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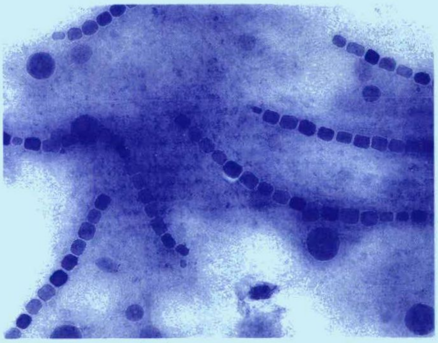

SYMPOSIA ON
ENVIRONMENTAL MINERALOGY
(Budapest, May 18–19, 2000)
AND
BIOGENIC IRON MINERALS
(Tihany, May 21–23, 2000)

ABSTRACTS

SZEGED, HUNGARIA

2000

NOTE TO CONTRIBUTORS

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Manuscript should be typewritten with double spacing, 25 lines on a page and space for 50 letters in a line. Each new paragraph should begin with an indented line. Underline only words that should be typed in italics.

Manuscript should be generally be organized in the following order:

Title
Name(s) of author(s) and their affiliations, in foot-note the address of the author to whom the correspondence should be sent.
Abstract
Introduction
Methods, techniques, material studied, description of the area investigated, etc.
Results
Discussion or conclusions
Acknowledgement
Explanation of plates (if any)
Tables
Captions of figures (drawings, photomicrographs, etc.)

Abstract

The abstract cannot be longer than 500 words.

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ACTA UNIVERSITATIS SZEGEDIENSIS

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COLLECTED ABSTRACTS
OF SYMPOSIA ON

ENVIRONMENTAL MINERALOGY
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Edited by
M. Pósfai, T.G. Weiszburg, K. Török, E. Tóth, T. Váczi and P. Pazonyi

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COVER

Chains of magnetite crystals in helicoid magnetotactic bacteria from Gyöngyös stream, Szombathely, Hungary. The size of the individual crystals is about 70 nm. The dark, circular features are phosphatic granules. TEM micrograph obtained by M. Pósfai (abstract on page 57).

NOTE

Abstracts were subjects of revision and were sent back for corrections to the authors. Additional minor grammatical corrections were also made on some of them by the editors.

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HEAVY METAL RETENTION IN POLYMINERAL CLAYS

ADAMCOVÁ, R. (Comenius University, Bratislava, Slovak Republic)

Heavy metal pollution of groundwater endangers not only areas of mining activities (acid mine waters, mine wastes), chemical industry, municipal landfills, but also those of intense agricultural production etc. However, the geological environment is able to retard the migration of heavy metals and to reduce the leachate concentration, especially in porous media like soils and partly soft rocks as well. The reliability of such groundwater protection depends on one hand on solution parameters, on the other hand on rock specific parameters. Among them, mineralogical composition plays a crucial role, influencing directly not only the physical and chemical interaction of the leachate with the soil particles, but also other rock specific parameters often used in prediction of pollutant mobility: cation exchange capacity, specific surface, soil pH and grain size (CZURDA & WAGNER, 1990).

The last effect is most evident in clays that represent the best pollution barriers. The small sized platy clay mineral particles are responsible for the low hydraulic conductivity of clays. Expandable clay minerals ensure the closing of cracks in the clay liner. Due to the "inner surface", their sorption capacity is very high. Moreover, they are able to exchange their primary cations for other ones. That is why the properties of pure clays have been studied for years (GRIM, 1968; NEWMAN, 1987). Today they are quite well known and they are successfully used also in mineral liners and geocomposites in the construction of landfills.

However, it is not easy to predict the final retention effect in polymineral clays. There, heavy metal retention is a complex of very different chemical and physical processes that cannot be studied separately. Manifold competitive reactions and clay selectivity determine the result.

The retention of lead, copper and zinc in 12 natural polymineral clays (soils in geotechnical terms) was studied using a mixture of heavy metal solutions in batch tests. A comparison of the sorption isotherms and the mineralogical composition of the clays indicated the affinity of individual metals to certain minerals in the soil. But the behaviour of every metal was quite different. Therefore, a new term "summary heavy metal sorption" was used in order to assess the whole sorption capacity of the soils. Because these results are very conditions-dependent, another way of more universal evaluation was searched for. When forming the sequence of best sorbing soils based on the batch tests and looking at their specific parameters, the cation exchange capacity together with the content of carbonates yielded the best correlation. Later these parameters were used in a simple graph for a qualitative prediction of the heavy metal retention properties of natural clayey soils.

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ENVIRONMENTAL ASPECTS OF THE BIODEGRADATION OF ORES CONTAINING REFRACTORY GOLD FROM WESTERN CARPATHIANS

ANDRÁŠ, P. (Slovak Academy of Sciences, Banská Bystrica, Slovakia) & KUŠNIEROVÁ, M. (Slovak Academy of Sciences, Košice, Slovakia)

Important potential source of gold in Western Carpathians is represented by gold-bearing Sb-Au sulphidic ores. This type of mineralization forms impregnations of fine-grained euhedral arsenopyrite and arsenian pyrite. The gold content in arsenopyrites is ranging usually from zero up to 250 ppm (crystals containing up to 0.6 wt% Au in point analyses were described only from the Trojárová deposit) and in pyrites from zero up to 100 ppm. Mössbauer spectroscopy showed that most of the invisible gold incorporated in sulphide minerals is chemically bound (András et al., 1995).

Gold-bearing sulphides exhibit strong zonation patterns. Two extreme types of growth zones can be distinguished, both with different compositional trends. The first one has high Sb and the second one high As and low Sb content. Progressive enrichment in As is generally in correlation with a decrease in the S and Sb content. As and S are strongly negatively correlated. The As-rich zones are considered to be the carriers of the substantial majority of chemically bound gold. Gold-bearing crystals with rims rich in Au-As are described from the Pezinok and Trojárová deposits (Malé Karpaty Mts.), while crystal cores rich in Au-As were found at the Dúbrava and Vyšná Boca deposits (Nízke Tatry Mts.).

From an environmental point of view, the industrial treatment of gold-bearing sulphidic ores has negative consequences for the landscape. It is difficult to find convenient technology for gold production from ores with invisible gold.. The biological-chemical oxidation of these ores is environmentaly satisfactory but usually very tedious.

Our study proved that the process of bacterial oxidation is a selective one, with preferential oxidation of arsenopyrite in As (Au) enriched zones. This process is followed by dissolution of As (Au) enriched zones of pyrite crystals preferentially along cracks, veins and growth zones of crystals, and, as a result, tunnels and various depressions form on the crystal surface. Their space orientation is directly related to the orientation of different crystal faces. The oxidation is also influenced by the galvanic interaction of crystal parts with different As content.

Our results have practical use in the industrial treatment of sulphidic ores. The preferential biochemical solving of the arsenopyrites, which contain about 80% of the gold, and the preferential oxidation of the As-rich zones of arsenopyrite and pyrite, which contain about 90% of the gold in each grain, substantially speed up the technological process of gold leaching and enable the use of the tedious biological-chemical technology for gold production from arsenopyrite-pyrite ores containing refractory gold in a convenient way from the environmental viewpoint.

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SELF-PURIFICATION OF Zn AND OTHER HEAVY METALS IN MINING EFFLUENTS: A NATURAL PHENOMENON

ATANASSOVA, R., KERESTEDJIAN, T. & BONEV, I. (Geological Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria)

The lead-zinc vein and skarn-replacement deposits of the Madan ore district in South Bulgaria, embedded in the high-crystalline gneissic rocks of the Rhodope massif, are one of the greatest ore concentrations in Europe, intensively exploited during the last 50 years. Descending waters actively interact with ore sulphides in the set of underground mining works and become enriched in heavy metals. Going out on the surface of the high mountain terrain they usually infuse into fresh running river waters. Specific reactions occur at their infusing points. Such a case of spontaneous precipitation has been studied in the upper parts of the Erma River in the southern part of the district.

The outflowing mining waters gathered from the higher levels of the exhausted Stratiev Kamuk Mine are of calcium sulphate composition with high contents of Zn (93.1 mg/dm^3) and Mn (48.63 mg/dm^3) and high TDS (1739 mg/l). Pb is rather low (< 0.02 mg/dm^3). The main stream waters are of Ca Mg sulphate hydrocarbonate composition with only a small content of Zn (1.75 mg/dm^3), Mn (0.14 mg/dm^3), Fe (0.05 mg/dm^3), and lower TDS (642 mg/l).

In the discharge zone where the mining effluents run into the fresh water stream, spontaneous mineral precipitation has been observed. The newly deposited and weakly lithified mineral mass consists mainly of amorphous zinc hydroxides with high contents of Fe, Al and Mn. The Zn:Al:Fe atomic ratio is about 4:2:1. Small contents of clay material (illite + kaolinite) and minor detrital quartz are also observed.

Interesting organic constituents of the new sediment are two types of algae – *Sargassophitae* and *Diatoms*. Characteristic are the µm-sized spindle-like diatom frustules of the genus *Achnanthes*. The microanalyses of these frustules show that Zn plays an important role in their composition, too. Si, which normally forms the skeletons of these *Diatoms*, is too low here. Their Zn:Al:Fe ratio is about 4:2:1 again. The probable presence of bacteria is suspected to cause the observed intensive gas bubble formation.

The mineral precipitates have a peculiar cellular texture with some circular micro-atoll forms. It is suggested that they have been formed around adhered gas bubbles. Due to their high porosity and included bubbles, some of these light mineral crusts are floating on the water surface.

The observed phenomenon results in a significant diminishing of the heavy metal concentration (esp. of Zn) in the river area after the discharge point, which is a specific kind of self-purification of the mining effluents. A detailed understanding of this process can contribute to the creation of an effective and sustainable remediation technology applicable in active or abandoned mining areas.

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MINERALS INERT, FRIENDLY AND AGRESSIVE TO THE ENVIRONMENT

BĂLAN PITIŞ, O.M. (North University, Baia Mare, Romania)

One of the subjects of major importance all over the world is the environment. The great polluting industries have a severe impact on the environment, but looking from this perspective only means a superficial approach to this problem.

Having the ecological laws stated by Barrens as a starting point, we considered a study from the basis important for a correct analysis, taking into consideration the raw material sources.

The cause-effect relations are sometimes difficult to recognize in natural geological systems as several mineralogical and geochemical parameters vary simultaneously and in different ways.

In this study, mineral species will be dealt with following the system of mineralogy, not according to their frequency in the Earth's crust. In order to describe a mineral as being „inert", „friendly" or „aggressive", we will consider the impact they have on the fauna and flora, directly or as a result of natural biochemical processes.

Some examples are listed here to emphasize the importance of mineralogy in understanding natural processes and thus contributing to environment protection.

Soils can lose elements through leaching, plants remove elements necessary for their growth selectively from the soil and animals intensify the degree of uptake of a certain element through selective feeding. Thus, to restore the original state of disturbed, cultivated or polluted soils it is essential to know all processes that mobilize elements in one way or another.

Pollutions can be both of human and „natural" origin. Under the action of atmospheric agents (wind, variations in temperature, rain fall etc.) radioactive minerals are partially altered, dissolved and thus radioactive elements – for example uranium originating from certain phosphates or arsenates containing UO_2 – are dispersed by waters, contributing to environment pollution. On the other hand, absorbing properties of clay minerals can be used to eliminate pollution.

Last but not least, a strong relation exists between minerals and living organisms. In the last centuries the idea that geology could be associated with aspects of health was suggested by geographical correlation. The frequency of some diseases seems to be more characteristic in some areas than in others, thus the relations between the geological environment and human health are extensively researched recently by medical geology.

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DETECTION OF ASBESTOS AND OTHER SILICATES IN THE URINE OF GENERAL POPULATION AND IN NORMAL AND CANCEROUS HUMAN KIDNEY AND VESICAL TISSUES

BELLIS, D. (ASL4, Torino, Italy), BELLUSO, E., CAPELLA, S., GULA, A. (DSMP, University of Torino, Torino, Italy), COVERLIZZA, S. (ASL4, Torino, Italy) & FERRARIS, G. (DSMP, University of Torino, Torino, Italy)

The presence of asbestos and other silicates in urine and in bladder/kidney tissues can be used as an indicator of environmental and/or occupational exposure to minerals via inhalation and ingestion (GUILLEMIN et al., 1989; POLLICE et al., 1995; FINN & HALLENBACK, 1984). Mineralogical analyses are suitable to assess the intensity of exposure when data from other sources are unavailable or unreliable.

The purpose of this research was to prove the feasibility of using optical microscopy and SEM/EDX to detect asbestos and other silicate fibres in neoplastic and non-neoplastic kidney/bladder tissues and in urine. The urine of the following persons were analysed: (1) a 66-year-old woman with kidney cancer surgery and paraoccupational asbestos exposure; (2) a 6-year-old child with environmental asbestos exposure; (3) a 43-year-old woman with environmental asbestos exposure and without neoplasia; (4) a 62-year-old man with pleural mesothelioma and without asbestos exposure. Besides, (a) cancerous and normal kidney tissue of a patient without asbestos exposure, (b) transitional cancerous and normal bladder tissue of a patient without asbestos exposure and (c), as control, autoptical normal bladder tissue of an adult were analysed.

The results show that (*i*) while silicates are present in all cases, asbestos occurs only in two cases of urine and kidney/bladder tissue samples, with the higher concentration in the neoplastic kidney tissue; (*ii*) confirm previous data reported in literature (PATEL-MANDLIK, 1981; KOBAYASHI et al., 1987; ROGGLI et al., 1986) and (*iii*) suggest a possible role of asbestos in urological neoplasia, especially in the kidney. However, only three studies of human material are available in literature and they cannot be statistically significant to detect an excess mortality due to kidney cancer among workers professionally exposed, thus further research is necessary.

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THE ECOLOGICAL ACCIDENT FROM “AURUL”, BAIA MARE (ROMANIA): CAUSES, CONSEQUENCES AND ACTIONS

BOLCHIŞ, R. (Environmental Protection Agency, Baia Mare, Romania), FLAUT, C., COSTIN, D., BENEA, M. & POP, D. (Babeş–Bolyai University, Cluj-Napoca, Romania)

Bozânta dams complex is located 6 km downstream of Baia Mare city, close to Săsar and Bozânta Mare villages. It consists of three ponds: Bozânta Veche (in conservation, conceded by AURUL S.A. for future exploitation), Bozânta Nouă (active, exploited by REMIN mainly for base metals) and Bozânta Aurul (active, exploited by AURUL S.A. for precious metals). The first two are of a slope-type and consist of materials which are suitable for being used for the elevation of the external walls, whilst Aurul dam is of a plain-type and its constituent material cannot be used for similar purposes due to its high toxicity.

Aurul tailings dam (94 ha) was built up in a short time in 1998 by Australian engineers, and it is located between Săsar river and Morii Brook. A plastic base-lining method using polyethylene film was selected for groundwater protection. The dam surrounding the pond was built of a settled sand core covered by soil. A second, safeguard dam does not exist. Aurul dam became active on 8 April 1999, when the gold leaching activity started.

The ecological accident

At the end of January 2000, a major ecological accident took place at Aurul dam, which in the following days focused the attention of the whole world. 6–7 accidents have been reported previously. Among them 4 pipe breaks, 1 at the pipe from the factory to the basin, and 3 at the pipe back from the basin to the factory carrying “pure water” in May, September and December 1999. On 28 January 2000, the water table in the pond was rising visibly, but no action was undertaken. On 30 January 2000, 8:30 p.m., after heavy rains, the top of the dam broke giving birth to an originally 25 m wide breach. Thus, in 11 hours a spill of about 100,000 cubic meters with suspensions and cyanide covered more than 4 ha surface of soil and then was discharged in the hydrographic system. The standard limit of cyanide in fresh water in Romania and Hungary is 0.01 mg/l.

Causes and consequences

The previous experience in building tailing dams in the region was not used for the new construction (absence of a clay core); specific local meteorological conditions (heavy rains, frost and snow in winter) were not taken into consideration; the dam was overcharged with highly concentrated cyanide solutions.

Cyanide contamination of the rivers Săsar, Lăpuş, Someş (values between 19.2–7.8 mg/l), Tisza and Danube (in Romania, Hungary and Yugoslavia); flora and fauna in the contaminated rivers were affected; contamination of about 20 ha agricultural land and of 9 water wells in Bozânta Mare village.

Actions

Cessation of AURUL’s operations; early warning of Hungarian authorities from the Romanian regional authority (10 hours after the dam broke); filling the breach with soil (51 hours); controlled discharge of the spill from the dam (40–50 l/s); neutralization of the discharged waters with sodium hypochloride; monitoring of the toxic elements along the rivers and water supply source for the population; further consolidation of the embankment; mass-media, diplomatic and legal feed-back.

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OLD MINING SITES AND DUMPS RECOGNITION BY FLUID INCLUSION CHARACTERISTICS IN QUARTZ, RUDE, NW CROATIA

BOROJEVIĆ, S., PALINKAŠ, L.A. & BERMANEC, V. (Department of Geology, Faculty of Sciences, University of Zagreb, Zagreb, Croatia)

The ore deposit of Rude is situated within the Dinaric geotectonic unit, 25 km NW from Zagreb. It is a complex SEDEX type ore deposit consisting of a feeder zone with siderite, Cu, Pb, Zn sulfides, barite and quartz and a stratiform ore (siderite, hematite, barite, quartz, gypsum and anhydrite). The host rocks are Upper Paleozoic clastics overlain by Scythian sandstones and shales (ŠINKOVEC, 1971). The ore zone is beneath a thick cover of Mesozoic sediments, including Cretaceous melange with masses of spilites and pillow lavas in allochthonous position. Interpillow spaces are filled with secondary quartz.

Mining was abandoned in the sixties, therefore research of the ore deposits is possible only on minerals from old dumps and streams draining the mining area. Fluid inclusion study revealed the presence of two different generations of quartz, one is related to the mineralization itself and another to the Mesozoic pillow lava formation. Fluid inclusion data from pillow lavas bear the following characteristics:

Quartz contains the following types of inclusions: 1. monophase, (L), 2. liquid-rich, (L+V) and 3. vapor-rich, (V+L), with possible addition of some CO_2 or methane. Cryometric measurement data confirm the presence of the H_2O-NaCl-$CaCl_2$ type fluids.

Temperature of the hydrohalite melting are in two ranges: between -38.5 – -35.1 °C and between -30.0 – -27.6 °C. The situation is similar with temperature of the last melting of ice; first maximum between -15.5 – -13.1 °C and the lower between -7.0 – -4.1 °C. The three component diagram of the H_2O-NaCl-$CaCl_2$ system also separates these two groups. These indicate the mixing of highly concentrated ore bearing hydrothermal fluid with less saline fluids, sea water or pore water trapped during the emplacement of the pillows.

Homogenization temperature is around 105–115 °C, occasionally as high as 155 °C, indicating low temperature of the hydrothermal solutions. It differs greatly from the expected chemistry and thermal characteristics of the fluids from the ore bearing minerals, and offers a possibility to distinguish ore bearing and country rock quartz (PALINKAŠ, 1989). The data can be used for the exploration of forgotten and unknown historical mining sites in the area and the evaluation of the extent of old mining activity.

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PARTITIONING OF CHROMIUM IN THE SYSTEM $MgO–Al_2O_3–SiO_2–Cr_2O_3$ AT 1 atm

BRIGIDA, C. (Dipartimento di Scienze della Terra, Universitá di Milano, Milano, Italia), VALLE, M. (ICRA SpA, S. Paolo d'Argon, BG, Italia) & POLI, S. (Dipartimento di Scienze della Terra, Universitá di Milano, Milano, Italia)

Storage and inertization of toxic wastes containing heavy metals (Cr, Cd, Pb) should be approached by appropriate technological recycling processes. Chromium can be reinserted in a number of crystalline phases forming in the system $MgO–Al_2O_3–SiO_2$, profiting from petrological knowledge at supersolidus conditions. This way a complete bonding of chromium in a refractory phase assemblage and thus inertization can be obtained.

Phase equilibria were investigated in the spinel, corundum and mullite primary phase fields of the system $MgO–Al_2O_3–SiO_2–Cr_2O_3$, aimed to study chromium partitioning between solid and liquid phases, at temperatures up to 1560 °C. Six different bulk compositions were prepared: three of them with $SiO_2:Al_2O_3 = 1:1$ and three with $SiO_2:Al_2O_3 = 2:3$. All compositions had $Cr_2O_3:Al_2O_3 = 1:9$ in molar proportions. A first set of runs was performed in platinum capsules, heated in a vertical furnace with controlled atmosphere, and quenched in water.

Preliminary chemical characterization of the phases by electron probe microanalysis shows strong partitioning of chromium relative to coexisting liquids in spinel, corundum–eskolaite series phases and Cr-mullite, for appropriate bulk compositions. Cr_2O_3 content in mullite coexisting with Cr_2O_3-Al_2O_3 solid solutions in the most Al-Si-rich sample is up to 11 wt%; such amount is very close to the upper limit known of chromium solid solubility in the mullite structure, as reported by RAGER et al. (1990). Cr_2O_3 content in glass ranges from 0.3 to 0.9 wt% and Cr_2O_3 increases with the Al_2O_3 content of the liquid phase, in agreement with previous work by SCHWESSINGER & MUAN (1992). Al_2O_3 partitioning between spinel and coexisting liquids shows a major dependence on the composition of the bulk system, i.e. on the composition of the coexisting phases, as found by SCHWESSINGER & MUAN (1992) in Al-poor systems. Relationships between chromium and aluminum partitioning in spinels, Cr-mullite and glass are discussed.

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THE INFLUENCE OF THE ALTERATION OF MINERALS FROM THE JOINT SURFACE UPON THE STABILITY OF ROCK BLOCKS

BUD, I. & DENUT, I. (Faculty of Mining and Metallurgy, North University, Baia Mare, Romania)

The instability of rock blocks limited by joint surfaces is determined by: the orientation of the joint surface; rugosity of the surface and the presence of argillaceous minerals. Such an instability is very frequently met in underground excavations (mining works, civil works and storage), in quarries or on the slopes near the roads.

The alteration phenomena of minerals from rocks having joints (natural or blasting) increases in time because of the changes that appear in the environmental parameters (water and air) after excavation. These factors lead to the decrease of the friction angle and dilatation, and swelling occurs, creating additional effects, as a result of the presence of certain minerals such as anhydrite, montmorillonite and pyrite.

The alteration phenomena (with the formation of argillaceous minerals, chlorite, fine muscovite, etc. as a result) lead, generally, to decreasing the values of mechanical and elastic properties, and for the fissured rocks these phenomena are more accentuated on and around the joints. Minerals more affected by alteration are plagioclase and orthoclase feldspar, biotite, hornblende and pyroxene. In the case of the Baia Mare basin there is also a biological cause which contributes to the emphasized alteration of the joints. Prevailing bacteria are the autotrophic species of the *Thiobacillus* genus (*ferrooxidans* and *sulfooxidans*; OROS & PETERFI, 1991). These oxidize sulphide minerals yielding sulphuric acid and trivalent iron.

The outcome of our research is a study concerning the influence of the friction angles by using the computer program UDEC (ITASCA, 1996). In all the simulations of the blocks around underground excavations, the value of the friction angle is 25° where an inflexion occurs in the curve of the movement, and the critical value is 20°.

By decreasing the friction angle and dilatancy, the computer program UDEC was used to represent the movement of one block related to others, as well as to the "key block", i.e. the block which has the maximum movement and which will establish the failure of the blocks.

The presence of argillaceous minerals on the joint surface leads to the decrease of the friction angle to less than 20°; for example, for montmorillonite the angle can be 6–12°.

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DEGRADATION OF CLAY MINERALS AND SOILS IN THE SODA WORKS: A POST-INDUSTRIAL AREA POLLUTED WITH ALKALINE SOLUTIONS

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The XRD, TEM, SEM, FTIR and ESCA methods as well as sorptive and chemical examination have been applied to studying changes in structure, morphology and porosity of mineral and soil samples treated with alkaline solutions. The main purpose of our studies was to explain the nature of the dramatic environmental transformations on the plot of the former Kraków Soda Works "Solvay" in the southern part of Kraków.

Research covered both examination of polluted soil samples and experimental studies on clay minerals (smectite, kaolinite and illite) degraded with NaOH solutions in different periods of time.

It was found that alkaline solutions influence very strongly the properties of soils, causing degradation of their microstructure and chemical composition as well as transformation of mineral substances. Changes in soil microstructure included mostly breakdown of the pore systems, decomposition of soil aggregates and destruction of soil stability. Changes in the chemical composition of polluted soils were connected to the removal of soil organic matter (mostly of humic type) and dissolution of mineral components. Transformation of the mineral components of soil comprise evolution of fine-grained mineral fractions (mostly clay minerals), leaching of chemical components, deep etching and partial dissolution of clay flakes and aggregates, and also crystallization of secondary mineral phases (among others of zeolite type).

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BINDING AND SOLIDIFICATION OF RADIOACTIVE WASTES IN HOT PRESSED CEMENT SYSTEMS

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Blended cement systems, which are characterized by an increased degree of binding of some radioactive wastes, have been developed. Along with ordinary Portland cement (OPC), these systems include other mineral components (blast furnace slag, fly ash and bentonite), which improve the chemical fixation of radionuclides inside solidified compounds. Different cement compositions were utilized for the investigation of the processes of binding and solidifying radioactive wastes while hot pressing (i.e. the simultaneous effect of increased temperature and pressure upon a hardening system).

The influencing parameters of hot pressure (temperature, pressure and time of their duration) on processes of forming the structure of the cement paste have been investigated. Hot pressing with a pressure of 25–50 MPa, temperature of 150–200 °C and duration of 30–45 min have proved to have an influence upon most processes of structure forming. In contrast to samples obtained by traditional cementation, in the composition of hot pressed cements calcium hydroxide, the most easily leached hydrate phase, is not present.

The study of physical and mechanical properties of hot pressed cements including radioactive wastes has shown them to be characterized by decreased porosity (< 10%), increased water resistance, and a decreased level of the leach rate of radionuclides ($< 1\times10^{-5}$ g/cm^{2}xday). In addition, obtained products have an increased compressive strength (30–100 MPa).

It has been proved that hot pressed cements have a several times higher capacity of radioactive wastes with respect to traditional cements, and at the same time exhibit a leach rate of radionuclides several orders lower than those produced by traditional methods. As a result of these researches, the technology and a plant for hot vibro-pressing for the immobilization of radioactive wastes in Chernobyl Exclusion Zone have been designed.

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GEOLOGICAL AND PROCESSING RELATED ASPECTS OF THE PRECIOUS METALS URBAN ORE NEAR BAIA MARE (MARAMUREŞ REGION, ROMANIA)

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Baia Mare has been a traditional mining region for precious and base metals since the Roman times. The ores have an epithermal genesis, their structures are of vein- and breccia-type and they are related to the Neogene volcanism of the Carpatho-Pannonian area. The metallic mineral assemblages consist of common sulfides, sulfosalts and native gold and silver. Gold appears as free gold, especially in the upper part of the ore deposits, and included in sulfides (mainly in pyrite). Quartz, carbonates, adularia and clay minerals represent the gangue minerals (BORCOŞ & VLAD, 1994).

The active precious metal urban ore (KELLER, 1992) westwards Baia Mare is represented by the Meda tailings dam, built up between 1956 and sometime in the '70s, very close to the residential area. It is an old mining solid waste tip resulted from the mineral processing of the ores from the Ilba, Nistru and Săsar deposits. Quartz, adularia, pyrite, sphalerite, galenite and submicroscopic gold (0.6 g/t) represent the average mineralogical composition of the tailings. The same processing technology was used since the '60s and it was based on the use of cyanide for gold concentration (cyanide leaching). In 1992, S.C. AURUL S.A. company was established as a joint venture between Esmeralda Ranger Exploitation Ltd. (Australia, 50%), REMIN Baia Mare (44.8%) and others (5.2%). Its first objective was gold recovery from the Meda tailings dam. The amount of solid waste at that time was 4.43 million tons. The expected yearly amounts of recovered metals were 1.6 t Au and 9 t Ag.

The technological flow of S.C. AURUL S.A. (courtesy of EPA Baia Mare) involves the mixing of the fluidized solid waste from Meda dam and calcines from Phoenix plant with industrial water containing a high concentration of free cyanide (about 120 mg/l), HCl, and NaOH. The mixture is then electrically dried and melted. The final product is a doré bullion, which is transported to the Metallurgical Plant for refinement. At the end of the process, the solution has 20 mg/l cyanide and it is neutralized by sodium hypochloride down to 4 mg/l. The resulting aqueous solution is stored in another tailings deposit dam, located near Bozânta village (Aurul dam). All the process operate in closed circuit, the waters after the sedimentation of solids in the Aurul pond being reused. The maximum capacity of the AURUL plant: 3.5 million tons/year, the approved operating capacity: 2.0 million tons/year, the total amount of wastes processed until now: 1.6 million tons.

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ARSENIC IRON CRUST DEVELOPED WITHIN FORMER METALLIC MINE TAILINGS

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Oxidation of sulfides in mining environments is an important problem regarding the acid drainage it induces (ALPERS et al., 1994) and the release of potentially toxic elements such as metals or arsenic, which frequently occur as by-products of various ores.

Located in the southern part of the French Massif Central, the tailings of an arsenopyrite-rich former metallic mine present a local induration by an oxidized cement rich in As and Fe. These "ferri-crusts" are constituted by millimetric to centimetric quartz and other mineral grains proceeding from the ore gangue. They are well developed in the gullies recently (< 20 years) created by the runoff of drainage waters.

We aimed at characterizing this material in order to understand its formation and to forecast its potential to release its arsenic content under these conditions. The first step was to determine the As-bearing phases. Mineralogical and chemical observations were performed by XRD, ICP/MS and AAS analyses on the whole sample or on mechanically separated cement. Combining optical microscopy observations determinations with SEM + EDX system, and with microprobe (WDX) analyses, we defined five types of cements: a dark reddish cement (~ 1.4 wt% As and ~ 47 wt% Fe) and a red cement (~ 3 wt% As and ~ 45 wt% Fe) which both formed collomorph structures, a yellow cement (~ 1.4 wt% As and ~ 40 wt% Fe), a resinous As-rich cement (As ~ 17 wt%, Fe ~ 23 wt%) and a fleecy cement (As ~ 5.7 wt%, Fe ~ 27.5 wt%). Small amounts of sulfur were found, which could be explained by the fact that a few sulfide relicts were observed.

The affinity of As with Fe was pointed out in many studies (DAUS et al., 1998; PIERCE & MOORE, 1982). It was also observed in these ferri-crusts that the largest quantities of As were found either in association with Fe as an As-bearing K-jarosite or as an amorphous gel corresponding to the so-called "resinous" cement. The formation of jarosite is consistent with the pH-Eh conditions measured in drainage waters (2.8 and 481 mV, respectively). However, arsenic seems to be mainly trapped by the well-developed amorphous iron hydroxide: no arsenate minerals were observed. It is now important to investigate the long-term stability of these ferri-crusts under variable pH-Eh conditions.

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ENVIRONMENTAL IMPACT PRODUCED BY ECOLOGICAL ACCIDENT FROM THE TAILING POND OF NOVĂŢ STREAM (BAIA BORŞA ZONE – NW ROMANIA)

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General setting

Baia Borşa Mining Exploitation – proprietor of the Novăţ Pond – belongs to National Company REMIN S.A. Baia Mare (state capital society) that is working on the exploitation and mineral processing of the non-ferrous ore deposits. The Novăţ Tailing Pond is a "valley type" waste flotation dump, placed between slopes of the Novăţ stream, a left tributary of the Vaser River. There are two access routes from Baia Borşa: a country road, with a length of 13 km, hard to pass in winter and an underground gallery, with a length of 8 km.

Causes and accident evolution

The causes of the accident are: Increase in the water level, due to abundant rains and thawing of snow; flood of pumping station which transports the clean water from the pond to the Processing Plant of Baia Borşa (09.03.2000, 10:10 pm).

In spite of all the preventive measures of E.M. Baia Borşa S.A. (the stop of Processing Plant, 09.03.2000, 11:00 am), on 10.03.2000, 10:30 am, the dam downstream of the pond was broken. Polluted water and tailings were let out through this breach contaminating the rivers Novăţ, Vaser, Vişeu and Tisa with heavy metals. The size of the breach rapidly increased to 40 m in length and 18 m in height. The entire mass of overflowed material was 70 000 m^3 of water and 40 000 m^3 of gangue (but approximately 20 000 m^3 were hold back by the downstream dams).

Emergency measures

After the accident – until 15.03.2000, 06:00 pm – the next actions were undertaken: Sampling and analysation of the water from the rivers Vaser, Vişeu and Tisa; cleaning of snow and mud (of landslides) from access routes to the tailing pond; restoration of the pumping station; pumping clean water from Novăţ Pond temporarily to Colbu Pond; controlled evacuation of the water through pipes leading to tumbling bay; construction of a supplementary dam to stop the breach advance; reconstruction of the dam upstream of the eroded zone.

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CRYSTAL SIZE AND SHAPE DISTRIBUTIONS OF MAGNETITES FROM MAGNETOTACTIC BACTERIA

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Magnetite crystals from magnetotactic bacteria are typically characterized by sizes within the single magnetic domain range, growth habits that can differ from equidimensional morphologies, and structural perfection. It is of great interest to find criteria that could unambiguously distinguish such bacterial magnetites from inorganic ones when crystals are no longer organized in chains, as can be the case in ancient rocks.

We showed (DEVOUARD et al., 1998) that "structural perfection" should not be considered a valid criterion for distinguishing magnetite from magnetotactic bacteria, since both biological and synthetic crystals of magnetite can display similar twinning according to the spinel twin law, also known in macroscopic magnetite.

The size and shape of magnetite crystals from magnetotactic bacteria appear to be statistically different from those of synthetic crystals (DEVOUARD et al., 1998). We studied four samples of cultured magnetotactic bacteria (*Magnetospirillum magnetotacticum*, strains MV-1, MV-4 and MC-2) and compared their size and shape distributions with those of synthetic crystals similar mean size. The crystal size distributions (CSDs) of bacterial samples appear to be species dependent, narrower than that of synthetic crystals, and their skewness is inverted compared to the synthetic sample (Fig. 1a, c). The anisotropy (elongation) of the crystals was estimated from the ratio of their measured width over length (W/L). Those "shape" distributions differ from those of synthetic material for the strains that show consistently elongated morphologies (strain MV-1, Fig. 1b, and less markedly strain MC-2), while cubooctahedral crystals from *M. magnetotacticum* are indistinguishable from synthetic ones (Fig. 1d).

Two questions remain to be addressed in order to apply this size and shape criterion to unknown samples. (i) The CSD from a mixture of species of magnetotactic bacteria can be estimated by summing those of pure species: in most cases, the resulting distributions could still be distinguishable from those of non-biogenic samples. (ii) The synthetic sample we used for this study can not be considered as representative of all possible non-biogenic samples. However, observed CSDs of various non-biogenic crystals are properly described by lognormal distributions similar to that of Fig. 1c (EBERL et al., 1998). These authors show that crystals evolved from supply-controlled Ostwald ripening (i.e., volume diffusion being the limiting process) can display negatively skewed CSDs similar in shape to the one observed in magnetite from magnetotactic bacteria.

Analyzing CSDs with the desired accuracy raises two additional problems. The first one is that it is difficult to define width and length for a non regular shape (Fig. 2a). This issue can be addressed by approximating the crystal shape by a best-fitting ellipse of same area (Fig. 2b), and taking the mean of minor and major axis lengths as the size, and the ratio of these lengths as the W/L ratio. These calculations are easily performed by image analysis softwares. The second problem in quantifying CSDs of crystals observed by TEM is that the observed distribution can strongly differ from the real one. If one considers a set of identical but randomly oriented cubes (Fig. 3), the CSD obtained from measuring the different projections of the cubes will lead to an overestimation of the mean size, while the apparent W/L ratios will be less than 1. Because we know of no way to infer the real CSD from the observed one, we conducted numerical simulations of CSDs for randomly oriented simple shapes (cubes, octahedra, and parallelepipeds). The results show that for most shapes, the CSDs are significantly biased and show a larger spread than the real distributions. The shape distributions are affected in similar ways.

Although problems remain, crystal size and shape distributions seem to be a useful criteria for distinguishing magnetites from magnetotactic bacteria from non-biogenic ones. However, we suggest that studies using quantitatively CSDs should try to take into account the measurement bias.

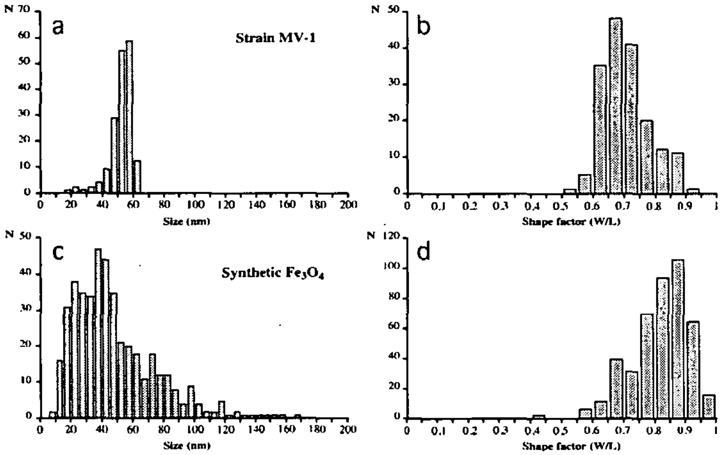

Figure 1: CSD and shape (W/L ratio) distribution for (a, b) strain MV-1 magnetotactic bacteria and (c, d) synthetic magnetites.

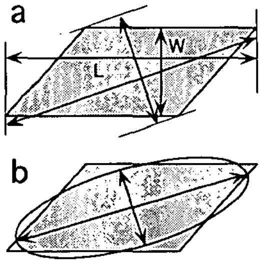

Figure 2: Measurement of an irregular shape

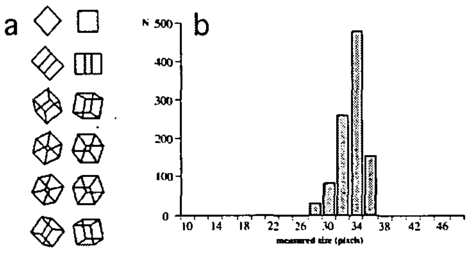

Figure 3: Measured CSD of randomly oriented cubes

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MINERALOGY OF WELTZ-CLINKER WASTE – WAYS FOR USEFUL COMPONENT EXTRACTION AND ENVIRONMENTAL DECISIONS

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About 250 000 t of waste weltz-clinker have been deposited near the factory for non-ferrous metals in Plovdiv, Bulgaria, for the last 30–35 years. The waste contains 2% Cu, 0.7% Zn, 0.5 g/t Au, 200 g/t Ag and coke. This is a typical technogenic polymetallic deposit of specific mineral composition, as explored by boreholes. Over 30 minerals were identified there: elements (metals and alloys), oxides, silicates, sulfides, carbonates of copper, iron, zink, lead and noble metals (gold and silver). In the group of sulfide minerals pyrrhotite and non-stoichiometric iron-copper sulfides, chalcopyrite, bornite, chalcocite, covellite, sphalerite, wurtzite and galena are present. Copper (metal), copper oxides and sulfates are considered to be the most essential in this mineral association owing to their solubility in sulfuric acid. A large number of iron oxides formed under changeable redoxy conditions: magnetite, Zn-ferrite, hematite, wüstite, goethite and lepidocrocite were proved. Iron (α-Fe) is generated by reduction under solid state conditions in close association with iron carbides.

The artificial deposit is determined as very similar to the natural cementation zone, but it is considered that the specific primary composition and physical, mechanical and physico-chemical properties of the clinker have been decisive for the self-organization of the system, which is in a significant contrast with natural processes.

This mineral association underwent natural leaching and the great part of the heavy metals precipitated in the alluvial formation of the Chaja river. However, a part of copper is cemented on α-Fe in the clinker.

The clinker studied is found to be a product containing useful and valuable metals, and, from another point of view, a very hazardous waste for natural equilibrium. On the basis of these results, technological and projective works for processing of this deposit were performed. Economic balance of plant building, production and its effectivities were calculated.

The main practical conclusion is that application of combined schemes, i.e. biogeochemical leaching with cementation or extraction of copper and flotation of coke and sulfides enriched in Au and Ag to extract useful components is possible. In addition to the economic benefit, one more important result of this exploitation could be the environmental effect, as the clinker deposit is situated on the river terrace.

Finally, the methodological steps and results of this investigation together with the technological treatment can be applied successfully to other technogenic objects of similar kind.

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OFF-AXIS ELECTRON HOLOGRAPHY IN THE TEM AND ITS APPLICATION TO MAGNETOTACTIC BACTERIA

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Off-axis electron holography in the transmission electron microscope (TEM) allows the amplitude and phase of the electron wave that has passed through a sample to be recorded. Here, we outline how holography can be used to characterize the magnetic microstructure of magnetite nanocrystals in magnetotactic bacteria (DUNIN-BORKOWSKI et al., 1998).

Figure 1a shows a bright-field image of a single cell of the marine vibrioid strain MV-1, recorded at 200 keV in a Philips CM200 field-emission-gun TEM. A chain of magnetite crystals, which are each ~60 nm in length, can be seen next to a hole in the C film. The presence of the hole allows a reference wave from vacuum to be overlapped onto the cell to form a hologram (Figs. 1b and 2a). This is achieved by applying a positive voltage to a biprism (a 0.6 μm Au-coated quartz wire) located in the selected-area aperture plane of the microscope. The amplitude and phase of the electron wave leaving the sample are determined by extracting one 'sideband' from the Fourier transform of the hologram. This sideband is inverse-Fourier-transformed and the amplitude and phase of the resulting complex image are calculated. The phase is 'unwrapped' to remove discontinuities that result from the fact that it is initially calculated modulo 2π.

Neglecting dynamical diffraction, the measured phase is given in one dimension by

$$\phi(x)=\left(\frac{2\pi}{\lambda}\right)\left(\frac{E+E_0}{E(E+2E_0)}\right)\int V(x,z)dz-\left(\frac{e}{\eta}\right)\iint B_\perp(x,z)dxdz \qquad (1)$$

where z is the incident beam direction, x is a direction in the plane of the sample, $B_\perp$ is the component of the magnetic induction perpendicular to both x and z, V is the mean inner potential (MIP), λ is the wavelength and E and E_0 are, respectively, the kinetic and rest mass energies of the incident electron. Equation (1) shows that the phase is sensitive to both the MIP of the sample and the magnetic induction. For magnetic nanocrystals of this size, the MIP contribution dominates the phase and must be removed to characterize the magnetic microstructure of the sample. This can be achieved by recording two holograms with the chain of crystals magnetized in opposite directions. If the magnetic field in the sample reverses exactly, the magnetic and MIP contributions are given by half the difference and half the sum of the phases of the two holograms, respectively.

Figures 2b and 2c show two phases images obtained from the region in Fig. 2a, between which the magnetization direction of the chain was reversed using the field of the microscope objective lens. The two images are almost identical as they are dominated by the MIP contribution to the phase. The magnetization of the crystals produces a slight change in background across the chain; as a result, the top right of Fig. 2c is very slightly darker than in Fig. 2b. Figures 3a and 3b show the MIP and magnetic contributions to the phase determined from four pairs of holograms. The MIP contribution to the phase of each crystal is proportional to its thickness and can be used to provide information about its morphology. The magnetic contribution, which is more slowly-varying, can be used to measure the magnetic moment of the cell. Alternatively, contours can be added to it to represent magnetic field lines, which are most closely-spaced along the line of crystals.

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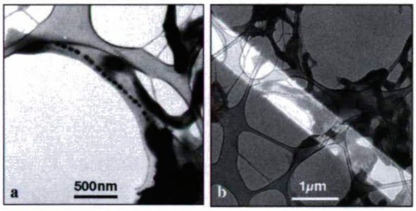

Figure 1: (a) TEM bright-field image of single cell of magnetotactic bacterium strain MV-1 located next to hole in carbon film. Chain is ~1600 nm in length and contains 15 magnetite crystals that are elongated along [111] and ~60 × ~35 nm in size. (b) Low magnification bright-field image obtained in field-free conditions showing effect of applying 120 V to biprism wire placed over region shown in (a).

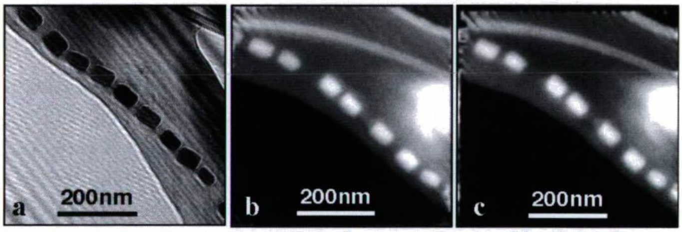

Figure 2: (a) Individual off-axis electron hologram obtained in field-free conditions by increasing magnification from condition shown in Fig. 1b, after tilting sample and applying large vertical field using conventional objective lens along axis of cell. Coarse fringes are Fresnel fringes from edge of biprism wire and fine fringes are holographic interference fringes which carry information about amplitude and phase of electron wave at exit surface of sample. (b) Phase image reconstructed from hologram shown in (a). (c) Phase image obtained after magnetizing chain in opposite direction to (b).

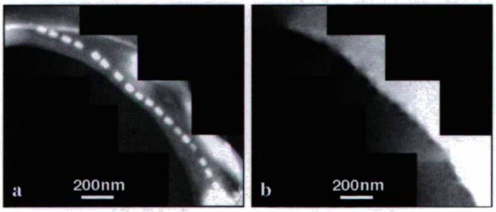

Figure 3: Composite images obtained by combining four pairs of phase images such as those shown in Figs. 2b and 2c. (a) and (b) show mean inner potential and magnetic contributions to phase and are formed by calculating half of the sum and half of the difference of each pair of images, respectively.

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ENVIRONMENTAL POLLUTION STUDY IN THE ARIEŞ VALLEY (APUSENI MOUNTAINS, ROMANIA) USING FACTOR ANALYSIS

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The chemical systems of river water are complex ones in which groups of chemical species are reacting and become correlated whereas others behave in an independent manner. In order to investigate and identify such inter-element alignments, the analytical results have to be checked for correlations. This is best done by factor analysis which, as a statistical technique, tries to explain the observed variations in terms of a smaller, unobserved number of statistical associations or factors. Such factors can then be interpreted in terms of processes or reactions, i.e. one searches for a geochemical control over data variations. The most common type of factor analysis is the R-mode analysis, which is based on the relationships between variables (RUIZ et al., 1990; JAYAKUMAR & SIRAZ, 1997). Fourteen variables and samples from fourteen sampling sites were selected for R-mode factor analysis.

The analytical data used were transformed values, in order to obtain near normal distributions (GUPTA & SUBRAMANIAN, 1998). The factor analysis was performed using SPSS software.

An evaluation of the results showed that about 88% of the internal variance of the data set could be explained by the re-arrangement of the data into factors. The interpretation of the factors allowed an identification of several groups of ionic species and parameters, which were connected by internal correlation.

The high factor loadings for Ca^{2+}, Sr^{2+}, K^+, Na^+, Mg^{2+} and EC values in Factor 1 are interpreted as large-scale water–rock interactions, i.e. the influence of the rock types exposed locally. Since the cations grouped under this factor contribute the most to the conductivity of the water, their correlation to the EC values is expected.

Factor 2 contains the variables pH, Cu^{2+}, Zn^{2+} and Mn^{2+} and it can be interpreted as the fingerprint of mining activities and related pollution.

Factor 3 is characterized by high loadings for NO_3^-, Cl^-, and SO_4^{2-} and is interpreted as the interaction of river water with settling pond effluents and also as the continuous interaction of river water with Neogene sediments.

Factor 4 could be interpreted as representative for domestic effluents.

Factor 1 explains 39.2% of data variance and points to the importance of water–rock interaction processes in the control of the composition of the river water. The high percentage represented by the sum of Factors 2, 3 and 4 (48.3%) supports the interpretation of a high pollution of the Arieş river system as a result of mining and other human activities within the region under study.

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GASTROPOD SHELLS AS POLLUTION INDICATORS IN MINING REGIONS: PRELIMINARY STUDY IN THE ARIEŞ VALLEY (APUSENI MOUNTAINS, ROMANIA)

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The pollution effect increased in the last decades due to the industrial progress and also due to the orientation of economy towards a consumption society. An increased degree of pollution determines the scientist to find ways to diminish the effects. The technical development allowed new high performance instruments to be used for pollutant detection. In many cases, pollutants are present in the environment in small concentrations and for their detection high performance and expensive devices are necessary.

Due to specific biological activity, pollutants can be concentrated in different plants and animals, at levels several orders higher than those recorded in the environment (HAAS et al., 1998). This increased concentration can cause major perturbation in the biological cycle or even the death of the individuals.

The increased concentration of different pollutants in certain plants and animals can be used for monitoring pollution with the help of less expensive methods.

Previous research has been focused mainly on the study of metals present within shells and skeletons of different marine animals in order to use these values as pollution indicators (AUERNHEIMER et al., 1984; BOURGOIN, 1990; GUZMAN & JIMENEZ, 1992; AUERNHEIMER & CHINCHON, 1997).

The present study intends to demonstrate the possibility of using terrestrial gastropod shells as pollution indicators. 28 gastropod shells from 8 regions affected by pollution in various degrees were analyzed. The analysis was done by using X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD). The analyzed shells where compared with shells collected from non-polluted areas.

Our results indicate that the gastropod shells collected from the neighbourhood of settling ponds and mine waste dumps accumulate significant amounts of Pb, Zn, Cu, Fe and Mn.

In conclusion, gastropod shells can be successfully used in the study of heavy metal pollution in mining regions and also in establishing the geochemical lower limits for different bivalent metals in non-polluted regions.

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POTENTIAL USE OF CLINOPTILOLITE–SMECTITE CLAYSTONES FROM THE OUTER FLYSCH CARPATHIANS (POLAND) FOR REMEDIATION

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The aim of this work was the comparison of physico-chemical properties of a clinoptilolite–smectite claystone with a zeolite fraction separated from this rock, and the evaluation of their potential use for remediation. The claystone outcrops are found near Rzeszów (SE Poland) as the Trójca Red Shale Member of the Variegated Shales Formation (Upper Paleocene–Lower Eocene) within the Skole Unit of the Outer Flysch Carpathians (RAJCHEL, 1990). The rock consists of 60–80% smectites, 15–30% clinoptilolite, and 15–30% quartz, feldspars, illite/glauconite and kaolinite (FRANUS & DUDEK, 1999). Zeolite concentrate 90–95% purity) was separated by sedimentation as a fraction > 25 µm.

Cation exchange capacity (CEC, NH_4Oac static method), specific surface area (A_s, BET method), sorption of heavy metals from aqueous solutions (Cr(III), Cu(II), Pb(II), Zn(II)) and sorption of gases (SO_2, CO_2, NH_3) were compared for the raw claystone and clinoptilolite separate (KŁAPYTA et al., 1999; BAJDA et al., 2000).

The CEC of the shale (380 meq/kg) is lower than that of the zeolite (660 meq/kg), whereas the specific surface area of the shale is higher (46 m^2/g) compared to 20 m^2/g for zeolite).

The amount of heavy metals removed from solutions by the shale is higher than that removed by the zeolite and equals to 562 mM/kg for Cr, 221 mM/kg for Cu, 190 mM/kg for Pb, and 256 mM/kg for Zn, the zeolite removes 260 mM/kg Cr, 172 mM/kg Cu, 136 mM/kg Pb and 142 mM/kg Zn. Desorption from the shale is higher for Cu and Pb while desorption from the zeolite is higher for Cr and Zn.

The zeolite fraction shows a very high adsorption capacity for CO_2 and SO_2 gases, 1060 and 1270 mM/kg, respectively. The shale adsorption equals to 250 mM/kg for CO_2 and 640 mM/kg for SO_2. However, adsorption of gaseous ammonia (NH_3) is higher for the shale (2740 mM/kg) than for the zeolite (1870 mM/kg).

From the above data it can be seen that both the shale and the zeolite separate show physico-chemical properties making them suitable for their use for remediation or in various branches of industry and agriculture. Their characteristics, however, are significantly different. Therefore, separation of zeolite concentrate is recommended for certain applications.

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CASE STUDY OF ST. KATHREIN, SOUTH TYROL, ITALY – GRÖDEN SANDSTONE MATERIAL AND WEATHERING PROPERTIES

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The preservation of monuments implies maintenance as well as restoration. Two aspects are essential for those campaigns: i) documentation of the materials used and the damages occurring at the object and ii) the properties of the applied materials to assure high quality restoration. In the frame of an Italian–Austrian EU-Interreg program we performed such preparatory work for the church of St. Kathrein in Hafling, a prominent roman–gothic stone monument in South Tyrol/Italy built of reddish brown Gröden sandstone, a widely employed stone material in that region. St. Kathrein is located on a mountain saddle eastward and some 1000 m above Meran (300 m), where winds and rain from the west are dominant. The general weathering situation is characterised by a south Alpine climate and little air pollution.

The nave (15 m in length) was erected in form of a rough stone construction with edges and opening frames out of square stone. Originally the walls were covered by roughcast. The 26 m high tower is constructed of big seized quartzitic Gröden square stones. Other materials such as regional mica schists, gneisses and (Laas-) marble as well as (Bozen-) rhyolite were used as fillings and are found only in small quantities.

For the detailed mapping with respect to material inventory, damage spectrum and distribution of different mortars and masonry, digitally converted orthophotographs of the facades were produced. Geological exploration in the area disclosed the location of the medieval quarries. The most striking weathering features on the sandstone were black coatings which were irregularly distributed throughout the building. This phenomenon seems mainly governed by the hygroscopic properties and stone geometry. The most common stone damage is surface erosion. On quartzitic sandstone (tower) the material losses amount to some 2 mm over a period of about 600 years. The erosion increases significantly with clay content. Most severe stone damages, which were the main cause for the restoration campaign, have been fractures up to 20 cm size at all weathered mouldings and heavily at the SE edge of the tower. The latter is related to a lightning event in the 19th century.

The Gröden sandstone applied as building material is to be classified as quartz arenite to subarcosic sandstone (PETTIJOHN et al., 1973) of medium to fine grained size. The clay mineral content in the rock varies; the best qualities are characterised by quartzitic grain contacts. Fresh material from the quarries and weathered building material were examined for characteristic petrological and petrophysical properties such as mineral components, fabric, soluble compounds, porosity and hygroscopic properties.

Porosity and specific surface display an inversed tendency (fresh material: pore volume 5.4%, surface 1.2 m^2g^{-1}; weathered material: pore volume 9.9%, surface 0.8 m^2g^{-1}). Correspondingly, the hygroscopic sorption behavior, the capillary water uptake properties as well as the water capacity are different due to the different pore sizes.

A surprising refinding in some fresh material was the rare mineral dawsonite $NaAl_2[(OH)_2|CO_3]$, confirming observations by WOPFNER & HÖCKER (1987). Its disappearance in weathered material has been experimentally simulated by leaching experiments and thus proves to be a good weathering indicator.

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DISPERSION AND CONTENTS OF INDUSTRIAL DUST AND SOIL SAMPLES FROM BAIA MARE AREA, NORTH - WEST ROMANIA

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Our study shows the dispersion of several heavy metals (Cu, Pb, Zn, Cd) in industrial dust and soil samples collected from the Baia Mare area, northwest Romania. The town of Baia Mare is the site of two major plants for processing Pb and Cu ore supplied by mining companies from the nearby mountains. Consequently, the atmosphere is polluted with airborne particles, which contain mainly Pb, Cu and Zn and traces of other heavy metals, such as Cd. Samples were collected in several points appropriately established based on the location of industrial sites and meteorological factors.

In the particular case of the Baia Mare area, the polluting elements occurred in the form of oxides, carbonates, silicates, sulfides and sulfates. To accomplish specification, samples were processed by selective and successive dissolution by using specific reagents. The collected fractions were then analyzed by optical emission spectrometry (CORDOS et al., 1999; FRENTIU et al., 2000). Results indicate that sedimented dust shows a high metal content in the form of sulfates while sulfides predominate in soil samples. For a total content of 0.879% Pb, 0.892% Zn and 0.136% Cu, the proportion of sulfides in soil samples is up to 88%, 68% and 46%, respectively. The corresponding proportions of sulfates is 10%, 2% and 5%. Similarly, for a total content of 2.282% Pb, 1.411% Zn and 1.001% Cu in sedimented dust, the proportion of sulfides is 52%, 40% and 42%, respectively, while the proportion of sulfates is 31%, 34% and 21%. Along with these metals, Cd was determined in dust samples after acid digestion. The total content of Cd traces covers the range 0.0001–0.0004%.

Relationship between sedimented particles and soil was established with regard to the total level of metals and their chemical forms in accordance with depth and distance from the polluting sources.

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CHANGES IN THE MINERALOGICAL COMPOSITION OF THE GYÖNGYÖSOROSZI MINE WASTE SPREAD OUT ON THE FLOODPLAIN OF THE TOKA CREEK

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In the Gyöngyösoroszi base-metal mine approx. 3.7 million tons of ore were produced between 1952–1985. Because of different kinds of operational accidents some 200 000 m^3 of flotation waste entered the beds of Toka and Száraz Creeks. A considerable part of this material has been deposited in the reservoirs built in the valley, but a still important quantity has been spread about by floods on the floodplain. This is the essential factor of the contamination here. The flotation waste mixed with the products of natural weathering is deposited in lenticular bodies along the Toka Creek. In these deposits the Pb and Cd contents are frequently above 500 ppm and 5 ppm, respectively. In most cases As, Zn and Cu are above the C_2 limits of tolerable values for soils (40, 1000 and 300 ppm, respectively).

Predominant commodities of the mine were Zn and Pb, while Cu, Ag and Au were less important. Sulphide minerals include sphalerite, galena and chalcopyrite; they are accompanied by several % of pyrite. The associated minor elements like Cd, As and Sb deserve attention from an environmental point of view.

The flotation waste is a grey fine grained material. The lens formed on the floodplain originally had the same colour, but because of the intensive oxidation they became yellow. During the oxidation to sulphate, part of the excess iron becomes soluble, another part turns into ferric iron and this is bound in jarosite or in oxi-hydroxide phases. As a consequence, there are less iron minerals in the samples taken on the floodplain than in those collected on the flotation dump. There are many white gypsum needles in the oxidised waste, and mineral grains are also overgrown by these thin gypsum crystals.

The mobility of the base and heavy metals responsible for environmental pollution is quite different. This process was studied on the floodplain by the use of two geochemical profiles. Isotope data made it possible to determine the age of the different layers: the lowermost layers which contain no detectable amount of Cs^{137} had probably been deposited before the first atmospheric hydrogen bomb tests took place. The "yellow sand" layers were deposited during the operation of the mine. The effect of the Chernobil accident (1986) is reflected by the uppermost sample, this layer was deposited after the closing of the mine. These profiles show that Zn and Cd are washed out of the "yellow sand" by the infiltrating water and they are now enriched in the underlying layers formed prior to mining activity. This way the contamination progresses downwards. The process for elements (Pb, Hg, As and Sb) less mobile under hypergene conditions seems to be much slower.

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DISCOVERY OF BOTANICAL IRON BIOMINERALS BY ELECTRON DIFFRACTION AND MICROSCOPY

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Introduction

Characterization of soil profiles often shows enhanced magnetism in the top soil, attributed to higher concentration of ferrimagnetic iron oxides (CORNELL & SCHWERTMANN, 1996). Two contrary routes, an inorganic (MAHER & TAYLOR, 1988) and a bacterial (FASSBINDER et al., 1990), have been proposed for the formation of ultra-fine magnetite in soil, and the soil magnetite controversy is yet unresolved. Soil by definition supports plant life, and it is known that plants, like animals, store iron in their cells. Based on magnetic studies of various plant material, McCLEAN & KEAN (1993, 1996) have proposed that plants can be contributors to the soil magnetism. These saturation isothermal remanence magnetization studies and hysteresis measurements were indicative of magnetite as the dominant magnetic mineral, in the grain size range of superparamagnetic to pseudo-single-domain, with minor antiferromagnetic components. This size range of magnetite is consistent with the findings of many transmission electron microscopy studies of sectioned plant cells, which have revealed micron sized phytoferritin agglomerates made of nanometer sized electron dense cores with ordered, semi-ordered and random self assembly (e.g. review by SECKBACK, 1982). However, the crystal structure of these phytoferritin iron cores has remained unknown, as biominerals are seldomly available in the quantities needed for characterization by X-ray diffraction. In our work we use electron diffraction to get the first determination of the plant iron biomineral phases.

Experimental

Leaf and stem clippings from normal grass (*Festuca* species) were harvested in August 1995 from a rural location in southeast Wisconsin. We used the biochemical procedure of HYDE et al. (1968) to extract and isolate phytoferritin, which was then dispersed on thin amorphous carbon films for studies with transmission electron microscopy (TEM: Hitachi H-9000 NAR, operated at 100 keV). Digitally recorded selected area transmission electron diffraction patterns (SAED) were used to determine the crystallography of the phytoferritin iron core. Two kinds of TEM samples were investigated: standard ultracentrifuged extracts with dispersed phytoferritin nanoparticles; and novel low-speed centrifuged and filtered extracts with micron-sized phytoferritin agglomerates. We used energy dispersive X-ray (EDX) spectrometry (Noran Voyager II) to discriminate between various sub-cellular extracts present in the low-speed centrifuged samples. Only those specimen areas that displayed characteristic Fe peaks in the EDX spectra were analyzed with electron diffraction and imaging. This approach allowed us to investigate the crystallography of both ferromagnetic and antiferromagnetic phases that might be present, as suggested by our magnetic measurements of plant clippings, ashes, and soil phytoliths.

Results

Detailed correlative analysis of 36 SAED patterns and their corresponding TEM images indicate that phytoferritin occurs as crystalline magnetite (Fe_3O_4), ε-Fe_2O_3, and hematite (α-Fe_2O_3), with typical sizes of single crystallites in the 1–50 nm range and agglomerate grain sizes up to 4 μm. The three dimensional agglomerates are built with different biomineral nanocrystals in three distinct modes of biological self-assembly: 1) ordered magnetite; 2) semi-ordered mixture of magnetite and ε-Fe_2O_3; and 3) random hematite. These self-assemblies correspond to prior TEM reports of crystalline, paracrystalline and amorphous phytoferritin arrangements in sectioned cell samples. A fourth plant iron biomineral, tentatively assigned as calcium ferrate hexahydrate, has morphology and diffraction patterns distinct from the phytoferritin aggregates. We did not detect diffraction patterns that are consistent with the 2-line or 6-line ferrihydrite, the postulated form of phytoferritin based on analogies with the animal ferritin (BIENFAIT & VAN DER MARK, 1983).

These diffraction results mark the first discovery of crystalline iron biominerals in plants. Of these four new iron biominerals, three are antiferromagnetic, while magnetite is the only ferromagnetic phase. These results are consistent with the SIRM measurements of McCLEAN & KEAN (1993, 1996). The properties of the observed botanical magnetite are of particular interest in the context of its contribution to plant and soil magnetism. The majority of plant magnetite nanocrystals display cubo-octahedral shapes and narrow size distributions typical for intracellular boundary organized biomineralization processes (LOWENSTAM, 1981). The botanical magnetite nanocrystals are self-organized in ordered micron range agglomerates, distinct from magnetite strings in magnetotactic bacteria (BLAKEMORE, 1975, PETERSEN et al., 1986) and similar to some pedogenic magnetite currently attributed to inorganic processes (HOUNSLOW, M.W. & MAHER, B.A., 1996).

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DISSOLUTION MECHANISMS OF JAROSITE UNDER DIFFERENT CONDITIONS: AN AFM STUDY

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As a result of the oxidation of FeS_2 in brown coal open pit mines, toxic elements are released and then partly fixed in secondary minerals, e.g. in jarosites $[(K,H_3O)Fe_3(SO_4)_2(OH)_6]$. Dissolution reactions of jarosite are of great environmental importance for the reason that flooding a pit possibly results in release of sulfate and toxic elements due to the limited stability of jarosites in a relatively narrow range of acidic conditions. Therefore an understanding of its dissolution behavior is critical to any model of the dynamics of water–dump interaction. Only a few studies have sought to elucidate the dissolution process from a bulk chemical perspective (BARON & PALMER, 1996). Thus mechanisms are still unknown. The dissolution process is influenced by mineral chemistry, surface microtopography and structure. That is why atomic force microscopy (AFM) is used to study at real time mineral surface reactions by monitoring its microtopography during dissolution. The primary advantage of Fluid Cell AFM are *in situ* observations of nanoscale processes at the mineral–water interface, offering unique and complementary features to commonly used techniques.

Synthetic jarosite (012) surfaces grow by a spiral mechanism. The spirals form a single plane like a "staircase" with monolayer steps of about 5 Å in height ($d_{012} \cong 5.1$ Å) originating around a screw dislocation. It could be expected that screw dislocations provide a source of energetically favoured edge sites for dissolution, but neither in acidic solution (HCl, pH 2), in pure water nor in alkaline solution (KOH, pH 10), step retreat has been observed. Spiral breakdown on (012) faces starts at the outcrop of the screw dislocation by a dissolution process reverse to that of spiral growth. But the dominant dissolution process remains the displacement of steps by terrace vacancies, thus removing the topmost layer. It seems that dissolution mechanisms do not depend on the type of solvent (acidic, alkaline or containing complexing agents). The changes of morphology in the presence of an iron complexing agent occur at a significantly faster rate than in pure water and we suggest that the formation of thin iron oxyhydroxide layers by the interaction with water may retard dissolution kinetics. This might be of importance in coal dump sediments containing iron complexing agents like humic acids.

Ex situ AFM observations indicate biologically catalized sulfate reduction under anaerobic conditions. Sulfate reducing bacteria settled on jarosite surfaces. Decomposition of jarosite is proved by the formation of black FeS layers and strong morphological changes due to microbial activity. Runs under identically but bacteria free conditions did not reveal black covers and growth spirals remain almost unchanged. Thus laboratory experiments clearly show that bacteria are able to reduce sulfate from a solid phase.

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USE OF NON-SPECIFIC BACTERIA IN BIOSOLUBILISATION PROCESSES

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Bacillus megatherium, isolated from soil, is used especially in genetic and enzimatic studies. Its use in geochemical investigations like non-specific bacterium (GAVRILOAIEI et al., 1998) may be an interesting alternative of actual biotechnologies.

The use of the *B. megatherium* strain (cultivated in a nutrient medium containing molasses as a source of carbon and energy) in leaching processes lead to some good results in the biosolubilisation of some ionic metals from a sulphide concentrate and a phosphatic rock (GAVRILOAIEI et al., 1998). The solubilisation of ionic metals (Fe, Co, Cu, Zn, Ca) is due to the formation of a weak acidic medium and of the secretion of different amino acids by the bacterium (alanine, serine, glycine) which act like complexing agents for the analysed ions (BURGSTALLER & SCHINNER, 1993). The study of the influence of time on the phosphatic rock solubilisation show a considerable yield in the first 14 h from the beginning of the experiment for Fe, Co, Ca, P, while for the other cations the process is slower.

The presence of some trace elements in the analyzed solutions leads to the conclusion that the non-specific bacterium is also capable to mobilise other metallic cations. The use of the bacterium in biosolubilisation processes is one of the future challenges for ionic metal recovery from mine or waste waters, sterile dumps or in soil bioremediation processes.

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MODELLING OF THE SCALE EFFECT IN MASS ROCK WITH A CASE STUDY IN THE BAIA MARE AREA (NW ROMANIA)

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The paper presents some problems, aspects and novelties related to the modelling of the scale effect in mass rock (Hoek-Brown and Palmstrom criteria, HOEK & BROWN, 1997; PALMSTROM, 1997), along with a case study on fissured massifs from the Baia Mare area, NW Romania, at different values of the RMR parameter.

A matter of permanent interest for ecological engineering in mining zones is the way in which rocks behave in the massif. Such data are important for an economic sizing of the support of mines, as well as for the preservation of the zones after exploitation.

The discipline "resistance of rocks" means decision in certain matters such as stability and deformation resistance of the massifs in the presence of mining works.

The correlation of laboratory data with practical situation is confronted with many difficulties connected to the modelling of the so-called "scale effect".

The traditional procedure consisting of the non-discriminating application of a "reducing coefficient" has often proved to be non-economic and insecure.

Recent research, which led to the elaboration of different indices (e.g. RMR, "Rock Mass Ration", RMI) with regard to the behaviour of rocks in the massif, and the stability criteria recommend more flexible ways of estimating the massif resistance.

In the case study, after the laboratory determination of the RMR parameter and the values of resistance to compression of andesites and sedimentary rocks often seen in the Baia Mare mining area, the differences between the results obtained through the application of the theoretical methods included in our paper are concisely presented.

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SIGNIFICANCE AND FATE OF JAROSITES IN BROWN COAL MINING SITES: A FIELD AND LABORATORY STUDY

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In disused brown coal mining pits ascending groundwater is expected to change chemical conditions and to mobilize hazardous elements. With it, the stability relations of minerals containing iron and sulfur like jarosite $AFe_3(SO_4)_2(OH)_6$ ($A = Na, K, H_3O, NH_4$), schwertmannite $Fe_{16}O_{16}(SO_4)_2(OH)_{12}$ and goethite FeOOH influence the distribution of metals, mainly iron and sulfur between solid phases, surface and ground water.

The present study focuses on jarosite because it has been detected in large amounts in brown coal sites of the Central German and the Lusatian District (Germany). From its iron to sulfur ratio of 1.5 in comparison with 0.5 in the original iron disulfide, jarosite enriches iron and high amounts of sulfate result in the related surface waters. Formation of mainly K-rich jarosite is due to the release of K^+ from the most common K-bearing silicate minerals (muscovite, K-feldspar) of the Tertiary sediments through reaction with sulfuric acid. But also Na-rich jarosites and NH_4-bearing jarosites have been detected. NH_4 might result from nitrate stimulated oxidation of FeS_2. No end member oxonium jarosites have been found in the dump sites until now. But from lattice constants it is likely that part of the alkalis in the jarosite structure is replaced by H_3O.

Investigations of site materials often give only partly information about location, duration and mechanisms of mineral formation. Just these data are needed to reconstruct acidification processes. Therefore mineral precipitation on test substances placed in an acidic mining lake (pH 2.6, Lusatian District) show the most intensive coatings close to the lake surface which have been identified by Raman spectroscopy as jarosite.

Jarosite precipitated in the lake water takes part in the sediment formation: up to 40 wt% jarosite have been measured. Assemblage of goethite, jarosite and rarely schwertmannite in the sediments ($pH \geq 3$) of the lake under investigation indicate instability of jarosite under aerobic conditions. An aim of remediation measures could be to initialize neutralization processes by microbial sulfate reduction. Thus, the behaviour of jarosite under both aerobic and anaerobic conditions has to be known. Laboratory experiments show that by hydrolysis under aerobic conditions sulfate release decreases in the order of H_3O-, Na-, K-, K(Fe,Cr)-jarosite. Cr(III) in the structure seems to stabilize K-rich jarosites. Red-brown coloured surface coatings indicate iron oxyhydroxides. Increasing run duration confirms goethite as a product of hydrolysis for K-rich jarosite. Under anaerobic conditions in the presence of sulfate reducing bacteria, K-rich jarosite decomposes and iron sulfides precipitate as black coloured covers. Jarosite surfaces during and after hydrolysis are characterized using atomic force microscopy (AFM).

Structure refinement from X-ray powder and single crystal investigations as well as IR and Raman spectroscopic measurements supply crystallographic and crystallochemical data which are necessary to calculate the stability of jarosite crystal faces to get to know its surface properties.

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MICROBIAL GENERATION OF ACID DRAINAGE WATERS IN A URANIUM DEPOSIT

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The uranium ore deposit Curilo is located in Western Bulgaria, about 35 km north from Sofia. Uraninite ("nasturane" and "pitchblende") and torbernite are the main uranium minerals in the ore. Some copper is present in the form of minerals such as chalcopyrite, covellite and chalcocite. The ore is rich in pyrite and different iron hydroxides.

For a long period of time the deposit was a site of intensive mining activities, initially by both open-pit and underground mining of high-grade ores and later, by in situ leaching of low-grade ores by means of diluted solutions of sulphuric acid. The uranium recovery was stopped in 1990 but since that time the acid drainage waters generated in the abandoned mines and dumps consisting of mining wastes have been a persistent environmental problem. These waters have a pH in the range of about 2.0–3.5 and contain radioactive elements (uranium, radium, thorium), toxic heavy metals (copper, cadmium, manganese, iron), arsenic and sulphates in concentrations much higher than the relevant permissible levels in waters intended for use in agriculture and/or industry.

The formation of the acid drainage waters was connected with the oxidative activity of the acidophilic chemolithotrophic bacteria which inhabited the uranium deposit. *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* were the most widely distributed and the most numerous species in this microbial community. Their densities in some parts of the deposit exceeded 10^8 cells per g of ore and per ml of drainage waters. Some of the strains of these bacteria differed markedly from each other with respect to their ability to oxidize sulphide minerals, ferrous iron, tetravalent uranium and sulphur. *Thiobacillus thiooxidans* and *Thiobacillus acidophilus* as well as some moderately thermophilic bacteria related to *Sulphobacillus thermosulphidooxidans* and the genus *Thiobacillus* were also found but almost always in lower numbers than *T. ferrooxidans* and *L. ferrooxidans*. The extremely thermophilic chemolithotrophic bacteria related to the genera *Sulpholobus* and *Acidianus* were not detected in the deposit. Several heterotrophic microorganisms were found but it seemed that only those related to the genus *Acidiphilium* were typical members of the microbial community inhabiting the uranium deposit.

It was found that the microbial activity depended on some essential environmental factors such as humidity of the ore, presence of oxygen inside the ore mass, pH and composition of the waters percolating through the ore, and ambient temperature. It was possible to change this activity by suitable changes in the levels of these environmental factors.

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MINERALOGICAL OBSERVATIONS ON DECAY OF HISTORICAL MONUMENTS FROM TRANSYLVANIA

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This paper is part of a larger work dedicated to study the monuments from Transylvania. In this part we try to present some observations on the processes of decay on monuments from Cluj and Braşov and the newly formed minerals which appear.

A video recording presents categories of deterioration and associated minerals present on some monuments from Cluj-Napoca. The second part is dedicated to the monuments from Braşov.

Generally, deterioration begins with the appearance of a net of cracks on the surface. It continues with exfoliation that can reach 1 cm. The undercover material is dusty, irregular and it can be very easily attacked by other factors. The rich vegetation makes the alteration process faster as it keeps humidity high and increases the quantity of CO_2. Deterioration is intense on the W and NW sides of monuments. All the processes lead to the appearance of minerals like gypsum, aragonite and wollastonite. Statues and sculptures not exposed directly to precipitation water are well preserved despite their age. Results presented here lead to the conclusion that the studied limestones are more suitable for ornamentation inside buildings and in protected areas.

In the Braşov region we have studied the following monuments: Weaver's Tower (Braşov), City Walls (Braşov) and Fortress Prejmer (Braşov District). These monuments are built of sandstone, bricks and limestone.

Pollution information is structured in two parts: air pollution and soil pollution. Restoration of Fortress Prejmer was documented two times: July 1998 and March–April 1999. X-ray analysis was also made on samples from these three monuments.

Many X-ray analyses were made to detect newly formed minerals which appear due to processes of dissolution, solvation and precipitation affecting the rocks. The samples were from different materials such as limestone, bricks and black crust. Among the minerals we found aragonite, albite, tobermorite and afwillite.

We can conclude that air pollution plays an important role in the deterioration process. Also, precipitation of soluble minerals and the freeze–unfreeze cycle lead to major exfoliation. Sulfates and sulfites from cement produce gypsum and anhydrite and the growth of the crystals leads to the exfoliation of cement.

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SUPERPARAMAGNETIC MAGNETITE IN THE UPPER BEAK TISSUE OF HOMING PIGEONS

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Introduction

Ferromagnetic material is commonly detected in many organisms, although it is normally present only in minute amounts. With the exception of magnetotactic bacteria its role is not clear. It could be a merely accidental by-product of metabolism, it could play a role in the iron household of the organism, or it could serve a particular function as in the case of magnetite dentical capping in chitons or represent part of a magnetoreceptor.

Here we try to study this question for the case of homing pigeons. WALCOTT et al. (1979) were the first who detected permanently magnetic material in the pigeon head. They found it in tissue between the dura and the skull and identified the concentrated material by Curie temperature measurement as magnetite. This result was in contrast to similar experiments of PRESTI & PETTIGREW (1980) who found no visible magnetic structures in the skull, but reproducible, inducible, magnetic remanence in the neck musculature of the pigeon, which they attributed to the presence of magnetite. Both of these investigations did not come so far to resolve size and nature of individual magnetic particles, nor identify their exact location and possible structural arrangement within the tissue.

Measurement of induced and remanent magnetization

We obtained a first indication of the presence of ferromagnetic material in the pigeon upper beak tissue by a series of magnetization measurements with a SQUID magnetometer, carried out in a similar way as described by WALCOTT et al. (1979) or PRESTI & PETTIGREW (1980). The fresh unfixed tissue did not show a detectable remanent magnetization, but an induced magnetization when measured in 1 Oe. After appr. 30 min, the tissue changed to a state where it did acquire a remanent magnetization (10^{-6} to 10^{-7} emu) after exposure to 1000 Oe. These results indicated to us that the fresh tissue must have been changing rapidly its original structure, probably due to desiccation, thus altering the magnetic particle configuration.

Identification of iron concentrations by Prussian Blue reaction

As next step in our attempt to localize the magnetic material we looked for concentrations of Fe(III) using the Prussian Blue reaction (Tanka and Berschauer, 1969). We made serial histological sections of paraplast and plastic (Epon) embedded upper beak skin from 7 homing pigeons. In the Prussian Blue treated sections iron enrichments show up intensively blue. This way we found in the upper beak skin up to six isolated sites of Fe (III) enrichments arranged in sets of cellular elements, which extend over appr. 200 µm and always occur in the same skin layer (Stratum laxum of the subcutis). They are arranged in connective tissue strands between fat cells. At higher magnification, the Prussian Blue stained regions are resolved to accumulations of discrete, opaque and intensely blue granules of 1 to 3 µm diameter.

Transmission electron microscopy

These granules can be resolved as clusters of extremely fine-grained particles with diameters between 1.5 and 5 nm. Selected area diffraction patterns of these particles show a powder diagram characteristic of fine-grained crystalline magnetite. In combination with the black colour of the clusters in the light microscope these findings are diagnostic for magnetite. We did not detect any other magnetite particles outside the clusters, although the entire tissue was scanned very carefully. Our detection of magnetite in the pigeon tissue confirms the earlier findings of WALCOTT et al. (1979) and PRESTI & PETTIGREW (1980) as described above. However, the grain size observed here is such that superparamagnetic behaviour should be expected for the material at room temperature (BUTLER & BANERJEE, 1975).

Low temperature magnetization measurements

In order to further characterize the magnetic properties of the observed magnetic particles in the tissue low temperature measurements were carried out using a Quantum Design MPMS-XL SQUID magnetometer. A section of the upper beak skin (thickness approx. 1 mm) was embedded in a diamagnetic resin. "Zero-Field cooled" (ZFC) and "Field-cooled" (FC) curves were measured for different applied fields. The ZFC-FC-curves show paramagnetic behaviour up to temperatures of around 20 K. A broad peak is visible at higher temperatures (around 140 K). At applied fields of 100 and 150 G this peak is shifted to slightly higher temperatures (~ 160 K) and disappears at 200 G.

For the remanence decay the sample was initially cooled in zero applied field, then magnetically saturated (H_{appl} 25 kG) at 5 K, and then the remanent magnetic moment was measured in zero field as a function of the temperature. In order to obtain the distribution of the blocking temperatures the remanence curve was differentiated. The data were fitted assuming a log-normal distribution of blocking temperatures as described by BLANCO-MANTECÓN & O'GRADY (1999). We have fitted the data with 3 log-normal distributions. The occurrence of a low and an intermediate blocking temperature (3.4 and 17.3 K) is similar with the studies on synthetic magnetites by BLANCO-MANTECÓN & O'GRADY (1999) who described a bimodal distribution in blocking temperatures due to the growth process by which the particles are formed. The third component is characterized by a blocking temperature of ~ 110 K.

The influence of an applied magnetic field on the peak temperature of ZFC-curves has previously been observed for magnetite (LUO et al., 1991) and γ-Fe_2O_3 (SAPPEY et al., 1997). LUO et al. attribute the increase of T_B with H to the dipole interaction of the particles in a system with a random anisotropy. They also observed an increase of the peak temperature with increasing concentration of magnetite particles.

Taking into consideration the electron microscopical observation the results of the magnetic measurements are interpreted as a combination of two effects: The rapid decay of the magnetization at low temperatures is an indication for very small superparamagnetic particles. The peak at higher temperatures can be attributed to the clusters which consist of agglomerated magnetite particles. This interpretation is supported by the TEM investigations which showed that within the cluster the distribution of the magnetite particles is not completely homogeneous. There are regions with agglomerated and dispersed particles. The results do not give any evidence for single domain particles.

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PHASE COMPOSITION OF ATMOSPHERIC DUST COLLECTED AT DIFFERENT HEIGHTS

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Samples of suspended and fallen dust were collected in two cities (Katowice and Sosnowiec) in the industrial region of Upper Silesia (Poland), at the heights of 2.5, 60 and 90 m above ground level (a.g.l.). Samples were collected monthly from December 1994 to June 1997.

Dust particles were analysed by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and transmission electron microscopy (TEM).

Regardless of the collection height, all the samples contained the same major phases: quartz, aluminosilicates (with different amounts of K, Fe, Na, Mg, Ti, Mn, Zn), calcium sulphates (gypsum, bassanite), iron oxides (hematite, magnetite, wüstite), coke and soot. Some of them were reported earlier (MANECKI et al., 1984; RIETMEIJER & JANECZEK, 1997; ZELECHOWER et al., 1998).

However, the samples had significantly different minor phase compositions. Minor phases were particularly abundant in fallen dust collected at 60 and 90 m a.g.l. and in suspended dust at 2.5 m a.g.l. Minor phases include: feldspars, calcite, lead sulphide, lead chloride, barite, halite, sylvite, magnesium sulphate and ilmenite. Lead oxide, TiO_2 and Al_2O_3 were only observed at 2.5 m a.g.l. Sulphur, olivine, spinels and ankerite were identified solely at 60 and 90 m a.g.l.

Size and shape have strong impact on the residence time of those particles. Particles larger than 10 µm fall to the ground very fast. Smaller particles in the form of spheres also reach the ground faster, because their air resistance is relatively small. Studies of natural dust in the lower stratosphere describe non-spherical particles which are a few nm in size, reside in the air long, and are also influenced by long distance transport (RIETMEIJER, 1987, 1993).

Samples collected at 60 and 90 m a.g.l. were enriched in respirable particles. They commonly contained rare phases with heavy metals. Due to their small size and irregular shape, respirable particles reside in the air for a long time and can be transported far away from their source of origin.

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ENVIRONMENTAL MINEROLOGICAL STUDY OF SOIL OF THE CSEPEL ISLAND (HUNGARY): TRACING THE TOXIC HEAVY METALS (V, Ni)

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The „Dunamenti" Thermal Power Plant (DTPP) has been working since 1959 at Százhalombatta, 20 kilometres south from Budapest. The power plant operates on extra heavy fuel oil containing 3.5% S on average and small amounts of vanadium (50 ppm) and nickel (15 ppm). It has emitted more than 1000 tons of heavy metal containing solid pollutants into the air for the last 40 years. More than 95% of the flying ash's metal content are vanadium and nickel compounds. The flying ash settled down on the ground according to its morphology, size and density. Considering the dominant direction of wind, the main area of dustfall pollution is the Csepel Island in the Danube.

Up to now no extensive investigation has been carried out to discover the penetration of heavy metal pollution into the soil. Beside the assessment of environmental damage, our primary goal was to describe the mobilisation–fixation properties of the soil-forming minerals. We took 5 drill core soil samples (from surface down to 1 meter depth) from different locations of the Csepel Island. Each location is 5–10 km far from the thermal power plant (this might be the maximum spread of significant pollution, GANOR et al, 1988). The soils are alluvial meadow soils and alluvial soils (Fluvisols, FAO classification).

XPD qualitative and quantitative phase analyses, thermoanalythical, ICP-MS, and different chemical separation methods were used. The XPD and thermoanalytical results show a very similar composition for the soils samples. They consist of quartz (40–50% on average), a significant amount of feldspars and carbonates (calcite and dolomite, up to 40%) and small quantities of clay minerals and other sheet silicates (illite, smectite, chlorite, kaolinite), as measured by XPD quantitative phase analysis. Different chemical digestion methods were used. To determine the total amount of V and Ni aqua regia microwave digestion was used. The total amount of V and Ni are 14–28 and 10–35 ppm, respectively. The main interacting soil constituents are: calcite (5–10% of the total amount of V and 10–20% of Ni, acetic acid digestion), organic matter (5–7% of both V and Ni, NaOH digestion), amorphous iron (oxy)hydroxide (50–70% of both V and Ni, hydrochloric acid digestion) and clay minerals (1–10% of both V and Ni, KNO_3 digestion). Good correlation were found between the amount of Fe and V, and V and Ni contents.

In order to be able to draw a general conclusion from the data obtained by these investigations, our analytical results are subjected to the fuzzy logic statistical method.

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ZEOLITIZED VOLCANICLASTIC MATERIALS FROM GREECE TO BE USED IN TACKLING ENVIRONMENTAL PROBLEMS

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The investigation of a series of volcaniclastic deposits from various places in Greece proved that the matrix of these materials has been greatly altered to a variety of authigenic zeolite and clay minerals. The formation of such mineral types within volcaniclastic materials is the result of the alteration of volcanic glass. Zeolitized materials from various deposits in Northern Greece and the Santorini, Milos, Kimolos, Polyegos, and Samos Islands were examined. By using XRD, SEM and EPMA it was shown that the dominant zeolite mineral is either clinoptilolite or mordenite. Materials containing up to 80% of zeolite minerals were identified. Smectite, occasionally illite/smectite is the dominant clay mineral. Opal-CT, cristobalite, quartz, kaolinite, feldspar, amphibole, Fe-Ti oxides, biotite and halite often complete the mineralogy of these materials.

The cation exchange capacity (CEC) is one of the most important property of zeolites. CEC results from the presence of loosely bound cations in the structure of the zeolites which are easily exchanged when the zeolites come in contact with solutions of "saturating" or "indexing" ions. The CEC of the zeolitized materials was measured using the ammonium acetate saturation method. The obtained CEC values exceeded 200 meq/100 g in some cases.

So, the composition, purity and high CEC value of zeolitic materials from certain deposits indicate that the Greek zeolitic materials could have numerous applications with respect to the environmental protection area. They can be effectively used **a)** to remove NH_4^+ and phosphate from various types of wastewaters such as municipal effluents, wastes from urban landfills, animal sewage, and other agricultural and aquacultural effluents; **b)** to remove heavy metals such as Pb, Cd, Zn, and Cu from industrial waste effluents; and **c)** to be added to clay-based (with relatively low CEC) liners of waste repositories, in order to enhance the total CEC of the liner and, thus, its retardative properties.

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COPPER CONTAINING MINERALS BEFORE AND AFTER ELECTRODIALYTIC REMEDIATION

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Electrodialytic remediation (EDR) is a method that has proven to be useful for the remediation of soil polluted with heavy metals (HANSEN et al., 1997; KLIEM et al., 1999). Earlier experiments have shown that addition of reacting agents will improve the electrodialytic soil remediation process (e.g. OTTOSEN et al., 1999).

Soil polluted with copper has been investigated. The pH of the soil was 7.5, content of carbonates was 12%, and the copper concentration 20000 mg/kg DM. After remediation, the copper concentration was 1050 mg/kg DM. The soil was investigated by different analytical methods: scanning electron microscopy (SEM), connected to an EDX-analyser, X-ray powder diffraction (XRD), and X-ray absorbance fine structure (XAFS).

Sample of the soil <250 µm showed that copper could be found in mainly three different phases. The first phase showed almost pure copper in EDX spectra (H, C and O cannot be detected) and minor amounts of Zn, Fe, Al and Si, in the second phase Ca and Cu were found together, and in the third phase copper was found in particles in connection with Si and Ca. When a separation of the particles <20 µm was made, only the first copper phase was found. Here copper was found in spherical particles, which were hollow. These particles were most probably malachite also found in XRD and EXAFS. In the sample remediated as much as possible by EDR, copper could not be found as malachite, which contained the main part (90%) of copper before remediation.

SEM analytic methods showed that copper in the untreated soil was situated as pure copper (H, C and O were not included), and XRD showed that copper was bound in copper hydroxycarbonates. EXAFS measurements verified these results, as they showed a good agreement between the pure copper hydroxycarbonate reference and the soil sample. EXAFS showed no significant peaks for copper hydroxycarbonates in the soil that was remediated by the EDR technique. This means that the copper hydroxycarbonates were the part of the copper that was remediated, and the remaining copper was situated in some other minerals, which are obviously more difficult to extract. The main problems seem to be the possibility of slow kinetics of the reaction between the copper compounds and the desorbing agent, and the risk for no reaction.

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THE GEOMORPHOLOGICAL STUDY OF THE COMPLEX LANDSLIDE IN TULBURE VALLEY, CHIUZBAIA (NW OF ROMANIA)

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The geomorphological study of the complex landslide in the Tulbure Valley zone has pointed out the presence of a landslip from the category of those formed through water saturation.

Taking into account the geological structure and the morphology of the region, the following ways of formation of the sliding beds have been distinguished: bed formed through the saturation of a Pannonian clay marl intercalation by meteoric water, Levels 1 and 3 (see picture: the precipice and the sledded body with transversal fissures); bed formed in the Pannonian clay marl deposits, through saturation by meteoric and phreatic water, Level 2; bed formed in the zone of lithological contact through the saturation of the Pannonian clay marls that have slided onto the rough andesitic substratum by meteoric water, Level 4; bed formed along a stratification through the saturation of the Pannonian clay marl intercalation, Level 5, protruding precipice on the left; bed formed through the saturation of the clays resulted from hydrothermal alteration by meteoric water, Level 5, precipice on the right.

The presence of some morphological aspects that have rarely been described has also been made evident.

The conclusions present a summary regarding the activity of the landslide and the affected areas.

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DISSOLUTION RATE OF RECRYSTALLIZED CARBONATE ROCKS FROM THE BÜKK MOUNTAINS (NE HUNGARY): THE EFFECT OF ROCK TEXTURE

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The investigation of dissolution kinetics of carbonate rocks has been an important issue since the late 1970s. The early works were focused primarily on the understanding of carbonate dissolution and precipitation processes in marine environments and during the diagenesis. The dependence of dissolution rate on the composition and dynamics of the dissolving fluid as well as on textural factors such as grain size and surface roughness were studied in detail. Recent works focus on the dissolution processes of karstic regions, which are environmentally highly sensitive areas (e.g. the IGCP 379 project or the FRACFLOW project).

This paper summarises the results of dissolution experiments completed on samples of different carbonate facies from the Bükk Mountains (NE Hungary). All investigated limestones are of Triassic age and had been recrystallized by the Alpine metamorphism up to very low – low grade. Some of these stratigraphic units have been the scene of recent and ancient karst formation. Our experiments include runs of dissolution tests on both karstic and non-karstic limestone formations.

The rotation disk technique (see e.g. ZAIHUA & DREYBOLT, 1998) was applied to investigate the dissolution rate. Since the main question was how the dissolution process depends on textural parameters of the rocks, the experimental conditions were set up for "reaction-controlled" dissolution. Consequently, low degree of undersaturation and high rotation speed were chosen (3×10^{-4} mol/l initial $CaCO_3$ solution, low CO_2 pressure, 600–2500 rpm).

To control the changes at the rock's surface (a polished and etched disk cut from a drill core), the surface roughness was measured before and after a dissolution cycle by a laser scan micrometer and the texture was characterised by optical methods.

The results show that - considering textural parameters -, the dissolution rate depends not only on the grain size and surface roughness but also on the textural position of the grain. Coarse grains of calcite vein fillings that are of pre-metamorphic origin are dissolved at the same rate as the microcrystalline matrix. Conversely, the post-metamorphic vein fillings are dissolved significantly slower.

Mrs. Tolvaj (Department of Production Technology, University of Miskolc) is thanked for the surface roughness measurements. The help of Mrs. Emese Szántó (Department of Physical Chemistry, University of Miskolc) in the dissolution experiments is gratefully acknowledged.

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THE ETRUSCAN-TO-MIDDLE AGE COPPER-SILVER-LEAD SLAGS FROM CAMPIGLIA MARITTIMA

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The Campiglia Marittima area (Southern Tuscany) has been long exploited for Cu-Pb-Ag mineralizations (skarn deposits formed mostly by hedenbergite, johannsenite and ilvaite with Cu, Pb, Zn and Fe sulphides).

An important mining activity started there in Etruscan time (8th–3rd c. BC). The mining activity was mostly addressed to the extraction of Cu (from chalcopyrite), Pb and Ag (from silver-rich galena). The centre of metal processing was the Capattoli Valley, where abundant slag heaps occur. The segregation of metals was obtained by smelting in appropriate ovens and subsequent gravimetric separation of metals (at the bottom of the oven) and silicate melts (at the top of the oven).

Slags are mainly formed by SiO_2 (mean value 27.7 wt%), FeO (47.5 wt%) and CaO (9.1 wt%), with minor Al_2O_3, MgO and MnO contents: major element contents reflect the original composition of the raw material used in the process. The Cu, Pb and Zn contents give information about the effectiveness in metal segregation. The Cu content is always low (mean value 2700 ppm), whereas Zn is systematically higher (mean value 36700 ppm), as this element was neglected in the smelting process. Pb occurs in variable amounts, ranging from 5300 to 33900 ppm. In particular, we identified two different compositional groups, high Pb in CaO-poor slags and low Pb in CaO-rich slags, the latter corresponding to higher segregation effectiveness.

The slags are mostly formed of olivine, with variable Fe/Ca ratio: in particular, CaO-poor slags consist of fayalite whereas CaO-rich slags contain two different olivines, a Ca-rich fayalite and a Fe-rich kirschsteinite. Pb and Zn occur as sulphides (galena and sphalerite, respectively), whereas no evidence for chalcopyrite has been found, possibly due to the low Cu content. Slags also contain an amorphous silicate glass, formed by Si, Ca, Fe and Al, with minor Na and K. Na and K could be derived from the charcoal and/or firewood as well as from the oven walls, which were built of porphyry and clays.

The mineralogical characterization of slags from Capattoli has been useful to understand the ancient metallurgic technique used in this area and the effectiveness of the metal segregation process. Cu segregation was attained in all the slag heaps. In contrast, the segregation of Pb was successfully attained only in the ovens working with CaO-rich charges: this could reflect different ore compositions as well as different processes (for instance, addition of limestone fluxes).

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IMMOBILIZATION OF LEAD – AN EXAMPLE OF AFM APPLICATION TO ENVIRONMENTAL MINERALOGY

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Apatite has been used to remediate Pb contamination. Apatite dissolution releases phosphate, which combines with Pb to form highly insoluble Pb phosphate mineral pyromorphite $Pb_5(PO_4)_3Cl$ (PY). A combination of atomic force microscopy (AFM) with scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and atomic absorption spectroscopy (AAS) were used for *in situ* and *ex situ* examinations of the interface and the reaction products. Experiments were performed with natural chlorapatite (CAP) and fluorapatite (FAP), and with synthetic hydroxylapatite (HAP).

Heterogeneous and homogeneous precipitation of PY was observed. Heterogeneously grown PY crystals form by epitaxy, exhibiting spiral growth patterns on AFM images. For a better understanding of possible epitaxial relationships between the atomic structures of Ca- and Pb-apatites, atomic models for different crystallographic planes were computed using the program ATOMS^{TM}.

In situ Tapping Mode AFM imaging with the aid of fluid cell attachment coupled with *ex situ* SEM/EDX revealed that heterogeneous PY precipitation did not prevent the continuation of apatite dissolution. The presence of Pb_{aq} increased apatite dissolution rates, most probably because formation of PY acted as a sink for dissolved phosphate hence increasing the thermodynamic drive for dissolution. The results indicate that *in situ* immobilization of Pb_{aq} by apatite amendments to contaminated soils may take place both on the apatite surface in contact with Pb_{aq} (mostly heterogeneous precipitation) as well as in the soil profile as a result of a reaction between Pb^{2+} and dissolved phosphates released from leaching apatite (mostly homogeneous precipitation).

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MICROBIAL INTERACTIONS IN THE ALTERATION PROCESSES OF NATURAL BASALTIC GLASS: TEXTURAL EVIDENCES IN PILLOW BASALTS FROM THE EASTERN FLANK OF THE JUAN DE FUCA RIDGE

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Many recent studies have shown the importance of microbial interaction in the alteration processes of natural basaltic glass (FISK et al., 1998; FURNES & STAUDIGEL, 1999). This interaction may be direct, through release of specific enzimes, or indirect, through chemical action of their metabolic products, through the immobilization of specific substances on their cell surface, or through modification of pH and Eh conditions of the environment (THORSETH et al., 1992). Pillow basalts (0.8 to 3.5 Ma old), with glass rims up to 5 mm thick, were recovered during ODP Leg 168 from nine sites drilled across the eastern flank of the Juan de Fuca Ridge (from about 20 km to roughly 100 km east of the ridge axis). The glassy rims show variable degree of palagonitization which increases regularly with the age of the oceanic crust. The degree and the style of the glass alteration are strictly related to the presence of concentric and radial cracks and veins (generally < 0.5 mm wide). Most of the cracks and veins are characterized by the presence of palagonite rinds, often showing different altered zones. Microscopic textures suggestive of a microbiological origin have been found adjacent to hair-sized fractures and clay-filled veins and vesicles in some samples from the oldest sites (2.6–3.5 Ma). The most common features are elongated channels, up to 5 μm in diameter, which occur along fractures or clay veins and extend for several tens of micrometers into unaltered glass. Most channels taper down in diameter and are irregular and frequently convoluted. Some channels bifurcate into two or more branches and are commonly characterized by distinctly segmented or septate textures. Other channels may contain one or more small spherical balls with a diameter that fills the channel, usually at a bend or near the tip. Other features that might be related to microbial alteration include isolated hemispherical patches of alteration that occur along fractures in glass, and coarse optically fuzzy protrusions, tens of micrometers across and slightly elongated, that extend from clay-filled vesicles into fresh glass. Features very similar to all of these have been explained as a result of bacterial activity on alteration of glass from a number of subseafloor samples (FISK et al., 1998). Preliminary statistical studies performed with epifluorescence microscopy observations on DAPI (diamidino-2-phenylindole)-stained samples systematically show the presence of DNA within some of the channels and in scattered areas around the hair-sized fractures. Further studies are in progress to confirm the presence of bacterial activity during the alteration of the glassy rims and to clarify the relationship between microbiological and inorganic/hydrothermal palagonitization processes.

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SOILING OF STONE MONUMENTS: MINERALOGICAL AND CHEMICAL ANALYSES OF DARK SURFICIAL LAYERS (CASTLES AROUND CRACOW IN POLAND)

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Optical microscopy, scanning electron microscopy with energy dispersive spectrometry (SEM-EDX), X-ray diffraction (XRD) and atomic absorption spectroscopy (AAS) were used for examination of black patinas coating the surface of stones in the monuments made of Jurassic limestones. Jurassic limestone has been used in the Cracow architecture since the 11th century. It was also applied for constructing defence castles near Cracow in the Ojców National Park (SCHEJBAL-CHWASTEK & MARSZAŁEK, 1999).

The crust contains mainly fly ashes (porous, partly coked carbon particles, smooth and porous spheres of glass particles), iron oxide and gypsum crystals. Gypsum shows several morphologies from euhedral to anhedral crystals. It also fills pores inside the stone: gypsum was found in layers 300 μm distant from the surface.

Chemical analyses have revealed higher than natural surface concentrations of Zn, Pb, Cd, Fe, Mn, Cu and Ni of the rock.

The main source of the chemical composition of these surficial layers is seen in overall air pollution (MANECKI et al., 1997).

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GREIGITE FROM ROCKS: BIOGENIC OR NON-BIOGENIC?

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Iron sulfides that commonly occur in rocks include pyrrhotite ($Fe_{1-x}S$) of magmatic or metamorphic origin, pyrite and marcasite (both FeS_2), and greigite (Fe_3S_4). Pyrite and marcasite are paramagnetic, i.e., they contribute only to the magnetic susceptibility. Monoclinic pyrrhotite and greigite have ferrimagnetic properties; thus, they may also contribute to the remanence. When greigite was discovered and identified in rocks, it was first considered to be rare. However, greigite and pyrrhotite as carriers of the natural remanent magnetization in sediments have been increasingly reported over the last decade, and magnetic methods to screen rocks for the presence of ferrimagnetic iron minerals and for their identification have been developed.

Iron sulfides in sediments can be of either inorganic or biogenic origin. Biologically-induced mineralization (BIM) is known to produce greigite as an intermediate in a reaction sequence that starts with precipitated amorphous iron sulfide and terminates with pyrite (MORSE et al., 1987). Greigite is also produced by biologically-controlled mineralization (BCM) in magnetotactic bacteria (HEYWOOD et al., 1990). Except for a study that described presumably BCM greigite from soil (STANJEK et al., 1994), we have no information about the potential contribution of bacterial greigite to the magnetic signal of sediments or rocks.

In the Pannonian basin and its surroundings there are several occurrences of dark grey clay and marl that have been studied in the last three years primarily for obtaining paleomagnetic directions of tectonic value or for magnetostratigraphy; these rocks display magnetic properties characteristic of magnetic iron sulfides. We selected half a dozen samples from the above outcrops in which greigite was the likely carrier of the remanence, and studied them using analytical transmission electron microscopy (ATEM).

Electron diffraction and energy-dispersive X-ray spectra confirmed the presence of greigite and pyrite in two samples, a marl that deposited in a brackish environment (Laki, Poland), and a salty marl that formed in a hypersaline basin (Mihalovce, Slovakia). In the Laki specimen greigite crystals occurred in clusters, attached to the surfaces of clay minerals. The crystals typically showed non-uniform, blotchy contrast in the TEM (Fig. 1b). Similar spotty contrast was observed in BCM greigite from magnetotactic bacteria (Fig. 1a), and interpreted as resulting from a partially completed solid-state transformation of a precursor sulfide (mackinawite) into greigite (PÓSFAI et al., 1998). Greigite grains in the Mihalovce sample looked different from those in the Laki rock; they occurred in large clusters together with pyrite, and showed uniform black contrast (Fig. 1c).

A knowledge of the crystal size distribution (CSD) of a population of crystals is useful for assessing possible growth mechanisms (EBERL et al., 1998). We compared the CSDs of three populations of iron sulfide crystals, including bacterial (BCM) greigite and greigite from two rock specimens (Fig. 2). The CSD of bacterial greigite shows an almost perfect bell-shaped or normal distribution (Fig. 2a), in contrast to CSDs of BCM magnetite crystals that are asymmetric (DEVOUARD et al., 1998). The CSD of greigite from the Laki sample (Fig. 2b) is similar to that of bacterial greigite; however, the maximum of the curve is at 120 nm, indicating that greigite crystals in this rock are about twice as large as those from the MMP. The CSD for the Mihalovce sample differs significantly from both the bacterial and the Laki greigite CSDs: it has an asymmetric "tail" extending to large crystal sizes, and a maximum of the frequency at 400 nm (Fig. 2c).

The CSD for the Mihalovce sample can result from surface-controlled growth in an open system (EBERL et al., 1998), and both the CSD and the peak value are consistent with a framboidal (BIM) origin (WILKIN et al., 1998). On the other hand, the CSD and typical contrast features of greigite crystals in the Laki sample make it very likely that these grains are of BCM origin, even though they are larger than greigite crystals produced by contemporary magnetotactic bacteria.

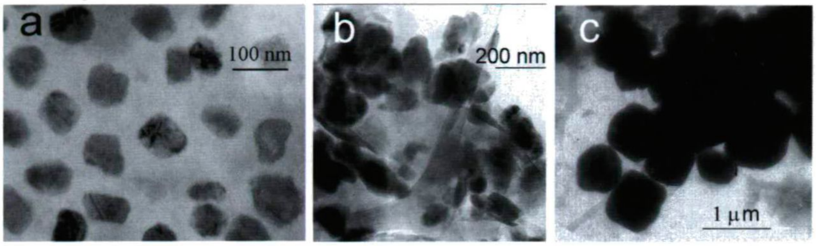

Figure 1. Bright-field electron micrographs of clusters of greigite crystals from (a) a multicellular magnetotactic prokaryote (MMP), and from rock specimens from (b) Laki, and (c) Mihalovce. Note that in (a) and (b) greigite crystals show uneven, spotty contrast in the TEM, whereas in (c) the rounded and relatively thick crystals produce uniform and dark contrast.

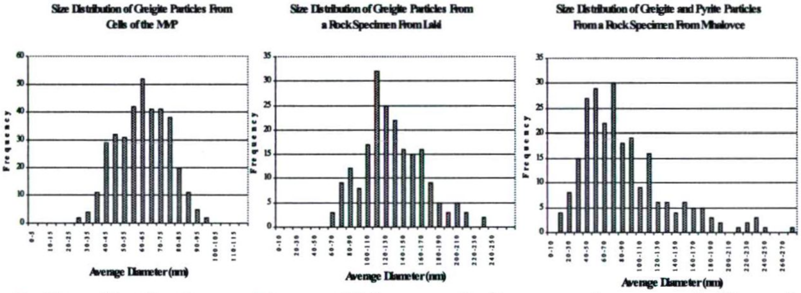

Figure 2. Size distributions of iron sulfide crystals from specimens as indicated on top of the figures

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ENVIRONMENTAL INFLUENCE ON STONE DAMAGES OF THE MONUMENT “OSLOBODIOCIMA BEOGRADA 1944” (SERBIA)

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The monument “Oslobodiocima Beograda 1944” is located in a highly polluted district of Belgrade, about 1.5 km southeast from the center of town. All surrounding streets have heavy traffic virtually throughout the day, which results high atmospheric (SO_2, CO_2, NO_x) and acoustic pollution around the monument. The city has a typically medium continental climate with wet and hot summers, and long cold winters, often with fog and snow. Average yearly precipitation, number of frosty days and high relative humidity in winter undoubtedly accelerate the degradation of sandstone and limestone. The yearly average pollutant concentrations are relatively high, with yearly maximum average above the sanitary limits in Belgrade. SO_2 in the air changes the pH of rain. These acid rains attack stone blocks. During the last ten years, contents of SO_2 and smoke show a descending trend, but even their lower contents are pernicious for rocks.

The monument was built in 1954. The main portal, platforms and steps were made of sandstone blocks and the base-reliefs of limestone. Forms of weathering observed on the monument were: exfoliation, cracking, grain disaggregation with loss of reliefs. The particular types of deterioration of the stone are black crusts and the appearance of efflorescence along the mortar joints of sandstone blocks and on the surfaces of base-reliefs built of limestone.

The data of X-ray diffraction show that the efflorescence consists essentially of halite [NaCl], thenardite [Na_2SO_4], aphthitalite [$(K,Na)_3Na(SO_4)_2$] and gypsum [$CaSO_4 \cdot 2H_2O$].

The black crust, a typical weathering phenomenon on buildings in urban areas, is formed on the block surfaces that are not exposed to rain influence. They are composed of gypsum mixed with soot particles. Blistering and peeling off of the crust cause disintegration of stone surface.

Halite is originated from streets salted during winter. SO_2 from the atmosphere affects the surface of limestone and sandstone containing $CaCO_3$ as a binder as well as the mortar between blocks. When sulfur compounds are adsorbed on the stone surface or along joints of blocks, a series of reactions begin and gypsum is generated as end product. Na and K (thenardite and aphthitalite) probably derive from air pollution or the material of the mortar.

The rate of stone decay is effected by a number of factors, both natural and man-made, of which humidity, temperature and atmospheric (urban) pollution are the most important as well as superficial working of stone blocks. The obtained results suggest that the main causes of sandstone decay are water and frost, but also important are the sulfur compounds precipitating from atmospheric pollutants.

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PHYSICAL AND MAGNETIC MICROSTUCTURE OF BACTERIAL MAGNETITE FROM ELECTRON HOLOGRAPHY

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Introduction

Magnetite crystals in magnetotactic bacteria are typically organized in chains and have specific crystal morphologies within each cell type. In some bacterial strains, the crystals are cuboctahedra comprised of {100} and {111} forms. In other bacterial strains, the crystals are elongated along a [111] axis parallel to the chain direction and have idealized habits comprising {100}, {111}, and {110} forms. In these habits, the six, eight, and twelve symmetry-related faces of the respective forms expected for the face-centered (Fd3m) spinel structure are not equally developed (DEVOUARD et al., 1998). The elongated magnetite crystals are typically ca. 40 to 100 nm long, within the permanent, single-magnetic-domain size range.

Magnetotactic bacteria collected from a brackish lagoon at Itaipu', located on the coast of Brazil north of Rio de Janeiro, contain chains of magnetite crystals with lengths up to 200 nm (FARINA et al., 1994; LINS et al., 1994). As the magnetic single-domain to multi-domain transition dimension in magnetite is not well understood and varies with axial ratio (DUNLOP & OZDEMIR, 1997), it is uncertain whether the magnetite crystals in the Itaipu' bacteria are permanent single domains or metastable single domains resulting from magnetostatic interactions between crystals in the magnetosome chains. Here we report on a study of the micromagnetic structure and crystal morphology of magnetosome magnetite crystals in the magnetotactic bacteria from Itaipu' by off-axis electron holography (EH), high-resolution transmission electron microscopy (HRTEM), and electron diffraction (ED).

Methods

Two strains of coccoid magnetotactic bacteria, IC-1 and IC-2, were collected and whole cells, or magnetosomes extracted from disrupted cells, were deposited on TEM grids. EH, HRTEM, and ED measurements were carried out as previously reported (DUNIN-BORKOWSKI et al., 1998; DEVOUARD et al., 1998).

Results and Conclusions

IC-1 cocci contain two chains of large magnetosomes with quasi-rectangular planar crystal projections. IC-2 cocci have smaller magnetosomes with elongated rectangular projections. From HRTEM and ED, it was inferred that the idealized habit of the crystals in IC-2 cocci consists of combinations of {100}, {111} and {110} forms, with pseudo-hexagonal prisms of six elongated (110) faces. This morphology is consistent with the electronic contribution to the EH phase deviations in [110] and [112] zones perpendicular to the [111] elongation axis, which show a (110) face (flat top) perpendicular to the beam, and an intersection between adjacent (110) faces (tent-top) perpendicular to the beam, respectively (figure 1). The corner faces of the crystals in IC-1 cocci are less prominent, but the HRTEM, ED, and EH data show that these crystals also have idealized habits consisting of pseudo-hexagonal prisms comprising six slightly elongated (110) faces. This is the first report in which three-dimensional information obtained by EH has been used to confirm the morphology of bacterial magnetites derived from two-dimensional projections.

Based on the magnetic contribution to the EH phase deviations, the crystals in IC-2 cocci are true single-magnetic domains. The crystals from IC-1 cocci are also single magnetic domains when in a chain configuration. A fortuitous configuration was also found in the crystals extracted from disrupted cells that comprised three large crystals and three elongated crystals, from IC-1 cocci and IC-2 cocci, respectively, with the large crystals forming a right angle. Analysis of the magnetization before and after application of a magnetic field greater than the coercive field indicate that the large crystals can support domain walls. Hence the large crystals in magnetosome chains in IC-1 cocci from Itaipu' are metastable single-magnetic domains.

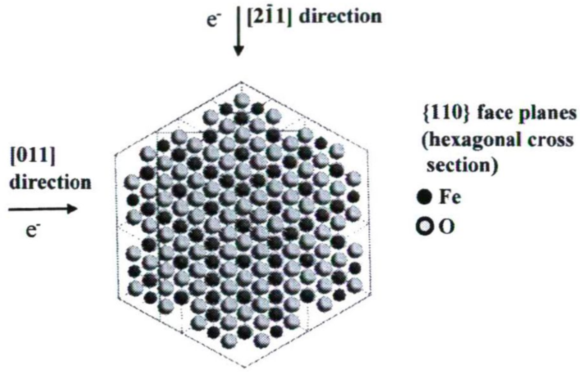

Figure 1. Model of a cross-section of the magnetite structure viewed along the [111] axis of elongation in which six [110] face planes are seen edge-on.

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MAGNETIC CHARACTERISATION OF URBAN DUST AND POTENTIAL USE OF MAGNETIC MONITORING AS A METHOD OF HEALTH RISK ASSESSMENT

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In recent years there has been a renewed interest in the magnetic properties of dusts, and in particular the potential of using magnetic techniques as a method of health risk assessment. To do this it is necessary to have a good understanding of the magnetic constituents of dust both of natural and anthropogenic origin. Although previous studies have been revealing, there are still uncertainties as to the nature and origin of the magnetic signature. In this study, we have conducted a detailed magnetic study of several dust samples collected from various localities in and around Munich, and attempted to characterise magnetic properties. We have utilized several different approaches; from standard techniques such as magnetic hysteresis and SEM analysis to non-standard rock magnetic techniques such as Mössbauer spectroscopy and rotational hysteresis. When used with magnetic techniques, Mössbauer analysis is a particularly powerful tool which has not been readily utilized in previous dust magnetic studies. Early results suggest that the magnetic signature is carried by a combination of near-iron and magnetite-like grains in the smallest and most dangerous grain size fraction (< 1.1 μm). In an attempt to correlate the dust studies with dust actually trapped within the lung, preliminary results from dogs' and cats' lung tissue are also presented, and compared to the dust measurements.

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VITRIFICATION OF JAROSITE WASTE FROM ZINC ELECTROLYTIC EXTRACTION PROCESS

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Wastes arising from primary raw materials refining and metal extraction plants are presently landfilled. Projects of re-utilisation as secondary raw materials have been presented proposing interesting solutions to the environmental problems generated by waste disposal and providing a new source of raw materials. Jarosite is a by-product generated in zinc hydrometallurgy during the separation of iron after the hot acid leaching of roasted sphalerite concentrate. The jarosite process is a simple and low cost technology but involves the production of a huge quantity of hazardous waste (0.4 t per ton ore).

In this study, the possibility of reutilising jarosite as a secondary raw material by means of vitrification has been investigated.

The wastes were characterised by XRF spectroscopy and the results showed the presence of the elements Fe, S, Si, Zn and Pb. They were subjected to the TCLP (Toxic Characterization Leaching Procedure) by putting them in contact with distilled water for 24 h at constant pH 5 and the leachate was analysed by means of atomic adsorption. In the leachate, zinc (15.5 mg/l) and lead (4.0 mg/l) concentrations largely exceeded the European limits.

Different batch compositions were prepared by mixing jarosite with silica-rich wastes such as granite mud and glass cullet. Fusion was carried out in corundum crucibles in an electric furnace in the 1400–1450 °C temperature range. Glass frit, glass-ceramic tiles and glass fibres were obtained. The materials were characterised in order to investigate their stability and the possibility of re-utilising them in the building industry.

The results obtained highlighted the possibility of incorporating a consistent amount of wastes into glass form products. It has been possible to stabilise hazardous components in glass batches containing up to 50% of waste. The final glass easily passes the TCLP test. The jarosite glasses have characteristics such as density 2.8–3 g/cm^3, thermal expansion 7–8$\times 10^{-6}$ K^{-1}, and chemical durability in acid and basic media, comparable to that of commercial materials.

The vitrification-recycling of wastes is a combined process that offers solutions to the environmental impact of zinc extraction activities and opens large opportunities for the valorisation of wastes.

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MAGNETOTACTIC BACTERIA AND SIZE DISTRIBUTIONS OF THEIR MAGNETITE INCLUSIONS FROM HUNGARIAN STREAMS AND LAKES

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Magnetotactic bacteria play a significant role in the formation of single-domain magnetic iron minerals on a geological scale. Studies of the sizes, habits, compositions, and microstructural characteristics of iron oxides and sulfides from magnetotactic bacteria can provide information on biogenic mineral-forming processes, and the results can be used to define criteria for identifying bacterial crystals in geological samples. We collected sediment and water samples from 20 lakes and streams in Hungary during August and September, 1999; these freshwater bodies can be regarded distinct and typical environments of current sediment formation. All samples contained magnetotactic bacteria. Based on size, morphology, speed and mode of swimming, we distinguished six common magnetotactic organisms. In some samples magnetotactic bacteria occurred in such large numbers that they may be dominant species in the microaerobic zone of the sediment.

The morphologies and size distributions of magnetite inclusions were studied in two widespread magnetotactic species, a helicoid bacterium from Gyöngyös stream, Szombathely (designated MH-1) and a diplococcus from Malom Lake, Tapolca (MDC-1). We performed statistical analyses of the sizes and habits of magnetite crystals from both organisms; we used the same procedure as described by DEVOUARD et al. (1998). The shape factor (elongation) distribution has a sharp maximum around 0.85 in MH-1 and between 0.60 and 0.65 in MDC-1. The size distribution histograms show distinct asymmetry with sharp cut-offs towards larger sizes (consistently with earlier observations on other magnetotactic species by MELDRUM et al. [1993] and DEVOUARD et al. [1998]), with maxima between 55–70 (MH-1) and 80–90 nm (MDC-1). The shapes of the size distribution curves for length and width values match those model results of EBERL et al. (1998) that result from Ostwald ripening, during which the relative rate of crystal dissolution and growth is controlled by differences in specific surface area and by diffusion rate. It is possible that several crystals nucleate within the same magnetosome vesicle, but only one will grow to the strain-specific size at the expense of the other nuclei. The distribution histogram for magnetite particles from MH-1 contains a small peak at 30–35 nm, the presence of which may be explained by crystal agglomeration that is known to produce multimodal size distributions (EBERL et al., 1998). Such agglomeration of crystals could take place at the ends of chains, and may be responsible for the production of twinned crystals.

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TENGIZITE – A NEW JEWELLERY STONE

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Tengizite is a new jewellery stone from the melting zone of rocks that occur near burned oil wells. Chemically it is an analogue of the andesite-dacite obsidian with high contents of calcium and iron. Character of iron distribution, its coordinating position in stone structure and also partial crystallization of melt with formation of diopside-wollastonite veins and spherolites result in a colour and texture rare for natural stones. Tengizite is characterized by certain decorative qualities: deep dark blue and black colours with transitions from one colour to another; charoite plication; massive and vein-spheroidal texture resulting from crystallization of olive-green aggregates of wollastonite and diopside. It is easily cut like obsidian and is processed similarly, getting ideal polishing. Tengizite is related to the II group of jewels such as agate, rodonite and obsidian.

Certified properties of tengizite are as follows: Mineral composition: silicate-calcium glass matrix with quartz, diopside, wollastonite, anorthite, magnetite and less pronounced trydimite, chalcedony and chlorite. Texture: vitrophyric, locally crystalline. Structure: massive, less often spheroidal, vein-spheroidal and porous. Colour: brown, brownish green, black, dark blue, light blue, greyish light blue (turquoise), white and light blue (plication). Jewel varieties have dark blue, black, white and light blue colours (colour list is given in order of reduction of stone quality as jewel material on the basis of ESR data). Decorative pattern: homogeneous, massive with alternation of colour strips from black through dark blue to light blue; olive green or less often brown spherolites and veins on a black and dark blue background; plication figure as at charoite from contortion in folds, thin alternating dark blue, light blue and white (rarely cream-coloured) strips; and various combinations of the above mentioned figures. Hardness: as of obsidian, 5–5.5 on the Mohs scale. Glass lustre. Transparency: transparent in thin edges up to 2 mm in various shades of brown, brownish green colour. Conchoidal fracture. Density: 2.5–3.0 g/cm^3, that is essentially higher than that of obsidian. Refractive index: 1.522–1.539, higher than that of obsidian, for which refraction index is about 1.48–1.51. Workability: because of its greater density, it is not as workable as obsidian; massive and plication varieties accept ideal polishing.

Tengizite is suitable for manufacturing of brooches, rings, bracelets, earrings and other jewelry. Tengizite is a pretty rare stone. As well as for charoite, only one deposit of tengizite is known all over the world. Moreover, each jewelry from tengizite due to the wide colour range and various graphic pattern of the stone is exclusive and therefore most attractive.

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TRANSFORMATION OF ROCK FORMING MINERALS OF A SALT BED IN A TECHNOGENIC FIRE ZONE

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In January 1995 a technogenic earthquake took place in one of the mines of Verkhnekamsky deposit (North Ural). As a result of it a local fire rose in mine workings which proceeded for 5 days. The breaking of high-voltage cables ignited combustible gases and dispersed organic matter. Salt rocks were exposed to warming up to 900 °C in the fire center and to 170–200 °C in the distant parts. The “motley” sylvinites of a salt bed have been exposed to an ignition.

Rock forming minerals are halite and sylvite, both presented by large, up to 2–3 cm, grains; while gypsum, clay minerals from the illite-montmorillonite group and dolomite fill in the intergranular space or compose thin beds. As a result of heat affecting minerals of a bed have undergone structural and compositional changes.

In the zone of intensive warming-up sylvinite has gained more light tints with contrasty dark spots in places of accumulation of unsoluble minerals. Primary mineral composition and mineral relations were not transformed practically. Occasionally it is possible to find the traces of dissolution of salt minerals. In the unsoluble residuum of salts of this zone all of the above mentioned minerals are found.

The field of rocks transformed under the action of volatile combustible products formed at a distance of 30–50 m from the combustion zone. Water and pitch-like organic matter were formed as a result of burning of hydrogen, methane and other hydrocarbons. Water and pitch-like matter were carried out of the zone of high temperatures as gases condensed on decreasing of temperature. Water condensed on drift walls also solved sylvite. As a result of sylvite solution fields of high porosity were formed containing mainly transparent halite and rare relics of not completely dissolved white sylvite grains. Pitch-like matter settled in these pores and painted the rock black. In the unsoluble residuum except for organic matter rare rhombohedra of dolomite and intergrowths of needle-like crystals of gypsum were established.

Directly in a combustion zone temperature was risen up to 900 °C and above. Halite and sylvite have been fused, and the salt melt has flowed down a wall drift. Dark brown sinters with a thickness of 3–5 mm were formed. X-ray and optical immersion studies revealed that the unsoluble residuum of fused salts practically consists of small grains of microcline with small admixing dark brown concretions of ferric oxides. (The latter appear in an immersion liquid as dark red isotropic flakes with high refractive index.) The minerals of the unsoluble part, unrepresentative for the original salt rocks, were formed by the thermal transformation of clay minerals and ferric oxy-hydroxides. Original sulphates and carbonates were thermally decomposed.

This study revealed that the transformed salt rocks show a clear zonation of mineral composition relative to the center of burning and therefore were formed during a fire.

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ASSESMENT OF POLLUTING ELEMENTS IN SOIL SAMPLES FROM THE AREA OF ZLATNA TOWN, ROMANIA

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Metal contamination from the mineral processing plant of the town of Zlatna (Romania) lead to environmental degradation in a wide area around the smelter emission. The plant processes a variety of complex, mainly sulphide ores for Cu, with Au, Ag, Pb, Zn, Bi, Cd, and Mo as major by-products.

The degree of soil contamination depends on the type of the present metals, their concentration and their bioavailability. The bioavailability of different metals is dependent on the type of organisms that are present as well as on a wide range of environmental variables.

Different metals polluted sites of soil (7 points) were sampled in order to perform chemical analyses. Cu, Pb, Zn, Cd, Fe and Ni were identified and analysed with ICP using a widely accepted extractant DTPA. The location of the studied soil sites is to the west and east (200–300 m) from the Zlatna plant's chimneys and 25 km down in the Ampoi Valley (Fig. 1). The concentration of polluting elements is controlled by the pH of the soil, which has always acidic values (pH =3.20 – 4.42).

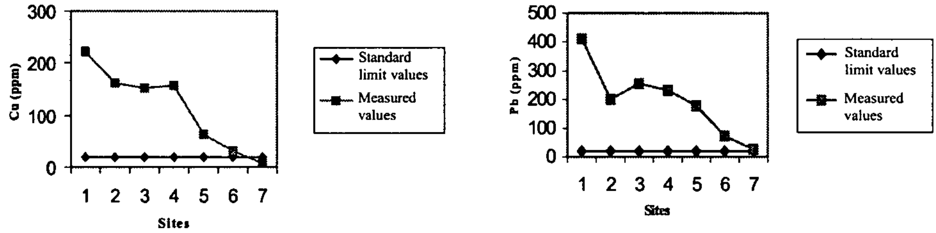

Fig. 1. Cu and Pb distribution profiles in the sites along Ampoi Valley (Site 1 represents the emission point near the Zlatna plant)

The study points out the following behavior of the polluting elements:

- Cu and Pb concentrations are above the standard limit values in all sampled sites.
- Cd concentration has a variable distribution. Only some sites have Cd concentrations above the standard limit values.
- Zn and Ni concentrations are usually below the standard limit values.

The most heavily polluting element is Pb, even 25 km away from Zlatna.

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SORPTION OF IODINE BY HYDROTALCITE AND HYDROTALCITE-LIKE COMPOUND - PROPERTIES AND EFFECT OF CARBONATE ION

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For the long-term safety assessment of radioactive waste disposal, anionic species in radioactive waste, e.g. $^{99}TcO_4^-$ and $^{129}I^-$ are of serious environmental and critical regulatory concerns. Due to poor sorption onto common minerals, their transport from constructed repositories into the biosphere is predicted to be very rapid. In this context, extensive efforts have focused on identifying minerals that might impede the movement of the anionic species. From the result of such previous studies, sulfide and selenate minerals containing Fe, Cu, Sb, Hg and Pb are derived as efficient anion scavengers (OSCARSON et al., 1986; BALSLEY et al., 1998). However, addition of such minerals to the backfill is still a desk plan because of their uncertainty of long-term stability, geochemical complexity and toxicity of such heavy metals. Hydrotalcite (CO_3- HT) has also been investigated for the retardation of the anionic species due to its high anion exchange capacity (for example KANG et al., 1996). Given the relatively low selectivity of CO_3-HT for I^-, OSCARSON et al. (1986) concluded that CO_3-HT would not be effective buffer additive for the immobilization of $^{129}I^-$.

In this study, iodine sorption experiments at pH 9.6 for the synthesized CO_3-HT and hydrotalcite-like compounds with NO_3^- (NO_3-HT) as an interlayer anion were performed in laboratory batch tests at 20 °C to elucidate and compare sorption characteristics of each phase. In addition, to obtain information on the sorptive competition between I^- and CO_3^{2-} for NO_3-HT, sorption experiments for the synthesized NO_3-HT were also conducted in CO_3^{2-}-bearing solutions with different concentrations of KCO_3.

As the results of adsorption experiments with KI concentration range between 10-1000 mg/l, much of the I^- in solution may be exchanged for the NO_3^- in the NO_3-HT (see Figure). The amount of I^- sorbed to contacting NO_3-HT increased linearly with an increase in the equilibrium concentration of I^- in solution, and was totally larger than that to CO_3-HT. On the other hand, in the adsorption isotherm of the CO_3-HT, the saturation was around 1 mg adsorbed per g CO_3-HT, whereas the same linear increase was observed at lower equilibrium concentration of I^- in solution. From the competitive isotherms of I^- with CO_3^{2-}, no effects on adsorption properties and linear isotherms were observed in the experiments with KCO_3 concentration less than 10^{-3} mol/l (here, CO_3^{2-} was 5.1×10^{-5} mol/l). Although the adsorption of I^- by NO_3-HT would not be practical under such high carbonate conditions, the NO_3-HT is presumably an effective scavenger of $^{129}I^-$ under high Ca conditions such as cementitious repositories.

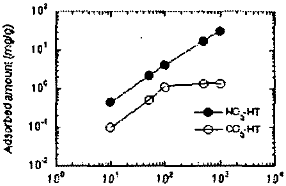

Figure Adsorption isotherms of iodine onto CO_3-HT and NO_3-HT at 20°C.

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GEOCHEMICAL ANALYSIS OF SOILS IN THE OJCÓW NATIONAL PARK (POLAND)

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This research project is aimed at the determination of the level of soil contamination in the area of the Ojców National Park, with particular emphasis on the pollution caused by a major transport route. The locality of the park is heavily unfavourable as it is situated within the immediate sphere of influence of large industrial centres such as the Upper Silesian Region and the cities of Olkusz, Jaworzno, Trzebinia-Siersza and Kraków.

The authors collected soil samples along the major transport route crossing the Ojców National Park area. Chemical analyses have revealed high concentrations of toxic elements (higher than the natural background) in the surface soil layers. All the samples collected contain amounts of hydrocarbons, both aromatic and aliphatic, significantly exceeding norms (the norm was exceeded over 100 times; PIOŚ, 1994). A comparison of concentrations of toxic substances in soils from the centre of the park and an area situated outside its borders shows small differences, with Cd contents within the park area even higher than in samples collected close to the heavily used Kraków–Katowice E-40 motorway (KABATA-PENDIAS & PENDIAS, 1993).

The soils of the Ojców National Park, however highly polluted, reveal good protective properties based on high sorption capacities associated with the presence of organic matter. The soils of the park also reveal substantial buffering properties, controlled by the presence of carbonate minerals. Due to their presence the pH of the soils is relatively high and, therefore, toxic elements are partly immobilized.

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MINERAL DUSTS IN SNOW COVER (SOUTH URALS, RUSSIA)

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Snow cover sampling is widely used for the purpose of environmental monitoring in such Russian regions where snow cover is stable for a few months. On melting a snow sample is divided into soluble (snow water) and insoluble (snow dust) parts. From the mineralogical point of view, the latter is a fine-grained polymineral mixture which may be researched with the aid of appropriate methods of mineral determination.

For example, snow dust from Miass (South Urals, Russia) is characterised by high concentrations of Cd, Cr, Pb, W, Fe, Zn. With the use of X-ray diffractometry it was established that these metals formed various oxides among which the technogene analogues of such minerals as monteponite CdO, picotite $(Mg,Fe)(Al,Cr)_2O_4$, litharge PbO, minium $Pb^{4+}Pb_2^{2+}O_4$, stolzite $PbWO_4$, magnetite $Fe^{2+}Fe_2^{3+}O_4$ and maghemite γ-Fe_2O_3 were found. These compounds are mainly produced by devices and mechanisms burning various kinds of fuel and are accumulated in the heavy fractions of snow dust.

In addition, quarries mining non-metallic resources generate dust waste consisting of silicate and carbonate minerals. It was found that every quarry produced dust waste of well-defined mineral composition – only calcite, only talc or only quartz–feldspar. These minerals are well distinguished on the basis of key lines of their X-ray diffraction patterns, and this fact allows to outline the zone of influence for each quarry, using mass X-ray diffractometry of snow dust samples for this purpose. In principle, specific indicative mineral(s) or compound(s) may be found for every particular pollution source – quarry, plant, factory, mine and so on.

Knowledge of mineral nature of snow dust gives possibility not only to connect a definite source of pollution with a definite indicative mineral and outline the zone of its influence, but also to estimate real scales of various pollutions and to predict correctly the future effects of snow dust on the environment.

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AUTOCONSERVATION OF SOME WASTE OF MINING INDUSTRY (SOUTH URALS, RUSSIA)

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In the South Urals (Russia) semi-liquid flotation waste of Cu-Zn ores are disposed as a pulp to the open tailing ponds. During storage, some valuable components such as Au and Ag accumulate and may be utilised as technogene deposits.

The fresh tailings contain on average (wt%): pyrite 45, quartz 35, aluminosilicates of K, Na, Ca 10, carbonates 5, primary Cu-Zn sulphides 2–4. In old tailings aluminosilicates and carbonates practically disappear, and Cu and Zn sulphides occur as single grains only in the deeper levels of the settling ponds. The major minerals of old tailings are pyrite, quartz and gypsum. Pyrite content varies from 20–80%, with the general trend of decreasing from deeper levels to the surface of the settling ponds along with the relative concentration of fine-grained shlam bands. On the surface of old, closed settling ponds, the pyrite content is significantly lower up to the absolute disappearance of this mineral. Quartz content varies from 10–35%, increasing towards the top levels of old settling ponds where as a rule a sharp increase of the average size of quartz grains is also observed. Gypsum content varies from 5–40%, generally increasing towards the surface of the settling ponds. In the near-surface parts of tailing ponds Fe sulphates are abundant: jarosite (up to 15%) and rozenite (up to 10%) are found in most old settling ponds; and szomolnokite (10–15 %) occurs in young ponds. Melanterite, rhomboclase, coquimbite and copiapite occur rather rarely.

The features of the structure and composition of tailings indicated consistent stages of tailing transformations as a result of prolonged storage, in relation to the age of the settling ponds. In the transformation processes of tailings, pyrite is oxidised under the action of oxygen enriched atmospheric waters to form sulphuric acid and hydrous ferroan sulphates $FeSO_4 \cdot nH_2O$ ($n = 1–7$), firstly in the surface zone with coarse-grained bands of tailings. Sulphuric acid has a major role in the chemical transformation of tailings resulting in direct crystallisation of ferroan sulphate phases of low water content, oxidation of ferroan sulphates to ferrian ones and decomposition of aluminosilicates and carbonates of tailings with the formation of secondary SiO_2 along with Ca, K, and Al sulphates. As a result of these processes, the originally friable tailings are transformed into compact rocks (technogenic sandstones) in which separate mineral grains (mainly quartz and pyrite) are cemented by the newly formed sulphates. In the deeper levels of settling ponds pyrite concentrations reach 70–80%. In contrast, a quartz–sulphate crust is formed on the settling pond surface. In the composition of this crust water-soluble sulphates (melanterite, rozenite) are replaced by an insoluble one (jarosite) for a time. Such crusts, varying in thickness from 0.5–0.7 m, cover the surface of settling ponds completely within 15-25 years, isolating them and causing difficult access to the inner parts for atmospheric waters and preventing the further oxidation of pyrite. Any attempt to develop the settling pond as a potential technogene deposit will likely result in disturbance of the surface crust and the established equilibrium, and pose renewed environmental risk.

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NEW FORMING MINERALS OF Cu AND Zn FROM THE SELF-BURNING SLAG OF ZINC SMELTING PLANT (BELOVO, WEST SIBERIA, RUSSIA)

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Heavy metal migration from waste piles is a severe problem in regions of coal and metal mining and in areas where ore smelting industries are concentrated. Approximately 70000 tons of slags, containing a high concentration of fine-grained carbon (up to 20%) and heavy metals (up to 2.5% Cu and up to 1.5% Zn) were accumulated in the town of Belovo (Kemerovo region, Russia) as a result of Zn-smelting between 1950 and 1994. The combustion of these wastes resulted most likely from spontaneous ignition of the fine-grained carbonaceous material, and is analogous to the process of self-burning, observed in coal mining waste dumps. Primary phases of copper are their alloys with iron and sulfur. Zinc was detected in Zn-Fe-S fusion, gahnite $((Zn_{0.7}Fe_{0.3})(Al_{1.9}Fe_{0.1})O_4)$, fayalite $((Fe_{1.3}Mg_{0.5}Zn_{0.2})SiO_4)$ and glass. In this study, we describe mineral associations forming in the waste heaps and compare the metal retention capability of primary and secondary phases.

The phases and minerals were studied with reflected light and scanning electron microscope (JEOL JSM-36), X-ray diffraction (Cu Kα radiation, DRON-UM diffractometer), and electron microprobe (CAMEBAX MICRO).

Spontaneous ignition of fine-grained carbonaceous material and the subsequent burning of the waste heaps produced a zonation pattern, which is characterized by three types of assemblages of Cu and Zn minerals. Each of the types is observed at different distances from the combustion centre of burned wastes.

The first assemblage occurs very close to the combustion centre and is presented by willemite (Zn_2SiO_4), zincite (ZnO) and johillerite ($Na(Mg,Zn)_3Cu(AsO_4)_3$), which covered hematite–magnetite aggregates. The second assemblage was observed in the weakly altered waste located away from the combustion centre. Minerals identified are: antlerite ($Cu_3(SO_4)(OH)_4$), devilline ($CaCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$), boyleite ($ZnSO_4 \cdot 4H_2O$) and two unnamed Zn-sulfates which are distinguishable on the basis of their XRD patterns and which can be described by the formulae $Cu_{1.5}Zn(SO_4)(OH)_3$ and $Na_2Zn(SO_4)_2 \cdot 4H_2O$ (JCPDS card numbers: #28-405 and #19-1263, respectively). The third assemblage was further found as crusts deposited on the surface of the waste heaps in the close vicinity of active fumaroles. These crusts are composed of chalcanthite ($CuSO_4 \cdot 5H_2O$), Mn-free gunningite ($ZnSO_4 \cdot H_2O$) and an unnamed mineral with the formula $Zn_3Al_4(SO_4)_9 \cdot 36H_2O$ (JCPDS card #28-1458).

Mineralogical compositions of different assemblages reflect stages of Zn and Cu-rich phase transformations. In chemical terms, the transformation patterns are schematically shown as follows: sulfide, oxide and silicate → oxide, silicate and arsenate → sulfate (for Zn); sulfide alloys → elements and arsenate → sulfate (for Cu). On the basis of these patterns, we can conclude that, as a result of combustion, metals were redistributed from relatively resistant phases into less resistant phases, and finally into relatively soluble minerals.

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ROLE OF ORGANIC MATTER AND FERRIC/FERROUS IRON IN CHROMIUM CONCENTRATION IN VOLKONSKOITES

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Heavy metals in sediments are bound in various components, the most important being clay minerals, Fe-Mn oxyhydroxides and organic substances.

Volkonskoite is a unique mineral from the smectite group, containing dominantly chromium in the octahedral position. This mineral is formed on different organic remains buried in productive sandstone from West Ural (Perm and Kirov regions). Besides veinlets, volkonskoite forms complete pseudomorphs of even large tree trunks ("volkonskoite tree").

Chemical analysis shows great variations in the chromium content of volkonskoites (Cr_2O_3 ~ 14–30 wt%). In volkonskoite-bearing rocks Cr accumulated in the clayey cement of sandstone (Cr_2O_3 ~ 2%). The silicified wood fragments retained well their original texture, which is often marked by finely disseminated inclusions of iron hydroxides, so the presence of ferric and ferrous iron can promote the concentration and fixation of chromium in clayey matter. Inner structure of such inclusions indicates their organic origin. The accumulation of chromium in silicified wood takes place firstly at the inner part of such ferric or ferrous inclusions.

The formation of "volkonskoite tree" can be explained as follows: in relics of silicified wood that keeps the original inner "biological" structure chromium accumulates firstly on clayey matter that has been formed on cell membranes, grain boundaries of quartz, small cracks and other parts where organic matter can endure and microorganisms can be present.

SEM investigations of volkonskoites show besides typical smectite structures (globular, acicular and curved-platy) the vermicular structure of bacterial cells unique for volkonskoite. So the reduction and fixation of chromium in clay minerals may be provided by microorganisms or by ferrous iron that is microbiologically reduced from ferric iron.

Laboratory experiments were carried out for modelling the chromium sorption and desorption on smectite at the combined or separate presence of humic acids, FeOOH and Fe^{2+}. Whole rock samples from Vychegda (Triassic montmorillonite) and Efimiata (Permian clay from volkonskoite-bearing rocks) were used as model materials.

These experiments show that chromium sorption is especially high on the montmorillonite clay at the presence of Fe^{2+} and goethite, and desorption of sorbed chromium after pH decrease is relatively low. Desorption of chromium from volkonskoite under oxic and anoxic conditions is also small. The influence of humic acids and ferrous iron increased the sorption capacity of clay minerals.

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ENVIRONORAMAN: ENVIRONMENTAL APPLICATIONS OF NON-DESTRUCTIVE POLYVALENT MRM (MOBILE RAMAN MICROSCOPY)

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ENVIRONORAMAN has been defined (SMITH, 1999) as the study of bio- and geomaterials of relevance to environmental questions using the Raman spectrometric (RS) technique. As such it is one of a group of topics that compose the wider theme previously called GEORAMAN (SMITH, 1987): applications to geological science. Although biomaterials can also be analysed by RS, as it is one of the rare analytical techniques that can identify organic or inorganic solids, liquids or gases, we are mainly concerned here by geomaterials, especially crystals and their associations (e.g. rocks; deterioration products) in environmental mineralogy. RS has recently become transportable or portable, i.e. mobile, hence the symbol "MRM" which also emphasises the fact that one can observe a material under a microscope before choosing which micron-sized particle to analyse; there is no need to prepare a material or extract a sample in any way. Also, by employing optical fibres, one can analyse materials *in situ* far from the spectrometer by bringing an analytical apparatus to an object (on a ceiling or wall; inside a cave or drawer; under water) rather than taking a sample to a laboratory.

The technique is based on interatomic vibrations in crystals or molecules being excited by a laser and diffusing light with characteristic wavelength shifts. Transformed into a spectrum the result is a unique fingerprint which, through comparison with spectra of standards, identifies both the structure and chemistry of the material, and of each phase in the case of mixtures. MRM carries a unique range of advantages, and in certain circumstances provides the only possible way of acquiring identification data. Of course where materials are not precious, many alternative powerful physico-chemical, but destructive techniques may be convenient so that MRM would not be necessary.

It is difficult to conceive of a problem in environmental mineralogy where MRM cannot be of use as it is appropriate for identifying: dusts; particles suspended in liquid; components of soils or sediments; products of climatic, microbial or animal/vegetal degradation; corroded metals; minerals in domestic or industrial waste (and at the same time non-minerals if desired); as well as rocks. Concerning minerals in human health one can examine teeth, stones and implants (MEDICORAMAN). Concerning minerals within the cultural heritage (ARCHCORAMAN including art and architecture, as well as anthropology and ethnology) where most artefacts are indeed precious, the range of applications are enormous, e.g. rough, cut or mounted gems, and their inclusions and treatments; earthenware and other ceramics; stone axes or columns; corroded metal statues or weapons; and especially pigments on glass, wood, paper, pottery, plaster...

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LABORATORY REACTOR FOR IRON(II) OXIDATION /PRECIPITATION BY *GALLIONELLA FERRUGINEA*

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The bacterium *Gallionella ferruginea* is reported to grow within the limits of a pH range from 6.0 to 7.6 and Eh range of +200 mV to +320 mV, corresponding to rH_2 from 19 to 21. Oxygen content should be in the range 0.1–1 mg/l (HANERT, 1992).

However, in a pilot plant built to investigate the possibility to adsorb the pollutants trichloroethene and several hydrophobic pesticides onto the stalks (exopolymers) of *Gallionella ferruginea*, we observed that at pH of about 5.5 and oxygen contents of about 5.4–7.5 mg/l the bacterium created very big amounts of stalks in the ferrihydrate precipitate (SØGAARD et al., 2000).

A laboratory reactor was built for the purpose of iron(II) oxidation / precipitation in a biological way, based on the results from the pilot plant. The reactor was made of a glass cylinder – top and bottom were sealed with stainless steel covers, each with 5 ports for inlets and outlets. The reactor was filled with silica sand grains of size 1.5–3 mm in diameter, all covered with iron (hydr)oxides precipitated by *Gallionella ferruginea*. Tap water was used with a flow rate of about 215 ml/min. Iron was added as iron(II) sulphate to the reactor in a content of about 3.5 mg/l. To avoid oxidation of iron(II) in its container, oxygen free water was used as solvent. Hydrogen carbonate and phosphate were added in form of their sodium salts. The pH of inlet water was adjusted, regulated and controlled by computer to 5.2–5.8 and was not changed from top to bottom of the filter. Eh was measured between 90 mV and 200 mV in top of the filter – normally an increase of 5–50 mV was observed from top to bottom. Oxygen contents were high. The inlet water to the reactor had oxygen contents of about 6.2–6.3 mg/l, which were only slightly changed during the filtration process.

Visible optical microscopy showed an increasing gradient of stalks in the precipitate of iron (hydr)oxide down through the filter. Kinetic calculations showed an increase in the rate of oxidation / precipitation of about 10000 times as compared to purely physico-chemical oxidation / precipitation.

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BURNED COAL-BEARING WASTE HEAPS FROM THE CHELYABINSK COAL BASIN, RUSSIA

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Intense human industrial activity results in the formation of technogenic lanscapes over a large area. Extraction and storage of a large body of rock on the earth's surface is a dramatic impact on the geological environment. The creation of dumps in the surroundings of coal mining enterprises presents an additional severe problem. The detailed mineralogical and geochemical investigation of waste mass composition must be a necessary procedure, preceding the decision on the waste heap destruction. Burned heaps in the Chelyabinsk coal basin are favourable objects for study on environmental mineralogy and investigation of ecological problems.

In the considered region there are about 50 heaps. The majority of these are 40–70 m in height, their volume reaches 1 000 000 m^3. The original waste material supplied contains mudstones, siderite concretions and coal-bearing material. Spontaneous oxidation of coal material in the heaps, with associated flame combustion, took place between 1960 and 1980. Coal combustion has been completed by now, and the heaps are composed of variably altered rocks. The emission of hot gases ($T = 200–400\ ^{o}C$) can be observed. The essential factors that are responsible for the mineralogical variety of technogenic combustion metamorphic rocks are temperature (up to 1000–1200 °C), chemical heterogenity of initial wastes; aggressive gaseous medium (O_2 – from the atmosphere; S, F, Cl – from coals and waste rocks); high porosity of the heap rocks and active gas circulation.

The predominant process observed in silicate rocks during annealing is the decomposition of clay materials. The initial quartz–hydromica association in the mudstones is replaced by a quartz–mullite–hercynite association, and further gives way to refractory clinker: trydimite–mullite–cordierite (± hematite). This material constitutes the major part of the heaps. In the process of oxidative annealing of waste mass there is no active fractionation of Si, Al, Mg, Ti, Mn. Nevertheless the redistribution of Fe, Ca, F, and removal of Na, K, S, C outside the heaps are apparently to take place.

Some parts of the waste sedimentary rocks, the so-called "black blocks", were subjected to annealing under very reducing conditions and high temperature, dry refining of coal as well as carbonate dissociation were realized here. In these zones we identified monosulfides and carbides of iron, a wide variety of high temperature oxides and silicates, and abundant minerals of fluorine. One of the general mineral forming processes is precipitation from gaseous phase, either directly, similarly to the way ice crystallizes from vapour, or through interactions between different volatile cation and anion complexes ("reactions of gas–transport synthesis"). Where combustion has already terminated, "black blocks" remain the sustained source of nitrogen, chlorine and sulfur compounds.

At least three types of rocks, differing in hazardous effect on the environment, can be distinguished in the burned heaps: a) clinker, which is the chemically most tolerant part of the burned heaps; b) "black blocks", the source of toxic gases, containing S, F, Cl, N; c) asphalt-like crusts and the products of fumarole activity, the potential sources of sulfate contamination of soils and ground waters.

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WEATHERED FELDSPAR, MUSCOVITE AND TOURMALINE FROM PEGMATITES OF THE SOMEŞ SERIES (APUSENI MOUNTAINS, ROMANIA)

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The present paper deals with a short description of some weathering features we have put in evidence on pegmatites hosted by medium-grade metamorphic rocks of the Someş series (mica schists, gneisses, migmatites etc.). The pegmatite bodies occur as veins and lenses; their mineralogy is simple: quartz, feldspars, muscovite as principal minerals, while biotite, garnets and tourmaline as subordinate minerals. The composition of pegmatites is a granite-like one; genetically they are products of both metamorphic differentiation and anatectic processes (MÂRZA, 1980; STUMBEA, 1999).

Analytical techniques we have used are wet chemical analysis, electron probe microanalysis (CAMECA SX 50), XRD analysis (PHILIPS PW 1730) and scanning electron microscopy – SEM (JEOL 100).

The physical and chemical behaviour of feldspars, muscovite and tourmaline was followed in vertical and horizontal profiles; the presence of tectonic phenomena have also been considered.

Physically, loss of smoothness, appearance of cracks (particularly following the cleavage directions) and even of powder (tourmaline especially) in the mineral mass have been recorded. The relationship between the width of cracks and the depth at which the sample was taken is revealed by a negative correlation we noticed for this pair of parameters. On the contrary, in terms of feldspars a positive correlation between the abrasion hardness and depth was recorded. Horizontally, these relationships have not been found at all or they are much less evident. In the last case they seem to be connected with local tectonic phenomena, the same ones that made possible the formation of the vein-like pegmatite bodies.

In terms of chemical composition, loss of SiO_2 in both potassium feldspar and plagioclase, partial removal of Na_2O and CaO in plagioclase and a relatively constant amount of Al_2O_3 in all feldspars have been noticed. The geochemical balance concerning muscovites shows reduced changes during the weathering process: more or less marked oxydation of Fe(II) with the appearance of Fe(III); loss (sometimes pronounced) of MgO; variable removal of K_2O and Na_2O. Moreover, XRD analyses show a reduced presence of secondary minerals (1.80–8.00% montmorillonite + chlorite) in muscovite samples. Tourmaline is generally quite resistant at the earth's surface in terms of chemical composition; the most pronounced change we have noticed is the oxydation of Fe(II).

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MAGNETOSOMAL MATRIX: POSSIBLE ROLE IN THE BIOMINERALIZATION OF MAGNETITE (Fe_3O_4) AND GREIGITE (Fe_3S_4)

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Marine, brackish and freshwater magnetotactic bacteria were analysed using transmission electron microscopy (TEM). Stained ultrasections of gutaraldehyde-fixed and Epon®-embedded magnetotactic bacteria were examined in a JEOL® JEM 1010 transmission electron microscope at 80 kV. Unstained, dehydrated whole-cell preparations of magnetotactic bacteria were analysed by analytical TEM (selected area electron diffraction, phase-contrast lattice imaging and energy dispersive X-ray spectroscopy), in a JEOL® 4000 FX high resolution transmission electron microscope fitted with an Oxford-Link® windowless silicon X-ray detector.

An organic iron-containing matrix was detected encapsulating magnetite and greigite magnetosomes in unstained whole-cell preparations, unstained ultraviolet-B-irradiated whole-cell preparations and stained ultrasections of fixed embedded magnetotactic bacteria. The magnetosomal matrix was detected using all three methods, which indicates that the magnetosomal matrix was not an artefact of specimen preparation. Pseudo-hexagonal prismatic magnetosomes in a variety of cells were surrounded by a mildly anionic capsule that extended 30–70 nm beyond the surface of the magnetosomes. The matrix was ~50 nm thick around bullet-shaped magnetosomes. In some cells the space between adjacent magnetosomes were consistently 1.8–3.0 nm wide, which is too small to contain two magnetosome boundary membranes each 5.7 nm thick, as reported by GORBY et al. (1988).

Phase-contrast lattice images of magnetosomes revealed lattice fringes in the magnetosomal matrix with approximately the same widths and orientations as lattice planes in the encapsulated magnetosomes. This correlation indicates that the magnetosomal matrix may act as a template for spatially defined catalysis of magnetite and greigite. A magnetosomal matrix was found encapsulating two types of pseudo-hexagonal prismatic, bullet-shaped and cubo-octahedral magnetite magnetosomes. A feint matrix was also detected encapsulating greigite magnetosomes. These data indicate a second biological mechanism for the mineralization of magnetite.

The magnetosomal matrix is hypothesised to be a semicrystalline polysaccharide gel that acts as a template (mother matrix) for spatially defined catalysis of precursors in magnetite and greigite biomineralization (unpublished data). The matrix may also control the influx of reactants and excretion of product(s) (e.g., iron chelation). The magnetosomal matrix may explain the structural integrity of some magnetosomal chains and the ultrafine-structural coordination between adjacent magnetosomes (e.g., mirroring).

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HAZARDOUS FREE SURFACE AREA OF ASBESTOS: CHANGES DURING REMOVAL

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Since attention was drawn to the diseases that can be induced by asbestos, removal of asbestos containing materials from buildings has become an increasingly important issue. Asbestos fibres entering the human body by means of inhalation can cause a wide range of both chronic inflammatory and malignant diseases, dominantly in the respiratory system.

Among asbestos containing products, sprayed asbestos carries the greatest health risks due to the high concentration of asbestos (60–90%) and the great free surface area of the fibres. Containing practically no binding agent, fibres in sprayed insulation materials are completely exposed, can easily increase the concentration of airborne fibres, and thus endanger human health.

Sprayed asbestos was widely used for insulation purposes in buildings built or renovated between 1940 and 1982 in Hungary. Assessment of the amount of asbestos built in as sprayed insulation material has already begun in Hungary and removal of these materials is most cases executed according to the strict regulation of the European Union.

Removal is the only long-term solution to the problem of asbestos, but it raises new problems as well. During removal, the concentration of airborne fibres can be extremely high, which should be avoided even if preventive measures are taken to protect the workers' health. On the other hand, removal produces a high amount of hazardous waste that must be disposed completely isolated from the environment.

Soluble glass is used to coat sprayed asbestos in order to decrease the concentration of airborne fibres during removal. A patented new Hungarian removal method applies different additive agents to improve the adhesive properties of soluble glass to asbestos fibres. This special material is also used to decrease the free surface area of other asbestos wastes. Thus, isolated by the treatment, the fibrous waste can be utilised as filler in core concrete. According to the inventors this development offers solution to both problems raised by the removal of asbestos. Our study aims to characterise the relation between asbestos fibres and this special soluble glass with the help of optical microscopy, XRD and SEM-EDX analyses.

XRD analyses were performed on both untreated and treated insulation material. XRD patterns revealed that the treatment did not altered the original chrysotile. SEM studies of untreated and treated chrysotile justify that fascicles of chrysotile got covered with soluble glass, so the potential of fibre emission to the air decreases significantly, however, the degree of coverage slightly decreases inwards from the surface of the thick samples. The study of concrete samples confirmed that the glassy coating of fascicles did not get hurt during the production of concrete.

Our results are in accordance with air concentration tests done on asbestos removal areas: in areas where the described method is used, the concentration of airborne fibres is significantly lower than in areas where insulation materials are not treated before removal.

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THEORETICAL MODELS OF MAGNETIC-FIELD RECEPTORS BASED ON SUPERPARAMAGNETIC MAGNETITE

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Numerous animal species use the Earth's magnetic field for their orientation (see WILTSCHKO & WILTSCHKO, 1995). However, the nature of the postulated "magnetic-sense organ" is still a matter of speculation. Recently, a structural candidate for a magnetic field receptor in homing pigeons could be identified (HOLTKAMP-RÖTZLER et al., 1997): clusters of superparamagnetic (SP) magnetite crystals (with grain sizes between 2 and 5 nm) in close association to magnetically sensitive nerves; the cluster size typically amounts to 3 μm.

The question therefore rises as to how a magnetoreceptor based on SP magnetite could work, for SP particles do not behave like compass needles as, for example, single-domain magnetites found in magnetic bacteria. In SP particles, the magnetisation vector **m** can rotate more or less freely within the crystal; as a consequence, the external magnetic field $\mathbf{H}_0$ will (on average) align **m** parallel to $\mathbf{H}_0$ but not the SP particle itself. A torque receptor therefore will not work in the case of SP particles.

Three new receptor models were developed to the point of making quantitative predictions which are testable by experiments. The working principle of each model receptor is a transformation of magnetic field energy into mechanical strain, an idea originally presented by KIRSCHVINK & GOULD (1981). However, as shown in WINKLHOFER (1999), their model, the so-called elastic rod transducer, is founded on physically wrong assumptions leading therefore to results that stand in contradiction with experimental facts. The newly formulated receptor models predict an extension of the SP clusters along the axial direction of an externally applied magnetic field $\mathbf{H}_0$ with the amount of deformation being a measure of field intensity. Since the strain ellipsoid indicates the axial direction of $\mathbf{H}_0$ but not its polarity, such a receptor would be in accordance with the characteristics of the inclination compass of migratory birds as deduced from behavioural experiments.

The amount of strain depends on the viscoelastic properties of the embedding medium, where three cases are distinguished here:

A) SP particles in an elastic matrix (e.g., the cytoskeleton);
B) SP particles in a liquid surrounded by a vesicle membrane;
C) SP particles attached to the membrane of a vesicle or a cell.

It is demonstrated for each model that – even in the comparatively weak geomagnetic field – the magnetic field induced strain is sufficiently large to be detected by molecular mediators of cellular mechanotransduction such as the cytoskeleton or mechanosensitive ion channels in the cell membrane.

Several possibilities are discussed of how small variations in geomagnetic field intensity could be resolved by a so-called active magnetoreception, that is by reversing magnetic field induced changes in receptor shape through regulation of internal control parameters, as for example the osmotic pressure difference across the receptor membrane.

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REGION OF BAIA MARE: INVENTORY OF AREAS AFFECTED BY MINING ACTIVITIES

ZAHARIA, E. & CHIS, C. (North University, Baia Mare, Romania)

The activities of geological research and exploitation of base metal ores contribute in a certain way to the degradation of the environment. Among the positive results of geological exploration and mining activities on the Neogene hydrothermal ore deposits of the Baia Mare area, we could also consider the fact that 14 new mineral species as well as several mineral varieties were identified here. The famous „mineral flowers" from this zone are also present in mineral collections all over the world. Some base metal ore deposits contribute extensively to the national economy, which defines the state of Baia Mare as a mining region, providing about 60% of the base metal production of Romania.

Exploitation and mineral processing are the principal pollutants in this zone. Pollution and degradation are caused by:

A. Mining wastes – they represent sterile deposits resulting from the mining works done outside the ore. When talking about these deposits we must take into consideration the following aspects: water pollution by leaching and the washing out of fine grains. Mining waste heaps can slide and block the valleys, can cause floods, not to mention marring of the landscape. In the region of Baia Mare there are 60 mining waste deposits among which 6 are still active, having a volume of 1,047,892 m^3 in an area of 7.22 ha, and the rest of them are abandoned, covering a surface of 38.98 ha and having a total volume of 1,863,272 m^3.

B. Tailing ponds – these represent waste deposits resulting from mineral processing. The depositing technology is realized by hydro-transport, therefore the wastes are found as submillimetric fine grains. The problems associated with tailing ponds are the pollution of rivers, phreatic water, and soil, pollution of villages and towns with dust from the surface of tailing ponds, and again, the marring of the landscape. In the region of Baia Mare there are 8 such tailing ponds, stretching on a surface of 308.7 ha. The quantity of their waste was estimated to be 77,026,944 t on 31 December 1997.

C. Quarries – from economical reasons, the exploitation rate of qarries is constantly increasing, because considerably bigger productivity is realized compared to those obtained in underground works, now that the exploitation of low content ores has become possible. But these, after having been exploited, are deserted and raise great environmental problems: they cause landslides, block valleys, pollute waters and mar the landscape. In this region there exist 6 quarries of a total surface of 53.6 ha, out of which only 10.3 ha have been re-integrated in the economical cycle.

D. Underground works affect the physical stability of the soil surface. Especially the deserted galleries raise problems because of their susceptibility to collapse and the implicit danger to cause accidents (zones of Baia Sprie and Suior Mining Exploitation).

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IRON AND ZINC SULPHIDE MINERALIZATIONS IN ALVINELLA POMPEJANA TUBES: SPECIFIC MINERALOGICAL MARKERS OF BACTERIAL ACTIVITY AT HYDROTHERMAL VENTS?

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The deep-sea hydrothermal environments at mid-oceanic ridges are appropriate for studying biologically induced mineralizations (BIM), since an abundant biomass lives in highly mineralizing environments. In order to sudy BIM in this context, proteinaceous tubes of Alvinella pompejana, a thermophilic polychaete (DESBRUYÈRES et al., 1985; CARY et al., 1998), have been collected with a special experimental device (GAILL et al., 1996; TAYLOR et al., 1999) on active smoker walls at deep-sea vents of the East Pacific Rise. Minerals precipitated within the animal tubes were studied by analytical transmission electron microscopy. The unique sulphide mineral observed within the exoskeleton of the animals is nanocrystalline Zn-Fe suphide, forming typical alignments parallel to the main tube layering. These minerals are closely associated with layers of bacteria present within the tubes and, in some cases, they are observed within bacterial cells. The structure of the nanocrystals is consistent with both blende or wurzite forms, but with some particular space group modifications. We show that these minerals are very different structurally and chemically from the sulphides precipitated inorganically in the hydrothermal environment immediately outside of the living organisms. This makes them interesting as mineralogical biomarkers. Both their particular microstructure and their close association with the bacterial cells present within the proteinaceous tube leave open the possibility that this BIM might indeed correspond to biologically controlled mineralization. In any case, the significance of this Zn-Fe-S BIM or BCM will be discussed with regard to metal detoxification mechanisms by these organisms. Such alignments of nanocrystals might also be searched in fossilized hydrothermal vent systems and used as specific mineralogical markers in paleometabolical studies.

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ENVIRONMENTAL MINERALOGY RESEARCH IN CHINA

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Environmental mineralogy focuses on studying chemical behavior of minerals in the processes of natural and man-made environment, looking for technical methods and measures to prevent the environment from deterioration using mineralogical knowledge. At present, environmental mineralogy owns definite research goals: to explore the pollutants leading to environment pollution and to research the minerals that can eliminate pollution, employing some of their characteristics to transform and protect the environment.

Environmental mineralogy in mining industry

There are many ways of endangering human beings in coal mining: the vast amount of coal ashes and other harmful matters carried by ashes released during exploitation, the polluted water discharged from the pit and the harmful materials resulting from the leaching of dumps.

Coal mine dust pollution takes place mainly in the mines, directly damaging the workers' health (HAN, 1996). The mineral components in the dust, such as carbonates, quartz, clays, sulfides, silicates and other fine particles take key roles in producing pulmonary diseases, furthermore, the different mineral combinations can lead to various types of pulmonary damage.

Hazardous elements in minerals occurring in coal have been investigated in China (ZHUANG et al., 1999). Potentially toxic elements and some minerals entering the human body by means of exhalation, for example, will lead to abnormalities in metabolism and pathological changes. Due to their physico-chemical properties, minerals can cause different kinds of damages to human tissues. Thus mineralogical speciation is really important in preventing illnesses.

Treatment of Cr^{6+}-bearing waste water using natural sulfide

Some waste water containing soluble Cr^{6+} ion was released endangering the environment. Sulfide was used to absorb Cr^{6+}-bearing waste water (LU et al., 1997). At $pH < 7$, absorption efficiency increased.

The role of environmental mineralogy in protecting the environment

Many minerals have proved useful in reducing waste and dust pollution, deodorization and other aspects. The application of minerals in decontamination is mainly based on their adsorption properties. The mineral sorption agents usually used in curing waste water are tripolite, bauxite, zeolite, activated carbon, etc. With the development of technology, various kinds of new mineral sorption agents appear constantly. Moreover, some wastes are also utilized in decontamination, for example, slags can be modified to create absorption agents. Similarly, many minerals play an important role in curing waste gas. It can be ensured that environmental mineralogy, a new subject, will play an increasingly important role in protecting and curing the environment as it is developing.

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AUTHOR INDEX

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