CHARLES UNIVERSITY PRAGUE
FACULTY OF SCIENCE

INSTITUTE OF GEOCHEMISTRY, MINERALOGY AND NATURAL RESOURCES

ACADEMY OF SCIENCES
of the Czech Republic

INSTITUTE OF GEOLOGY, v. v. i.

Contribution to arsenic solid phase speciation in soils and mine wastes

DISSERTATION

Michal Filippi

FIELD: APPLIED MINERALOGY AND GEOCHEMISTRY

Supervisor: Prof. RNDr. Zdeněk Pertold, CSc.

May 2007, Prague

Statement of originality

This dissertation consists of three original papers published in international scientific journals dedicated to environmental issues. The results of the presented studies are supplemented by an extensive introduction. Some parts of this introduction can also be considered as a new study, literature search and review, giving summarizing information about the present state of knowledge of the subject discussed.

In papers where two or more authors are stated, the first author performed most of the fieldwork, sample preparation, analysis or data processing, writing and interpretation. Other co-authors provided a review of the manuscript and/or helped with data collection and interpretation.

This dissertation is an original work of the author and is presented for the degree of "Doctor of Philosophy" at the Faculty of Science at Charles University in Prague.

Michal Filippi M.Sc.

Prohlášení originality

Tato disertační práce se skládá ze tří původních článků publikovaných v mezinárodních vědeckých časopisech zaměřených na environmentální problematiku. Výsledky prezentovaných prací jsou doplněny rozšířeným společným úvodem. Některé části tohoto úvodu lze také považovat jako novou práci, rešeršně - revizní, poskytující shrnující pohled na současný stav řešené problematiky.

V článcích, kde je uvedeno více autorů, první autor provedl většinu terénní práce, zpracování vzorků, analýz či zpracování dat a sepsání interpretací a závěrů. Ostatní spoluautoři pomohli s revizí textu a/nebo se podíleli na získávání a interpretaci dat.

Tato disertační práce je originální prací autora a je předložena pro dosažení titulu „Doctor of Philosophy" na Přírodovědecké Fakultě University Karlovy v Praze.

Mgr. Michal Filippi

Statement of co-authors

On behalf of both co-authors of the paper titled "Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ)", I can confirm that Michal Filippi performed most of the field and research work and interpretations of the results. The co-authors helped with sampling, and their critical comments helped to improve the final version of the manuscript.

M.Sc. Viktor Goliáš, Ph.D.

On behalf of both co-authors of the paper titled "Mineralogical speciation of arsenic in soils above the Mokrsko-west gold deposit, Czech Republic", I can confirm that Michal Filippi performed most of the field and research work and interpretations of the results. The co-authors contributed by obtaining and interpreting data from sequential leaching and Raman spectroscopy. Co-authors' critical comments helped to improve the final version of the manuscript.

M.Sc. Barbora Doušová, Ph.D.

Prohlášení spoluautorů

Jménem obou spoluautorů práce nazvané „Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ)" mohu potvrdit, že Michal Filippi provedl většinu terénní a výzkumné práce a interpretací výsledků. Spoluautoři se podíleli především na odběru vzorků a dále pak kritickými připomínkami pomohli ke zlepšení definitivní verze textu.

Mgr. Viktor Goliáš, Ph.D.

Jménem obou spoluautorů práce nazvané „Mineralogical speciation of arsenic in soils above the Mokrsko-west gold deposit, Czech Republic" mohu potvrdit, že Michal Filippi provedl většinu terénní a výzkumné práce a interpretací výsledků. Spoluautoři se podíleli především na získání a interpretaci dat sekvenčního loužení a Ramanovy spektroskopie. Kritickými připomínkami pak pomohli ke zlepšení definitivní verze textu.

Ing. Barbora Doušová, CSc.

Acknowledgements

Results of the research presented in this dissertation was supported by project No. 79-502 881 – Elemental mobility in the oxidation zone of mineral deposits (EMOZMiD), financed by the Rio Tinto Technology Development (in years 2000-2001) and by the Institutional Research Plan No. Z3-013-912 of the Institute of Geology, v.v.i., AS CR, Prague (2002-2004).

The author would like to thank all persons who helped to provide data and/or helped by consultation or other types of assistance: A. Langrová, V. Böhmová, J. Dobrovolný, and V. Sedláček (Service Laboratory of Physical Methods, Institute of Geology, AS CR, v.v.i., Prague); M. Burian, J. Rohovec, A. and Žigová (Department of Environmental Geochemistry and Geology, Institute of Geology, AS CR, v.v.i., Prague); V. Goliáš, J. Haloda, J. Hovorka, and O. Šebek (Laboratories of Geological Institute, Faculty of Science, Charles University, Prague); B. Doušová, V. Machovič, and S. Randáková (Institute of Chemical Technology, Prague).

Special thanks belong to my supervisor Z. Pertold and to my colleague P. Drahota: they both helped in improving the text of the dissertation by their numerous consultations and comments. My wife Renata is acknowledged for her help with the technical revision of the text, and R. Lewis, J. Adamovič, R. Pažout and Z. Wilhelm are acknowledged for improving the English.

Poděkování

Výzkum prezentovaný v této disertaci byl podpořen projektem č. 79-502 881 – Elemental mobility in the oxidation zone of mineral deposits (EMOZMiD), financovaným společností Rio Tinto Technology Development (v letech 2000-2001) a výzkumným záměrem č. Z3-013-912 Geologického ústavu, AV ČR, Praha (2002-2004).

Autor by rád poděkoval všem, kteří přispěli ke vzniku práce, resp. se podíleli na získávání data či pomohli konzultacemi či jiným způsobem. Jmenovitě to jsou: A. Langrová, V. Böhmová, J. Dobrovolný a V. Sedláček (Servisní laboratoř fyzikálních metod*); M. Burian, J. Rohovec, A. Žigová a především P. Drahota (Oddělení environmentální geochemie a geologie, *Geologický ústav, v.v.i., AV ČR, Praha); V. Goliáš, J. Haloda, J. Hovorka a O. Šebek (Laboratoře geologického ústavu, Přírodovědecké fakulty, University Karlovy, Praha); B. Doušová, V. Machovič a S. Randáková (Vysoká škola chemicko technologická, Praha).

Speciální dík patří mému školiteli Z. Pertoldovi a kolegovi P. Drahotovi, kteří svými poznámkami a konzultacemi pomohli zlepšit text této disertace. Díky také mé ženě Renatě za pomoc při technické revizi textu. R. Lewisovi, J. Adamovičovi, R. Pažoutovi a Z. Wilhelmovi patří poděkování za revizi Angličtiny.

Table of contents

List of figures **8**

List of tables **10**

Abstract **11**

Abstrakt **13**

Preface **15**

Field of interest, its topicality and relevance 15
Purpose of the dissertation 16
An overview of the contents of the dissertation 17

CHAPTER 1. Basic data on arsenic with emphasis on As-bearing minerals in soils and mine wastes **19**

- 1.1. Arsenic as a chemical element 19
  - 1.1.1. Basic data 19
  - 1.1.2. Main usage of arsenic 21
  - 1.1.3. Chemical speciation of As in the environment 21
  - 1.1.4. Arsenic toxicity 24
- 1.2. Arsenic in soils and mine wastes 24
  - 1.2.1. Sources and concentrations of As 24
  - 1.2.2. Physico-chemical behaviour of As and releasing mechanisms 26
  - 1.2.3. Microbial activity 28
- 1.3. Arsenic minerals in soils and mine wastes: a brief overview 28
  - 1.3.1. General terms and relationships in environmental mineralogy 28
  - 1.3.2. Primary As minerals 29
  - 1.3.3. Secondary As minerals 31
    - 1.3.3.1. As oxides 32
    - 1.3.3.2. Fe arsenates 32
    - 1.3.3.3. K-(Ba-) Fe arsenates 32
    - 1.3.3.4. Ca-Fe arsenates 33
    - 1.3.3.5. Ca, Mg and Ca-Mg arsenates 33
    - 1.3.3.6. Crystalline Fe sulpho-arsenates 33
    - 1.3.3.7. Pitticite and other amorphous Fe sulpho-arsenates (AISA) 34
    - 1.3.3.8. Other secondary As minerals 34
    - 1.3.3.9. Rare secondary As minerals and unidentiffied phases 34
  - 1.3.4. Stability of secondary As minerals 35

CHAPTER 2. Determination of As-bearing minerals in contaminated soils and mine wastes – a literature review **38**

- 2.1. Introduction 38
- 2.2. Methodological approaches 39
  - 2.2.1. Sampling, sample treatment and preparation 39
  - 2.2.2. Instrumental methods 41
    - 2.2.2.1. Binocular and optical microscopy 41
    - 2.2.2.2. XRD, DXRD, μXRD 41
    - 2.2.2.3. XRF 42
    - 2.2.2.4. XPS, XAES, TOFSIMS, and TOFLIMS 43
    - 2.2.2.5. SEM-EDS/WDS and EMPA 44

      - 2.2.2.6. TEM, STEM, HRTEM, and related techniques 45
      - 2.2.2.7. AFM, BFM, BAFP 46
      - 2.2.2.8. PIXE 46
      - 2.2.2.9. Synchrotron-based radiation methods: µXRF, µXRD, XAS - (µ)EXAFS and (µ)XANES 47
        - 2.2.2.9.1. µXRD and µXRF 47
        - 2.2.2.9.2. XAS techniques 48
      - 2.2.2.10. Infra-Red spectroscopy and other related techniques 49
        - 2.2.2.10.1. IR 49
        - 2.2.2.10.2. FT-IR and MAS 49
        - 2.2.2.10.3. RS........ 50
      - 2.2.2.11. Thermal analysis: TGA, DTA........ 50
      - 2.2.2.12. Vis DRS, VMP 51
      - 2.2.2.13. ND........ 51
  - 2.3. Summary........ 52

CHAPTER 3. Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ) 53

  - 3.1. Introduction 53
  - 3.2. Geological background 54
  - 3.3. Sampling 56
  - 3.4. Analytical methods........ 56
  - 3.5. Results 57
    - 3.5.1. Mineralogical composition 57
    - 3.5.2. Geochemistry 59
      - 3.5.2.1. Bulk chemical composition........ 59
      - 3.5.2.2. Arsenic content 59
      - 3.5.2.3. Soil pH........ 62
    - 3.5.3. Arsenic mineralogy........ 63
  - 3.6. Discussion 67
    - 3.6.1. Arsenic distribution 67
    - 3.6.2. Secondary phase speciation and stability 67
  - 3.7. Conclusions........ 70

CHAPTER 4. Oxidation of the arsenic-rich concentrate at the Přebuz abandoned mine (Erzgebirge Mts., CZ): the mineralogical evolution 73

  - 4.1. Introduction 73
  - 4.2. Geological setting and description of the concentrate 75
  - 4.3. Methods and sample description 75
  - 4.4. Results and discussion........ 76
    - 4.4.1. Mineral identification and description 76
    - 4.4.2. Oxidation of primary ore and succession of secondary minerals 81
    - 4.4.3. Arsenic contamination 82
  - 4.5. Summary and Conclusions 83

CHAPTER 5. Mineralogical speciation of arsenic in soils above the Mokrsko-west gold deposit, Czech Republic........ 84

  - 5.1. Introduction 84
  - 5.2. Site description 85
  - 5.3. Sampling and analytical methods........ 86
    - 5.3.1. Soil sampling and characteristics........ 86

    - 5.3.2. Preparation of the mineralogical samples 87
    - 5.3.3. Semi-quantitative bulk chemical composition 87
    - 5.3.4. Pedological characteristics 87
    - 5.3.5. Separation in heavy liquid 88
    - 5.3.6. X-ray diffraction analyses 88
    - 5.3.7. Raman spectroscopy 88
    - 5.3.8. SEM and microprobe study 89
    - 5.3.9. Sequential extraction 89
  - 5.4. Results 89
    - 5.4.1. Soil characteristics 89
    - 5.4.2. Identification and characterisation of the As-bearing secondary minerals 91
      - 5.4.2.1. Preconcentration and mineralogical composition of the concentrate samples 91
      - 5.4.2.2. Chemical composition of the minerals 93
      - 5.4.2.3. As-bearing secondary minerals in soils above the granodiorite bedrock 95
      - 5.4.2.4. As-bearing secondary minerals in soils above the volcanosedimentary bedrock 99
    - 5.4.3. Sequential extraction 103
  - 5.5. Discussion 104
    - 5.5.1. Representation and distribution of As-bearing minerals in soil profiles 104
    - 5.5.2. Selected soil properties versus secondary mineralisation: implication on stability of As-bearing minerals 104
    - 5.5.3. Succession model for mineralisation above the granodiorite bedrock 105
    - 5.5.4. Data from sequential extraction versus mineralogical observations 106
  - 5.6. Conclusion 107

CHAPTER 6. Prospects of future research 108

Literature 109

CURRICULUM VITAE of Michal Filippi 126

List of figures

CHAPTER 1. Basic data on arsenic with emphasis on As-bearing minerals in soils and mine wastes

Fig. 1. An Eh-pH diagram of aqueous, aerobic As-solution at 25 C and 1 bar of pressure (according to Smedley and Kinisburg, 2002)

Fig. 2. Summary of important inorganic, organic, and biological forms of arsenic in the environment (according to O´Day, 2006, modified).

CHAPTER 3. Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ)

Fig. 1. A: Location of the Mokrsko, Roudný and Kašperské Hory gold deposits in the Bohemian Massif; B: Mokrsko area, simplified geological map (adjusted after Morávek 1996). Legend: 1- mafic to intermediary volcanites, 2- felsic volcanites, 3- albite granite, 4- volcano-sedimentary sequence overlying the volcanites, 5- 6- amphibole-biotite granodiorite, 7- dikes (aplite, porphyrite, etc.), 8- Upper Proterozoic shales and graywackes, 9- gold-bearing zones, 10- faults; C: Roudný area, location of mining and ore treatment sites (adjusted after Komínek 1990, unpublished); D: Kašperské Hory, simplified geological map (adjusted after Pertold and Punčochář 1996). Legend: 1- biotite-sillimanite paragneiss, 2- biotite orthogneiss, 3- quartzite, 4- Au-W mineralised zones with old workings, 5- adits, 6- mylonitisation

Fig. 2. Quantitative mineralogical composition of selected samples (values are given in wt.%)

Fig. 3. Arsenic distribution in selected profiles from the: a) Mokrsko; b), c) Roudný; d) Kašperské Hory Quaternary covers

Fig. 4. X-Y plots of As and Fe concentrations in selected samples from different geological settings, and indication of As mineral groups (see the Appendix for sample characteristics)

Fig. 5. Microphotographs of secondary minerals containing arsenic: a) Pharmacosiderite relicts (darker) replaced by arseniosiderite (lighter) in quartz (black). Sample Mo1/6c. Back-scattered electron image (BEI); b) Arsenopyrite relicts (white) replaced by arsenates (darker). Sample Mo1/6c. BEI; c) Scorodite grain partly affected by dissolution at its margins. Sample Mo2/2. BEI; d) HFO with varied As contents (lighter parts have higher As contents) in phyllosilicate. Sample Mo6/4a; analyses are given in Table 3. BEI; e) Unidentified arsenate coating replacing arsenopyrite. Sample Ro4/7. BEI; f) Pitticite covering quartz surface. Sample Ro4/4. Secondary electron image (SEI)

Fig. 6. The XRD pattern of separated arsenate aggregate. Abbreviations: Ph – pharmacosiderite, A –arseniosiderite, Q – quartz

CHAPTER 4. Oxidation of the arsenic-rich concentrate at the Přebuz abandoned mine (Erzgebirge Mts., CZ): the mineralogical evolution

Fig. 1. Location map of the abandoned Přebuz mine and settings in the close proximity of the concentrate body (position of sections P1 and P2 are marked by arrows).

Fig. 2. Octahedral arsenolite crystals (ars) (about 200 micrometres across) associated with powdery scorodite aggregates (sco) growing in a cavity of the concentrate material. SEI photograph.

Fig. 3. Aggregate of acicular kaatialaite crystals. SEI photograph.

Fig. 4. An example of a slightly weathered sample. Arsenopyrite (aspy) and löllingite (lö) grains are sharply terminated, practically without dissolution features. Secondary cement is composed of scorodite (sco) mass with dispersed arsenolite (ars) grains. Pyrite (py) grain is partly decomposed and associated with secondary Fe-O phase. BSE photograph, scale bar 100 μm.

Fig. 5. An example of strongly weathered sample. Löllingite is absent and arsenopyrite grains occur in small relicts only (all white particles in the figure). Secondary cement is composed of scorodite mass (sco) and sulphur (S) that fills some cavities (c) after dissolved arsenopyrite grains. Feldspar occurs as unaffected grain (f). BSE photograph, scale bar 200 μm.

Fig. 6. a) Cavity (all black parts) after practically completely dissolved arsenopyrite (white relicts) in a strongly weathered sample. Relatively homogeneous cement is composed of scorodite. The whole cavity is partly lined by native sulphur (S). Scale bar 100 μm. BSE photograph.; b) Internal structure of the cavity is documented by secondary electron photograph (SEI), and the presence of sulphur is documented by its X-ray distribution analyses (S).

CHAPTER 5. Mineralogical speciation of arsenic in soils above the Mokrsko-west gold deposit, Czech Republic

Fig. 1 Location of the Mokrsko-west deposit and simplified geological map of the area (adjusted after Morávek, 1996). Legend: 1– amphibole-biotite granodiorite; 2 – shales; 3 – intermediate tuffs; 4 – intermediate and mafic volcanics; 5 – basic dyke rocks; 6 – barite dykes; 7 – surface prospecting from 80s´ (dashed line), gallery; 8 – fault; 9 – forest ways (thin line), road; 10 – approximate areas with high contents of As in soil (>1000 mg/kg).

Fig. 2 Soil profiles and location of the samples. For description of horizons see Appendix in Filippi et al. (2004)

Fig. 3. Typical morphology of various secondary mineral grains (identified by SEM-EDS, XRD, and Raman studies). (a) Dark brown coloured consistent grain composed from pharmacosiderite with admixture of arseniosiderite (sample Mo1/6). (b) Rusty brown incoherent grain composed from mixture of pharmacosiderite with arseniosiderite (Mo1/4). (c) Light brown porous and crumbled scorodite grain (Mo2/3); for XRD pattern see Table 5. (d) Ochre brown homogenous tabular jarosite grain (Mo5/4); for XRD pattern see Table 5 and for internal structure cf., Figure 9l. (e) Compact black goethite grain with smooth surface (Mo5/3); for XRD pattern see Table 5 and for internal structure cf., Figure 9a. (f) Compact black goethite grain with reniform (kidney-shaped) surface (Mo6/3); for XRD pattern see Table 5 and for internal structure cf., Figure 7b, and 7c. (g) Intergrowth of two cubic-like (pseudo)crystals (Mo1/1). (h) Aggregate of perfect cubic-like (pseudo)crystals (Mo6/3); the XRD pattern corresponds to goethite (see Tab. 5 and for internal structure cf., Fig. 9f).

Fig. 4. XRD powder patterns (parts in range 5-31° 2θ) of heavy concentrates obtained from the soil samples above (a) granodiorite and (b) volcanosedimentary bedrock. Key: A – amphibole, Al – albite, An – anorthite, Ar – arseniosiderite, Bt – biotite, C – chlorite, I – illite, J – jarosite, NJ – natrojarosite, Q – quartz, Ph – Pharmacosiderite, Sc – scorodite, X – unidentified peak.

Fig. 5. Chemical composition of secondary minerals. (a) CaO vs. As_2O_5 plot of the studied secondary minerals. (b) Variations of As_2O_5 as a function of Fe_2O_3 in the studied secondary minerals. Dashed circles border approximate areas of theoretical mineral compositions (adjusted according to Paktunc et al., 2004).

Fig. 6. X-ray mapping of an arsenate grain from Figure 7b, demonstrating heterogeneity in elemental distribution within the bounds of one arsenate grain. Compared to Figure 7b, this section is rotated.

Fig. 7. Backscattered electron micrographs of different secondary arsenates and other minerals from the soil above the granodiorite bedrock. Black squares and circles point at positions of the chemical (selected representative analyses are given in Table 4) and Raman analyses (selected representative spectra are given in Figure 8), respectively. (a) Complex grain composed from pharmacosiderite, arseniosiderite (lighter phases) and quartz (grey phase). (b) Predominant arsenopyrite crystal metamorphosed by pharmacosiderite (light) in quartz (grey); thin vein in the left corner and leaf-like aggregates near the right margin of the quartz are composed by arseniosiderite. (f), (c), (d) Complex grains composed by pharmacosiderite (lighter) and FOHs (darker). (e), (f), (g) Chemically and structurally homogeneous pharmacosiderites (lighter) overgrowing or replacing rock-forming minerals (darker). (h) Detail of the leaf-like texture of arseniosiderite (lighter) in quartz (darker). (i) Homogeneous scorodite grain (white) aggregated with rock-forming minerals (darker). (j) Scorodite (light) with jarosite (darker inclusion) aggregated with rock-forming minerals (darker). (k) Partly decomposed scorodite grain.

Fig. 8. Set of representative Raman spectra of the studied arsenates in range between 100 and 1200 cm^{-1}. For chemical analyses see Table 4.

Fig. 9. Backscattered electron micrographs of different secondary goethites and other minerals from the soil above the volcanosedimentary bedrock. Black squares and circles point at positions of the chemical (selected representative analyses are given in Table 4) and Raman analyses (selected representative spectra are given in Figure 10), respectively. (a) Chemically and structurally homogenous goethite grain. (b) Goethite with coloform internal structure. (c) Goethite with coloform internal structure (lighter parts) associated with jarosite crystals (grey parts – point 5/16) and FOH (dark grey parts – point 5/17). (d) Goethite (lighter) impregnating rock-forming silicates (darker). (e) Goethite displaying radial fibrous-like structure. (f) Pseudomorphs of goethite with hematite after pyrite. (g) Reticular grain composed by mixture of goethite with hematite (light phases) overgrowing unidentified FOH* (darker phase). (h) Mixture of star-like goethite (lighter phases) dispersed in unidentified FOH* (darker phase). (i) Polygonal grain composed by hematite (whiter) and goethite (darker). (j) Goethite impregnation (light phase) in rock-forming silicates (darker phases). (k) Mixture of goethite (white) with jarosite (darker). (l) Single jarosite grain. * The identification was not possible due to high fluorescence within the Raman study.

Fig. 10. Set of representative Raman spectra of the studied goethites and hematites in range between 50 and 1500 cm^{-1}. For chemical analyses see Table 4.

Fig. 11. Representative Raman spectrum of jarosite in range between 100 and 1300 cm^{-1}

Fig. 12. Relative amounts of extracted As from particular fractions obtained by sequential extraction of the Mokrsko soil samples

List of tables

CHAPTER 1. Basic data on arsenic with emphasis on As-bearing minerals in soils and mine wastes

Table 1. Basic characteristics of the arsenic

Table 2. List of the most common arsenic minerals in the nature

Table 3. Average As concentrations and/or ranges in various rocks and other geological environments (according to Smedley and Kinniburgh (2002), for references see therein, partly adjusted)

Table 4. As concentrations in common rock-forming minerals (according to Smedley and Kinniburgh (2002), for references see therein, partly adjusted).

Table 5. Several rare As minerals and artificial phases(*) occurring in some specific contaminated sites

Table 6. The most important secondary As minerals occurring in contaminated soils and mine wastes

Table 7. Selected unidentified secondary As phases mentioned in the literature

Table 8. Schematic representation of the progressive oxidation (paragenesis) in the soil/mine waste containing As-bearing primary minerals (compiled according to materials published by Jambor, 2003; Pfeifer et al., 2003; and others)

CHAPTER 2. Determination of As-bearing minerals in contaminated soils and mine wastes – a literature review

Table 1. List of abbreviation

CHAPTER 3. Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ)

Table 1. Bulk chemical composition of selected samples from the Mokrsko, Roudný and Kašperské Hory Quaternary covers

Table 2. Frequency of detected arsenic secondary minerals

Table 3. Chemical analyses of selected As-bearing HFO and goethite. Analyses designated as Mo6/4a (light part) and (dark part) come from the grains in Figure 5d. Designations Mo6/4a, Ka13/4, etc. specify the horizons from which the analysed grains were obtained (as in Tab 4). Explanation for sign: - not determined

Table 4. Chemical analyses of pharmacosiderite and arseniosiderite. Explanation for sign: - not analysed

Appendix Description of the samples, their As contents and the pH values of the leachates in distilled water and KCl for selected representative samples. Abbreviations and signs: Mo …Mokrsko; Ro …Roudný; Ka …Kašperské Hory; Q…quartz fragments; id. …identical characteristics; - …not determined

CHAPTER 4. Oxidation of the arsenic-rich concentrate at the Přebuz abandoned mine (Erzgebirge Mts., CZ): the mineralogical evolution

Table 1. Chemical analyses of secondary minerals from the Přebuz concentrate (EDAX)

Table 2. Brief characteristics of the sections sampled near the concentrate body

CHAPTER 5. Mineralogical speciation of arsenic in soils above the Mokrsko-west gold deposit, Czech Republic

Table 1. Semi-quantitative bulk chemical composition (XRF) of soil samples

Table 2. List of selected pedological parameters of soil samples

Table 3. Frequency of detected secondary minerals found in soils at the Mokrsko locality

Table 4. Selected electron microprobe analyses of As-bearing minerals (values in wt.%)

Table 5. X-ray diffraction lines obtained by Debye-Scherrer camera from a set of mineral grains

Table 6. Content of arsenic in particular fractions obtained by sequential extraction procedure (values in mg/kg)

Abstract

The presented dissertation attempts to contribute to the current knowledge on the arsenic (As) mineralogical speciation in diverse types of solid materials, such as contaminated soils and mine wastes.

Introductory part of the dissertation provides a general introduction to As chemical and physical characteristics and to the behavior in the environment, with the main emphasis on As solid phase speciation in soils and mine wastes.

Next part of the dissertation summarizes and briefly evaluates mineralogical methods to the study of primary and secondary As-bearing phases. The main aim is to help with better orientation in the application of these methods. The literature review showed that although a rank of modern methods have been developed in last years (HAADF-STEM, AFM, BFM, PIXE, XAS techniques, ND, etc.), there remain several established methods (XRD, SEM, etc.) as a starting step for mineralogical research. Some other group of methods has been found as possible useful for the study of As solid phase speciation (e.g., RS, DTA, TGA, Vis DRS, VMP).

The main part of the dissertation is presented as a set of three papers on similar subjects published in scientific journals - Environmental Geology, Science of the Total Environment and Geoderma.

The following geochemical and mineralogical methods and approaches were used to achieve the particular aims (summarized collectively): soil samples were characterized by its pH, chemical composition (by X-ray fluorescence, XRF), carbonate, humus, exchangeable cations and H^+, and oxalate extractable Fe contents. Mineralogical and chemical speciation of the As was studied by mineralogical methods and sequential extraction: the As-bearing minerals were concentrated by several ways (panning, heavy fluids) and determined using X-ray diffraction analysis (XRD), the Debye-Scherrer powder method, scanning electron microscopy equipped with an energy-dispersive microanalysis (SEM-EDX), electron microprobe analysis (EMPA) and Raman spectroscopy.

The first published paper titled "Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ)" describes research of the soil, mine tailing, and waste dump profiles above three mesothermal gold deposits in the Bohemian Massif with different anthropogenic histories. The amorphous hydrous ferric oxides, As-bearing goethite, K-Ba- or Ca-Fe- and Fe- arsenates pharmacosiderite, arseniosiderite, and scorodite, and sulphate-arsenate pitticite were determined as products of arsenopyrite or arsenian pyrite oxidation. The As behaviour in the profiles studied differs in dependence on the surface morphology, chemical and mineralogical composition of the soil, mine wastes, oxidation conditions, pH, presence of (or distance from) primary As-mineralisation in the bedrock, and duration of the weathering effect. Although the primary As-mineralisation and the bedrock chemical composition are roughly similar, there are distinct differences in the As behaviour amongst the Mokrsko, Roudný and Kašperské Hory deposits.

The aims of the second paper titled "Oxidation of the arsenic-rich concentrate at the Přebuz abandoned mine (Erzgebirge Mts., CZ): mineralogical evolution" were: i) To study the oxidation of two most common primary As minerals, arsenopyrite and löllingite, stored in a unique anthropogenic deposit; and ii) To evaluate As contamination in the close surroundings of this deposit. The studied concentrate (ore concentrate with up to 65 wt.% of As) contains very small proportion (<5 vol.%) of gangue minerals such as quartz and feldspars; the oxidation of arsenopyrite and löllingite (and accessory pyrite) is thus practically not complicated by interference with additional minerals and elements. Arsenolite, scorodite, kaatialaite and native sulphur were found to be the main secondary phases originating by dissolution of arsenopyrite and löllingite. New secondary phases precipitate on the surface of the ore-concentrate body but also form cement among the grains of finely milled material. The following succession of secondary minerals was determined: arsenolite, scorodite + native sulphur and kaatialaite. Significant As migration into the proximal environment was revealed: 2580 and 13,622 mg.kg^{-1} were the highest arsenic concentrations in two sections excavated at distances of 0.5 and 1.5 m from the concentrate body.

The third paper titled "Mineralogical speciation of arsenic in soils above the Mokrsko-west gold deposit, Czech Republic" was aimed at the natural soil profiles contaminated by As at the Mokrsko gold deposit. The aims of the paper were: i) To determine mineralogical speciation of As throughout the whole soil profiles. ii) To verify a possible relationship among some selected pedological parameters and As-bearing secondary minerals. iii) To test a representative sample of sequential extractions developed for soils contaminated by As and compare the obtained data with knowledge accomplished during the mineralogical studies. Results were compared and discussed regarding the two different types of soil environment: i) soil developed above the flat unforested granodiorite bedrock and ii) soil developed above the volcanosedimentary bedrock in a sloping forested area. Iron (III) oxyhydroxides; K(-Ba) pharmacosiderite, arseniosiderite, scorodite, and jarosite were identified as products of arsenopyrite. Arsenates of varying chemical compositions dominate the soil above the granodiorite, while goethite, minor hematite and other indistinguishable FOHs are observed in the soil above the volcanosediments. The diversity and stability of the As secondary minerals in the studied soils are influenced partly by variation in the bedrock composition and mainly by the presence/absence of vegetation cover which mirrors in various contents of exchangeable Ca^{2+}, content of Fe oxalate, and pH. The results of the sequential extraction show an average to high As retention by these soils, when As was extracted during the third and fourth extraction steps (NH4-oxalate buffer, ascorbic acid) in most samples. This finding indicates that As is more mobile in soils where arsenates dominate over well crystallized iron (III) oxyhydroxides.

Key words: soil, mine wastes, applied mineralogy and geochemisty, arsenic (As), As solid phase speciation, secondary As minerals

Abstrakt

Cílem předkládané disertace je přispět k dosavadním znalostem o arsenové (As) mineralogické speciaci v různých typech pevných materiálů jako jsou kontaminované půdy a důlní odpady.

Úvodní část disertace poskytuje obecné přehled o chemických a fyzikálních vlastnostech As a jeho chování v prostředí. Hlavní důraz je kladen na speciaci As v pevné fázi v půdách a důlních odpadech.

Další část disertace shrnuje a stručně zhodnocuje mineralogické metody používané pro studium primárních a sekundárních As obsahujících fází. Hlavním cílem je usnadnit v orientaci při aplikování těchto metod. Revize literatury ukázala, že ačkoliv bylo v posledních letech vyvinuto mnoho moderních metod (HAADF-STEM, AFM, BFM, PIXE, XAS techniky, ND, aj.), stále zde zůstávají některé osvědčené metody (XRD, SEM, aj.), které mohou být považovány za jakýsi startovní krok pro mineralogické výzkumy. Některé další skupiny metod byly pro studium speciace As v pevné fázi zjištěny jako potenciálně užitečné (např., RS, DTA, TGA, Vis DRS, VMP).

Hlavní část disertace je prezentována formou tří článků s podobným zaměřením publikovaných ve vědeckých časopisech Environmental Geology, Science of the Total Environment a Geoderma.

Pro dosažení jednotlivých cílů byly využity následující geochemické a mineralogické metody a přístupy (shrnuto společně): půdní vzorky byly charakterizovány pomocí pH, chemického složení (stanoveno rentgenovou fluorescencí, XRF), obsahem karbonátu, humusu, vyměnitelných bazických kationtů a vyměnitelného H^+ a obsahem oxalátového Fe. Mineralogická a chemická speciace As byla studována mineralogickými metodami a sekvenční extrakcí: As obsahující minerály byly několika způsoby koncentrovány (rýžování, těžké kapaliny) a určovány pomocí rentgenové difrakce (XRD), Debye-Scherrerovou práškovou metodou, skenovací elektronovou mikroskopií vybavenou energiově disperzním analyzátorem (SEM-EDX), elektronovou mikroanalýzou (EMPA) a Ramanovou spektroskopií.

První publikovaný článek nazvaný „Arsen v kontaminovaných půdách a antropogenních deponiích na zlatých ložiscích Mokrsko, Roudný a Kašperské Hory, Český masív (CZ)‟ popisuje výzkum půdních, odkalištních a haldových profilů nad třemi mezotermálními ložisky zlata s rozdílnou antropogenní historií. Amorfní hydratované oxidy železa, As obsahující goethit, K-Ba- nebo Ca-Fe- and Fe- arsenáty farmakosiderit, arseniosiderit a skorodit, a sulfoarsenát pitticit byly určeny jako produkty oxidace arsenopyritu a arsenového pyritu. Chování As se ve studovaných profilech liší v závislosti na morfologii povrchu, chemickém a mineralogickém složení půd a důlních odpadů, oxidačních podmínkách, pH, přítomnosti (nebo vzdálenosti od) primární As mineralizace v horninovém podloží a době zvětrávání. Ačkoliv jsou primární As mineralizace a chemické složení hornin relativně podobné, jsou zde zřetelné rozdíly v chování As na jednotlivých lokalitách.

Cíly druhého článku nazvaného „Oxidace arsenem bohatého koncentrátu na opuštěném dole Přebuz (Krušné hory, CZ): mineralogický vývoj‟ byly: i) studium oxidace dvou běžných primárních As minerálů arsenopyritu a löllingitu deponovaných v unikátní antropogenní deponii; ii) zhodnotit As kontaminaci v těsném okolí této deponie. Studovaný koncentrát (rudní koncentrát s obsahem až 65 hm.% As) obsahuje jen velmi malé množství (<5 vol.%) hlušinových minerálů jako křemen a živce; proto oxidace arsenopyritu a löllingitu (a akcesorického pyritu) probíhá prakticky bez dalších minerálů a tedy prvků. Jako hlavní produkty rozpouštění rudních minerálů byly zjištěny arsenolit, skorodit, kaatialaite a ryzí síra. Tyto nově vznikající sekundární fáze vznikají na povrchu koncentrátu, ale také

jako cement mezi zrny jemně namletého rudního materiálu. Byla zjištěna následující sukcese tvorby sekundárních minerálů: arsenolit, skorodit + síra a kaatialait. Bylo také zjištěno, že v okolí haldy koncentrátu dochází ke kontaminaci As, kdy nejvyšší obsahy ve dvou kopaných sondách ve vzdálenosti 0,5 m a 1,5 m byly stanoveny 2580, resp., 13,622 mg.kg^{-1}.

Třetí článek nazvaný „Mineralogická speciace arsenu v půdách nad ložiskem Mokrsko-západ, Česká republika" byl zaměřen na přírodně kontaminované půdní profily nad tímto ložiskem. Cíle tohoto článku byly: i) určit mineralogickou speciaci As v celých půdních profilech. ii) Ověřit možné vztahy mezi vybranými půdními parametry a výskytem As minerálů. iii) Otestovat zástupce metod sekvenční extrakce vyvinuté pro posouzení chemické speciace As v kontaminovaných půdách a porovnat získané výsledky s výsledky mineralogického studia. Výsledky byly hodnoceny především s ohledem na dva odlišné typy půdního prostředí, tj. půdu vyvinutou v rovném nezalesněném terénu nad granodioritovým podložím a půdu vyvinutou na svahu v zalesněném terénu nad vulkanosedimentárním podložím. Fe (III) oxyhydroxidy; K(-Ba) farmakosiderit, arseniosiderit, skorodit a jarosit byly identifikovány jako produkty zvětrávání arsenopyritu. Arsenáty s variabilním chemickým složením dominují v půdách nad granodioritem, zatímco goethit, minoritní hematit a další nerozlišené oxyhydroxidy Fe převládají nad vulkanosedimenty. Diverzita a stabilita sekundárních As minerálů je ve studovaných půdách ovlivněna částečně odlišnostmi ve složení horninového podloží a především odlišnými obsahy vyměnitelného Ca^{2+}, obsahem oxalátového Fe a odlišným pH. Výsledky sekvenční extrakce ukazují, že As je ve studovaných půdách vázán relativně silně, kdy většina As byla vyloužena ve čtvrtém loužícím kroku (kys. askorbová pufrovaná NH4 oxalátem). Výsledky také ukazují, že As vázaný v arsenátech v půdě nad granodioritem je poněkud mobilnější než As vázaný na Fe(III) oxyhydroxidy v půdách nad vulkonasedimenty.

Klíčová slova: půda, důlní odpady, aplikovaná mineralogie a geochemie, arsen (As), speciace As v pevné fázi, sekundární As minerály

Preface

Field of interest, its topicality and relevance

Arsenic-bearing minerals were already mined by ancient civilizations (e.g. Ascue and Nriagu, 1994; O'Neill, 1995). Historically, arsenic (As) was used for medicinal purposes in the treatment of ailments such as trypanosomiasis, amoebic dysentery and syphilis (Ascue and Nriagu, 1994; Eisler, 1994). Consequently, the poisoning effects of As on live beings in case of strong exposure have been known since very long time (Nriagu, 2002). However, the toxic effects caused by low-level and long-term exposure result in chronic As poisoning (arsenicosis) were recognized only recently (e.g., Stöhrer, 1991; Chappell et al., 1994; Nriagu, 1994; Liu et al., 2002; Ng et al., 2003).

Nowadays, As is still in the focus of wide public attention mainly due to heavy poisoning of hundreds of thousands people in Bangladesh and West Bengal and in other areas around the world (see e.g., Chatterjee et al., 1995; Das et al., 1995, 1996; Chen et al., 1999; Matschullat, 2000; Berg et al., 2001; Guo et al., 2001; Chakraborti et al., 2002; Ahmed et al., 2004; Vahter et al., 2006). Accidents with As poisoning related to drinking water provoked the legislation in many countries into tightening up the limits for As in drinking water (WHO, 1993; USEPA, 2001).

From 1990 to February 2007, about 17,000 papers have been published on As and its mineral species in different fields (Web of Science data). However, despite the multitude of data on As behavior in the different environmental compartments, from the lithosphere to the anthroposphere, many quantitative data published earlier are questionable, mainly due to analytical problems and oversimplified sampling methods (Matschullat, 2000). Moreover, after the application of more sensitive analytical facilities and more suitable techniques, As compounds became to be determined more commonly, and As behavior was found to be more complex than formerly assumed. These facts arose wide interest in this element. For about the last three decades, the As distribution, bonding and properties have been studied in all constituents of the geosphere. The speciation of As in, and its influence on, the living organisms are studied very attentively (see e.g., Eisler, 1988; Burguera and Burguera, 1997; Chappell et al., 1998; Cobb et al., 2000; Langdon et al., 2001; Sancha and Castro, 2001; Jung et al., 2002; Zhang et al., 2002; Alam et al., 2003; Langdon et al., 2003; Cava-Montesinos et al., 2005; Bruneel et al., 2006; Serafimovski et al., 2006; Schaeffer et al., 2006; Weldon and MacRae, 2006; etc.)

A complex study should be carried out for the identification of As bonding in the uppermost part of the Earth's crust and for the prediction of its behavior under variable environmental conditions. A combination of chemical and mineralogical approaches with laboratory experiments and geochemical modeling is useful and sometimes necessary.

As referred to by Pfeifer et al. (2004), there are many experimental studies focused on the sorption and extraction behavior of As in pure materials (e.g., Goldberg and Glaubig, 1988; Xu et al., 1988; Raven et al., 1998; Lin and Puls, 2000; Goldberg, 2002) as well as on theoretical predictions based on thermodynamic data (e.g., Brookins, 1988; Davis and Ashenberg, 1989; Vink, 1996; Sadiq, 1997). Not so many papers deal with natural materials such as soils that have been enriched in synthetic As compounds (Manning and Goldberg, 1996; Smith et al., 1999).

In the last two decades and mainly in recent years, many papers deal with sites contaminated by industrial and/or mining activities (e.g., Voigt et al. 1996; Dhoum and Evans, 1998; Corwin et al. 1999; Juillot et al., 1999; Weiss et al., 1999; Daus et al., 2000; Roussel et al., 2000; Savage et al., 2000; Lumsdon et al. 2001; Williams, 2001; Craw et al. 2002; Courtin-Nomade et al., 2003; Fukushi et al. 2003; Matera et al. 2003; Néel et al. 2003; Van Herreweghe et al. 2003; Frau end Ardau 2004; Ferreira da Silva et al. 2004). On the other hand, fewer papers concern soil contamination by natural sources (e.g., Jacobs et al., 1970; Dudas, 1987; Bowell, 1994; Morin et al., 2000; Strawn et al., 2002).

As implies from the above cited papers, contaminated soils and different types of mine wastes are important systems on the Earth's surface from the viewpoint of As mobility/stability. These settings are significant reservoirs providing As for the biosphere (food chains of living organisms), atmosphere (gas migration via biomethylation and wind transport of solid particles) and hydrosphere (interaction with rainfall, surface water, groundwater and soil waters). Arsenic behavior in soils and in other related materials depends mainly on the type of As bonding and on physico-chemical properties of soils (mine wastes).

The association of As with clay minerals, ferric (III) oxyhydroxides and organic matter has been well established and widely studied by many authors (see e.g., Bowell, 1994; Manning and Goldberg, 1996; Lin and Puls, 2000; Manning et al., 1998; Davis et al. 2001; Gräfe et al., 2001; Randall et al., 2001; Goldberg, 2002; Cao et al., 2003; Sherman and Randall, 2003; Ko et al., 2004; Fernández et al., 2005; Warwick et al., 2005). However, a much lesser attention was focused on As bonding to secondary As minerals in the contaminated soils and mine wastes (see e.g., Pierrot, 1964; Morin et al., 2000; Frau and Ardau, 2004; Paktunc et al., 2004). The main reasons for this are probably the scarcity and substantial dispersal of the secondary As minerals in such environments, their intergrowths with other minerals and often also an unknown structure of individual secondary phases. All these facts make the investigation of secondary As minerals difficult.

Purpose of the dissertation

Identification of As mineralogical/chemical bond is essential for all studies focused on As behavior in the uppermost part of the Earth's crust. Complex knowledge may be achieved only by a study of both the natural and anthropogenic inputs of As into the systems. Moreover, the application of computer models of As behavior in the environment as well as the developing of remediation procedures for treatment of contaminated areas depend closely on the quality of these data.

The presented dissertation attempts to contribute to the current knowledge on the As mineralogical speciation in diverse types of solid materials, such as contaminated soils and old mine wastes. The aims of individual selected topics are presented in more detail in introductions to the particular chapters; however, the main objectives were:

- A brief summary of the existing knowledge of secondary As mineralogy in highly contaminated soils and mine wastes
- A summary of the mineralogical approaches for the determination of As-bearing minerals in soils and mine wastes
- Determination of the As contents and main As-bearing minerals in the Quaternary sediments and soils at Mokrsko, Roudný and Kašperské Hory
- A detailed characteristic of the distribution of secondary As-bearing minerals throughout the Mokrsko soil profiles

- Determination and evaluation of the soil properties and their importance for the stability of As-bearing minerals at the Mokrsko locality
- Testing of the sequential extraction as a commonly used chemical tool for the evaluation of As speciation at the Mokrsko locality
- Identification of the secondary products of the arsenopyrite and löllingite oxidation in the unique As-rich dump from the case locality of Přebuz, and a preliminary evaluation of their environmental hazard

An overview of the contents of the dissertation

First Chapter of this dissertation provides a general introduction to As chemical and physical characteristics and to the behavior in the environment, with the main emphasis on As solid phase speciation in soils and mine wastes. It also contains a brief summary of the secondary As minerals that have been mentioned in the literature as important As carriers in this type of environment.

Chapter 2 is an important part of the dissertation. It summarizes and briefly evaluates mineralogical approaches to the study of primary and secondary As-bearing phases. This chapter will be submitted as a review-type publication to an appropriate international journal after some adjustment. As stated in Section 1 of this Preface, As behavior in the environment is a modern and widely studied subject. As a result, a huge number of papers have been published (cf., Section References). In this situation, review articles help significantly with the orientation in various parts of As investigations (cf. e.g., Matschullat, 2000; Smedley and Kinnisburgh, 2002; Ng et al., 2003; Langdon et al. 2003; Wang and Mulligan, 2006); Chapter 2 can be thus considered a useful result of this dissertation.

The main part of the dissertation is presented as a set of three papers on similar subjects published in scientific journals - Environmental Geology, Science of the Total Environment and Geoderma (Chapters 3, 4, and 5, respectively). Therefore, some repetition of the background and methods occurs in some sections.

The first published paper “Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ)” has its origin in the diploma thesis of the author. Some new chemical and mineralogical data were added to the previous results. The paper compares the As contents at three different localities with roughly similar primary mineralization and monitors As solid phase speciation in contaminated soils as well as in mine tailings and mine wastes of different ages.

Afterwards, a new research started at the very specific Přebuz locality. The principal aims were: i) To study the oxidation of two most common primary As minerals, arsenopyrite and löllingite, stored in a unique anthropogenic deposit; and ii) To evaluate As contamination in the close surroundings of this deposit. Unfortunately, after ca. 50 years of repose, this deposit was removed suddenly and the research could not be completely finished. A preliminary mineralogical evaluation was published in the paper titled “Oxidation of the arsenic-rich concentrate at the Přebuz abandoned mine (Erzgebirge Mts., CZ): mineralogical evolution.”

Further work was focused on the Mokrsko locality again, which was selected for the good knowledge of its geology and the high As contents in naturally contaminated soils. After disclosing the occurrence of arsenates and ferric oxides and oxyhydroxides in selected soil samples (Filippi et al., 2004), three main purposes were followed: i) To determine mineralogical speciation of As throughout the whole soil profiles. ii) To verify a possible relationship among some selected pedological parameters and As-bearing secondary minerals. iii) To test a representative sample of sequential extractions developed for soils contaminated by As and compare the obtained data with knowledge accomplished during the mineralogical studies. The results were published in the paper titled “Mineralogical speciation of arsenic in soils above the Mokrsko-west gold deposit, Czech Republic.”

Finally, the Chapter 6 tries to briefly outline the possible ways for future research planned by the author of this dissertation.

CHAPTER 1. Basic data on arsenic with emphasis on As-bearing minerals in soils and mine wastes

1.1. Arsenic as a chemical element

1.1.1. Basic data

The name arsenic comes from the Persian word Zarnikh meaning "yellow orpiment". Zarnikh was borrowed by Greek as arsenikon. Orpiment is a bright yellow mineral composed of arsenic sulfide (As_2S_3). Historians say that As was discovered in 1250 C.E. by Albertus Magnus, a German monk who spent his life studying and classifying natural materials. It is believed that he heated soap and orpiment together and isolated elemental arsenic.

Arsenic (As) is a metalloid, member of group V of the periodic table, which combines readily with other elements, manly it is very similar chemically to phosphorus (P), due to similar ionic radii (Peryea, 1991; Darland and Inskeep, 1997; Reynolds et al., 1999; Hongshao and Stanforth, 2001; Violante and Pigna, 2002). Especially in aerated systems, the As(V) ions closely resemble orthophospate ions (Walsh et al., 1977). Elemental As is found in two solid modifications: yellow, which is unstable, and gray/metallic that is stable. The metallic modification is a steel grey, very brittle, crystalline solid. It tarnishes in air and when heated it oxidizes to As trioxide which has an odour of garlic. Selection of main characteristics of the As is listed in Table 1.

Table 1. Basic characteristics of the arsenic

Name	Arsenic
Symbol	As
Date of Discovery	Known to the ancients
Discoverer	Unknown
Modifications	Yellow (unstable) and gray (described bellow)
Classification	Metalloid
Group	Non-metal, Nitrogen group
Stable isotope	As 75
Number of unstable isotopes	8
Atomic number	33
Number of Protons/Electrons	33
Number of Neutrons	42
Atomic mass	74.9216 g/mol
Atomic volume	13.1 g.cm3/mol
Crystal Structure	trigonal, orthorhombic
Point Group:	-3 2/m
Space Group:	R-3m
Density at 14 °C	5.72 g/cm^3 (grey), 1.97 g/cm^3 (yellow)
State	solid
Oxidation states in natural systems	-III, 0, +III, +V: arsines and methylarsines (-III), elemental arsenic (0), arsenite (+III), and arsenate (+V)
Most common compounds	H_2AsO^{4-}, $HAsO_4^{2-}$ and H_2AsO^{3-}
Melting point	817.0 °C (1090.15 K, 1502.6 °F)
Boiling point – sublimation	613.0 °C (886.15 K, 1135.4 °F)
Electronegativity according to Pauling	2.0
Vanderwaals radius	0.139 nm
Ionic radius	0.222 nm (-2) 0,047 nm (+5) 0,058 (+3)
Electronic configuration	[Ar] $3d^{10}$ $4s^2$ $4p^3$
Energy of first ionisation	947 kJ.mol^{-1}
Energy of second ionisation	1798 kJ.mol^{-1}
Energy of third ionisation	2736 kJ.mol^{-1}
Standard potential	- 0.3 V (As^{3+}/ As)

Natural As usually has a trigonal symmetry but two very rare orthorhombic As (named arsenolamprite and pararsenolamprite) are known from several localities over the world (e.g., Johan et al., 1959; Matsubara et al., 2001). Arsenic typically occurs in anionic form, which is different from most metals that form cations. Arsenic does not readily substitute into the structures of the major rock-forming minerals (Vaughan, 2006). The most important primary As-bearing minerals are mixed sulfides of the M(II)AsS type, where M(II) stands for Fe, Ni, and Co as well as other two-valent metals (Reimann and de Caritat, 1998). Secondary As minerals usually originate by oxidation of the primary As minerals. Most of them are arsenates, which reveal close crystalochemical relations to phosphates and vanadates. Some of the most common primary and secondary As minerals are listed in Table 2. The As is naturally associated mainly with sulfides (chalcophilic minerals), and usually occurs in hydrothermal types of mineral deposits. Less frequently it is associated with volcanic or magmatic rocks. Arsenic phases are also known to occur in fumeroles and geothermal systems. Occasionally As can also occurs associated with sedimentary pyrite in sedimentary rocks.

Table 2. List of the most common arsenic minerals in the nature

Mineral	**formula**
Algodonite	Cu_6As
Allemontite (stibarsen)	SbAs
*Annabergite**	$Ni_3(AsO_4)_2{\cdot}8H_2O$
Arsenolite	As_2O_3
Arseniosiderite	$Ca_2Fe_3(AsO_4)_3O_2{\cdot}3(H_2O)$
Arsenopyrite	FeAsS
Bayldonite	$PbCu_3(AsO_4)_2(OH)_2{\cdot}H_2O$
Beudantite	$PbFe(AsO_4)(SO_4)(OH)_6$
Bukovskyite	$Fe_2(AsO_4)(SO_4)(OH)\ {\cdot}7H_2O$
Enargite	Cu_3AsS_4
Erythrite	$Co_3(AsO_4)_2{\cdot}8H_2O$
Gersdorfite	NiAsS
Haidingerite	$CaHAsO_4{\cdot}H_2O$
Hornesite	$Mg_3(AsO_4)_2{\cdot}8H_2O$
Chloantite	$NiAs_2$
Kankite	$FeAsO_4{\cdot}3.5H_2O$
Kobaltite	CoAsS
Löllingite	$FeAs_2$
Mimetite	$Pb_5(AsO_4)_3Cl$
Mixite	$BiCu_6(AsO_4)_3(OH)_6{\cdot}3H_2O$
Nicolite	NiAs
Olivenite	$Cu_2(AsO_4)(OH)$
Orpiment	As_2S_3
Pharmacolite	$CaH(AsO_4)\ {\cdot}2H_2O$
Pharmacosiderite	$Fe(AsO_4)_3(OH)_4{\cdot}5\text{-}7H_2O$
Pitticite	amorphous iron sulpho-arsenate
Proustite	$3Ag_2S.As_2S_3$
Rammelsbergite	$NiAs_2$
Realgar	As_4S_4
Safflorite	$CoAs_2$
Scorodite	$Fe(AsO_4)\ {\cdot}2H_2O$
Skutterudite	$CoAs_3$
Tennantite	$(Cu, Fe)_{12}As_4S_{13}$
Weilite	$CaHAsO_4$
Zeunerite	$Cu(UO_2)_2(AsO_4)_2{\cdot}10\text{-}16H_2O$

***** Mineral printed in italic style are usually considered to be the secondary (or supergene) minerals; the other are primary As minerals.

The average content of As in the upper Earth's crust is about 2 mg/kg (Wedepohl, 1995) and it is 47th in abundance among the 88 naturally occurring elements (Vaughan, 2006). The total As amount in the Earth's crust was estimated to be 4.01×10^{16} kg, based on concentrations in different rocks (Matschullat, 2000). The same author also calculated the total As input to the litosphere to be of

8.46-14.22 × 10^7 kg per year. Fluxes and amounts of the As in other constituents of the geosphere were summarized and calculated by Matschullat (2000).

Arsenic pollution of the environment originates from both geochemical background and anthropogenic sources. Gaseous and solid emissions connected with volcanic activity, terrigenous dust, biogenic volatile compounds of both marine and terrigenous origin, oceanic spray and large forest fires, represent the natural inputs into the As cycle on Earth; whilst mining, ore dressing, non-ferrous metal production, steel/iron manufacturing and fossil fuel combustion are the main anthropogenic sources (Nriagu, 1989).

1.1.2. Main usage of arsenic

During the 18th, 19th, and 20th centuries, a number of As compounds were used as medicines, and copper acetoarsenite was used as a green pigment known under many different names (Ascue and Nriagu, 1994). Today, the most common usage of As compounds is in agriculture and forestry as arsenical pesticides such as insecticides, herbicides, fungicides, algicides, sheep dips, and some dyestuffs, and it is also used for the eradication of tapeworm in sheep and cattle (Adriano, 1986). After that follow manufacturing of ceramics and glass, chemicals, and other minor uses. Very important use is for wood preservatives in form of a compound called chromated copper arsenate (CCA). CCA prevents organisms from growing in the wood and causing it to rot. Trace amounts of As are alloyed with lead in accumulators.

At present, the major use for inorganic As except the wood preservation is in the microelectronics industry and in semiconductor manufacture. Alloys of gallium, arsenic, and phosphorous are used for the production of light-emitting diodes (LEDs) in watches, clocks, calculators, and numerous other instrument displays.

1.1.3. Chemical speciation of As in the environment

Arsenic forms a variety of inorganic and organic compounds in soil and mine waste environments. The most common forms are, however, inorganic arsenite As(III) and arsenate As(V) (e.g., Masscheleyn et al., 1991; Smith et al., 1998). Under common environmental conditions (pH in range 4-8) As(V) is present as $H_2AsO_4^-$ or $HAsO_4^{2-}$ species, while As(III) occurs as $H_3AsO_3^0$ species and is dominant only in low pH and low Eh environments (Cullen and Reimer, 1989; Smith et al., 1998; Goldberg and Johnston, 2001). For the main forms of the As see also Figure 1.

Other soluble forms of arsenate and arsenite may probably be present as minor constituents within aquatic or soil environments: e.g., methylated-arsenic (Smith et al., 1998; Smedley and Kinniburgh, 2002), thio-arsenic - $H_2AsOS_2^-$ and $H_2AsOS_3^-$ (e.g., Helz et al., 1995; Rochette et al., 2000; Wang and Mulligan, 2006) and carbonato-arsenic (Kim et al., 2000; Lee and Nriagu, 2003). The monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA), and partly also trimethylarsine oxide (TMAO) are the most common methylated species, which mainly dominate in biomass, but have also been detected in soils (Buchet and Lauwerys, 1981; Cullen and Reimer, 1989; Leonard, 1991; Turpeinen et al., 2002). In soils, water-soluble As species can be volatilized by microbes to the form of gaseous arsines (e.g., Gao and Burau, 1997). As(V) and As(III) can be volatilized to arsine (AsH_3), MMAA to monomethylarsine (MMA, $AsH_2(CH)_3$), DMAA to dimethylarsine (DMA, $AsH(CH_3)_2$), and TMAO to trimethylarsine (TMA, $As(CH_3)_3$) (Cullen and Reimer, 1989). Arsenobetaine (AsB) is a common organoarsenic species in marine mammals, while arsenosugars are the major species in plants like algae (Belzile and Tessier, 1990).

Soluble forms of As may also bind to organic matter in sediments (Gräfe et al., 2001, 2002; Redman et al., 2002; Ko et al., 2004). However, organic matter content tends to be poorly correlated to As in comparison to Fe, Al, or P (Chen et al., 2002), suggesting that its contribution to As retention in soils is limited (Herbel and Fendorf, 2006).

Inorganic, organic, and biological forms of As in the environment are listed in Figure 2.

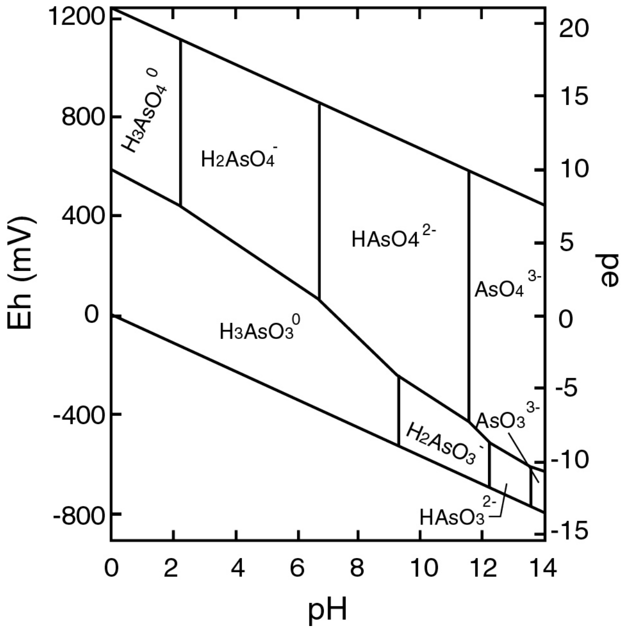

Fig. 1. An Eh-pH diagram of aqueous, aerobic As-solution at 25 C and 1 bar of pressure (according to Smedley and Kinisburg, 2002)

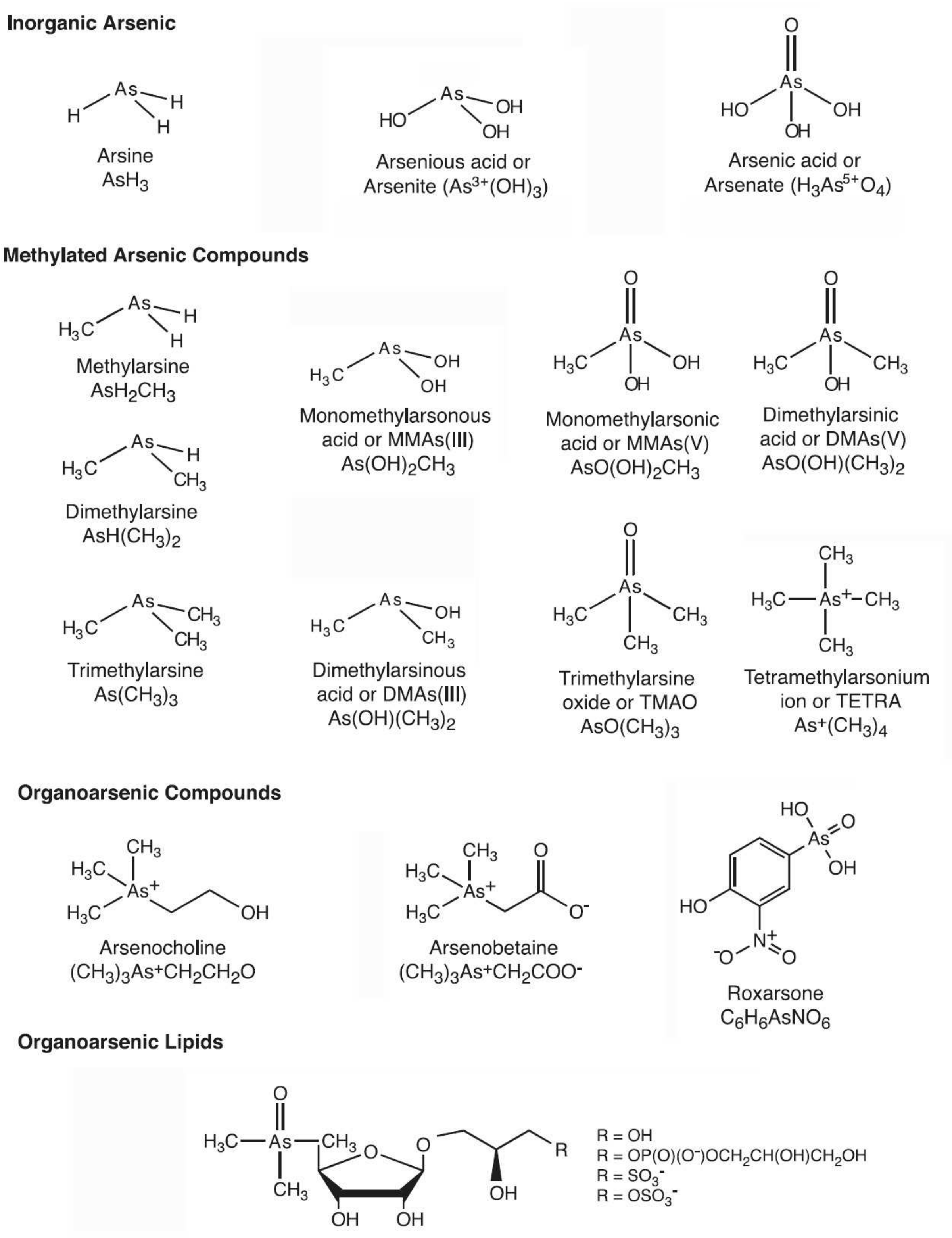

Fig. 2. Summary of important inorganic, organic, and biological forms of arsenic in the environment (according to O´Day, 2006, modified).

1.1.4. Arsenic toxicity

Arsenic is a toxic element for fauna and flora. Arsenic speciation influences its toxicity that decreases in following order: arsines > arsenite > arsenoxides > arsenate > tetravalent arsenicals > metallic As (Penrose, 1974). Humans may be exposed to As through various ways such as via ingestion of contaminated food or water, inhalation of polluted air in some industrial plants and also through direct dermal exposition with soil or water that contains high contents of As (e.g., Mitchel and Barr, 1995; Dudka a Miller, 1999). Certain hazard is posed by constructions that contain conserved wood. Also people who live or work on farmlands where As-containing pesticides have been applied in the past are exposed to a risk of intoxication. As well, mining areas and old mine dumps and tailings may represent hazard due to dust transport by air (Camm et al., 2003; Camm et al., 2004; Jamieson et al., 2006).

High exposure to inorganic As can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes, lung irritation, infertility and miscarriages with women, it can cause skin disturbances, declined resistance to infections, heart disruptions and brain damage. Finally, inorganic As can damage DNA (e.g., Oliver, 1997; Shi et al., 2004; Ding et al., 2005). A lethal dose will vary with compound, but 0.2-0.3 g of arsenic trioxide (As_2O_3) is usually fatal in an adult.

1.2. Arsenic in soils and mine wastes

1.2.1. Sources and concentrations of As

The main source of As in soils is the parent rock material (Yan-Chu, 1994); bedrock in case of natural contamination and waste dumps in case of so-called minesoils. For As concentrations in various geological environments and in particular minerals see Tables 3 and 4. The As content in rocks depends on contents of different rock-forming minerals. According to various authors the sedimentary rocks contain generally much higher concentrations than the igneous rocks (e.g., Wedepohl in Merian et al., 1991; Bhumbla and Keefer, 1994; Smedley and Kinnisburgh, 2002).

The content of As in natural nonpolluted soils varies with soil type, depending on the nature of the parent material (Smith et al., 1998). Usual As concentration ranges between ca. 4-20 $mg.kg^{-1}$, and rarely up to 40 $mg.kg^{-1}$ (Walsh and Keeney, 1975; Smith et al., 1998). These values are considered as safe for living organisms (Dudka and Miller, 1999). Recently, 5 $mg.kg^{-1}$ of As is considered as the global average content in uncontaminated soils (Koljonen, 1992). The content and distribution of As in minesoils is very variable as well, and it often mirrors the heterogeneity of the background material (mine/industrial waste). Generally, the contaminated soils (whether naturally or industrially) contain from tens up to hundreds of $mg.kg^{-1}$, and rarely up to several percent of the As (e.g., Peterson et al., 1979; Matschullat, 2000; Morin et al., 2000; Wenzel et al., 2001; Van Herreweghe et al., 2003; Taggart et al., 2004; De Brouwere et al., 2003; Ferreira da Silva et al., 2004; Filippi et al., 2004).

Nriagu and Pacyna (1988) calculated the anthropogenic As input into the soil as 9.4×10^7 kg per year, in the following approximations: 40 % wastages from commercial products; 21 % from coal ashes; 11 % from atmospheric deposition; 10 % from mine tailings materials; 7 % from agriculture, wood, animal, and food wastes; 6 % from smelter slags and wastes; 5 % from other minor sources.

More detailed information about various types of anthropogenic sources of the As in soils were reviewed by Smith et al. (1998).

Table 3. Average As concentrations and/or ranges in various rocks and other geological environments (according to Smedley and Kinniburgh (2002), for references see therein, partly adjusted)

Type of rock / sediment	**As concentration average and/or range [$mg.kg^{-1}$]**
Igneous rocks	
Acidic rocks (rhyolite)	4.3 (3.2–5.4)
Acidic rocks (granite, aplite)	1.3 (0.2–15)
Acidic rocks (pitchstone)	1.7 (0.5–3.3)
Basic rocks (basalt)	2.3 (0.18–113)
Basic rocks (gabbro, dolerite)	1.5 (0.06–28)
Intermediate (andesite, trachyte, latite)	2.7 (0.5–5.8)
Intermediate (diorite, granodiorite, syenite)	1.0 (0.09–13.4)
Ultrabasic rocks (peridotite, dunite, kimberlite etc)	1.5 (0.03–15.8)
Volcanic glasses	5.9 (2.2–12.2)
Metamorphic rocks	
Amphibolite and greenstone	6.3 (0.4–45)
Granulites	4[a]
Hornfels	5.5 (0.7–11)
Phyllite/slate	18 (0.5–143)
Schist/gneiss	1.1 (<0.1–18.5)
Quartzite	5.5 (2.2–7.6)
Sedimentary rocks	
Bituminous shale (Kupferschiefer,,Germany)	100–900
Coals	0.3–35,000
Evaporites (gypsum/anhydrite)	3.5 (0.1–10)
Iron formations and Fe-rich sediment	1–2900
Limestone/dolomite	2.6 (0.1–20.1)
Marine shale/mudstone	3–15 (up to 490)
Non-marine shale/mudstone	3.0–12
Phosphorite	21 (0.4–188)
Sandstone	4.1 (0.6–120)
Shale (Mid-Atlantic Ridge)	174 (48–361)
Unconsolidated sediments	
Alluvial mud/clay (Bangladesh)	6.5 (2.7–14.7)
Alluvial sand (Bangladesh)	2.9 (1.0–6.2)
Continental margin sediments (argillaceous, some anoxic)	2.3–8.2
Glacial till, British Colombia	9.2 (1.9–170)
Lake sediments, British Colombia	5.5 (0.9–44)
Lake sediments, Lake Superior	2.0 (0.5–8.0)
Loess silts, Argentina	5.4–18
River bed sediments (Bangladesh)	1.2–5.9
Stream and lake silt (Canada)	6 (<1–72)
World average river sediments	5
Soils	
Acid sulphate soils (Canada)	1.5–45
Acid sulphate soils (Vietnam)	6–41
Peaty and bog soils	13 (2–36)
Soils near sulphide deposits	126 (2–8000)
Soils (or eluvium) above gold deposit	up to ca. 26,300[b]
Various contaminated superficial anthropogenic deposits	usually up ca. 50,000; rarely up to ca. 60 wt.% [c]

[a] data from Wedepohl in Merian et al. (1991)
[b] data from Filippi et al. (2004)
[c] data from Filippi (2004)

Table 4. As concentrations in common rock-forming minerals (according to Smedley and Kinniburgh (2002), for references see therein, partly adjusted).

Mineral	As concentration range [mg.kg^{-1}]
Sulphides	
Galena	5–10,000
Chalcopyrite	10–5000
Marcasite	20–126,000
Pyrite	100–77,000
Pyrrhotite	5–100
Sphalerite	5–17,000
Oxides	
Haematite	up to 160
Fe oxide (undifferentiated)	up to 2000
Fe(III) oxyhydroxide	up to 76,000
Ilmenite	<1
Magnetite	2.7–41
Silicates	
Amphibole	1.1–2.3
Biotite	1.4
Feldspar	<0.1–2.1
Olivine	0.08–0.17
Pyroxene	0.05–0.8
Quartz	0.4–1.3
Other	
Apatite	<1–1000
Barite	<1–12
Calcite	1–8
Dolomite	<3
Halite	<3–30
Fluorite	<2
Gypsum/anhydrite	<1–6
Jarosite	34–1000
Siderite	<3

1.2.2. Physico-chemical behaviour of As and releasing mechanisms

Geochemical factors that may enhance As mobility are highly variable and complex. It includes ion displacement, oxidative dissolution of sulphides, reduction of As, and reductive dissolution of As containing Fe oxyhydroxides (Cullen and Reimer, 1989; Smith et al., 1998; Smedley and Kinniburgh, 2002). Common type of anthropogenic As contamination is related to exposure of As-bearing minerals to atmospheric O_2 upon the mine wastes storage, which leads to the formation of acid mine drainage (AMD) and acid minesoils with high concentration of As, SO_4, Fe(II), Fe (III) and other metals (e.g., Nicholson et al., 1989; Craw et al., 2002). Soils affected by AMD may have high concentration of inorganic As(III) or As(V) species depending on Eh-pH conditions (e.g., Bodénan et al., 2004; Sánchez-Rodas et al., 2005). Other potentially hazardous sites are those where As-bearing minerals oxidize in soils developed above the mineralized outcrops. Such sites may release As to the surrounding environment for very long time - from decades to millennia (Blowes et al., 1992; Pyatt et al., 2000; Frau and Ardau, 2003; etc.).

The reactions and mobility of As in soils, mine wastes and similar environments are highly governed by its oxidation state and in part by the tendencies of different As redox species to associate with particulate matter (e.g., Herbel and Fendorf, 2006). Thus As sorption to soil particles is one of the most important processes that immobilizes this element. Many studies were devoted to As sorption on well characterized minerals or soil particles (clays, oxides of Fe, less Al and Mn, phosphatic gels and/or organic matter) (e.g., Sadiq, 1997; Smith et al., 1998; Kabata-Pendias and Pendias, 2001). The adsorption capacity of these particles is dependent on different physico-chemical factors such as hydratation, crystallinity, pH, redox potential, presence of other elements and organic matter, etc. (Woolson, 1977; Sadiq, 1997). Although As(III) is generally more thermodynamically stable under reducing conditions and As(V) is more stable under well oxidizing conditions, both oxidation states will often exist concurrently because of the relatively slow redox transformations between As species. Also, the redox processes involving As are often biological and intracellular, where the redox conditions might be very different than those of the bulk soil. The result is that As(III) as well as As (V) are observed under both oxidized and reduced soil conditions (e.g., Drahota et al., 2006).

From experimental studies as well as from *in situ* observations, it is well established that As sorption on oxides is mainly pH dependant, when As(III) is preferentially sorbed at pH values raging from 7 to 10, whereas As(V) is preferentially sorbed on hydrous oxides at pH values ranging from 4 to 7 (Pierce and Moore, 1980). Frost and Griffin (1977) have also shown that As sorption on clay minerals (kaolinite and montmorillonite) is pH dependent and Lin and Puls (2000) confirm that As(V) is more strongly sorbed than As(III) on these minerals. Furthermore, As(V) adsorption on humic substances reaches its maximum at pH 5.5 in contrast to distinctly higher values of pH of about 8.5 for As(III) (Thanabalasingam and Pickering, 1986). As it was noticed by other authors (Frost and Griffin, 1977), adsorption of As(III) was lower than As(V). As species behaviour was largely attributed to humic acids that become more soluble with increasing pH. Alternatively, the observed pH effect could reflect the changes in protonation of both adsorbent and absorbate (Thanabalasingam and Pickering, 1986).

In most environmental materials, total As levels correlate with Fe content rather than Al or clay content (Smedley and Kinniburgh, 2002), and microbial reduction of Fe(III) in the iron (hydr)oxide minerals may release Fe(II) and adsorbed As(V) or As(III) into solution (Langner and Inskeep, 2000; Herbel and Fendorf, 2006). According to Xu et al. (1988); Manning and Goldberg (1997a,b) and Smith et al., (1998), As(V) is more strongly bound to clays and Al hydroxides than As(III). Ferric (hydr)oxides and magnetite, in contrast, exhibit a greater retention of As(III) than As(V) at all but acidic conditions (Raven et al., 1998; Goldberg, 2002; Dixit and Hering, 2003).

Releasing of As from the solid phase, and retardation of As adsorption, can occur when incoming solutions contain high levels of dissolved inorganic and organic ions (Manning and Goldberg, 1996; Reynolds et al., 1999; Dixit and Hering, 2003). Soluble Fe(II) and CO_3^{2-} may change As(V) and As(III) adsorption behaviour on the most common Fe minerals such as ferrihydrite and goethite (Van Geen et al., 1994; Villalobos and Leckie, 2001). Other anions, such as Cl^-, SO_4^{2-}, and NO_3^-, appear to have minimal effect on As desorption, yet these ions can contribute to ionic strength and salinization effects on As desorption in sediments (Gupta and Chen, 1978; Smith et al., 1998).

The most readily bioreducible Fe(III) oxyhydroxides are less thermodynamically stable phases of high surface area, such as ferrihydrite and lepidocrocite (Schwertmann and Taylor, 1989; Lovley, 1991; Roden and Zachara, 1996). Ferrous iron produced during Fe(III) reduction induces transformation of ferrihydrite and lepidocrocite to more stable Fe (III) minerals, such as goethite (α-FeOOH), and mixed Fe(II)–Fe(III) minerals, such as magnetite (Fe_3O_4) (Zachara et al., 2002; Hansel et al., 2004). Despite having a nearly equal affinity for As, transformation (due to ageing of biotransformation) of ferrihydrite and lepidocrocite to more crystalline phases (goethite, hematite) reduces the available surface area and thus diminishes their capacity to retain As (Dzomback and Morel, 1990; Fuller et al., 1993; Dixit and Hering, 2003; Herbel and Fendorf, 2005).

1.2.3. Microbial activity

The biotransformation of As has been recognized for many years, this process is considered as an important factor in redistributing As in soils (Cullen and Reimer, 1989; Ehrlich, 1996). Most important biochemical processes in soils are microbial oxidation of sulphides (Mandl et al., 1992; Blowes et al., 1995; Sampson et al., 2000), oxidation of As(III) to As(V) (Wakao et al., 1988), reduction of As (Harrington et al., 1998), dissolution of As induced by microbial reduction of Fe(III) (Nickson et al., 2000), and biomethylation (Woolson, 1977; Cullen and Reimer, 1989; Turpeinen et al., 1999; Carbonell et al., 1998; Turpeinen et al., 2002). Some other microbes can also demethylate organic forms back to inorganic species (Sohrin et al., 1997).

However, mainly two microbial processes, oxidation and reduction, are of current interest because of their possible application for bioremediation of contaminated soils (e.g., Smith et al., 1998; Gomez and Bosecker, 1999; Turpeinen et al., 1999) and for the oxidation of sulphides to recover the associated valuable metals for the industrial sphere (Sampson et al., 2000). Bacterial leaching is a pre-treatment step for the dissolution of metals from sulphidic minerals aided by the catalytic action of chemolithoautotrophic bacteria. Wide range of microorganisms are able to inhabit the extremely acidic environments associated with the oxidative dissolution of sulfide minerals or the oxidation of (reduced) sulfur (Johnson and Roberto, 1997). A number of heterotrophic As(III) oxidizing bacteria have been characterized, with many of them classified as *Bacillus* or *Pseudomonas* spp. (Smith et al., 1998). However, the commercially most important bacteria come from the *Thiobacillus* and *SulfobacilIus* genera (Sampson et al., 2000). Likewise, various microorganisms are able to reduce As compounds (Smith et al., 1998).

Many of microorganisms (bacteria, fungi, and algae organisms) that are capable to oxidize or reduce As-bearing compounds have been isolated from a diversity of natural environments (Osborne and Ehrlich, 1976; Lovley, 1991; Stolz and Oremland, 1999; Samson et al., 2000; Oremland et al., 2002; Oremland and Stolz, 2003). Some species of bacteria are able to reduce soluble arsenate and also adsorbed arsenate (Herbel and Fendorf, 2006) and solid arsenate such as scorodite (Newman et al., 1997), with recent evidence suggesting that reduction first proceeds through a step of dissolution (Saltikov and Newman, 2003).

Microbial activity, in combination with geochemical factors, may significantly control As speciation and uptake or release mechanisms in natural environments (Herbel and Fendorf, 2006).

1.3. Arsenic minerals in soils and mine wastes: a brief overview

1.3.1. General terms and relationships in environmental mineralogy

In environmental mineralogy, the **primary minerals** are those that are deposited within the various types of **mine** or **industrial wastes** and related **anthropogenic soils (minesoils)** or are present in weathered and decomposed rock outcrops (saprolith) covered by **natural soil**.

The **secondary minerals** are those that form by in-situ reaction of the primary assemblage; thus, the primary suite may contain **supergene minerals** that were in the ores and host rocks prior to mining or prior to the weathering processes under climate conditions in case of mineralized rock outcrops (c.f., Jambor, 1994; Jambor and Blowes, 1998). Therefore, some typical primary ore minerals such as pyrite (i), arsenopyrite (ii) or orpiment (iii) that, however, may form in: (i) water saturated tailings (Chappel and Craw, 2002), (ii) sediments (Rittle et al., 1995); or (iii) by microbial precipitation (Newman et al., 1997; Newman et al., 1998), could be classified as **secondary minerals from the environmental mineralogy point of view**. On the contrary, e.g., arsenolite described by Juillot et al. (1999) or scorodite described by Ahn et al. (2005), which both may be common products of industrial processes, could by considered as primary sources of the As in the industrial waste dumps.

Generally, the supergene As minerals often occur in form of well developed crystals or crystallized coatings and crusts close to primary ores in cavities of vein-minerals such as quartz, calcite, dolomite, etc. Supergene As minerals were mostly formed during the last stages of the **hydrothermal activity** in ore deposits. On the other hand, secondary minerals originated by direct oxidation of primary ores or by related **cold solutions** under the so-called **environmental conditions** are mostly developed as various types of amorphous-like or fine crystallized coatings, crusts and infillings of fractures in the primary ore minerals. Moreover, they often overgrow, impregnate or replace rock-forming minerals situated close to weathering ores.

In the following sections, important primary As minerals will be shortly described. The attention is, however, especially focused on the secondary As-bearing minerals which have been described as the major or significant sources of As in the environment. Those As low-temperature secondary associations which are formed from very rare primary ore associations or at very specific and isolated sites will not be included into this text. These random and specific settings may contain large amounts of rare secondary As-bearing minerals which, however, have no important influence on the As cycling in the environment. Table 5 presents some examples of such “mineralogical” occurrences of rare secondary As minerals.

Table 5. Several rare As minerals and artificial phases(*) occurring in some specific contaminated sites

Mineral	Formula	Selected reference
austinite	$CaZn(AsO_4)(OH)$	Bowel and Parshley (2005)
angelellite	$Fe_4As_2O_{ll}$	Leblanc et al. (1996)*
arsenolamprite	As	Johan (1959); Ahn et al. (2005)
arsenowaylandite	$BiAl_3(AsO_4)_2(OH)_6$	Courtine-Nomade et al. (2003)
bernardite	$Tl(As,Sb)_5S_8$	Ahn et al. (2005)
conichalcite	$CaCu(AsO_4)(OH)$	Pieczka et al. (1998)
cornwallite	$Cu_5(AsO_4)_2(OH)_4$	Bowel and Parshley (2005)
kaatialaite	$(FeAs_3O_9 \cdot 6\text{-}8H_2O)$	Filippi (2004)
legrandite	$Zn_2(AsO_4)(OH) \cdot (H_2O)$	Bowel and Parshley (2005)
ludlockite	$(Fe,Pb)As_2O_6$	Camm et al. (2003)
parascorodite	$FeAsO_4 \cdot 2(H_2O)$	Ondruš et al. (1999)
sarmientite	$Fe_2(AsO_4)(SO_4)(OH) \cdot 5(H_2O)$	Gieré et al. (2003)
schultenite	$PbHAsO_4$	Arai et al. (2006)
symplesite	$Fe_3(AsO_4)_2 \cdot 8(H_2O)$	Johnston and Singer (2007)
titanium oxide arsenate*	$Ti_2O(AsO_4)_2$	Ahn et al. (2005)
tooeleite	$Fe_{(8-2x)}[(As_{(1-x)},S_{(x)})O_4]6 \cdot 5(H_2O)$	Morin et al. (2003)
yukonite	$Ca_7Fe_{11}(AsO_4)_9O_{10} \cdot 24.3(H_2O)$	Pieczka et al. (1998); Paktunc et al. (2004)

1.3.2. Primary As minerals

Primary As minerals, no matter whether they arise from natural (e.g., rock outcrop) or anthropogenic (e.g., mine dumps) sources could be considered as the only source of As for soils/waste dump solutions and thus for the consequent precipitation of secondary As-bearing phases. Some of the most common primary As minerals occurring in nature are shown in Table 2. However, only several of them are significant from the environmental point of view.

The most widespread As mineral, globally, is arsenopyrite (FeAsS) (e.g., Ramdor, 1980; Vink, 1996). Arsenopyrite is common in many vein gold deposits and also occurs associated in granite hosted Cu-Sn veins as well as in many polymetallic Pb-Zn-Cu vein and stratiform deposits. Arsenopyrite is, however, of limited economic importance and is generally dumped during mining processes (Nesbitt et al., 1995), which makes this sulphide to be the most important As primary mineral pollutant in the environment and the most studied primary As mineral. Therefore, arsenopyrite stability, oxidation and dissolution were studied by many authors (e.g., Nesbitt and Muir, 1998; Craw et al., 2003; Jones et al., 2003; Yu, et al., 2004; Flemming et al., 2005; Mikhlin et al., 2006; Petrunic et al., 2006; Walker et al., 2006).

Arsenical pyrite (FeS_2) is also a relatively common sulphide in many, especially gold deposits (e.g., Fleet et al., 1989; Fleet et al., 1993; Fleet and Mumin, 1997; Savage et al., 2000; Strawn et al., 2002; Casiot et al., 2003; Akai et al., 2004; Lee et al., 2005; Loredo et al., 2005; Walker et al., 2005). Pyrite abundance in many types of rocks and deposits (and thus mine wastes) and its low stability under surface conditions, make it a very unstable As-carrier. Fleet et al. (1989) explained As contents in pyrites by the presence of pyrite/marcasite–arsenopyrite metastable solid solutions. Similarly, HRTEM and TEM studies made by (Pósfai and Buseck, 1997) demonstrated the presence of nonperiodic marcasite-type layers in some pyrites, namely in those with lower-temperature origin and spherulitic morphology. However, several authors have recently demonstrated that As substitutes for S in pyrite by the Fe $(As_xS_{1-x})_2$ substitution mechanism (e.g., Savage et al., 2000; Zachariáš et al., 2004). Zachariáš et al. (2004) discuss also possibility of an As–Fe (i.e. As1Fe–1) substitution mechanism. In anoxic environments As(III) was documented to be sorbed as precipitates on the pyrite surface (Bostick and Fendorf, 2003). Based on theoretical calculations Reich and Becker (2006) found that ca. 6 wt.% of As can be hosted in pyrite (or marcasite) in form of solid solution while beyond this concentration, arsenic segregates into arsenopyrite domains.

In the most recent work Blanchard et al. (2007) conclude that pyrite can incorporate up to ca. 10 wt% of As. They also result that the presence of As accelerates the dissolution of pyrite in oxidising conditions.

Löllingite ($FeAs_2$) is a somewhat less common primary mineral in ore deposits than the both above mentioned minerals and much less referred to as a (potential) source of As contamination (e.g., Morin et al., 2002; Ettler and Johan, 2003; Filippi, 2004). Similarly, orpiment (As_2S_3), realgar (AsS) and enargite (Cu_3AsS_4) were also rarely found to be significant As-pollutants in some areas (Reimann and Caritat, 1998; Fukushi et al., 2003; Loredo et al., 2005; Davis et al., 2006; Smuda et al., 2007). Other primary As minerals such as cobaltite (CoAsS), gersdorffite (NiAsS), niccolite (NiAs) tennantite ($(Cu, Fe)_{12}As_4S_{13}$) (e.g., Donahue et al., 2000, Shih and Lin, 2003) are rare and usually do not represent significant environmental risk. Special position has As (III) oxide arsenolite (As_2O_3), which is a relatively common product of some industrial processes and thus could represent a real risk of the pollution (e.g., Juillot et al., 1999).

Table 6. The most important secondary As minerals occurring in contaminated soils and mine wastes

Common indication (Dana Class)	**Mineral / Formula**	**Usual colour***	**Usual morphological forms***
As oxides (Simple oxides)	arsenolite [As_2O_3]	colourless, white, grey, light yellow	earthy to pulverulent; discrete grains; powder coatings, crust-like aggregates, well developed crystals
Fe arsenates (Hydrated phosphates, arsenates, vanadates)	kankite [$FeAsO_4 \cdot 3.5(H_2O)$]; scorodite [$FeAsO_4 \cdot 2H_2O$]	yellow green; green, grey, brown, blue green	powder aggregates and coatings, microcrystalline crusts; scorodite also as cements, discrete grains, crystals aggregates and rarely also crystals
K(-Ba) arsenates (Hydrated phosphates, arsenates, vanadates; containing hydroxyl or halogen)	pharmacosiderite [$KFe_4(AsO_4)_3(OH)_4 \cdot 6\text{-}7(H_2O)$]	brown, yellow-brown, olive green	discrete grains, impregnations, coatings, powder aggregates
Ca-Fe arsenates (Hydrated phosphates, arsenates, vanadates; containing hydroxyl or halogen)	arseniosiderite [$Ca_2Fe_3(AsO_4)_3O_2 \cdot 3(H_2O)$]	brown, yellow brown, reddish, rusty brown	massive, compositionally zoned, lief-like particles; discrete grains, spheroids, replacement products, infillings in fractures of mineral grains
Ca, Mg and Ca-Mg arsenates (Hydrated (acid) phosphates, arsenates, vanadates)	weilite [$CaHAsO_4$], haidingerite [$CaHAsO_4 \cdot H_2O$], hornesite [$Mg_3(AsO_4)_2 \cdot 8H_2O$], pharmacolite [$CaHAsO_4 \cdot 2H_2O$], picropharmacolite [$(Ca,Mg)_3(AsO_4)_2 \cdot 6H_2O$]	white, grey	powder aggregates and coatings, crusts, micro-crystalline matrix, discrete grains; pharmacolite and picropharmacolite also acicular crystals
Crystalline Fe sulpho-arsenates (Hydrated phosphates, arsenates, vanadates; compound anions with hydroxyl or halogen)	bukovskyite [$Fe_2AsO_4SO_4OH \cdot 7H_20$], zykaite,	brown, yellow brown, yellow; white, grey	concretions, micro-crystalline aggregates, crusts, component of stromatolitic formation, cement, nodular aggregates (namely zykaite)
Amorphous Fe sulpho-arsenates (AISA) (Hydrated phosphates, arsenates, vanadates; compound with anions and hydroxyl or halogen)	AISA and pitticite ca [$Fe_x (AsO_4)_y(SO_4)_z \cdot nH_2O$]	brown, yellow brown, rusty, gray, white	always amorphous, massive, coatings, crusts, gel-like cement, hardpan layers; typically reniform, botryoidal, stalactitic, in thin opaline crusts, crazed and crackled when dry; earthy
Other arsenates (several groups in Class of Phosphates, arsenates, vanadates)	beudantite [$PbFe_3AsO_4SO_4(OH)_6$]; annabergite [$Ni_3(AsO_4)_2 \cdot 8(H_2O)$]	brown, dark green, yellow, orange; apple green, greenish white, gray, yellow green, white	powdery aggregates, grains component of stromatolitic formation, crusts;

* only low-temperature forms of the presented minerals are characterized (not the hydrothermal and/or supergene)

1.3.3. Secondary As minerals

More than 260 As minerals are known to occur in nature. Of these ca. 60 % are arsenates, ca. 20 % sulfides and sulfosalts, 10 % are oxides and the rest are arsenides, native elements and metalloids (Bowell and Parshley, 2003). Although there are many species of supergene and secondary As minerals, only few of them have been identified as products of weathering of the primary As minerals in soils and waste dumps (Jambor, 2003). This implies that only several As-bearing minerals (mostly arsenates) play an important role in controlling the As mobility/stability and thus its general behaviour in the environment. These minerals are listed and shortly discussed in the following text. Minerals are sorted according to the chemical composition and divided into groups which are commonly used in the environmental literature. For the list, mineralogical clasification, chemical formulas and morphological forms of the minerals see Table 6.

1.3.3.1. As oxides

Arsenolite is the only one relatively "common" secondary mineral from the group of As-containing oxides. It is found on the walls of abandoned underground mine workings at As rich deposits (e.g., Ondruš et al., 1997) or it precipitates on fractures in As bearing rocks or in altered hydrothermal veins (Klopprodge et al., 2006). This mineral was found also under surface conditions in As-rich concentrate remaining after ore concentration process (Filippi, 2004). In environmental settings, arsenolite is usually associated with weathered arsenopyrite and/or löllingite and with other secondary product of the ore oxidation (usually with scorodite). Arsenolite is partly soluble in water, but well soluble in acids, thus its rich occurrence in the rock may strongly control As contents in mine/waste waters (Maggs, 2000).

1.3.3.2. Fe arsenates

Under acidic and relatively highly concentrated iron and arsenate conditions, **scorodite** is by far the most common natural arsenate solid phase, originating from the arsenopyrite or As-pyrite oxidation. Its persistence in nature suggests that its solubility may control the concentration of As in natural waters at many sites (Frau and Ardau, 2004). It is the most often secondary As-carrier in many types of environmental settings from lateritic tropical soils (Bowell, 1991), natural rock outcrops (e.g., Utsunomiya et al., 2003) various types of naturally contaminated soils in the ambient climatic area (e.g, Morin et al., 2002; Pfeifer et al., 2004; Filippi et al., 2007) to various mine/industrial tailings wastes and minesoils (e.g., Davis et al., 1996; Foster et al., 1998; Juillot et al., 1999; Craw et al., 2002; Néel et al., 2003 ; Pfeifer et al., 2003; Filippi, 2004; Frau and Ardau, 2004; Paktunc et al., 2004; Flemming et al., 2005; Mahoney et al., 2005; Mains and Craw, 2005; Salzsauer et al., 2005). Scorodite together with jarosite was also found as a solid-phase product of bacterial oxidation of As-pyrite (Carlson et al., 1992).

Due to the high environmental importance, scorodite stability was studied by many authors (e.g., Dove and Rimstidt, 1985; Nordstrom and Parks, 1987; Krause and Ettel, 1988; Craw et al., 2002; Harvey et al., 2006).

Kankite is a rare mineral in nature, however, in the last years it was determined from mine wastes as a relatively common mineral locally. At the type locality of this mineral, Kaňk near Kutná Hora (Czech Republic), kankite is associated with bukovskyite and scorodite (Čech et al., 1976). Relatively rich occurrence of this mineral was described from ca 300 years old mine dump in the famous Jáchymov ore district, Krušné Hory Mountains, NW Bohemia (Hloušek, 2000; author's own observation). Kankite occurs there as several centimetres large aggregates together with scorodite and rare zykaite. Kankite seems to be the youngest mineral in the association, so its importance in the As retention in mine waste material is probably high.

1.3.3.3. K-(Ba-) Fe arsenates

Pharmacosiderite appears to be a relatively important As-carrier in highly contaminated soils (Brown et al., 1990; Morin et al., 2002; Morin et al., 2006; Filippi et al., 2007) and mine wastes

(Paktunc et al., 2004). Pharmacosiderite has a slightly varying chemical composition namely in contents of K, Ba and Ca. Pharmacosiderite often forms discrete particles and/or various infillings of fractures in rock-forming minerals. This suggests its origin from As- and cation-rich solutions (Morin et al., 2002; Filippi et al., 2007). On the contrary, well developed cubic crystals are considered to originate in the weathered hydrothermal veins and than dispersed into soil during the pedogenesis (Morin et al., 2002). Presence of pharmacosiderite (together with arseniosiderite) in soils with near-neutral pH, suggests its higher stability in such conditions, compared to by far the most common arsenate scorodite.

1.3.3.4. Ca-Fe arsenates

Arseniosiderite is a scarse mineral in nature. Mostly it is a secondary product of the arsenopyrite weathering in Ca rich environment (Pieczcka et al., 1998). Rich occurrences of arseniosiderite in association with pharmacosiderite and scorodite were described from mine dumps and from cyanidation tailings (Paktunc et al., 2004) and from naturally contaminated soils where the As contamination rises from arsenopyrite mineralization in the bedrock (Filippi et al., 2007; Drahota et al., in prep). Although, the above mentioned environments (mine wastes, tailings and soils) are different by its origin and mainly time of development, the secondary associations are similar. These findings may point at a possible high importance in As binding into arseniosiderite on a long-term scale in some contaminated sites. This assumption is sustained also by other references concerning the As trapping in Ca-Fe arsenates (Frau and Ardau, 2003; Paktunc et al., 2003; Frau and Ardau, 2004; Paktunc et al., 2004).

1.3.3.5. Ca, Mg and Ca-Mg arsenates

Similarly as arsenolite, some arsenates from this group are often present on the walls of abandoned underground mine workings (Ondruš et al., 1997). However, Ca and Ca-Mg arsenates are important secondary products of reactions of As-rich solutions in various surface or near-subsurface environments. Pierrot (1964) described Ca and Mg arsenates from the Ca-Mg-rich oxidation zone of the Pb-Zn deposit; Voigt et al. (1996) described the precipitation of Mg-arsenate **hornesite** as a product of the reaction of Mg-rich ground waters with As-contaminated soils and Juillot et al. (1999) published a description of the precipitation of Ca-arsenates (**pharmacolite**, **haidingerite** and **weilite**) and Ca-Mg arsenate **picropharmacolite** as products of reactions of As-rich solutions derived from dissolved scorodite and arsenolite in mine waste affected by liming. Amorphous and weakly crystallized Ca arsenates have been also documented from reduced parts of some tailings (Donahue and Hendry, 2003). Pharmacolite and weilite have been found together with other secondary minerals on walls of a pit by Bowell and Parshley (2005).

Because liming is the common way of neutralizing AMD from sulphide-rich mine wastes, Ca and Ca-Mg arsenates are important As-bearing phases to participate in the As cycle in such environments. However, because of their high solubilities, this group of arsenates is not relevant candidate to immobilize As from contaminated soils on a long-term scale (cf., Juillot et al., 1999).

1.3.3.6. Crystalline Fe sulpho-arsenates

From this group, namely **bukovskyite** was found in a larger scale in some As-rich soils (Bowell, 1991), processing wastes (Marquez et al., 2006) and mine dumps or other related environments (Čech et al., 1976; Leblanc et al., 1996; Gieré et al., 2003; Bowell and Parshley, 2005;

Mains and Craw, 2005). It is usually associated with scorodite, kankite and rarely also with zykaite. The environmental stability of bukovskyite is not known. However, it may be significant as Mains and Craw (2005) found that bukovskyite is more soluble than scorodite under acid conditions (pH around 2). At Kaňk near Kutná Hora, bukovskyite forms up to several decimeters large fine crystalline concretions and thus it is a very important As immobilizer in the dump.

Zykaite is a very rare mineral (Čech et al., 1978); nevertheless, some recent references may point at its certain importance in As trapping under specific physico-chemical conditions. Zykaite was documented from As-rich mediaeval As mine dump by Hloušek (2000) and from wastes after bacterial oxidation process of a gold ore by Marquez et al. (2006).

1.3.3.7. Pitticite and other amorphous Fe sulpho-arsenates (AISA)

Pitticite is a generic name for amorphous gel-like Fe(III) arsenate with no apparent stoichiometry and with varying chemical composition from different localities (Dunn, 1982; Dunn et al., 1983). This mineral is usually closely associated with weathered arsenopyrite in sulphide-rich mine dumps (e.g., Jansa, 1997; Filippi et al., 2004).

Amorphous Fe sulpho-arsenates (AISA) are probably relatively common As-bearing phases in the mine wastes containing arsenopyrite or As-pyrite, though their presence may be often "invisible" due to its amorphous nature, variable chemical composition and occurrence in form of thin coating on clasts of the waste material. AISA of two various types have been described by Salzsauer et al. (2005); the first type is compositionally close to zykaite, the characteristics of the second type of AISA are comparable to pitticite. Amorphous As–Fe phase with similar morphology and chemical composition to pitticite was also described from mine tailings by Ahn et al. (2005).

1.3.3.8. Other secondary As minerals

Beudantite is probably the most common secondary As mineral from this group occurring and precipitating in mine wastes and soils. Beudantite was found as an oxidation product of arsenopyrite and was documented in association with gypsum, jarosite, ferric oxyhydroxides and other minerals (Leblanc et al., 1996; Roussel et al., 2000; Courtin-Nomade et al., 2003; Gieré et al., 2003; Néel et al., 2003; Romero et al., 2006). The precipitation of secondary beudantite is considered to play an important role in the natural attenuation of As and Pb in mine tailings, mainly those that contain Zn and Cu (Romero et al., 2007).

Annabergite is another mineral, which is considered to have a possible environmental significance (Langmuir et al., 1999; Mahoney at al., 2005).

1.3.3.9. Rare secondary As minerals and unidentiffied phases

Table 5 shows some of the rare As minerals, which were found at some specific places (surroundings of the ore veins in mineralized rock outcrops, or the walls in quarries, specific antropogenic deposts, etc.). These minerals are not considered to have some major environmental importance, however at some places they could partake on the As control in soils and waters.

Sometimes it is not possible to identify all As phases occurring at contaminated sites, althogh some of them could be important local As-carriers. Table 7 sumarizes some of these phases mentioned in papers with environmental direction. Further research and precise identification and characterization of these phases are important, because it could help to enlarge knowledge about As solid phase speciation in contaminated soils and mine wastes.

Table 7. Selected unidentified secondary As phases mentioned in the literature

Unidentified phases	**Selected references**
amorphous Fe(III) arsenate	Leblanc et al. (1996); Pichler et al. (2001); Ahn et al. (2005)
amorphous Ca-Fe-As arsenates	Alpers et al. (1994); Sidenko et al. (1998); Lazareva and Pospelova (1998); Donahue et al. (2000); Frau and Ardau (2004)
amorphous Fe(III) sulfate	Leblanc et al. (1996)
As phosphate	Davis et al. (1996)
metal Fe-As oxides	Davis et al. (1996); Hudson-Edwards et al. (1999)
Ca-As precipitates	Donahue et al. (2000)
amorphous and cristalline Fe-As phase (Fe_3AsO_7)	Ahn et al. (2005)

1.3.4. Stability of secondary As minerals

Primary As-bearing minerals exposed to atmospheric weathering (in soils, mine/industrial wastes dumps, etc.) become unstable, decompose and produce As rich solution from which As secondary minerals, As-bearing secondary Fe(III) oxides/hydroxides and sulphates precipitate (e.g., Alpers et al., 1994; Bowell, 1994). Generally, the precipitation of As-containing minerals could occur either (i) after their adsorption onto soil colloid surfaces or (ii) by direct precipitation of As solid phases (Davis et al., 1996; Sadiq, 1997). Generally, there are three main processes that lead to the immobilization of As from aqueous solutions interacting with solid matter: i) formation of secondary As-bearing phases; ii) sorption of arsenate on Fe(III) oxyhydroxides and eventually to a minor proportion by Mn (hydr)oxides (e.g., Manning et al., 1998; Sun and Doner, 1996; Raven et al., 1998), and iii) via sorption or coprecipitation processes or substitution of sulphate by arsenate in some sulphate minerals such as jarosite ($KFe_3(SO_4)_2(OH)_6$) and rarely also gypsum ($CaSO_4.2H_2O$), etc. (Bowell, 1994; Myneni et al., 1997; Foster et al., 1998; Savage et al., 2000; Gasharova et al., 2005).

Most of secondary As minerals form coatings on surface of primary ores, various weathering crusts and cements, massive or grained aggregates, as well as individual grains or crystals and other morphological forms. Simplified paragenesis (i.e., the sequence in which minerals have been formed) for As-bearing minerals is presented in Table 8, where also the main supposed physico-chemical processes active in their origin are listed.

The stability of secondary As minerals depends on various parameters. Generally known and crucial are the pH and redox potential (Eh) (e.g., Stumm, 1992; Pfeifer et al., 2003; Bodénan et al., 2004; Sánchez-Rodas et al., 2005). Other important factors are crystallinity, molar Fe/As ratios (Krause and Ettel, 1989; Papassiopi et al., 1988) and also microbial activity (Cullen and Reimer, 1989; Ehrlich, 1996; Pongratz, 1998; Smith et al., 1998; Zobrist et al., 2000; Jones et al., 2000; Mancur et al., 2001). Recently, several additional parameters have been found to be important for stability of some As-bearing phases. In soils as well as in mine waste of different age, the degree of maturity and thus amounts and type of cations in the pore-water may play a role in the chemical composition of arsenates (Morin et al., 2002; Filippi et al., 2007; Drahota et al., in prep). Diversification of arsenates during their precipitation under neutral and alkaline conditions is often strongly influenced by the Ca/As ratio (Donahue and Hendry, 2003; Paktunc et al., 2004).

Table 8. Schematic representation of the progressive oxidation (paragenesis) in the soil/mine waste containing As-bearing primary minerals (compiled according to materials published by Jambor, 2003; Pfeifer et al., 2003; and others)

Stage	**Main processes**
Initial	Exposition of primary As and supergene As minerals (mainly sulfides and arsenides such as arsenopyrite, arsenian pyrite, löllingite, and arsenolite, etc.).
Early (1)	Transformation (oxidation) of primary minerals in superficial parts (nano- and micro-scale changes), i.e., precipitation of secondary products such as native S, Fe^{2+} sulfates, amorphous or crystallised arsenites, arsenates, and As-bearing Fe oxyhydroxides, directly on the surface of primary minerals; Generation of As-rich solutions
Early (2)	Decrease of pH, acceleration of sulfide oxidation, start of decomposition of some rock-forming minerals; Fe^{2+} sulfates change to Fe^{3+} sulfates; amorphous Fe oxyhydroxides recrystallize and release part of the As; arsenites change to arsenates; common reaction of As-containing solutions with surroundings minerals; precipitation of the As secondary minerals and As jarosite from solutions
Mature	Slowing of sulfide oxidation; Mostly Fe^{3+} sulfates are stable; Partial transformation of Fe^{3+} oxyhydroxides onto goethite; Jarosite is stable and still precipitates
Late	Consuming of sulfides, increase of pH, advanced decomposition of some rock-forming minerals (=cations are available in solutions); Changes in arsenates chemical composition may occur? Most of Fe^{3+} oxyhydroxides are transformed onto goethite; Jarosite became unstable

According to Matera et al. (2003), three classes of arsenates can be distinguished according to their different stability: i) Fe arsenates, ii) Ca arsenates and iii) other metal arsenates. The proportions of these three classes are particularly linked to the nature of the mining site (type of ores, treatments used, etc.) or/and to the mineralogical composition of the parent bedrock material.

Some authors found that As solubility decreases when the Fe/As atomic ratio of the precipitates increases (e.g., Papassiopi et al., 1988). According to Krause and Ettel (1989) Fe arsenates with a Fe/As ratio superior or equal to 4 are relatively insoluble, and Harris and Monette (1989) estimated that a Fe/As ratio of 3 is sufficient to efficiently trap As in contaminated soils. However, Matera et al. (2003) found that the most of the analyzed arsenate grains in their soil samples presents a Fe/As ratio lower than 3.

According to Swash and Monhemius (1996), Fe arsenates are formed preferentially if sufficient Fe and Ca are available in the solution; however, Ca arsenate compounds will precipitate in solutions with Fe:As <1. As pointed out by Robins and Glastras (1987), the pH has the greatest influence on Fe or Ca arsenate type precipitation, where the Fe arsenates precipitate at significantly lower pH values than the Ca arsenates (pH 1-2 vs. pH 3-4). This finding agrees with conclusions of Dove and Rimstidt (1985) who showed that scorodite is stable for pH values close to 2 when $a(Fe^{3+}) = 10^{-3}$ and $a(AsO)_4{}^{3-}$ is higher than 0.1. For pH value higher than 3, the dissolution of scorodite leads to the precipitation of iron hydroxides (Escobar Gonzales and Monhemius, 1988). Dove and Rimstidt (1985), studying a synthetic scorodite, suggested that once arsenopyrite is consumed, scorodite dissolves incongruently with precipitation of goethite and release of aqueous arsenate. Arsenate ions released by this mechanism can be then sorbed onto iron oxides formed.

Usually, in acidic soils, which are the most common environments connected to AMD areas in mining districts namely Fe-arsenates occur, while Ca-arsenate, is the dominant species in basic and limy soils (Robins and Glastras, 1987; Fergusson, 1990, Fukushi et al., 2003). On the other side, Ca and Ca-Fe arsenates were found to be predominating in the neutral to slightly alkaline conditions of minesoils and tailings (e.g., Morin et al., 2002; Filippi, et al., 2004; Pactunc et al., 2004; Filippi, et al., 2007; Drahota et al., in prep).

Stability of Ca arsenate precipitates (namely in aqueous systems) has been investigated by many authors because they are a possible immobilizers of As in mine waste via liming (e.g., Nishimura et al., 1985; Robins, 1981; Donahue and Hendry 2000).

In fact, except the scorodite, the environmental stability of most secondary As minerals found in nature or mine deposits is not very well defined, therefore collecting data related to the conditions of their occurrence could help to understand their stability in natural systems.

CHAPTER 2. Determination of As-bearing minerals in contaminated soils and mine wastes – a literature review

Filippi M.

Institute of Geology, v.v.i., Academy of Science of the Czech Republic, Rozvojová 269, 165 00 Prague 6, Czech Republic

Stage: in preparation

Keywords: arsenic, secondary As-bearing minerals, soils, mine wastes, mineralogical methods

2.1. Introduction

Until recently, general knowledge about As cycling in the geosphere has been poor in comparison to other hazardous elements (Matschullat, 2000). There are considerable gaps in the knowledge about As solid phase speciation in soils (Matschullat et al., 2000; Kabata-Pendias and Pendias, 2001). However, in recent years increasing amounts of research has been aimed at solid phase speciation of As in the environment. Some focus on mine/industrial wastes and tailings (e.g., Gieré et al., 2003; Macklin et al., 2003; Paktunc et al., 2004; Bodénan et al., 2004; Filippi, 2004; Ahn et al., 2005; Petrunic and Al, 2005; Williams et al., 2006), whilst others focus on contaminated soils (e.g., Bowell, 1994; Voigt et al., 1996; Dhoum and Evans, 1998; Corwin et al., 1999; Roussel et al., 2000; Craw et al., 2002; Morin et al., 2002; Fukushi et al., 2003; Néel et al., 2003; Ferreira da Silva et al., 2004; Pfeifer et al., 2004; Matera et al., 2003; Moon et al., 2004; Ghosh et al., 2006; Filippi et al., 2007). Therefore, much progress has recently been achieved in relations between the crystal chemistry of As and its speciation and distribution at the Earth's surface (Morin and Calas, 2006).

Such information is fundamental, because understanding transformation of the primary As minerals into secondary species is an important step in order to understand the controls on groundwater chemistry and thus the general geochemical cycling of the As at polluted sites. Therefore, precise identification of the As-bearing minerals should be the first step of any research, as it provides structural information necessary for predicting the reactivity of As (c.f., Frank, 1998). Moreover, understanding the processes controlling the precipitation and transformation of secondary As species will help to model the long-term behaviour of As and aid the development of potential remediation strategies in contaminated areas (e.g., Camm et al., 2003).

There are several ways to determine and evaluate As solid phase speciation and mobility in soils and sediments. A large number of the chemical approaches have been comprehensively reviewed (e.g. Gleyzes et al., 2002a, b; Matera et al., 2003; Van Herreweghe et al., 2003; Francesconi and Kuehnelt, 2004; Hudson-Edwards et al., 2004; Terlecka, 2005), as well as some of the mineralogical approaches (e.g., Brown et al., 1998; Brown and Sturchio, 2002; Tamura et al., 2002; Vaughan et al., 2002; Weisener 2003; Pansu and Gautheyrou, 2006), however, information related to the solid phase speciation of As remain dispersed in many journals across the geo-branches.

The purpose of this review is, therefore, to summarize and briefly evaluate the mineralogical approaches covering the correct sampling, identification and analyzing the As-bearing minerals that are found in highly contaminated soils and mine/industrial wastes.

The application of the methods cited, are related not only to secondary As minerals, but also to other (mostly secondary) minerals that may contain significant amounts of the As.

For the list of abbreviation used in the text see Table 1.

Table 1. List of abbreviation

ADF	annular dark field detector
AFM	atomic force microscope
AMD, ARD	acid mine/rock drainage
As	arsenic
BAFP	biologically active force probes
BF	bright field detector
BFM	biological force microscopy
BSE	backscattered electron (image/micrograph)
DTA	differential thermal analysis
DXRD	differential X-ray diffraction
EELS	electron energy-loss spectroscopy
EFTEM	energy filtered transmission electron microscopy
EMPA	electron microprobe analyses
ESEM	environmental scanning electron microscopy
EXAFS	extended X-ray absorption fine structure spectroscopy
FT-IR	Fourier transform infrared spectroscopy
HAADF-STEM	high-angle annular dark field scanning transmission electron microscopy
HRTEM	high Resolution Transmission Electron Microscopy
IR	infrared spectroscopy
LV-SEM	low-vacuum scanning electron microscopy
MAS	Mössbauer absoption spectroscopy
ND	neutron diffraction
PIXE	particle (proton) induced X-ray emission
RS	Raman spectroscopy
SE	secondary electron (image/micrograph)
SEM (-EDS/WDS)	scanning electron microscopy (with combination of energy/wavelength dispersion) spectroscopy
STEM	scanning transmission electron microscopy
SXRD	synchrotron-based X-ray micro-diffraction
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TOFLIMS	time-of-fight laser-ionization mass spectroscopy
TOFSIMS	time-of-fight secondary ion mass spectroscopy
Vis DRS	Vis diffuse reflectance spectroscopy in the visible region
VMP	voltammetry of microparticles
WDS	wavelength dispersion spectroscopy
WDX	wavelength-dispersive X-ray analyzer
XAES	X-ray Auger electron spectroscopy
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near-edge structure spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

2.2. Methodological approaches

2.2.1. Sampling, sample treatment and preparation

For mineralogical and related geochemical analyses ca. 0.5-1 kg of sample is usually sufficient. Soil samples are mostly taken by trenching, hand auger drilling, or down-hole (non-rotational) hammer drilling. For sampling a stainless steel kit is widely used. Each different soil horizon (layer) should be sampled separately taking into account all macroscopic soil features, such as colour, structure, moisture, etc., to understand possible changes in mineral distribution throughout the whole soil profile (e.g., Morin et al., 2002; Fukushi et al., 2003; Van Herreweghe et al., 2003; Filippi et al., 2007). To sample various types of consolidated (cemented) tailings, a diamond drill core (e.g., Craw et al., 1999; Paktunc et al., 2004), the sonic drill core (Donahue et al., 2000; Salzsauer et al., 2005), or digging by a mechanical excavator in case of waste piles (Gieré et al., 2003) have to be employed. For further geochemical study only the inner parts of the cores should be separated to prevent chemical contamination from the tube core barrel. Attention should also be made to possible contamination by using a hammer during sampling of stones and hardened tailings materials as well.

As has been generally anticipated for a longer time and experimentally verified (Jen-How and Gunter, 2006), effect of sample preparation procedures, such as drying and storage, on the resulting As speciation may be significant. Hence consideration of sample storage and transport should be made. In the case of surface aerobic soils or well oxidized mine wastes, which are drained and exposed to climatic action, the sampled material may be stored in unfailing paper or plastic bags, in air-tight bags (e.g., Hudson-Edwards et al., 1999) or in polypropylene containers (e.g., Matera et al., 2003). In the laboratory these samples are usually dried slowly at a room temperature (e.g., De Brouwere et al., 2004; Salzauler et al., 2005) or oven-dried at temperatures up to ca 40 to 50 (C (Ferreira da Silva et al., 2004).

Samples from water saturated profiles or from reduced or just inner parts of hardened tailings materials, should be stored in air-tight bags or sealed polyethylene containers, glass vials or bottles (Hudson-Edwards et al., 1999; Donahue et al., 2000) or rather in N2 (Keon et al., 2001; Bodénan et al., 2004) or Ar atmosphere (Pfeifer et al., 2004).Freezing immediately after sampling is also commonly used (Blowes and Jambor, 1990; Donahue and Hendry, 2003; Salzsauer et al., 2005; Petrunic et al., 2006). Both frozen and unfrozen samples should be stored in the dark prior to other treatment (e.g., Donahue et al., 2000). In wet and reduced samples, freeze-drying preserves the features of the sample better than oven or air drying. For small samples (approximately 30 cm3) the use of a dehydration apparatus at CO2 critical point gives excellent results (Pansu and Gautheyrou, 2006).

All these procedures help to prevent possible oxidation of the chemical elements, undesirable crystallization or decomposition of mineral phases and other changes of physico-chemical parameters in soils and soil waters.

Prior to application of other methods, soil samples should be split into sub-samples by quartering to reduce bias in sub-sampling (Van Herreweghe et al., 2003) and separated by sieving, sedimentation, pipette or other methods (see Pansu and Gautheyrou, 2006) into various grain-size fractions, because the As mineralogical speciation depends on the grain size (e.g., Dudas, 1987; Manful et al., 1994; Kavanagh et al., 1997). Sieving can be performed dry or wet (in non-aqueous media such as denatured alcohol, pure acetone, etc.) to minimize possible dissolution of water soluble phases, which may be present (Blowes and Jambor, 1990; Filippi et al., 2004). In grain morphology studies, samples should be washed in non-aqueous media, because the grain surface could be disguised by some fine powder or by clay coatings (Filippi et al., 2007). Washing of sample may also disintegrate possible mechanical accumulations or clusters of grains, which can partly depreciate other procedures such as concentration in heavy liquids (see below).

Samples used for mineralogical study may be either bulk soils or selected fractions of a soil (Dixon and White, 1994). However, application of XRD as the most common method for the solid phase identification is often limited by lack of the studied As minerals. In diffractograms of bulk soil samples, peaks are untraceable due to high background counts of the other minerals (Van Herreweghe et al., 2003). Pre-concentration procedures for the As-bearing minerals is only rarely mentioned in the literature, although this approach may solve the above mentioned problem. The following methods have been referred in the literature: i) magnetic separation using Frantz isodynamic separator (Van Herreweghe et al., 2003); ii) pre-concentration of medium and heavy mineral fraction by panning in denatured alcohol (Filippi et al., 2004); and iii) density separation in heavy liquids such as tetrabromomethane, methyliodine, bromoform, etc. (Lin and Qvarfort, 1996; Pichler et al., 2001; Van Herreweghe et al., 2003; Thornburg and Sahai, 2004; Filippi et al., 2007). As a non-toxic alternative to bromoform, sodium polytungstate has also been used in heavy liquid separation (Munsterman and Kerstholt, 1996). Most As-containing minerals remain in medium or heavy mineral fractions (densities from ca. 2.5 g/cm3), therefore using heavy liquids of various densities (obtained by mixing with water, 1,4-dioxan, or other solvents) may help considerably to concentrate rare minerals.

Polished and thin sections should be performed carefully from samples of which the composition is poorly known. If water soluble minerals are expected, polished and thin section should be made in non-aqueous media to prevent dissolution (Salzsauer et al., 2005). Incoherent soil and tailing samples have to be impregnated with epoxy resin before cutting for polished thin section (e.g., Craw et al., 2002; Morin et al., 2002; Strawn et al., 2002).

2.2.2. Instrumental methods

2.2.2.1. Binocular and optical microscopy

Under binocular microscope, general information about mineral grains (secondary crusts, aggregates, etc.) may be gained and samples may be split for further procedures (Juillot et al., 1999; Filippi et al., 2007).

Although examination of polished and/or thin sections by optical microscopy may appear archaic in modern environmental research, it provides useful information about the sample and is often used as the first step of more complex mineralogical research (e.g., Craw et al., 1999; Juillot et al., 1999; Courtin-Nomade et al., 2003; Gieré et al., 2003; Néel et al., 2003; Van Herreweghe et al., 2003). Above all, knowledge about the rock-forming minerals; the relationship between individual mineral phases (overgrowths or intergrowths, replacements by younger phases, etc.), information about individual grains (inner structure, inclusions, fracturing, etc.) and about stability of minerals (dissolution features, presence/absence of the primary unstable minerals, etc.) is very useful. In addition, simple observation by optical microscopy can be supplemented with IR to UV radiation, cathodo-luminiscence, etc. and can be accompanied by digital photography or video images.

2.2.2.2. XRD, DXRD, µXRD

X-ray powder diffraction (XRD), together with scanning electron microcopy, are the most common methods used for identification (characterization) of As-bearing minerals in soils and mine wastes. Monochromatic X-rays are used to determine the interplanar spacings of the unknown crystalline solids. The spacing in the crystal lattice is determined using Bragg's law. The X-ray spectra generated (diffractograms or diffraction patterns) are compared with tabular data. Mixtures of crystalline materials can also be analyzed and relative peak heights of multiple materials may be used to obtain semi-quantitative estimates of abundances. Several types of diffractometers have been developed over the years to analyze various materials such as single crystals, powders, flat plates, thin films, etc. (Frank, 1998).

In environmental mineralogy, powder diffraction and monocrystal diffraction are commonly used. The XRD is applied for the first overview of the mineralogical composition in the bulk soil sample as well as for the detailed study of separated mineral grain fractions (e.g., Morin et al., 2002; Filippi et al., 2004) or individual mineral phases (e.g., Juillot et al., 1999; Gieré et al, 2003; Filippi et al., 2007). However, studied samples should comprise at least a few weight percent (ca. 5-10 %) of the As minerals displaying a high degree of crystallinity (e.g., Keon et al., 2001). In case of insufficient amount of the As minerals, pre-concentration of the sample has to be performed. For minerals displaying poor crystallinity, monocrystal powder X-ray diffraction or single crystal diffraction may aid identification.

Detection of poorly crystalline Fe(III) minerals such as ferrihydrite and schwertmannite in multiphase samples requires more sophisticated approaches. Differential X-ray diffraction (DXRD), based on the leaching of the sample in NH4-oxalate in the dark, is one of such special methods, but it requires at least a general knowledge of the dissolution kinetics (Schulze, 1981; Schulze, 1994; Šucha et al., 2002; Dold, 2003). However, other methods, which are not based on identification according to the atomic-scale periodicity, have to be used for amorphous species (see below).

Analyzing natural As-containing minerals may be complicated as they often occur in complex mixtures with common rock-forming minerals. Peaks of As-bearing minerals in diffractograms may be overlapped by other mineral peaks. A useful way to get relevant information is to simulate the experimental data, which may be done with Rietveld analysis using structural models for identified phases (Juillot et al., 1999; Morin et al., 2002). The basis of the Rietveld method lies in calculation of the simulated powder-diffraction pattern for each mineral phase. A detailed description of the principles of Rietveld method and its general utilization in environmental mineralogy is presented by Raudsepp and Pani, 2003, they also summarize difficulties associated to adequate grinding of the sample, as the size of powder particles was found to be significant for peak shape in diffractograms (see also Bish and Reynolds, 1989; Jenkins and Snyder, 1996).

For identification of fine grained (< 5 µm) secondary products of arsenopyrite oxidation Flemming et al. (2005) developed the modified micro X-ray diffraction (µXRD) based on a conventional (not synchrotron-based, see below) close-tube X-ray generator. This µXRD determination allows the in situ measurement in a rock slab (or thin/polished sections) and the µXRD can be directly compared, on grain-to-grain basis, to other micro-analytical data, such as electron microprobe analyses (EMPA).

Another potentially interesting tool for research of unstable secondary minerals (applicable probably also on some As phases) was presented by Peterson and Grant (2005). They developed a special sample stage and control system to enable powder XRD measurement during varying humidity and temperature. Such ability to study dehydration-hydrataion reactions of minerals in controlled environments creates an opportunity to evaluate reactions, which may play a role in transformations of secondary minerals in geological environments.

2.2.2.3. XRF

X-ray fluorescence (XRF) is based on the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. There are two main types of XRF instruments: energy dispersive XRF and wavelength dispersive XRF.

It is ideally suited to the measurement of film thickness and composition, determination of elemental concentration by weight of solids, and identification of specific and trace elements in complex sample matrices. This XRF technique is often used as a rapid analytical tool for determination of qualitative or semi-quantitative chemical composition of the solid samples such as soils and mine waste materials (Lumsdon et al., 2001; Donahue and Hendry, 2003; Fukushi et al., 2003; Filippi et al., 2007). It is also possible to analyze very small amounts of the sample, via mounting the selected fraction on a polyethylene film (Gieré et al, 2003). However, other methods such as EMPA have to follow for more detailed determination of chemical composition of individual As-bearing particles.

2.2.2.4. XPS, XAES, TOFSIMS, and TOFLIMS

X-ray photoelectron spectroscopy (XPS) is based on the photoemission that occurs when a sample is irradiated with highly focused monochromatised X-rays. It is a result of ionization of a core-level electron (Weisener, 2003). XPS is a useful method due to its ability to provide direct chemical composition of the mineral surfaces. Reasonably quantitative data of the surface atomic composition of primary As minerals is important in understanding processes related to oxidation and subsequent AMD generation and thus mobilization of various elements (such as As) into the environment (Weisener, 2003). Therefore oxidized pyrite and arsenopyrite surfaces have been studied extensively using this method (e.g., Buckley and Woods, 1987; Mycroft et al., 1990; Karthe et al., 1993; Evangelou and Eggleston et al., 1996; Rimstidt and Vaughan, 2003; and e.g., Richardson and Vaughan, 1989; 2003; Nesbitt et al., 1995; Nesbitt and Muir, 1998; Schaufuss et al., 2000; Jones et al., 2003; Mikhlin et al., 2006, respectively). Jones and Nesbitt (2002) published a comparative XPS study of the Fe and As of surfaces of pyrite, marcasite, arsenopyrite and löllingite. Recently, XPS in combination with other techniques has been used to identify other As-bearing phases (scorodite, As-plumbojarosite, ferrihydrite, etc.) in environmental samples (e.g., Frau et al., 2005).

In X-ray Auger electron spectroscopy (XAES), a highly focused and energetically defined electron beam interacts with the sample. Because of the low kinetic energies of the ejected Auger electrons, their escape depth is limited to a few atomic layers, therefore only the top atomic layers (~ 4 nm) of the sample is analyzed, and like EDX, the Auger microprobe can produce elemental maps by scanning (Weisener, 2003). Moretti (1998) and Weisener (2003) summarized the application of XAES to various sulphide minerals. Atzei et al. (2003) described the use of XAES (together with XPS) for characterizing the valence state of As in complex environmental samples.

To study surfaces of various sulphides from mine and processing wastes, Weisener (2003) proposed techniques based on secondary ion mass spectroscopy (SIMS), such as time-of-flight secondary ion mass spectroscopy (TOFSIMS) and time-of-flight laser-ionization mass spectroscopy (TOFLIMS).

SIMS is the mass spectroscopy of atomic or molecular particles which are emitted when the mineral surface is bombarded by energetic primary ions or neutral species such as Ar^+, O_2^+, Cs^+ or Ga^+. TOFSIMS uses a pulsed Nd-AYG laser beam to remove molecules from the outermost surface of the sample instead of an ion beam, and two laser beams (ablation and post-ionization laser) of various direction are used for the analysis. The particles removed from the surface (secondary ions) are accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (Weisener, 2003). TOFSIMS can detect trace elements and image the chemical distribution on surfaces with resolutions near 0.5 µm. A more detailed description of this method is given by Weisener (2003), and by Martin et al. (1997) who applied this technique to surface chemical composition analyses of As- and Pb- containing particles in mine tailings. Martin et al. (1997) and Al et al. (2000) consider TOFLIMS as a very surface-sensitive technique, that provides chemical information from surfaces of irregularly shaped mineral particles (< 100 µm in diameter), which are considered to be representative of particle surface coatings in the tailings pile. In addition, the combination of speed of analysis (ca 1 min), small beam-diameter (2-4 µm), surface sensitivity (2-10 nm), trace-element sensitivity, and capability to analyze rough surfaces makes this method very useful for studies of pore-water geochemistry and sulfide-rich mine tailings mineralogy.

2.2.2.5. SEM-EDS/WDS and EMPA

Scanning electron microscopy (SEM) combined with energy/wave dispersive spectroscopy (EDS/WDS) and electron microprobe analyses (EMPA) are the most commonly used methods in As solid speciation studies. In SEM, a fine focused, high-energy primary electron beam interacts with the surface of a specimen in a high vacuum environment (in most instruments). This probe is then rastered over the specimen and an image is built. The most common imaging modes are via detection of the low energy (<50 eV) secondary electrons (SE) and via high-energy (above 50 eV) back-scattered electrons (BSE). Due to their low energy, secondary electrons originate within a few nanometers from the surface, so they are used for imaging of surface morphology. Backscattered electrons consist of high-energy electrons originating in the electron beam, that are reflected or back-scattered out of the specimen interaction volume. Backscattered electrons may be used to detect contrast between areas with different chemical compositions, since the brightness of the BSE image tends to increase with the atomic number.

In the EMPA, the spectrometers EDS/WDS detects characteristic X-rays of the elements from the sample excited by the primary beam penetrating into the sample. Thus this tool is used for determination of small volumes of solid materials.

Geological samples for SEM and EMPA are usually coated with a conductive material to reduce charge buildup on the specimen (White and Dixon, 1995). Gold or rarely platinum or palladium are used for SE micrographs and carbon for EMPA. For morphological studies of individual grains, samples are fixed onto an aluminium stub using conductive carbon tape or glue. For both EMPA and X-ray element mapping polished and thin sections are used. Analyzing non-polished flat surfaces of coated particles may only be used to gain qualitative information about the sample. It is also possible to tentatively identify minerals by morphology combined with qualitative chemical composition (White and Dixon, 1995).

Recently however, low-vacuum SEM (LV-SEM) and environmental SEM (ESEM) have been developed and successfully used to study environmental samples without the need of a high vacuum or carbon coating (Mathieu, 1998; Pansu and Gautheyrou, 2006).

BSE and SE imaging combined with EDS and X-ray mapping are very powerful tools which may help to distinguish various groups of As minerals in samples, which may aid the selection of other methods (c.f., Lin and Qvarfort, 1996; Voigt et al., 1996; Hudson-Edwards, 1999; Chappell and Craw, 2002; Courtin-Nomade et al., 2003; Gieré et al, 2003; Camm et al., 2003; Fukushi et al., 2003; Lee et al., 2005; Filippi et al., 2007).

It is important, when using SEM to identify minerals, to be aware of secondary surface coatings on the studied mineral particles. Care must be also taken in identifying minerals using morphology alone, because, in same cases mineral pseudomorphs could occur (e.g., Filippi et al., 2007). The BSE imaging and X-ray element mapping is powerful tool to recognize mixed grains or various types of chemical heterogeneity in individual grains (Camm et al., 2003; Gieré et al, 2003; Matera et al., 2003; Filippi 2004; Lee et al., 2005; Filippi et al., 2007).

2.2.2.6. TEM, STEM, HRTEM, and related techniques

Transmission electron microscopy (TEM) is an optical instrument for imaging specimen structures at high resolution beyond that possible in an optical microscope and SEM. The TEM is based (similar to SEM) on an electron beam, which is focused toward a sample. The specimen must be very thin (typically < 200 nm), depending on the density and elemental composition of the sample (Weisener, 2003). The information is obtained from both deflected and non-deflected transmitted electrons, backscattered and secondary electrons, and emitted photons. Because of the high spatial resolution obtained, TEM is employed to determine crystallography of fine-grained nanoscale particles. With the addition of EDS or electron energy-loss spectroscopy (see below), TEM can be used to determine elemental composition of nanoscale particles and is capable of identifying the chemical composition in areas < 0.5 μm in diameter (Reimer, 1994).

Scanning transmission electron microscopy (STEM) combines features of both the TEM and SEM to produce transmission images obtained with a scanning probe. Images in the STEM are produced while scanning the beam over the specimen. Electrons transmitted through the specimen can be detected on a detector on the axis of the microscope (bright field detector - BF), or on an annular detector sensing electrons scattered through a range of angles (annular dark field detector - ADF) (Pansu and Gautheyrou, 2006). The main applications of a STEM are high spatial resolution microanalysis and imaging. X-ray spatial resolution of around 1 nm is possible with sufficient beam current to collect statistically significant EDX spectra in 100 seconds (Pansu and Gautheyrou, 2006). The scanned probe also allows the collection of X-ray maps and line scans. Imaging with a resolution equivalent to the minimum probe size is possible using electrons scattered through high angles onto the ADF detector. The intensity of the signal on the detector is proportional to the average atomic number under the probe, and in correctly oriented crystalline samples, it is possible to get Z contrast images at atomic resolution.

Electron energy-loss spectroscopy (EELS) is based on the incidence of the electron beam on a specimen, when part of the electron beam is inelastically scattered and loses energy. Elemental composition and atomic bonding state can be determined by analyzing the energy with the spectroscope attached (Weisener, 2003). Moreover, by selecting electrons with specific energy loss by a slit so as to image them, element distribution in specimen can be visualized (elemental mapping); similar to those obtained by SEM-EDS, but of a higher resolution. The EELS and related techniques have been used by Hochella et al. (1999) to study sediments from AMD sites. Garvie and Buseck (2004) applied EELS to study pyrites and Ouvrard et al. (2005) used a variety of mineralogical instrumental techniques including, EELS to understand the retention of As on a natural manganese sand.

High Resolution Transmission Electron Microscopy (HRTEM) is an imaging mode of the TEM that allows the imaging of the crystallographic structure of a sample at the atomic scale. Because of its high resolution, it is an invaluable tool to study nanoscale properties of crystalline material such as various oxidation products of primary As minerals. At present, the highest resolution realized is 0.8 Å, which allows the imaging of individual atoms and crystalline defects.

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) in combination with other standard TEM techniques is a relatively new technique for identifying and characterizing trace quantities of minerals at the nanoscale. The main advantages of this method are underlined by Utsunomiya et al. (2003) as follows: (i) High resolution HAADF-STEM images of minerals can provide near atomic-scale elemental information when the composition of the area of interest is known. In HAADF-STEM as the contrast increases, the atomic number increases. In contrast, TEM images never contain elemental information and energy filtered TEM (EFTEM) does not achieve atomic-scale resolution in elemental mapping. (ii) The contrast in HAADF-STEM does not change significantly as a function of defocus, while the contrast in TEM changes according to the contrast transfer function with changing defocus.

TEM and HRTEM have been used almost as often as SEM recently to study As bearing minerals in mine-related environments. Using TEM (HRTEM) in combination with other techniques is a particularly versatile method, because it provides a variety of imaging, analytical, and diffraction techniques with spatial resolution on the order from nm to µm, consistent with the fine-grained nature of most low-temperature minerals (see e.g., Bigham et al., 1996; Hochella et al., 1999; Al et al., 2000; Thornburg and Sahai, 2004; Frau et al., 2005; Petrunic and Al, 2005; Hochella et al., 2005). Utsunomiya et al. (2003) analyzed nanocrystalline hydrothermal alteration products on the surface of the arsenopyrite from natural rock outcrops using HAADF-STEM, and Petrunic et al. (2006) studied altered arsenopyrite grains from mine tailings.

2.2.2.7. AFM, BFM, BAFP

The atomic force microscope (AFM) is a very high-resolution type of scanning probe microscope. The AFM has several advantages over SEM. Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a true three-dimensional surface profile (Weisener, 2003). Samples viewed by AFM do not require pre-treatment and most AFM modes work well in ambient air or even in liquid environments. This makes it possible to study biological macromolecules and even living organisms which are often associated with As-bearing minerals.

Charlet et al. (2003) used an AFM to study naturally occurring As-bearing minerals and Mikhlin et al. (2006) studied oxidized arsenopyrite from tailings material. AFM has also used in experimental studies related to possible As-carriers, such as jarosite (Gasharova et al., 2005) or for studies dealing with remediation procedures from contaminated groundwaters (Kanel et al., 2005).

Bacteria often play an important role in the processes related to the As-bearing minerals surface changes, thus biological force microscopy (BFM) is a valuable tool for quantitative measurements of the in-situ interfacial and adhesion forces between native bacterial cells and mineral surfaces (Lower et al., 2000). The biologically active force probes (BAFP) are used for determining the natural and complex biomolecular networks on the surface of bacteria, and especially the complex nature of adhesive forces associated with bond formation, intra molecular forces, and extension of outer membranes that form the bridge between the mineral surface and bacterium (Weisener, 2003). More detailed descriptions of these techniques and their applications are given by Lower et al. (2001).

2.2.2.8. PIXE

Particle (usually proton) induced X-ray emission (PIXE), is a non-destructive elemental analysis technique which may help in identifying minerals in various matrices. The principle of the method lies in the interaction of accelerated protons with a sample, which causes inner shell ionization of atoms in a sample – outer shell electrons drop down to replace inner shell vacancies – however only certain transitions are allowed. X-rays characteristic of an element are emitted and detected and measured within an energy dispersive detector. The intensities of X-rays are then converted to elemental concentrations (Hill et al., 2003; Ryan, 2004).

Compared to electron based X-ray techniques, PIXE offers better peak to noise ratios and consequently much higher trace element sensitivities (Ryan, 2004). One of the most important advantages of PIXE is that a proton beam can be brought out from the high vacuum environment of the accelerator into the ambient environment of the laboratory.

PIXE has been used to determine As in contaminated soil samples (Rajander et al., 1999), in weathering products of primary sulphide mineralization e.g. goethite (Wilson et al., 2002), or to identify precipitates from mineralized hydrothermal fluids in coral reefs (Pichler et al., 1999).

Nevertheless, this method is not very commonly used in environmental mineralogy, though its powerful application in many projects illustrates its large potential (cf., Gill et al., 2002; Hattori et al., 2002; Ohnuki et al., 2004; Baker et al., 2006; Zucchiatti et al., 2006).

2.2.2.9. Synchrotron-based radiation methods: µXRF, µXRD, XAS - (µ)EXAFS and (µ)XANES

Synchrotron radiation methods have emerged as an incisive probe of local structures around selected atomic species in various solids (both the crystalline and amorphous), and also in liquids; thus is increasingly applied in modern mineralogical/environmental studies (Vaughan et al., 2002; Francesconi and Kuehnelt, 2004). The ability to provide increased intensity, collimation, tunability of specific energies of the source, and for most cases no vacuum environments for samples allowing the realistic in-situ experiments, distinguishes synchrotron techniques from conventional X-ray sources (Weisener, 2003). In addition, very small beam sizes are a powerful tool for analyzing very small grains (Tse, 2002).

In environmental studies, synchrotron radiation techniques used for As (and other elements) speciation studies include: X-ray micro-fluorescence (µXRF), X-ray micro-diffraction (µXRD), and the X-ray absorption spectroscopy (XAS) which covers both the extended X-ray absorption fine structure spectroscopy ((µ)EXAFS), and X-ray absorption near-edge structure spectroscopy ((µ)XANES).

2.2.2.9.1. µXRD and µXRF

Synchrotron µXRD (SXRD) is a structural analysis technique which enables the examination of very small sample areas. Like conventional XRD instrumentation, µXRD relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. This technique is a very powerful tool for identifying individual soil particles or to pinpoint the location of small mineral particles within a soil sample, which can be done neither by common X-ray diffractometry or by TEM (Vodyanitskii, 2006). Grain-by-grain µXRD, together with µXANES has been used to study As-rich mine wastes e.g., Walker et al. (2005).

Synchrotron-based µXRF in combination with other synchrotron methods (see below), is used to generate elemental distribution maps of soil/sediment thin sections with the main emphasis to reveal relationships between the distribution of the micro- and macroelements, and to recognize mineral aggregates in various environmental samples (Strawn et al., 2002; Weisener, 2003; Kirpichtchikova et al., 2006).

The combination of µXRD and µXRF inconjunction with other XAS techniques, may help considerably with the chemical and structural characterization of As solid state speciation in various types of very small samples, where conventional methods like SEM, TEM, etc. fail (e.g., Jambor et al., 2000; Arai et al., 2006).

2.2.2.9.2. XAS techniques

Synchrotron based X-ray Absorption Spectroscopy (XAS) is the main technique to obtain detailed information on the speciation and coordination environment of As in the solid phase in geological and environmental samples (e.g., Waychunas et al., 1993; Myneni et al., 1998; Strawn et al., 2002; Walker et al., 2005). However, access to this technique is difficult, and the analyses are very expensive (Frau et al., 2005). This technique is also sometimes not practical due to limited difficulty of data analysis for heterogeneous, natural samples (Fendorf and Sparks, 1996; Foster et al., 1997). XAS spectroscopy is based on the interaction of the X-ray radiation with the sample, when the oscillating electric field of the X-rays interacts with the electrons in an atom. The radiation is either scattered by these electrons or is absorbed and excites the electrons (Jalilehvand, 2006).

The (µ)EXAFS spectrum results when a photoelectron ejected by the absorption of an X-ray travels outward and is then backscattered by its nearest neighbor. The (µ)EXAFS region typically starts from ca 40 up to 1000 eV above the absorption edge. In contrast, (µ)XANES spectra are produced by multiple scattering resonances of an photoelectron among neighboring atoms. The (µ)XANES spectra provide qualitative information on the local coordination and oxidation state. The (µ)XANES region typically extends from ca 30-40 eV. The interpretation of (µ)XANES spectra is more complicated than (µ)EXAFS spectra, since the exitation process essentially involves multi-electron and multiple scattering interactions (e.g., Brown et al., 1988; Weisener, 2003). Combined (µ)EXAFS and (µ)XANES spectroscopy can provide information on both the chemical state and the local structural environment (in average interatomic distances up to 5-6 Å) for materials, such as fluids, colloidal precipitates, surface absorbed species, and poorly crystallized minerals, etc. (Weisener, 2003).

In environmental studies, the (µ)XANES is applied for the quantitative mineralogical microanalysis of undisturbed samples, as well as studying the relationship between the microelements and the solid phase of a soil (Strawn et al., 2002; Vodyanitskii, 2006). This microstructure-study technique requires an adequate sensitivity to the weakly ordered particles and a very low threshold of element discovery. This is equal to about 0.01 % of the bulk elements, which fits to their amount in soils (Vodyanitskii, 2006).

In recent years, XAS techniques (both the EXAFS and XANES) have been used to determine As solid phase speciation in various types of environmental samples. Waters affected by AMD were studied by e.g., Foster et al. (1997, 1998), Savage et al. (2000) or by Farquhar et al. (2002); mine wastes and related materials were studied by e.g., Pfeifer et al., (2003), Paktunc et al., (2004), Arčon et al., (2005), Walker et al., (2005), van Elteren et al., (2006); and contaminated soils (e.g., Manning (2005) Fendorf and Sparks (1996), Morin et al. , 2002; Strawn et al., 2002). Environmentally important synthetically produced compounds and other materials/minerals, were studied by e.g., Fendorf et al. (1997), Morin et al. (2003), Paktunc and Durtizac (2003), Sherman and Randall (2003), Ona-Nguema, et al. (2005), Savage et al. (2005), Smith et al. (2005) and Ouvrard et al. (2005).

2.2.2.10. Infra-Red spectroscopy and other related techniques

Infra-Red (IR) spectroscopy covers a range of techniques, which can be used to identify mineral phases in a sample based on characterizing energies of various vibrations of the molecules. IR radiation corresponds to these energy levels and IR absorption occurs when the frequency of the radiation is equal to that of the vibrations (see Pansu and Gautheyrou, 2006).

In order to analyze a sample, an IR radiation beam is passed through the sample, and the amount of energy absorbed at each wavelength is recorded. This may be done by scanning through the spectrum with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum may be plotted, which shows at which wavelengths the sample absorbs the IR, and allows interpretation of the bonds present (Pansu and Gautheyrou, 2006).

A disadvantage of the Infra-Red Spectroscopy is the relatively large amount of sample needed and complicated sample preparation (pellets composed of powdered sample and KBr, KCl, etc.).

2.2.2.10.1. IR

Infrared absorption spectroscopy (IR) deals with the infrared part of the electromagnetic spectrum (between visible and microwaves, ca 1-1000 μm). The IR region is usually divided into three energy sections: Near-IR, Middle-IR, and Far-IR.

IR spectroscopy is the most commonly used IR technique for phase identification in environmental (mineralogical) samples, and usually complements the XRD, because it is applicable also to amorphous phases.

Particular minerals can be identified, along with the nature and the direction of the chemical bonds. Thus the IR helps for better understanding of atomic structures and isomorphic substitutions in some cases. These data also help to quantify molecular water and constitutive hydroxyls and to detect presence of crystalline or non-crystalline impurities, which influence the regularity of the lattice structure (e.g., Tuddenham and Lyon, 1960; Taylor et al., 1970; Pansu and Gautheyrou, 2006). Gieré et al. (2003) used IR spectroscopy and thermogravimetric analysis (see below) for characterization of various amorphous As-bearing iron sulpho-arsenates, which were not possible to identify and characterize by SEM-EDS/WDS or XRD due to a lack of material and its amorphous nature.

2.2.2.10.2. FT-IR and MAS

Fourier transform infrared spectroscopy (FT-IR) is another technique for collecting IR spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator), the IR light is guided through an interferometer. Performing a mathematical Fourier Transform on the signal (so-called interferogram) results in a spectrum identical to that from conventional (dispersive) IR (Pansu and Gautheyrou, 2006). Measurement of a single spectrum is faster in FT-IR because the information at all frequencies is collected simultaneously. This allows multiple samples to be collected and averaged together resulting in an improvement in sensitivity (Griffiths and De Haseth, 1986).

Mössbauer spectroscopy is a technique based on the Mössbauer effect. In its most common form, Mössbauer Absorption Spectroscopy (MAS), a solid sample is exposed to a beam of gamma radiation, and a detector measures the intensity of the beam that is transmitted through the sample (Tuddenham and Lyon, 1960). In the resulting spectra, gamma-ray intensity is plotted as a function of the source velocity. At velocities corresponding to the resonant energy levels of the sample, some of the gamma-rays are absorbed, resulting in a drop in the measured intensity and a corresponding dip in the spectrum. The number, positions, and intensities of the peaks provide information about the chemical environment of the absorbing nuclei and can be used to characterize the sample.

In environmental sciences related to As solid speciation, IR techniques (mostly FT-IR and MAS) are usually used to determine and characterize natural or synthetic hydrated iron oxyhydroxides and oxyhydoxysulfates (Kosmas et al., 1984; Bigham et al., 1990; Sun and Donner, 1996; Carlson et al., 2002; Kanel et al., 2006; Lakshmipathiraj et al., 2006); clay minerals (Lin and Puls, 2000; Wang and Mulligan, 2006); or arsenate and other minerals (Brown et al., 1990 ; Murzin et al., 2003; Mollah et al., 2004; Raposo et al., 2004; Ouvrard et al., 2005; Marquez et al., 2006).

2.2.2.10.3. RS

Raman (vibrational) spectroscopy (RS) is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a sample. Typically, a sample is illuminated with a laser beam. Photons in the sample are absorbed or emitted by the laser light, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the photon modes in the sample (Pansu and Gautheyrou, 2006).

In the end of the ninetieths, this technique has been used for study of oxidized pyrite surfaces (Mycroft et al., 1990). Recently, the RS is employed increasingly in investigation of As-bearing secondary minerals from different types of geological environment (Courtin-Nomade et al., 2003; Frost and Kloprogge, 2003; Frost et al., 2003; Martens et al., 2003; Thornburg and Sahai, 2004; Kloprogge et al., 2006; Filippi et al., 2007). Application of RS for identification of As-bearing minerals may be useful. However, until now some rare arsenates found in soils/wastes has not been possible to identify because of a strong fluorescent effect of unascertained origin (Filippi et al., 2007). Similarly, the lack of published spectra of most arsenantes is a limiting factor. The main advantages of this method, compared to XRD, lie in the selectivity, simplicity of sample preparation and amount of the sample and in quickness of the measurement. Raman spectra can be collected from a very small volume of mineral phases (< 1µm in diameter) in polished sections and it is also simple to analyze tiny pulverized particles, which is very useful for research of scarce secondary As minerals.

2.2.2.11. Thermal analysis: TGA, DTA

Thermal analysis comprises a group of techniques in which a physical property of a sample is measured as a function of temperature, while the sample is subjected to a controlled temperature programme. The most commonly used methods in environmental science are based on changes of weight and energy of the sample during the heating. Used in combination with other mineralogical methods, thermal analysis is a valuable tool for the environmental samples that allow the qualitative identification and quantitative determination of many minerals, mainly clays and various iron oxyhydroxides.

Thermogravimetric analysis (TGA) is performed on samples to determine changes in weight during heating. Such analysis relies upon a high degree of precision in measurements of weight, temperature, and temperature change. TGA is commonly employed in research and testing the degradation temperatures, absorbed moisture content of minerals, the level of inorganic and organic components in soils, etc. Because many weight loss curves look similar, they may require transformation before results are interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent (Pansu and Gautheyrou, 2006).

Differential thermal analysis (DTA) enables quantification of exothermic or endothermic energy changes at various temperatures without inevitably modifying weight (Pansu and Gautheyrou, 2006). DTA is based on the record of difference in temperature between a measured sample and an inert reference material, when both are subjected to identical heat-treatments at a constant linear speed. This differential temperature is then plotted against time, or against temperature.

Gieré et al. (2003) used this technique to characterize amorphous As-bearing phases and sarmientite [$Fe_2(AsO_4)(SO_4)(OH)\cdot 5(H_2O)$] related to mine wastes. Using DTA Ghosh et al. (2006) detected arsenopyrite and marcasite (FeS_2) in a clay fraction of surface soils.

2.2.2.12. Vis DRS, VMP

The Vis diffuse reflectance spectroscopy in the visible region (Vis DRS) and voltammetry of microparticles (VMP) are relatively new methods which may be used in environmental sciences. Although, the both Vis DRS and VMP have still not been used directly in context of As-bearing phases, these methods have been used for characterization of ferric (III) oxides and oxyhydroxides, which are generally known as the most common As sorbents in the nature.

The Vis DRS of Fe(III) ions is based on the sensitivity of the energy of d–d electronic transitions of Fe ions to their nearest surrounding (Grygar et al., 2003). Thus, Vis spectra of Fe ions are phase-specific and are employed for the identification and quantification of Fe(III) species in the sample (Sherman and Waite 1985; Malengreau et al. 1996, 1997; Scheinost et al. 1998; Scheinost and Schwertmann, 1999).

VMP is an electrochemical method which reflects the reactivity of Fe oxide particles to reductive dissolution and therefore is specific to phase composition and to grain size and crystallinity (Grygar et al., 1995; Grygar, 1998). With VMP, information on the electroactive compounds in the sample is obtained by scanning over a specified potential range and looking for peaks in the current, which indicate the occurrence of electrochemical reactions (van Oorschot et al., 2001).

Grygar et al. (1995) studied the reductive dissolution behaviour of several synthetic Fe oxides and oxyhydroxides with VMP and they found that these minerals are reductively dissolved from the working electrode at different potentials typical of each phase, illustrating the diagnostic power of this technique. It is also possible to quantify concentrations of different minerals within a mixture, by making a calibration curve with mixtures of known amounts of well-defined minerals (cf., Grygar, 1995; Grygar et al., 1995; Grygar 1997; van Oorschot et al., 2001). Furthermore, the technique is simple, rapid (VMP could make it possible to derive the composition and characteristics of the Fe oxides in a sample within a matter of minutes) and no special sample pre-treatment is required. Therefore VMP could be a useful complementary method to standard techniques to identify powdered solids (minerals) and microparticles (e.g., Scholz and Meyer, 1998; Ettler et al., 2005). Although Vis DRS and VMP are relative methods, and require an internal standard or reference compounds to obtain absolute values (Grygar and van Oorschot, 2002; van Oorschot et al., 2001), both techniques are one order of magnitude more sensitive than XRD, i.e. with a limit of detection of ca. 0.1 % for free Fe oxides in soils and sediments (Grygar et al., 2003).

2.2.2.13. ND

Neutron diffraction (ND) is a crystallographic method for the determination of the atomic structure of a material. The technique is similar to XRD, but differs by the type of radiation (a neutron source) and provides complementary information to XRD. A sample is placed in a beam of thermal or cold neutrons and the intensity pattern around the sample gives information of the structure of the rock.

ND has only rarely been used in studies related to the As contamination of the environment. Fernández-Martínez et al. (2005) studied possible arsenate uptake by gypsum, which is a common industrial byproduct from a number of industrial processes, as well as a common mineral precipitate in mine dumps of sulphide rich deposits. Similarly, Roman-Ross et al. (2006) used ND for an experimental study of As(III) sorption by calcite.

2.3. Summary

A number of approaches and instrumental methods common in geology, soil and materials science are increasingly being applied in environmental sciences. Some have been used widely and for a long time, other are novel and seldom used; mostly due to its inaccessibility or cost.

The presented review summarizes and shortly introduces various methods that are (or could be) useful for characterizing As solid speciation in soils, tailings and mine wastes. It also tries to help with better orientation in the application of these methods.

Although a rank of modern methods have been developed in last years (HAADF-STEM, AFM, BFM, PIXE, XAS techniques, ND, etc.), there are several established methods (binocular/optical microscopy, XRD, SEM etc.) which remain a basic step for mineralogical research. Other group of methods has not commonly been used in environmental science, although they are well accessible, often do not need special sample preparation and may give good results (RS, DTA, TGA, Vis DRS, VMP). Wider usage of these methods for the identification of As-bearing minerals is still, in some cases, limited by a lack of comparative data of scarcer minerals.

As have been shown by several authors, a useful way how to obtain more detailed information via so-called conventional methods could be their improvement.

It can be concluded that usage of only sole mineralogical (or only geochemical) approach for the determination As solid speciation at polluted sites is insufficient and gained knowledge may not be complete. As demonstrated by many authors only complex research including correct sampling and sample preparation and application of a set of complementary methods can lead to complete results.

CHAPTER 3. Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ)

Filippi[a,b] M., Goliáš[b],V., Pertold[b] Z.

[a] *Institute of Geology, v.v.i., Academy of Science of the Czech Republic, Rozvojová 269, 165 00 Prague 6, Czech Republic*

[b] *Institute of Geochemistry Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic*

Status: Published in journal the Environmental Geology, 45, 5 (2004): 716-730

Abstract

Soil, mine tailing, and waste dump profiles above three mesothermal gold deposits in the Bohemian Massif with different anthropogenic histories have been studied. Their mineralogical, major element, and arsenic (As) contents and the contents of secondary arsenic minerals were analysed. The As-bearing minerals were concentrated and determined using X-ray diffraction (XRD) analysis, the Debye-Scherrer powder method, scanning electron microscopy (SEM), and energy-dispersive microanalysis (EDAX). The amorphous hydrous ferric oxides (HFO), As-bearing goethite, K-Ba- or Ca-Fe- and Fe- arsenates pharmacosiderite, arseniosiderite, and scorodite, and sulphate-arsenate pitticite were determined as products of arsenopyrite or arsenian pyrite oxidation. The As behaviour in the profiles studied differs in dependence on the surface morphology, chemical and mineralogical composition of the soil, mine wastes or tailings, oxidation conditions, pH, presence of (or distance from) primary As-mineralisation in the bedrock, and duration of the weathering effect. Although the primary As-mineralisation and the bedrock chemical composition are roughly similar, there are distinct differences in the As behaviour amongst the Mokrsko, Roudný and Kašperské Hory deposits.

Keywords: oxidation zone, Quaternary cover, arsenic, arsenopyrite, arsenate

3.1. Introduction

The toxicological effects of arsenic (As) have been generally recognised and documented (e.g. Stöhrer 1991; Chappell and others 1994; Nriagu 1994). The well known association of mesothermal gold mineralisation with As-bearing minerals has also been described for some gold deposits of the Bohemian Massif in Central Bohemia: in the metallogenic zone of the Jílové, Libčice, Mokrsko, Kasejovice, and Kašperské Hory deposits, and in the Roudný deposit (e.g. Morávek and others 1989; Morávek 1995). Prospecting plans and projects following the political and economic liberalization that began in 1989 have led to environmental concerns amongst the general public, especially in connection with As. No data is available on As bound in the weathered parts of these deposits, although the results of soil geochemical prospecting have revealed high As contamination (Janatka and Morávek 1990). This work is intended to supply such data, and encompasses an attempt to interpret this data in terms of As behaviour in the oxidation zone in the temperate climate zone. We decided to study the following three deposits because of their possible environmental impacts, and also because of their very different anthropogenic histories. Mining was terminated approx. 500 years ago at Kašperské Hory, 70 years ago at Roudný, and the Mokrsko deposit has never been mined so that its oxidation zone has been preserved in its natural form.

Numerous papers concerning As behaviour in contaminated areas have been published recently (e.g. Voigt and others 1996; Dhoum and Evans 1998; Craw and others 1999; Hudson-Edwards and others 1999; Juillot and others 1999; Donahue and others 2000; Savage and others 2000; Lumsdon and others 2001; Pichler and others 2001). These works are mostly concerned with a specific part of only one deposit: processing or mining wastes, contaminated waters and stream sediments or soils. Our study compares conditions at three different sites with roughly similar primary mineralisation and monitors conditions in contaminated soils as well as in mine tailings and mine wastes.

3.2. Geological background

The Mokrsko, Roudný, and Kašperské Hory deposits are situated in the central and southern parts of the Bohemian Massif (Fig. 1). The Roudný and Kašperské Hory deposits are hosted by high grade gneisses of the Moldanubian terrain, and the Mokrsko deposit is hosted by a granodiorite intrusion of the Central Bohemian Plutonic Complex, which generally borders the Moldanubian terrain on one side and the low grade Bohemicum terrain on the other.

The Mokrsko West deposit is a very regular sheeted veinlet system, mostly hosted by biotite-amphibole granodiorite of Variscan age, and extending across its contact into the Upper Proterozoic volcano-sedimentary complex, metamorphosed in the greenschist facies. The mineralisation consists mainly of quartz with relatively common calcite and minor chlorite, biotite, amphibole, and microcline. The total amount of sulphide minerals in the ore is <5% vol. (Morávek and others 1989). Arsenopyrite and pyrrhotite predominate, pyrite is frequent locally, and molybdenite, chalcopyrite and marcasite are common in minor amounts. Loellingite, ullmanite, sphalerite, galena, cubanite, tetrahedrite are accessories. Bi, Te and Sb minerals in the form of inclusions accompany microscopic gold. Cliff and Morávek (1995) estimated the general level of As in the ore at 300-500 mg/kg. A cross section in Morávek (1996) shows partial independence of the Au and As values, where most As values in the mineralised zone lie around 500 mg/kg, with local areas considerably above 1500 mg/kg. The soil cover mostly attains values of 0.5 to 2 m, with only local occurrences of larger thicknesses (Morávek and others 1990, unpublished data). The elevation of the deposit surface is between 400 and 488 m a.s.l., where precipitation reaches 500-550 mm p.a. with pH 4.5-4.7, and an average temperature of 7.8 oC (all cited climatic data come from the database of the Czech Hydrometeorological Institute - CHMI).

The Roudný deposit is a combined vein, impregnation and stockwork system hosted by biotite-sillimanite gneiss with intercalations of quartzite, calc-silicate rock, graphitic gneiss, and amphibolite, and by metagranite bodies and aplopegmatite dikes. Hydrothermally altered rocks (silicification, sericitisation and chloritisation) are widespread. The gangue consists mainly of quartz and also contains tourmaline, calcite, dolomite, siderite, fluorite, and barite. Microscopic gold is accompanied by four generations of pyrite, two generations of arsenopyrite, marcasite, and very minor sphalerite and chalcopyrite (Litochleb and Veselý 1992). Paterová and others (2000) found As contents in pyrite of up to 5% wt., in distinctly zoned patterns. Because pyrite is a dominant and frequent sulphide, it probably contains a considerable part of the As in the primary zone. The literature does not contain more detailed data on the As distribution in the ore. The Quaternary cover is of various types. Thick (more than 2 m) slope debris alternates with bedrock outcrops, and with surface workings from different periods, starting with the 14th century (Morávek and others 1990, unpublished data). Old tailings from the 18-19th centuries are preserved only in remnants, while the modern tailing pond (from 1900-1930) is preserved in its original shape. The deposit is situated between 440 and 500 m a.s.l. Climatic conditions are very similar to those at the Mokrsko deposit; precipitation equals 600-650 mm p.a. with an average pH value of 4.5, at an average temperature of approx. 8 oC (CHMI).

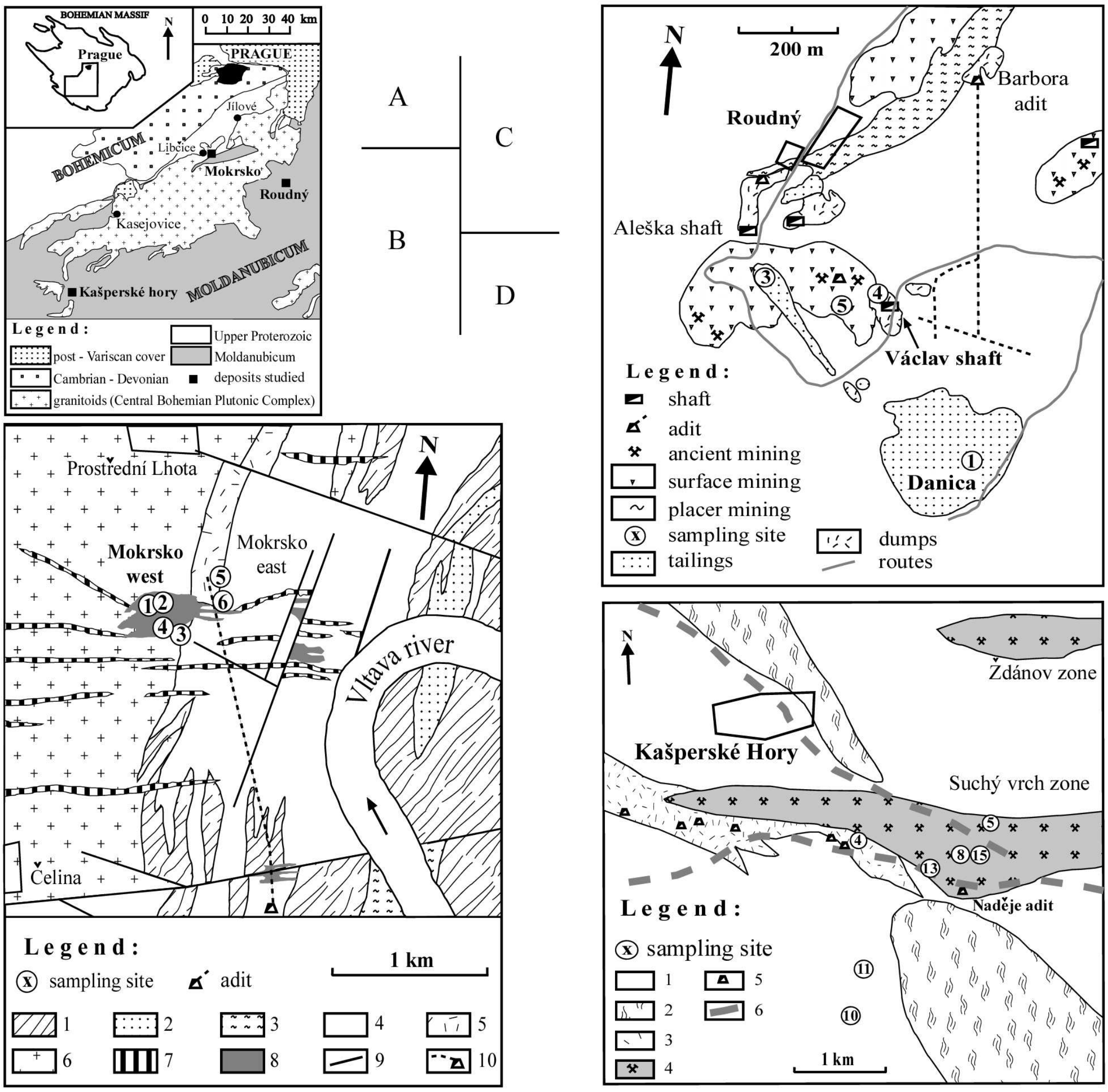

Fig. 1. A: Location of the Mokrsko, Roudný and Kašperské Hory gold deposits in the Bohemian Massif; B: Mokrsko area, simplified geological map (adjusted after Morávek 1996). Legend: 1- mafic to intermediary volcanites, 2- felsic volcanites, 3- albite granite, 4- volcano-sedimentary sequence overlying the volcanites, 5- 6- amphibole-biotite granodiorite, 7- dikes (aplite, porphyrite, etc.), 8- Upper Proterozoic shales and graywackes, 9- gold-bearing zones, 10- faults; C: Roudný area, location of mining and ore treatment sites (adjusted after Komínek 1990, unpublished); D: Kašperské Hory, simplified geological map (adjusted after Pertold and Punčochář 1996). Legend: 1- biotite-sillimanite paragneiss, 2- biotite orthogneiss, 3- quartzite, 4- Au-W mineralised zones with old workings, 5- adits, 6- mylonitisation

The deposits of the *Kašperské Hory ore district* (Pertold and Punčochář 1996) are hosted by different types of gneiss, with quartzite, leptynite, amphibolite, and calc-silicate rock intercalations. Rocks affected by the shear zone have been partly chloritised and sericitised. The explored Suchý vrch deposit is a complicated system of quartz veins following S- and steeper C-planes of the shear zone. Gold is accompanied by two generations of arsenopyrite, and by small amounts of Co, Ni sulphoarsenide gersdorffite, pyrite, glaucodote, sphene, apatite, molybdenite, pyrrhotite, and Bi-Te-S minerals. The As content in the ore is irregular, with frequent values of 300-700 mg/kg, but also attains values of over 1000 mg/kg and even as much as 2000 mg/kg (Janatka and Morávek 1992). The Quaternary cover has a thickness of more than 2 m in valleys and morphological depressions (Punčochář 1996, unpublished data). Large areas are covered by remnants of old surface mining from different historical periods: the circular depressions surrounded by elevations are the sites of former shallow shafts and their dumps. The deposits are mostly situated between 700 and 800 m a.s.l., where precipitation varies between 800-1600 mm p.a., at pH 4.5. The average annual temperature is approx. 4.5 oC (CHMI).

3.3. Sampling

Samples from the oxidation zone were taken by a combination of trenching, hand auger drilling (Eijkaelkamp kit), and down-hole (non-rotational) hammer drilling (Kobra equipment). Sampling sites were selected on the basis of the results of soil geochemical prospecting (Janatka and Morávek 1990) in sample areas highly contaminated by As. The profiles were sampled in small vertical segments, taking into account all lithological changes. The sampling was performed during a dry period in the summer. The locations of the profiles and characterisation are given in Fig. 1 and in the Appendix, respectively.

Mokrsko: Drill holes (Mo1 through Mo6) were situated in the natural oxidation zone of the deposit. Mo1 and Mo2 sampled the morphologically flat part of an agricultural field, while Mo3 and Mo4 were located in a sloping part of a forested area, consisting of granodiorite. Mo5 and Mo6 sampled the oxidation zone of the deposit hosted by volcanogenic and sedimentary rocks of Proterozoic age, in a sloping forested area.

Roudný: Drill hole Ro1 sampled the modern, mostly reduced tailings pond (called Danica) with a flat surface and sporadic vegetation cover; Ro3 was located in old, slightly sloping, mostly oxidised tailings. The Ro4 trench cut the slope of the Václav shaft dump (from the beginning of the 20th century), while the Ro5 trench penetrated the medieval surface workings (estimated origin in the 16th century, based on iron artifacts), both in a forested area.

Kašperské Hory: Most sampling sites were located so as to penetrate the remnants of old and younger surface workings, especially in the forested area of the main Suchý vrch zone. We focused on the oldest workings, from the 14-15th century (Ka4, Ka5) and from the 16th century in the case of sites Ka8, Ka13 and Ka15, estimating their age from their surface morphology and from the type of iron artifacts (hammers, etc.) that they contained. Sampling sites Ka10 and Ka11 were situated south of the mineralised shear zone in a natural soil environment, untouched by exploration and mining.

3.4. Analytical methods

After drying (at room temperature), the samples were sieved to 2 mm. Major element silicate analyses were performed by a combination of X-ray fluorescence analysis (XRFA) and wet chemical analysis (in the Gematrix laboratory, Prague-Černošice). The samples from selected profiles were prepared for As determination according to method A of Van der Veen and others (1985). The samples were treated in closed savilex pots by concentrated HNO_3 at 150 ^{o}C for three hours (1 g of sample and 7.5 ml of concentrated nitric acid). After cooling, they were diluted with distilled water. The As (and

Fe) concentration was determined by flame atomic absorption spectroscopy (FAAS, Varian Spectra AA 200 HT instrument) using an acetylene/nitrous oxide flame. The detection limit for As was 6 mg/kg. The pH values of selected solid samples were measured in the leachates consisting of distilled water and 1M KCl solution (leaching for 24 hours, ratio of 1:2.5). A calibrated digital 330/SET-2 pH-meter WTW was used with a SenTix 21combined electrode at 21 °C.

The samples were screened and quartered for mineralogical studies of rock-forming minerals and secondary As minerals in the soils. Two types of mineralogical specimens were prepared: from natural samples and from samples concentrated by panning in denatured alcohol. The purpose of panning was to concentrate the medium and heavy mineral fractions, where Fe- and the As-bearing minerals should be expected. Thin (from the 2-0.5 mm fraction) and polished sections (from the 0.125-0.5 mm fraction) and samples for X-ray analyses were prepared. First, they were studied by a Jenapol optical microscope, by a CamScan S4 scanning electron microscope (SEM) with a Link ISIS 300 energy-dispersive spectrometer (EDS), and by a JEOL JXA-50 electron microanalyzer with a PV 9400 (EDAX) energy-dispersive X-ray analyser. The following standards were used: GaAs (As), hematite (Fe), leucite (K), diopside (Ca), jadeite (Al, Si), ZnS (sulphide S) and barite (Ba, sulphate S). The samples were coated with carbon. The operating conditions were: voltage 20 kV, probe current 1.4 nA and counting 60 sec. ZAF correction procedures were used for calculation of all the analyses.

The X-ray diffraction analyses (XRD) were carried out using a DRON 2.1. diffractograph under the following conditions: CuKα radiation, graphite secondary monochromator, 35 kV, 30 mA, step scanning at 0.01 and 0.05°/3s in the range 2-60° 2θ. The quantitative mineralogical composition was estimated using the ZDS-system software, version 6.01 (Ondruš 1995, Ondruš and Veselovský 1995), combining X-ray data and silicate analyses. The powder diffraction file (PDF-2) database was employed for peak identification. The determination of minerals from soils and concentrates (it is multimineral) samples using the above mentioned XRD analysis is limited by ca. 5 vol. % of the determined mineral in the sample (of course in dependence on crystallinity of individual minerals). The Debye-Scherrer powder method with a 114.6 mm chamber and Cu/Ni and Co/Fe radiation was used for separated single grain identification. Time exposures were from 19 to 25 hours.

3.5. Results

3.5.1. Mineralogical composition

We employed a combination of silicate analyses, XRD data and normative minerals in an attempt to estimate the semi-quantitative mineralogical composition (data in wt.%) of selected samples. The result is depicted in Fig. 2. Optical microscopy and EDS help to identify the accessory minerals. The most frequent mineral in all the samples is quartz (32–48%), followed by muscovite + illite + biotite (13–38%), feldspars (3–33%), amorphous hydrous Fe oxyhydroxides (HFO) (3 – 13%) and Al oxyhydroxides (<1–3%), chlorite (<1–5%), minor Ti minerals (such as rutile, ilmenite), and some other minerals occurring at particular localities. The RECAL program used (Ondruš and Veselovský 1995) cannot distinguish amongst clay minerals such as kaolinite and illite, so the software includes them in the group of muscovite or amorphous Al oxyhydroxides. From the standpoint of the mineralogical and chemical compositions, the studied materials are roughly similar as a source of elements for newly forming secondary minerals. Of the primary minerals, which either weather and provide cations for solutions or can adsorb As, feldspars, phyllosillicates, secondary Fe-

Al- oxides and carbonates are important (e.g. Alpers and others 1994; Bowell 1994; Voight and others 1996; Juillot and others 1999; Lin and Puls 2000; Bhattacharya and others 2002), and thus resistant accessory rock-forming minerals will be not discussed here. Accessory arsenopyrite, which was found at all three localities, represents the main primary As carrier. However, at the Roudný deposit, pyrite, which occurs abundantly, can also be considered to be a significant source of As. There are, however, some important differences amongst the three deposits.

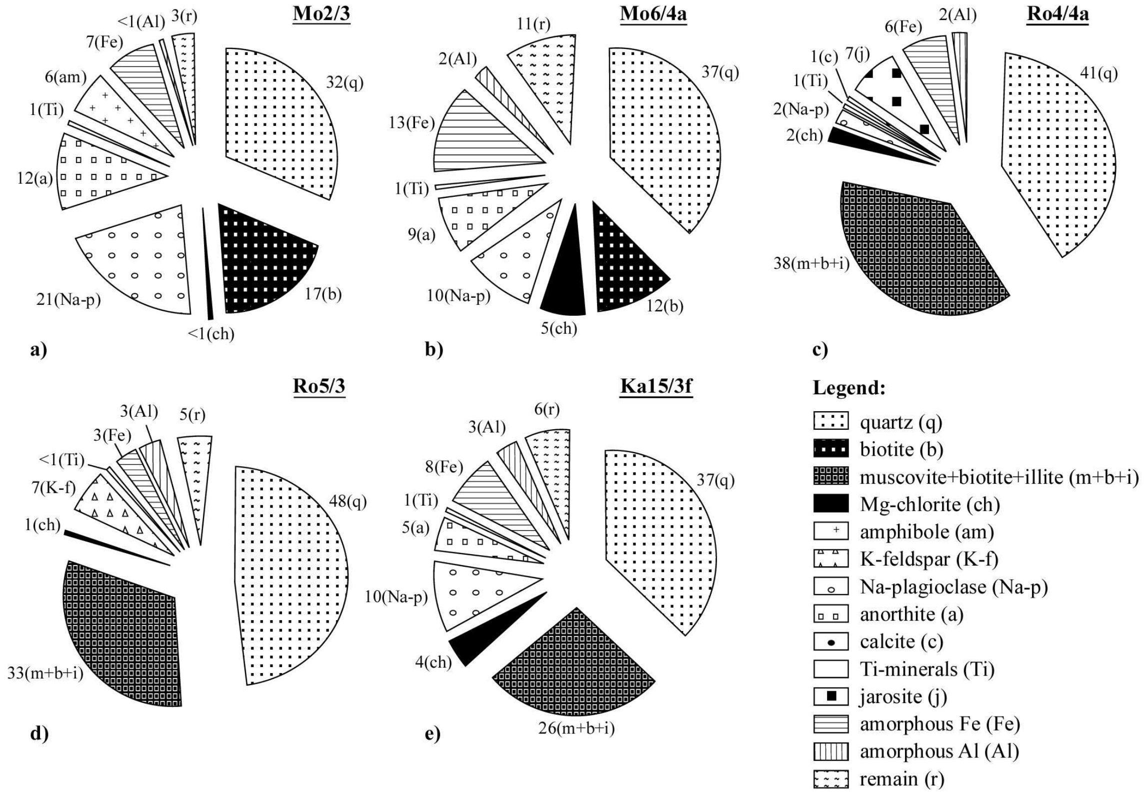

Fig. 2. Quantitative mineralogical composition of selected samples (values are given in wt.%)

The Mokrsko soil is richest in plagioclases. Above granodiorite, it contains amphibole, which has not been calculated or observed at other localities. The soil above the volcano-sedimentary bedrock contains maximum amounts of HFO and chlorite, and the highest portion of residual minerals, which probably points to the occurrence of a number of various minor minerals. The Roudný samples have the highest contents of quartz, muscovite + biotite + illite, and the lowest of feldspars. The Ro4 profile from the most recent dump contains jarosite and locally also gypsum (both observed macroscopically), which document the oxidation of the accessory pyrite well. Calcite was also calculated and found occasionally. The residual portion is missing in this sample, which could point to a low number of minor minerals present. The Kašperské Hory sample exhibits high contents of muscovite + biotite + illite, plagioclases, chlorite and a significant calculated proportion of HFO and Al oxyhydroxides.

3.5.2. Geochemistry

3.5.2.1. Bulk chemical composition

Nine samples have been analysed for chemical composition (Table 1). Low contents of MnO, P_2O_5, and TiO_2 (arithmetic means 0.09, 0.15, and 0.80 wt.%, respectively), as well as differences in the contents of MgO, Al_2O_3, and SiO_2 (means 1.51, 16.64, and 62.17 wt.%) seems not to be important from the viewpoint of the chemical composition of the determined secondary phases (see section 5.4). Variations in the rest of the parameters appear to be more important.

Samples from the Mokrsko and Kašperské Hory soils are richer in Fe_{tot} (mean 8.59 wt.%) than samples from the Roudný anthropogenic deposits (mean 4.47 wt.%), where the highest content was found in the Mokrsko soil above volcano-sedimentary bedrock (sample Mo6/4a 12.53 wt.%). The highest contents of CaO were found in samples from the Mokrsko soils above granodiorite (>3.2 wt.%), and in the sample above the volcano-sedimentary bedrock (2.29 wt.%). Considerably lower contents were found in samples from the Kašperské Hory (mean 0.90 wt.%) and Roudný locations (mean 0.48 wt.%). The trend in the contents of NaO is similar (see Tab.1), while the contents of K_2O are different: higher in the Roudný samples (mean 4.62 wt.%), than in the Kašperské Hory (mean 3.27 wt.%) and Mokrsko (mean 1.9 wt.%) samples. The higher contents of sulphur in samples from the reduced part of the tailing at the Roudný location (sample Ro1/5f 0.7 wt.%) and from the modern waste dump (sample Ro4/4a 1.16 wt.%) document the presence of sulphides and/or their oxidation products (for the Ro4 profile). The loss on ignition (l.o.i.) reflects the contents of free and fixed water in minerals and varies in the separate samples between 4.50 and 11.14 wt.%. The highest value was determined in the Mo6/4a samples with the highest amounts of HFO and the residual portion. Variations in the parameters described above correspond well with the data on the mineralogical composition of the studied samples (cf. Table 1 and Fig. 2).

Table 1. Bulk chemical composition of selected samples from the Mokrsko, Roudný and Kašperské Hory Quaternary covers

Sample [wt.%]	**Mo2/3**	**Mo2/5a**	**Mo6/4a**	**Ro1/3**	**Ro1/5f**	**Ro4/4a**	**Ro5/3**	**Ka13/3d**	**Ka15/3f**
SiO_2	62.97	58.34	57.97	65.70	63.12	60.96	68.50	62.09	59.90
TiO_2	0.67	0.73	1.15	0.85	0.80	0.78	0.41	0.91	0.89
Al_2O_3	15.50	15.80	14.02	16.33	16.82	18.16	17.50	17.10	18.49
$Fe_{tot.}$	7.31	7.98	12.53	4.76	4.46	6.18	2.47	7.33	7.78
MnO	0.11	0.13	0.25	0.05	0.05	0.07	0.02	0.07	0.11
MgO	1.65	2.46	2.07	1.01	1.61	0.79	0.40	1.97	1.59
CaO	3.22	4.23	2.29	0.56	0.85	0.39	0.10	0.89	0.90
Na_2O	2.44	2.65	1.19	0.36	0.28	0.22	0.16	1.64	1.17
K_2O	2.08	1.94	1.63	4.35	4.47	4.73	4.93	3.26	3.28
P_2O_5	0.08	0.13	0.25	0.16	0.15	0.12	0.14	0.14	0.15
l.o.i.	5.47	4.98	11.14	4.84	4.50	8.45	7.13	5.98	7.61
CO_2	0.32	0.00	0.22	0.43	2.10	0.38	0.26	0.28	0.21
$S_{tot.}$	0.04	0.00	0.13	0.09	0.70	1.16	0.15	0.13	0.08
Total	99.73	99.37	99.78	99.44	99.56	99.67	99.58	99.79	99.79

3.5.2.2. Arsenic content

The As content has been analysed in 119 samples from 17 sites at all three localities (Appendix and Fig. 3). To assess the possible relationship between As and Fe (Savage and others

2000), the Fe content has been analysed in 56 samples from 8 selected sites. The results are given in Figure 4.

The highest As values in the soils at Mokrsko vary from approx. 1500 to 2400 mg/kg. They occur at or close to the base of the profiles in the morphologically sloping area (profiles Mo3, Mo4, Mo5, Mo6). The lowest values occur in upper parts and vary from approx. 330 to 700 mg/kg. In the morphologically flat area (Mo1, Mo2), the highest values are located below the topsoil, at a depth of 0.2-0.7 m, but a high As concentration (>26 000 mg/kg) was also found in highly weathered granodiorite (C horizons in the Mo1 profile, see the Appendix). This anomalous content is caused by the occurrence of primary As minerals (arsenopyrite and loellingite) and by the great abundance of secondary arsenates. Differences in the As contents depending on the surface morphology suggest higher drainage on slopes, associated with elutriation of As from the upper soil horizons and formation of an illuvial horizon at the base of the soil profile.

The As values in the modern tailing pond down to 5 m at the Roudný deposit are between 1535 and 2490 mg/kg in its unoxidised part (Ro1/4 through Ro1/5g), and about 1000 mg/kg (Ro1/1 and Ro 1/2) in the oxidised upper part. The transitional layer (Ro1/3) contains 1800 mg/kg. The oxidised remnants of old tailings (Ro3) in a profile down to 6 m contain between 425 and 1230 mg/kg As. The dump (Ro4) shows irregular values between 418 and 1667 mg/kg, while the remnants of medieval surface workings (Ro5) exhibit quite steady values with a maximum of 524 mg/kg at the base.

At Kašperské Hory, sampling site Ka4 (from the part of the Suchý vrch zone that has been slightly disturbed by old surface workings), exhibits As contents (max. 480 mg/kg) that increase with the depth of the soil profile. Sampling sites Ka5, 8, 13, and 15 were situated in the same Suchý vrch zone, but in a part with many remnants of old surface or shallow mining works. They are all characterised by uneven distribution of As values, between 139 and 818 mg/kg. The highest As content was found in the upper part of the B-horizon, directly beneath the topsoil in the Ka13 profile. The sites located to the south of the mineralised shear zone (Ka10, Ka11) yielded lower values (mean 60 mg/kg) than the Suchý vrch zone.

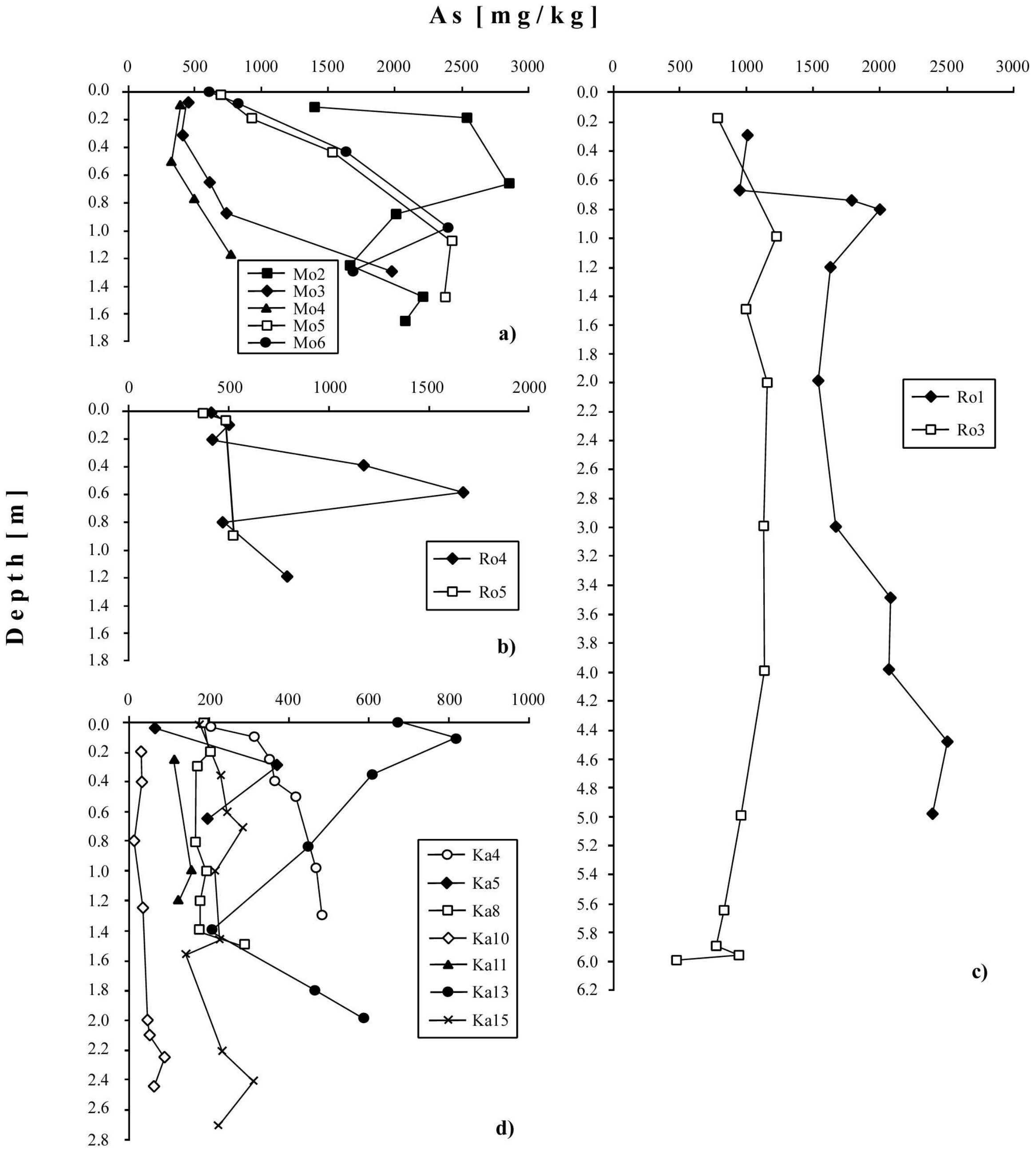

Fig. 3. Arsenic distribution in selected profiles from the: a) Mokrsko; b), c) Roudný; d) Kašperské Hory Quaternary covers

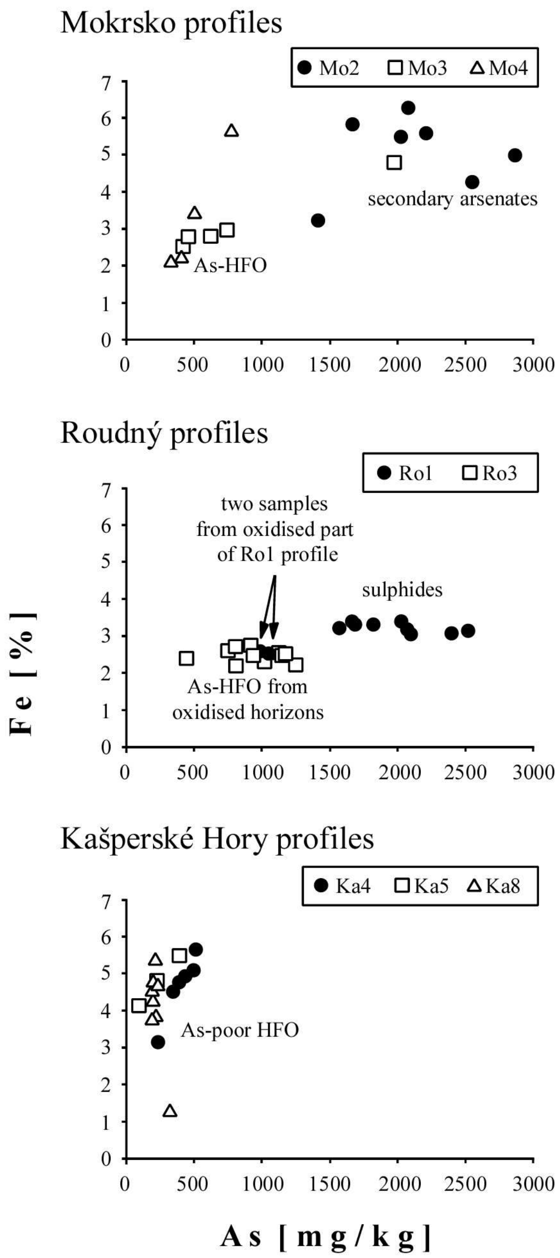

Fig. 4. X-Y plots of As and Fe concentrations in selected samples from different geological settings, and indication of As mineral groups (see the Appendix for sample characteristics)

3.5.2.3. Soil pH

Comparison of pH values determined in leachates in distilled water and in 1M KCl (the values are given in the Appendix) reflect the content of organic matter, the degree of weathering (or soil development), the binding of H^+ ions, and suggests the stability range for secondary minerals. There are distinct differences between the pH values, mostly of about one unit for both leachates in all samples from well developed soil horizons (profiles Mo1, 2, 3, 5 and 6 with median (med.) ΔpH [H_2O-KCl] = 1.1; samples Ro4/1-3 and Ro5/3 with med. ΔpH = 0.7; samples Ka8/2, 8/6, and Ka10/3a with med. ΔpH = 1.0). The considerably higher acidity in KCl leachates compared to H_2O leachates is caused by H^+ ions released from soil colloids, organic matter and clay minerals. In the samples from the youngest waste dump (profile Ro4 with the exception of the reclaimed upper loamy part) and tailing pond (profile Ro1), all the H^+ ions are already available for leaching with distilled water (ΔpH = 0.1). There are no differences between natural soil profiles and new soil profiles formed on anthropogenic deposits in relation to the contents and binding of H^+ ions.

Samples from the lower parts of the Mo1 profile above the granodiorite bedrock at the Mokrsko locality probably reflect the local influence of acidic solutions caused by sulphide weathering in mineralised quartz veins, where a lowering of the pH value starting from the B horizon and increasing with depth is apparent. On the other hand, conditions in the Roudný tailings are characteristic for this type of deposit: the pH is low (about 3) in the oxidised parts above the groundwater level, compared to the reduced parts below the groundwater level, where the pH value is above 7.

3.5.3. Arsenic mineralogy

The As-containing minerals identified in the Quaternary cover of the three deposits are listed in Table 2.

Hydrous ferric oxide (HFO) with As usually contains up to 7 wt.% of As_2O_5. Its texture and chemical composition vary (Fig. 5d, Table 3). It replaces primary minerals and also forms individual grains. Some grains exhibit heterogeneous structure with different As and Fe contents in the individual parts. At the Mokrsko deposit, HFO has been identified especially in the soils above the volcano-sedimentary bedrock but, as can be seen in Figure 4, it is most probably also present above granodiorite, especially in the profiles with lower As contents (Mo3 and Mo4). As-bearing HFO was also found at Roudný in samples from an oxidised part of the tailings and in the As-richest soils at the Kašperské Hory deposit. *Goethite* with more than 16 % wt. As_2O_5 has been identified at Mokrsko above the granodiorite (Table 3). A separate grain was also confirmed by XRD.

Pharmacosiderite is the most frequent secondary As mineral in the Mokrsko oxidation zone above granodiorite. Its grains, which rarely attain a size of 3 mm, and which have a brown to rusty brown colour under a binocular microscope, are both of homo- and heterogeneous composition (Table 4). Some are intergrown with and replace feldspars. The cations are K and Ba. The calculated lattice parameter (for a cubic structure) of a = 7.954 Å is in good agreement with the published data (Walenta 1966). Another pharmacosiderite type occurs in association with arseniosiderite (Fig. 5a). It is characterised by its Ca content (up to several wt.%). The XRD patterns (in agreement with PDF no. 17-0466 or 34-0155) were obtained from concentrated samples as well as from separate grains (Fig 6). Pharmacosiderite has also been found, though rare, in the soil above volcano-sedimentary rocks at Mokrsko (sample Mo6/4a). Generally, pharmacosiderite from Mokrsko soils has a variable composition (variable amounts of K, Ba cations and Ca contents) compared to known pure members of the pharmacosiderite series (cf. Strunz and Nickel 2001). However, some analyses are complicated by its chemical heterogeneity on a microscale and by intimate intergrowth with arseniosiderite and feldspars.

Table 2. Frequency of detected arsenic secondary minerals

Mineral	**General chemical formula (after Strunz and Nickel 2001)**	**Locality / Frequency**			
		Mokrsko		**Roudný**	**Kašperské Hory**
		granodiorite	vulcanosediments		
arseniosiderite	$Ca_2Fe^{3+}{}_3(AsO_4)_3O_2{\cdot}3(H_2O)$	++	-	-	-
pharmacosiderite	$KFe^{3+}{}_4(AsO_4)_3(OH)4{\cdot}6\text{-}7(H_2O)$	+++	+	?	-
pitticite	Hydrous ferric arsenate sulfate	-	-	++	-
scorodite	$Fe^{3+}(AsO_4).2H_2O$	+	-	-	-
goethite (with As)	$Fe^{3+}O(OH)$	+	-	-	-
HFO (with As)	Hydrous ferric oxide	++	+++	-	++
unidentified phases with As		?	-	++	-

Explanations for symbols: +++ very common, ++ common, + rare, - not found, ? probably present

Table 3. Chemical analyses of selected As-bearing HFO and goethite. Analyses designated as Mo6/4a (light part) and (dark part) come from the grains in Figure 5d. Designations Mo6/4a, Ka13/4, etc. specify the horizons from which the analysed grains were obtained (as in Tab 4). Explanation for sign: - not determined

Sample [wt%]	**Mo6/3**	**Mo6/4a (light part)**	**Mo6/4a (dark part)**	**Ka15/3f**	**Ka13/4**	**Mo1/3 (goethite)**
MgO	-	-	-	-	-	2.1
Al_2O_3	2.0	0.8	0.1	9.0	3.8	1.3
SiO_2	1.0	3.2	1.1	6.1	2.8	6.0
P_2O_5	0.6	0.7	0.1	5.5	1.1	-
SO_3	0.2	-	0.1	-	-	-
K_2O	-	-	-	-	-	1.3
CaO	1.1	0.7	0.2	0.8	0.6	-
TiO_2	-	-	-	-	1.4	-
CuO	0.2	0.5	-	-	-	-
MnO	-	-	-	3.1	0.2	-
Fe_2O_3	72.5	70.8	79.7	60.9	71.8	61.6
As_2O_5	5.2	5.7	2.0	2.0	2.5	16.2
WO_3	-	-	-	-	1.8	-
Total	82.8	82.4	83.35	87.3	85.9	88.5

Table 4. Chemical analyses of pharmacosiderite and arseniosiderite. Explanation for sign: - not analysed

	Pharmacosiderites						**Arsoniosiderite**
Sample [wt %]	**Mo1/6c**	**Mo1/6c**	**Mo1/6c**	**Mo2/2**	**Mo2/2**	**Mo6/4a**	**Average from 3 analyses (Mo1/6c)**
Al_2O_3	-	1.2	-	-	-	4.8	-
SiO_2	-	0.9	0.1	0.2	0.3	-	-
P_2O_5	-	-	-	-	-	1.0	-
K_2O	5.2	2.5	1.3	7.3	4.7	0.2	0.6
CaO	0.5	2.4	3.7	0.1	0.2	-	12.0
BaO	-	-	-	3.7	5.6	9.2	-
SO_3	-	-	2.5	-	-	-	-
Fe_2O_3	35.6	35.1	35.9	31.3	33.2	27.4	32.6
As_2O_5	39.7	38.6	37.6	38.2	37.1	38.3	43.3
Total	81.0	80.6	81.0	80.9	81.0	81.0	88.9

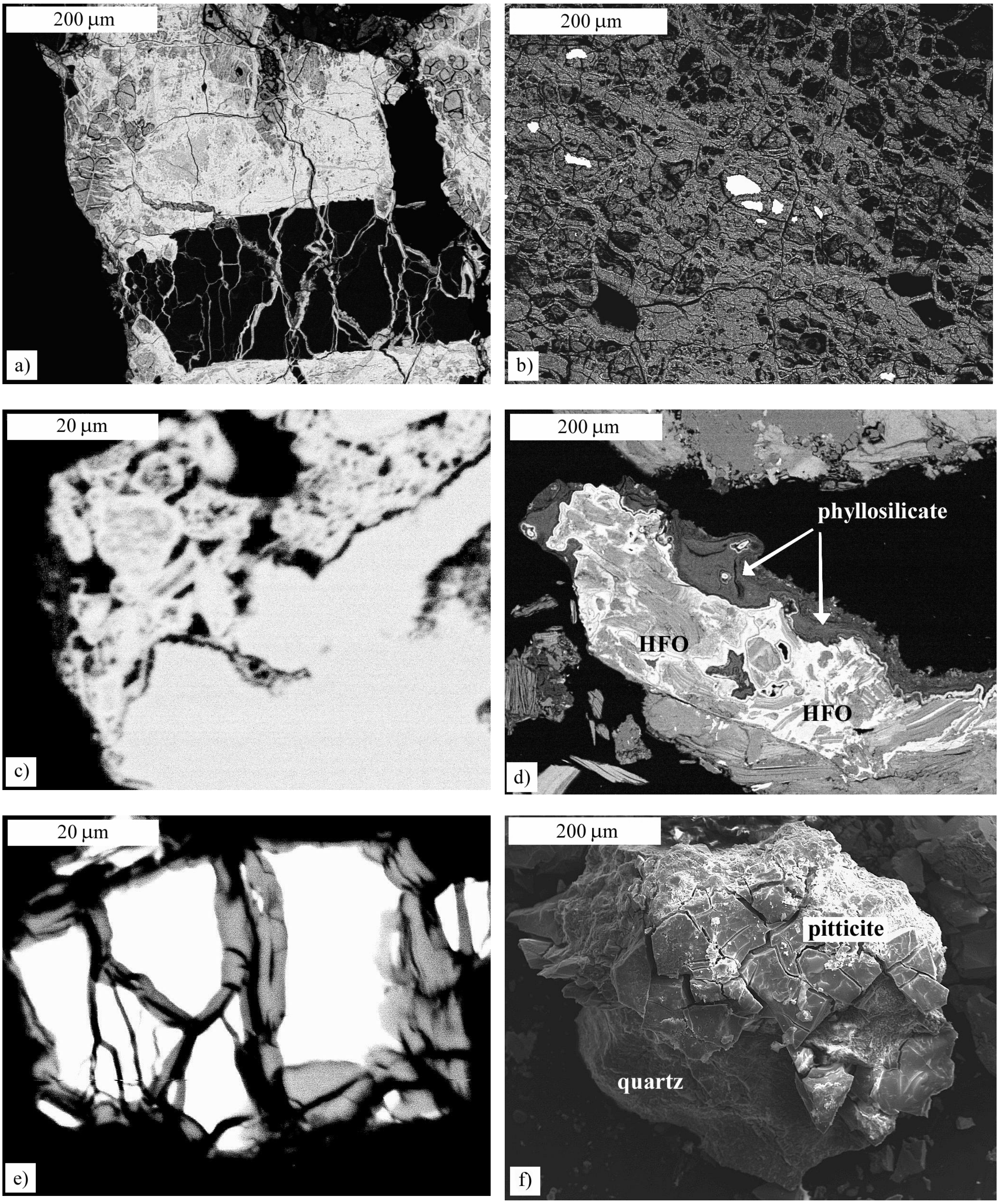

Fig. 5. Microphotographs of secondary minerals containing arsenic: a) Pharmacosiderite relicts (darker) replaced by arseniosiderite (lighter) in quartz (black). Sample Mo1/6c. Back-scattered electron image (BEI); b) Arsenopyrite relicts (white) replaced by arsenates (darker). Sample Mo1/6c. BEI; c) Scorodite grain partly affected by dissolution at its margins. Sample Mo2/2. BEI; d) HFO with varied As contents (lighter parts have higher As contents) in phyllosilicate. Sample Mo6/4a; analyses are given in Table 3. BEI; e) Unidentified arsenate coating replacing arsenopyrite. Sample Ro4/7. BEI; f) Pitticite covering quartz surface. Sample Ro4/4. Secondary electron image (SEI)

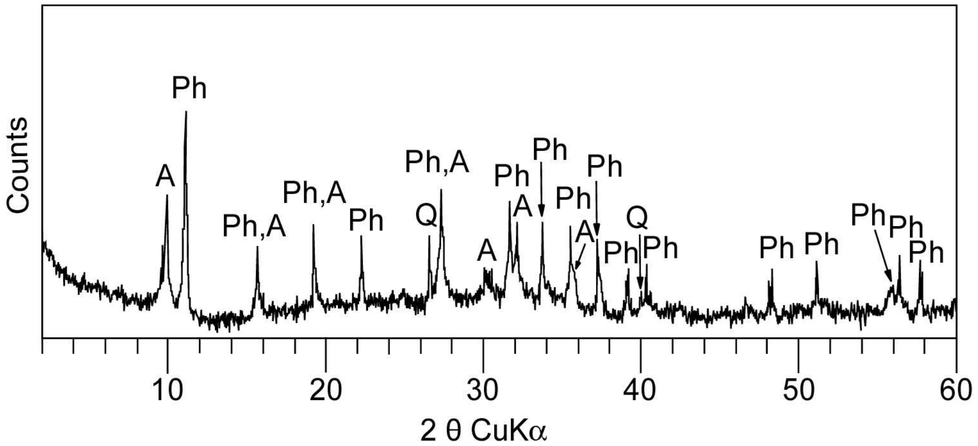

Fig. 6. The XRD pattern of separated arsenate aggregate. Abbreviations: Ph – pharmacosiderite, A – arseniosiderite, Q – quartz

Arseniosiderite has been found only at Mokrsko, in soils above the granodiorite bedrock (samples Mo1/4-6). Its identification is based on XRD analysis of numerous concentrated samples or separate grains and on chemical analyses of polished sections (Table 4). Under a binocular microscope, its grains are brown and are difficult to distinguish from HFO and pharmacosiderite. Arseniosiderite most frequently fills fractures in quartz. The grain size in aggregates is mostly a few tens of microns. Microscopic textures probably indicate replacement of pharmacosiderite by arseniosiderite (Fig. 5a,b).

Scorodite (Fig. 5c), though very frequent in the oxidation zone of many mineral deposits, has been identified only at Mokrsko, as a rare mineral above the granodiorite bedrock (samples Mo2/2 and Mo1/6). In polished sections, it is occasionally intergrown with pharmacosiderite in grains up to 60 μm in size. Its quantitative chemical composition exhibits the following average for three analyses (all values in wt.%): Fe_2O_3 – 28.7 and As_2O_5 – 51.9. Scorodite was also confirmed by XRD patterns in admixture with pharmacosiderite. Its pattern agrees with PDF no. 37-0468.

Pitticite (Fig. 5f) has been found in the dump material of the Václav shaft at Roudný (profile Ro4). Generally, this mineral is not very well described in the literature. Its chemical analyses exhibit variable composition from individual localities (Dunn 1982). According to Dunn, pitticite is a general name for iron-rich amorphous arsenates, originating from gels as the last oxidation product of As-rich primary ores. It occurs as yellowish to brownish coatings of vitreous habit up to 1 mm thick on quartz and host rocks. Pitticite surfaces are smooth with a glassy lustre. Chemical analyses were carried out only on the unpolished planar surface and represent an average for five spots (all values in wt.%): Fe_2O_3 - 36; As_2O_5 - 39; and SO_3 - 9.

At Roudný, *unidentified As-phases* were been detected only by EDAX. The identification is impossible without XRD, but the amount of material is too small for this technique. All the samples were obtained from sample site Ro4, located in the most recent waste dump. According to the chemical composition and the form, three types can be distinguished. The Al and Ba contents and predominance of Fe over As are characteristic for one type (in sample Ro 4/4b). The following chemical composition was found (all values in wt.%): Fe_2O_3 – 37; As_2O_5 – 27; Al_2O_3 – 6; BaO – 10; plus admixture of Si and P. This phase fills thin fractures in the silicate of chlorite composition. A second type (in Ro4/7) has been observed as several μm-thick coatings on arsenopyrite grains (Fig.

5e). It also exhibits a lower content of As than of Fe (all values in wt.%): Fe_2O_3 – 44; As_2O_5 – 28; CaO – 3; plus admixtures of S and Si. A third type (in Ro4/4b) occurs in a fracture of an arsenopyrite grain and has heterogeneous composition. The As/Fe ratio is the opposite of that in the previous two phases. It exhibits the following chemical composition (all values in wt.%) : Fe_2O_3 – 32; As_2O_5 – 37; Al_2O_3 – 6; CaO – 5 with variable contents of Al, Ca and admixture of S, Si and K. Thin secondary coatings on oxidizing sulphide grains were documented, e.g., by Alpers and others (1994). These coatings outline pyrrhotite, which is associated with arsenian pyrite and arsenopyrite, and consist of goethite with an As content of up to 13 wt.% and with max. 3.5 wt.% of Ca, Si and S. The Roudný coatings are richer in As and other elements and indicate the presence of arsenate, similar to coatings reported by Lazareva and Pospelova (1998) or Williams (2001).

3.6. Discussion

3.6.1. Arsenic distribution

In the morphologically flat area at Mokrsko, the maximum As concentrations in the B-horizon could be explained either by the rise of and sorption from solutions during relatively dry periods, and/or by As fixation in minerals that are stable in the specific soil horizon and are not soluble during the more humid periods. In the sloping area (profiles Mo3, 4, 5, 6), As is removed from the upper horizons (Fig.3).

At Roudný, the As content is steady in the soil profile in the old surface working (Ro5), whereas at the modern dump (Ro4), the As concentration is uneven, reflecting the material composition in the profile (see the Appendix, and section 5.3.). The Roudný tailings (modern Ro1 and old Ro3) clearly point to a decrease in the As contents in the oxidised parts compared to the reduced ones. Arsenic must have been partly transported into the surrounding environment during the oxidation processes (oxidation of old tailings proceeded for 100-200 years, partial oxidation of more recent tailings for about 70 years).

In the Kašperské Hory soil profiles in areas affected by surface mining (old as well as younger areas), the As distribution is more or less irregular, suggesting that the period of approx. 550 years was not long enough to produce a smooth geochemical profile in the heterogeneous material left after mining. While the As concentrations are roughly uniform or slowly increase to the base of the soil profile in natural areas (Ka10, Ka11), the elutriation of the upper parts of these soil profiles is probably a consequence of higher precipitation in this area. The increasing trend to depth is also obvious in the Ka4 profile in the old mining area situated on the slope.

The studied soils and anthropogenic deposits are significantly contaminated by As. Plotting of As- versus Fe- concentrations (Fig. 4) indicates clear differences in As solid phase speciation in individual environments (see also section 5.4.).

3.6.2. Secondary phase speciation and stability

Differences in As solid phase speciation for the studied geological locations (soils, waste dumps, tailings) can be explained by slightly different bedrock compositions, i.e. by the contents of Ca and Fe, by the degree of parent rock weathering (soil development, rock-forming mineral decomposition), and by the presence of primary mineralised zones. Because all the samples studied here were readily accessible for oxygen (except the reduced part of the new Roudný tailing), the pH conditions should play a significant role in the differing As behaviour and stability (Bowell 1994).

At Mokrsko, As is partly adsorbed on HFO, which occurs most frequently in volcano-sedimentary bedrock, and is also present in minerals with As in their lattice, mainly above the granodiorite bedrock. The Mokrsko pharmacosiderites display a great variety of compositions with variable contents of K, Ba and Ca cations, or with admixtures of Al. All of these cations are available in the soil, which is the product of bedrock weathering. It is probably the relatively high contents of Ca (higher at Mokrsko than at the other two localities) that keep the pH in the soil relatively high and Ca-ions available; therefore the Ca-Fe arsenates are stable and most widespread (Nishimura and others 1985; Swash and Monhemius 1996). Otherwise, if there is no excess Ca, the Ca- and Ca-Fe-arsenates are generally much more soluble than Fe arsenates (Swash and Monhemius 1995). Scorodite, which is an omnipresent phase during arsenopyrite oxidation and is generally the most frequent secondary As mineral in many types of oxidation zones and mine wastes (Dove and Rimstidt 1985; Foster and others 1998), is surprisingly scarce in the studied samples. According to Swash and Monhemius (1996), Fe arsenates are formed preferentially if sufficient Fe and Ca are available in the solution; however, Ca arsenate compounds will precipitate in solutions with Fe:As <1. As pointed out by Robins and Glastras (1987), the pH has the greatest influence on Fe or Ca arsenate type precipitation, where the Fe arsenates precipitate at significantly lower pH values than the Ca arsenates (pH 1-2 vs. pH 3-4).

Current information about secondary minerals, which originated from As-rich solutions in contaminated areas, exhibits a great dependence on the chemical composition of the location. For example Pierrot (1964) described Ca- and Mg-arsenates from the Ca-Mg-rich oxidation zone of the Pb-Zn deposit; Voigt and others (1996) described the precipitation of hoernesite (as a product of the reaction of Mg-rich ground waters with As-contaminated soils). Relatively rich paragenesis of Fe-secondary arsenate and arsenate-sulphate minerals (bukovskyite, kankite, pitticite and scorodite) was described by Bowell (1991) as a product of lateritic weathering in tropical Ferrasols. Juillot and others (1999) also published a detailed description of the precipitation of Ca-arsenates (pharmacolite, haidingerite and weilite) and Ca-Mg-arsenate picropharmacolite as products of reactions of As-rich solutions with limestone.

The mineralogical/chemical soil composition and soil pH seems to be the main factors influencing precipitation of secondary minerals in the Mokrsko oxidation zone. We prefer the following interpretation: oxidation of arsenopyrite (and other minor sulphides) in the rock produced a low pH value around the sulphide grains, which facilitated the precipitation of scorodite (e.g. Dove and Rimstidt 1985; Bowel and others 1994; Krause and Ettel 1988). After most arsenopyrite was depleted (arsenopyrite dissolution in soils was documented by Lumdsdon and others 2001) and after rock weathering advanced, decomposition of rock-forming minerals (including calcite in the ore) caused an increase in the pH. Under these conditions, scorodite became unstable (Krause and Ettel 1988) and, because the K^+, Ba^{2+} and Ca^{2+} ions were available in soil solutions, As-rich goethite and pharmacosiderites were formed, followed by more hydrated arseniosiderite. Arsenic could also be partly released into solutions. Dove and Rimstidt (1985) reported incongruent scorodite dissolution and As release owing to a decrease in the arsenopyrite oxidation rate followed by an increase in the pH and goethite precipitation. Juillot and others (1999) also explain scarce scorodite occurrence in their materials as being due to an increase in the pH following scorodite dissolution.

Different chemical composition causes different As mineralogical speciation in profiles above the volcano-sedimentary bedrock (profiles Mo5, 6). Arsenic is absolutely dominant in HFO. Swash and Monhemius (1994) found that the Fe/As ratio in amorphous ferrihydrites greatly influences the release of As into solution at low temperatures. The Mokrsko HFOs, with a high Fe/As ratio, are safely in the insoluble field.

Arsenic behaviour at the Roudný locality varies depending on the site. The very different morphology of the As phases (coatings on arsenopyrite grains or on rock fragments) in the samples from the modern waste dump (profile Ro4) probably indicates a different origin than the Mokrsko soils: 1) through direct oxidation of the arsenopyrite grains followed by dissolution (unidentified arsenates); 2) through consolidation of As-rich gels inside the dump (pitticite). Weathering of abundant pyrite led to the formation of powdery jarosite. According to Foster and others (1998), a certain amount of As^{5+} could be substituted for SO_4 in the structure of jarosite, while Savage and others (2000) suggest that part of the arsenate could also be adsorbed. Jarosite is generally assumed to be stable under acidic oxidizing conditions and can precipitate at pH below 3 (Bigham 1994). We found a value of pH 5.7, which suggests that this parameter has increased since the time of the formation of the dump and the jarosite-related weathering process. The presence of jarosite and pitticite in an environment with pH between 4 and approx. 6 (samples Ro4/3 and Ro4/4) and their coexistence with calcite and Ca-bearing arsenate indicate that the modern dump geochemistry and mineralogy are far from steady state conditions. The presence of secondary As-rich coatings documents the initial stage of the arsenopyrite oxidation. The absence of scorodite can be explained by the relatively high pH (about 6) of these samples (see the Appendix). As stated by Baron and Palmer (1996), when the pH increases above 5.89, transformation of jarosite to ferric hydroxides can begin, but the mechanism of As release is not known.

The presence of a sufficient amount of HFO in the oxidised part of the new Roudný tailing pond (samples Ro1/1-1/3) suggests adsorption of part of the As not removed during oxidation. At a pH value close to 3, pyrite and other sulphides were totally decomposed, so that further acidification and release of As from HFO are not occurring at the present time. The absence of secondary As minerals is probably caused by the simple mineralogy of the tailings, characterised by predominant quartz, with only rare and slightly weathered (chemically unmodified) feldspars and micas. Conditions seem to be very similar in older fully oxidised tailings (Ro3). Under the groundwater level (samples Ro1/4-1/5g) at pH>7, the sulphides have been stable for 70 years in the modern pond (similarly observed by Craw and others 1999) and consequently no As migration is likely, unless conditions change.

In the Kašperské Hory area, relatively low As contents caused by dispersion of primary ore during surface mining activities do generally not allow the precipitation of secondary As minerals; this is also true of the Ro5 profile penetrating the old waste dump at the Roudný deposit. The As contents are higher in the layers richer in Fe compounds or clay admixture (see Fig. 2 and the Appendix), so it is highly probable that these features control the As behaviour at these sites (Bowell 1994; Lin and Puls 2000; Bhattacharya and others 2002). More research is required to confirm this consideration and specify the As speciation. For example, some of the sequential methods developed recently especially for As could be employed (e.g. Wenzel and others 2001)

3.7. Conclusions

Very high As contents in the Quaternary cover (more than 2800 mg/kg) were found in agriculturally exploited flat areas at the Mokrsko gold deposit (these values are more than 70 times the Czech health limits for agricultural soils). The maximum content (approx. 26 000 mg/kg) was determined in weathered granodiorite with relicts of quartz veins rich in primary and secondary As minerals at the base of the Mo1 profile. Also high As contents (up to approx. 2500 mg/kg) were found in the tailings pond at the Roudný deposit. The As contents in the cover of the Kašperké Hory district are relatively low (from 10 up to approx. 670 and rarely 820 mg/kg). The terrain morphology has a certain influence on the As distribution in the studied profiles. The As in the sloping area is being partly removed from the upper horizons. In tailing ponds at Roudný, the permeable sandy layers are oxidised and depleted in As, compared to the impervious, clay-rich and reduced layers. In the Kašperské Hory district, the distribution is much more irregular in historical waste dumps compared to the Mokrsko soils.

Certain differences in the contents of Ca and Fe, various degrees of mineral decomposition, and the pH cause different As speciation in the Quaternary cover at selected sites. At Mokrsko above the granodiorite bedrock, As is bound in pharmacosiderite, arseniosiderite, scorodite, goethite, and also in HFO. Above the volcano-sedimentary bedrock, As adsorption onto HFO is the main process, with a smaller contribution from speciation in pharmacosiderite. Arsenic adsorption on HFO is also the main process in the oxidised parts of the Roudný tailing ponds, and also for samples from old waste dumps in Roudný and Kašperské Hory. In the younger Václavka waste dump at Roudný, the As speciation in pitticite and in several unidentified arsenate phases has been determined.

Acknowledgements

This research was supported by project no. 205/97/0829 of the Grant Agency of the Czech Republic, by project no. 79-502 881 (EMOZMID), financed by Rio Tinto Technology Development, and by project no. CEZ: Z3-013-912. The authors would like to express their thanks to A. Langrová (Institute of Geology, Academy of Science of the Czech Republic, Prague) and J. Hovorka for assistance with the SEM and microprobe, and to O. Šebek for help with FAAS analyses (both of the Faculty of Science, Charles University, Prague).

Appendix Description of the samples, their As contents and the pH values of the leachates in distilled water and KCl for selected representative samples. Abbreviations and signs: Mo …Mokrsko; Ro …Roudný; Ka …Kašperské Hory; Q…quartz fragments; id. …identical characteristics; - …not determined

Samples characteristics [depth in cm]	Arsenic content [mg/kg]	pH H_2O; (pH KCl)
Both profiles are drill holes in a field (ca 10 m asunder) in a flat area, consisting of granodiorite bedrock		
Mo1/1 (0,00-0,25); **Mo2/1** (0,00-0,13): light humous dun sandy soil with Q*	1403; 1410	6.6 (5,9); 6.3 (5.3)
Mo1/2 (0,25-0,40); **Mo2/2** (0,13-0,21): darker dun soil with Q	1756; 2545	7.3 (6.9); 6.9 (6.3)
Mo1/3 (0,40-0,57); **Mo2/3** (0,21-0,69): light ochre-brown sandy soil with Q	- ; 2855	7.1 (6.4); 6.8 (5.6)
Mo1/4 (0,57-0,77); **Mo2/4a** (0,69-0,90): rusty sandy loamy-alluvium of weathered granodiorite	1680; 2010	7.2 (5.7); 6.9 (5.6)
Mo1/5a (0,77-0,90); **Mo2/4b** (0,90-1,27): rusty brown clayey and loamy alluvium of granodiorite	- ; 1660	7.2 (5.6); 6.9 (5.3)
Mo1/5b (0,90-1,20); **Mo2/5a** (1,27-1,50): id. as above	3489; 2200	6.7 (5.5); 5.7 (4.7)
Mo1/5c (1,20-1,30); **Mo2/5b** (1,50-1,66): id.; slightly darker	- ; 2065	6.6 (5.1); 6.5 (5.0)
Mo1/6a (1,30-1,50): rusty brown, weathered granodiorite	- ;	6.2 (5.2);
Mo1/6b (1,50-1,60): darker rusty limonitic layer	- ;	6.4 (5.5);
Mo1/6c (1,60-1,70): dark rusty brown to rubicund weathered granodiorite with fragments of Q-veins	26325	6.2 (5.2);
Mo1/7 (1,70-1,96): rusty brown weathered granodiorite with fragments of Q-veins	- ;	6.5 (5.1);
Both profiles are trenches (ca 40 m as under) in the sloping forested area, above the granodiorite bedrock		
Mo3/1 (0,00-0,08); **Mo4/1** (0,00-0,10): light humous dun sandy soil	450; 405	4.2 (3.5); -
Mo3/2 (0,08-0,32); **Mo4/2** (0,10-0,50): ochre-brown sandy soil with Q and fragment of granodiorite	405; 330	4.5 (3.6); -
Mo3/3 (0,32-0,65); **Mo4/3** (0,50-0,78): light ochre-brown sandy soil with fragment of granodiorite	615; 500	5.0 (3.6); -
Mo3/4 (0,65-0,88): darker brownish sandy soil with fragment of granodiorite	735	5.4 (3.9);
Mo3/5 (0,88-1,31); **Mo4/4** (0,78-1,18): weathered clayey rusty brownish granodiorite (sample Mo3/5 is markedly more rusty)	1970; 770	5.8 (4.3); -
Both profiles are drill holes (ca 110 m as under) in a sloping forested area, above volcanosedimentary bedrock		
Mo5/1 (0,00-0,03); **Mo6/1** (0,00-0,02): forest litter	712; 613	4.1 (3.5); 3.9 (3.2)
Mo5/2 (0,03-0,20); **Mo6/2** (0,02-0,10): clayey-sandy rusty brown soil with fragments of metasediments and quartzites	941; 821	4.3 (3.6); 4.0 (3.3)
Mo5/3a (0,20-0,45); **Mo6/3** (0,10-0,45): id.; increase in clayey component; the colour changed to rusty yellow in Mo6	1548; 1634	4.6 (3.6); 4.9 (3.6)
Mo5/3b (0,45-1,10); **Mo6/4a** (0,45-1,00): id.; increase in fragments of quartzites; the colour became yellowish brown in Mo6	2430; 2388	5.2 (4.2); 5.7 (5.2)
Mo5/4 (1,10-1,50); **Mo6/4b** (1,00-1,30): id.; increase in fragments of metasediments	2368; 1682	5.6 (3.6); 5.0 (3.8)
Drill hole in modern, mostly reduced tailings pond in flat area with sporadic vegetation cover		
Ro1/1 (0,00-0,30): dark rusty fine-grained sand, horizontal laminated (variation of darker and lighter layers by 0,5-1 cm)	1015	3.4 (3.0)
Ro1/2 (0,30-0,68): more laminated fine-grained sand	960	-
Ro1/3 (0,68-0,76): ochre-orange highly smeary clay (= in the sense of the grain size) with fine-grained sand, without lamination	1800	-
Ro1/4 (0,76-0,82): light green clay with fine-grained sand; underground water level of the tailings body	2010	7.3 (7.3)
Ro1/5a (0,82-1,22), **Ro1/5b**, **c**, **d**, **e**, **f**, **g** (1,22-5,00): greyish blue highly smeary clay, locally sandy with laminae of sulphides	1640, 1535, 1660, 2065, 2050, 2490, 2375	for all ca 7.7 (7.6)
Drill hole in old (mostly oxidised) tailings pond in slightly sloping area with sporadic vegetation cover.		
Ro3/1 (0,00-0,17): light brownish laminated sand with humous admixture and with organic matter	795	
Ro3/2 (0,17-1,00): brownish rusty laminated sand	1230	
Ro3/3 (1,00-1,50): brownish rusty sand – less laminated	995	
Ro3/4 (1,50-2,00), **Ro3/5a**, **b**, **c**, **d** (2,00-5,65): brownish rusty sand	1145; 1115, 1105, 920, 785	
Ro3/6 (5,65-5,90), **Ro3/7** (5,90-5,95): dark brownish rusty sand; darker in sample Ro3/7	730, 895	
Ro3/8 (5,95-6,00): grey sand with clay admixture	425	
Trench cutting the slope of the Václav shaft dump (from the beginning of the 20th C.), in a forested area.		
Ro4/1 (0,00-0,01): forest litter	418	4.6 (4.1)
Ro4/2 (0,01-0,10): light yellow grey sandy soil with fragments of Q and rocks	499	4.2 (3.4)
Ro4/3 (0,10-0,20): orange rusty soil with fragments of Q and rocks	417	4.7 (4.0)
Ro4/4a (0,20-0,40), **Ro4/4b** (0,40-0,60): sharp-edged gravel of rock-fragments, quartz with primary sulphides and anthropogenic artefacts; the material is covered by yellow powdered sulphate and coatings of limonite	1170, 1667	- ; 5.7 (5.5)
Ro4/5 (0,60-0,80): layer with black slag, ash and charred woods	472	6.4 (6.3)
Ro4/6 – not sampled (0,80-1,00): block of rocks	-	-
Ro4/7 (1,00-1,20): wet, fine grey sand	784	7.2 (7.2)
Trench penetrating the mediaeval surface workings (estimated origin in the 16th C.), in a forested area.		
Ro5/1 (0,00-0,02): forest litter	381	-
Ro5/2 (0,02-0,07): light sandy-clayey soil with fragments of weathered granites and aplites	486	-
Ro5/3 (0,07-0,90): id., but with limonitic admixture	524	4.2 (3.4)
Trench penetrating the mediaeval surface workings (estimated origin in the 14-15th C.), in a sloping forested area.		
Ka4/1 (0,00-0,03): forest litter	205	
Ka4/2 (0,03-0,10): brown humous soil	315	
Ka4/3 (0,10-0,25): slightly sandy humous soil	355	
Ka4/4a, b, c (0,25-1,00): light brown sandy soil	365, 415, 465	
Ka4/5 (1,00-1,30): rusty yellow sandy soil	480	
Trench penetrating the mediaeval surface workings (estimated origin in the 14-15th C.), in a forested area.		
Ka5/1 (0,00-0,04): forest litter	65	
Ka5/2 (0,04-0,30): brown humous soil	370	
Ka5/3 (0,30-0,65): clayey humous soil	195	
Trench penetrating the mediaeval surface workings (estimated origin in the 16thCc.), in a forested area		
Ka8/1 (0,00-0,02): forest litter	185	-
Ka8/2 (0,02-0,20), **Ka8/3** (0,20-0,30): slightly humous brown soil with fragments of Q; there is more Q in sample Ka8/3	205, 170	4.2 (3.3); -
Ka8/4 (0,30-0,80): slightly greenish grey clayey soil with Q	165	-
Ka8/5 (0,80-1,00): slightly greenish grey soil with Q and ashes from old grate	190	-

Samples characteristics [depth in cm]	Arsenic content [mg/kg]	pH H_2O; (pH KCl)
Ka8/6 (1,00-1,20), **Ka8/7** (1,20-1,40): greenish grey sandy soil with Q and ashes; the soil in sample Ka8/7 is darker	175, 170	5.3 (4.3); -
Ka8/8 (1,40-1,50): orange rusty sandy soil	285	-
Both profiles are cores from drill holes in the mineralised zone, in a slightly sloping field area		
Ka10/1 (0,00-0,20); **Ka11/1** (0,00-0,25): brown humous soil with Q and fragments of gneisses	29; 112	- ; -
Ka10/2 (0,20-0,40); **Ka11/2** (0,25-1,00): rusty brown clayey-sandy soil with Q and fragments of gneisses	32; 153	- ; -
Ka10/3a (0,40-0,80), **Ka10/3b** (0,80-1,25); **Ka11/3** (1,00-1,20): brownish sandy soil with fragments of weathered gneisses and Q	10, 32; 119	-, 5.5 (4.4) ; - -, - ; -
Ka10/4a (1,25-2,00), **Ka10/4c** (2,00-2,25), **Ka10/4c** (2,00-2,25): wet clayey soil of slight brown colour with limonitic admixture	40, 46, 82	-, - ; - -, - , -
Ka10/5 (2,25-2,45): weathered bedrock	54	- ; -
Trench penetrating mediaeval surface workings (estimated origin in the 16th C.), in a forested area		
Ka13/1 (0,00-0,02): forest litter	669	
Ka13/2 (0,02-0,13): slightly dun sandy soil with fragments of gneisses	818	
Ka13/3a (0,13-0,35), **Ka13/3b** (0,35-0,85), **Ka13/3c** (0,85-1,40), **Ka13/3d** (1,40-1,80): light yellow brown sandy soil with fragments of gneisses	608, 448, 203, 458	
Ka13/4 (1,80-2,00): darker rusty weathered gneiss	582	
Trench penetrating the mediaeval surface workings (estimated origin in the 16th C.), in forested area		
Ka15/1 (0,00-0,02): forest litter	180	
Ka15/2 (0,02-0,35): slightly humous brown soil with fragments of Q and rocks	229	
Ka15/3a (0,35-0,60), **Ka15/3b** (0,60-0,70): yellow brown sandy soil with fragments of Q and rocks	244, 285	
Ka15/3c (0,70-1,00), **Ka15/3d** (1,00-1,45): slightly greenish grey clayey soil with fragments of Q	212, 223	
Ka15/3e (1,45-1,55): layer of ashes; minimum of soil and Q	139	
Ka15/3f (1,55-2,20): slightly greenish grey clayey soil with ashes	228	
Ka15/4 (2,20-2,40): id.; more fragments of gneiss	303	
Ka15/5 (2,40-2,70): weathered gneiss; practically without soil admixture; probably the base of the dump	215	

CHAPTER 6. Prospects of future research

Two directions of possible future research will be prefered. The first is a continuation in the study of the Mokrsko soils. The unusually rich occurrence of arsenates in these soil calls for a more detailed mineralogical study combined with the study of the soil−groundwater interaction. Understanding of the precipitation and stability of the secondary As minerals in the studied soils should help in the understanding of the arsenopyrite transformation during the pedogenesis on the bedrock of As-bearing granite in general.

The second direction will be focused on mineralogical and geochemical research of the As speciation and mobility in old As-rich mining dumps and related contaminated soils.

Why this topic??

Because the most recent studies are focused on relatively modern and often managed mine wastes, namely on tailings, sludge pits and ponds. However, numerous small isolated mediaeval mine dumps exist in many areas in central Europe, which have environmental impact and great scientific potential for study. These dumps have been rarely studied so far, although they represent in situ long-term models of As cycling and mobilization among the geosphere, hydrosphere, biosphere and atmosphere. Because of the old age of these dumps, the present day reaction rates of water−solid−gas interactions can be very slow and the system of the soil and waste dump might be near the geochemical equilibrium. Retention of As in old dump wastes and contaminated soils is, however, metastable because any change of physico-chemical conditions may induce geochemical disequilibria of the system. Research on As mineralogy and geochemistry in old mining dumps or soils is therefore essential for a better understanding of in situ mobility-limiting step of As in the soil (waste)−water system. It is also very helpful in elucidating their potential risk for the environment.

The history of several mining districts in the Czech Republic has een long, dating back to the mediaeval times. Old mining dumps are unique in many respects but, at the same time, may represent a common type of the local source of As input into the environment worldwide. One of these unique sites is the former Giftkies mine in the NE part of the famous Jáchymov ore district (Krušné Hory Mountains, NW Bohemia). Arsenic in the Giftkies mine was mined for arsenious oxide in the medieval ages (Kořan, 1947). The tailing dump was spread out along a steep slope covering approximately 400 m^2. Below mentioned factors make the locality interesting and favourable for research of As behaviour, and allow considering the soil as a natural laboratory representing in situ natural conditions. Above all, a very specific mineralogical association of As with a large quantity of As-bearing minerals has been reported from the waste dump. Hloušek (2000) described scorodite, kaňkite and rare zykaite from the dump. The present mineralogical situation in the waste dump is interesting for the quantity as well as for quality of As-bearing mineral phases (large and pure aggregates), having no parallel in the whole of Europe (comparable only with the well-known Kaňk locality). Then, the favorable position and the sharp limits of the waste dump on the slope offer a good opportunity for studying As migration from the dump to the close surroundings. And finally, negligible anthropogenic impact in the mine area for more than 300 years guarantees conservation of the mineralogical/geochemical settings at the site.

Literature

Acero, P., Ayora, C., Torrentó, C., Nieto, J.-M., 2006. The behavior of trace elements during schwertmannite precipitation and subsequent transformation into goethite and jarosite. Geochimica et Cosmochimica Acta, 70 (16): 4130-4139.

Adriano, D.C., 2001. Trace elements in the terrestrial environment. (2nd edition) New York: Springer, 867 p.

Ahmed, K.M., Bhattacharya, P., Hasan, M.A., Akhter, S.H., Alam, S.M.M., Bhuyian, M.A.H., Imam, M.B., Khan, A.A, Sracek, O., 2004. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. Applied Geochemistry, 19 (2): 181-200.

Ahn, J.S., Park, J.S:, Kim, J.-Y., Kim, K.-W., 2005. Mineralogical and geochemical characterization of arsenic in an abandoned mine tailings of Korea. Environmental Geochemistry and Health, 27: 147-157.

Al, T.A., Martin C.J., Blowes, D.W., 2000. Carbonate-mineral/water interactions in sulfide-rich mine tailings. Geochimica et Cosmochimica Acta, 64 (23): 3933-3948.

Akai, J., Izumi, K., Fukuhara, H., Masuda, H., Nakano, S., Yoshimura, T., Ohfuji, H., Anawar, H.M., Akai, K. 2004. Mineralogical and geomicrobiological investigations on groundwater arsenic enrichment in Bangladesh. Applied Geochemistry, 19 (2): 215-230.

Alam, M.G.M., Snow, E.T., Tanaka, A. 2003. Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. Science of the Total Environment, 308: 83–96.

Alpers, C.N., Blowes, D.W., Nordstrom, D.K., Jambor, J.L., 1994. Secondary minerals and acid-mine water chemistry. In: Jambor, J.L., Blowes, D.W., (eds). Environmental Geochemistry of Sulfide Mine-wastes. Mineralogical Association of Canada Waterloo Ontario, 22: 248-270.

Anawar, H.M., Komaki, K., Akai, J., Takada, J., Ishizuka, T., Takahashi, T., Yoshioka, T., Kato, K., 2002. Diagenetic control on arsenic partitioning in sediments of the Meghna River delta, Bangladesh. Environmental geology, 41 (7): 816-825.

Arai, Y., Lanzirotti, A., Sutton, S.R., Newville, M., Dyer, J., Sparks, D.L., 2006. Spatial and temporal variability of arsenic solid-state speciation in historically lead arsenate contaminated soils. Environmental Science & Technology, 40 (3): 673-679.

Arčon, I., van Elteren, J.T., Glass, H.J., Kodre, A., Šlejkovec. Z., 2005. EXAFS and XANES study of arsenic in contaminated soil, X-Ray Spectrometry, 34 (5): 435-438.

Ascue, J.M., Nriagu, J.O., 1994. In: Nriagu, J.O. (Ed.), Arsenic in the Environment. Part 1: Cycling and Characteristics. Vol. 26. Advances in Environmental Science and Technology. John Wiley & Sons, Inc, USA, 1–15.

Atzei, D., Da Pelo, S., Elsener, B., Fantauzzi, M., Frau, F., Lattanzi, P., Rossi, A., 2003. The chemical state of arsenic in minerals of environmental interest - An XPS and an XAES study. Annali di Chimica, 93 (1-2): 11-19.

Baker, T., Ebert, S., Rombach, C., Ryan, C.G., 2006. Chemical compositions of fluid inclusions in intrusion-related gold systems, Alaska and Yukon, using PIXE microanalysis. Economic Geology, 101 (2): 311-327.

Baron, D., Palmer, C.D., 1996. Solubility of jarosite at 4-35°C. Geochimica et Cosmochimica Acta, 60 (2): 185-195.

Belzile, N., Tessier, A., 1990. Interactions between arsenic and iron oxyhydroxides in lacustrine sediments, Geochimica et Cosmochimica Acta, 54: 103-109.

Berg, M., Tran, H.C., Nguyen, T.C., Pham, H.V., Schertenleib, R., Giger, W., 2001. Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat. Environmental Science & Technology, 35: 2621–2626.

Bhattacharya, P., Mukherjee, A.B., Jacks, G., Nordqvist, S., 2002. Metal contamination at a wood preservation site: characterisation and experimental studies on remediation. Science of the Total Environment, 290 (1-3): 165-180.

Bernard, J.H., 1981. Mineralogie Československa. Academia, Praha: 645 p. (in Czech).

Bish, D.L., Reynolds, R.C., Jr., 1989. Sample preparation for X-ray diffraction. In Modern Powder Diffraction (D.L. Bish and J.E. Post, eds.) Rev. Mineral. 20: 86-91.

Bigham, J.M., Schwertmann, U., Carlson, L., Murad, E., 1990. A poorly crystallized oxyhydoxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters. Geochimica et Cosmochimica Acta, 54: 2743–2758.

Bigham, J.M., 1994. Mineralogy of ochre deposits formed by sulfide oxidation. In: Blowes, D.W., Jamdor, J.L., (eds). The environmental geochemistry of sulfide mineral-wastes. Mineralogical Association of Canada Waterloo Ontario, 22: 103-132.

Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., Wolf, M., 1996. Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochimica et Cosmochimica Acta, 60 (12): 2111-2121.

Bhumbla, D.K., Keefer, R.F., 1994. Arsenic mobilization and bioavailability in soils. In: Arsenic in the Environment, Part I: Cycling and Characterization (J.O. Nriagu, ed.), 51-82. Wiley and Sons, New York.

Blanchard, M., Alfredsson, M., Brodholt, J., Wright, K., Catlow, C.R.A., 2007. Arsenic incorporation into FeS2 pyrite and its influence on dissolution: A DFT study. Geochimica et Cosmochimica Acta, 71 (3): 624-630.

Blowes, D.W., Jambor, J.L., 1990. The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings, Waite Amulet, Quebec, Canada. Applied Geochemistry, 5, 327-346.

Blowes, D.W., Jambor, J.L., Appleyard, E.C., Reardon, E.J., Cherry, J.A., 1992. Temporal observations of the geochemistry and mineralogy of a sulfide-rich mine-tailings impoundment, Health Steele Mines, New Brunswick. Explor. Mining Geol., 1: 251-264.

Blowes, D.W., Al, T.A., Lortie, L., Gould, W.D., Jambor, J.L., 1995. Chemical, mineralogical and microbiological characterization of The Kidd Creek mine-tailings impoundment. Timmins area, Ontario, Geomicrobiology, 13: 13-31.

Bodénan, F., Baranger, P., Piantone, P., Lassin, A., Azaroual, M, Gaucher, E., Braibant, E.G., 2004. Arsenic behaviour in gold-ore mill tailings, Massif Central, France: hydrogeochemical study and investigation of in situ redox signatures. Applied Geochemistry, 19 (12): 1785-1800.

Bostick, B.C., Fendorf, S., 2003. Arsenite sorption on troilite (FeS) and pyrite (FeS2). Geochimica et Cosmochimica Acta, 67 (5): 909-921.

Bowell, R.J., 1991. The mobility of gold in tropical rain forest soils. PhD thesis. University of Southampton.

Bowell, R.J., 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. Applied Geochemistry, 9 (3): 279-286.

Bowell, R.J., Parshley, J., 2003. Arsenic Cycling in the Mining Environment. in: U.S. EPA Workshop on Managing Arsenic Risks to the Environment: Characterization of Waste, Chemistry, and Treatment and Disposal, Proceedings and Summary Report, May 1-3, 2001, 10-11.

Bowell, R.J., Parshley, J.V., 2005. Control of pit-lake water chemistry by secondary minerals, Summer Camp pit, Getchell mine, Nevada. Chemical Geology, 215 (1-4): 373-385.

Brookins, D.G., 1988. Eh– pH Diagrams for Geochemistry Springer, Berlin.

Brown, G.E., Calas, G., Waychunas, G.A., Petiau, J., 1988. X-ray absorption spectroscopy and its applications in mineralogy and geochemistry. In Spectroscopis Methods in mineralogy and geology (F.C. Hawthorne, ed.). Rev. Mineral., 18: 431-512.

Brown, L.J., Gutsa, E.H., Cashion, J.D., Fraser, J.R., Coller, B.A.W., 1990. Mössbauer effect study of ferric arsenates from an abandoned gold mine. Hyperfine Interactions, 57 (1-4): 2159-2166.

Brown, G.E., Sturchio, N.C., 2002. An overview of synchrotron radiation applications to low temperature geochemistry and environmental science. In Applications of synchrotron radiation in low-temperature geochemistry and environmental science (P.A. Fenter, M.L., Rivers, N.C., Struchio, S.R., Sutton, eds.), Reviews in Mineralogy & Geochemistry, 49: 1-115.

Bruneel, O., Duran, R., Casiot, C., Elbaz-Poulichet, F., Personne, J.C., 2006. Diversity of microorganisms in Fe-As-Rich acid mine drainage waters of Carnoules, France. Applied and Environmental Microbiology, 72 (1): 551-556.

Buchet, J.P., Lauwerys, R., 1981. Evaluation of exposure to inorganic arsenic in man. Analytical techniques for heavy metals in biological fluids. Amsterdam: Elsevier, 75-89.

Buckley, A.N., Woods, R., 1987. The surface oxidation of pyrite. Appl. Surf. Sci., 27: 437–452.

Buckley, A.N., Walker, W., 1988. The surface composition of arsenopyrite exposed to oxidizing environments. Applied Surface Science, 35: 227-240.

Burguera, M., Burguera, J.L., 1997. Analytical methodology for speciation of arsenic in environmental and biological samples. Talanta, 44: 1581–1604.

Buurman, P., van Lagen, B., Velthorst, E.J., 1996. Manual for Soil and Water Analysis. Backhuys Publishers, Leiden.

Camm, G.S., Butcher, A.R., Pirrie, D., Hughes, P.K., Glass, H.J., 2003. Secondary mineral phases associated with a historic arsenic calciner identified using automated scanning electron microscopy; a pilot study from Cornwall, UK. Minerals Engineering, 16 (11): 1269-1277.

Camm, G.S., Glass, H.J., Bryce, D.W., Butcher, A.R., 2004. Characterisation of a mining-related arsenic-contaminated site, Cornwall, UK. Journal of Geochemical Exploration, 82: 1-15.

Cao, X., Ma, L.Q., Shiralipour, A., 2003. Effect of compost and phosphate amendments on arsenic mobility in soils and arsenic uptake by the hyperaccumulator, Pteris vittata L. Environmental Pollution, 126: 157-167.

Carbonell B.A.A., Burlo F.M., Mataix J.J., 1998, Arsenite sorption in Spanish soils as affected by temperature, Communications in Soil Science and Plant Analysis, 29 (5-6): 657-670.

Carlson, L., Lindström, E.B., Hallberg, K.B., Tuovinen, O.H., 1992. Solid-phase product of bacterial oxidation of arsenical pyrite. Applied and environmental microbiology, 58 (3): 1046-1049.

Carlson, L., Bigham, J.M., Schwertmann, U., Kyek, A., Wagner, F., 2002. Scavenging of As from acid mine drainage by schwertmannite and ferrihydrite: A comparison with synthetic analogues. Environmental Science & Technology, 36: 1712-1719.

Casiot, C., Leblanc, M., Bruneel, O., Personné, J.-C. , Koffi, K., Elbaz-Poulichet, F., 2003. Geochemical Processes Controlling the Formation of As-rich waters within a Tailings Impoundment (Carnoulès, France). Aquatic Geochemistry, 9 (4): 273-290.

Casiot, C., Pedron, V., Bruneel, O., Duran, R., J.C. Personné, J.C., Grapin, G. , Drakidès, C., Elbaz-Poulichet, F., 2006. A new bacterial strain mediating As oxidation in the Fe-rich biofilm naturally growing in a groundwater Fe treatment pilot unit. Chemosphere, 64: 492-496.

Cava-Montesinos, P., Nilles, K., Cervera, M.L., de la Guardia, M. 2005. Non-chromatographic speciation of toxic arsenic in fish. Talanta, 66 (4): 895-901.

Claassen, R., 1993. Mineralogical controls on the bacterial oxidation of refractory Barberton gold ores. Microgiology Reviews, 11: 197-206.

Cliff, D.C., Morávek, P., 1995. The Mokrsko gold deposit, Central Bohemia, Czech Republic. In: J. Pašava, B. Kříbek and K. Žák (Editors), Mineral Deposits: From their Origin to their Environmental Impacts, Balkema Rotterdam, 105-108.

Cobb, G.P, Sands, K., Waters, M., Wixson, B.G., Dorward-King E., 2000, Accumulation of heavy metals by vegetables grown in mine wastes, Environmental Toxicology and Chemistry, 19 (3): 600-607.

Coleyshaw, E.E., Griffith, W.P., Bowell, R.J., 1994. Fourier-transform Raman spectroscopy of minerals, Spectrochimica Acta, 50A: 1909-1918.

Cornell, R.M., Schwertmann, U., 1996. The iron oxides – Structure, properties, Reactions, Occurrence and Uses. VCH (Federal Republic of Germany), Weinheim, New York, Basel, Camridge, Tokyo. 573 p.

Cornu, S., Saada, A., Breeze, D., Gauthier, S., Barranger, P., 1999. The influence of organic complexes on arsenic adsorption onto kaolinites. C R Acad Sci Earth Planet. Sci., 328: 649-654.

Corwin, D.L., David, A., Goldberg, S., 1999. Mobility of arsenic in soils from the Rocky Mountain Arsenal area. Journal of Contaminant Hydrology, 39: 35-58.

Courtin-Nomade, A., Bril, H., Néel, C., Lenain, J.-F., 2003. Arsenic in iron cements developed within tailings of a former metalliferous mine—Enguiale` s, Aveyron, France, Applied Geochemistry, 18: 395-408.

Courtin-Nomade, A., Grosbois, C., Bril, H., Roussel, C., 2005. Spatial variability of arsenic in some iron-rich deposits generated by acid mine drainage. Applied Geochemistry, 20 (2): 283-396.

Craw, D., Chappell, D., Nelson, M., Walrond, M., 1999. Consolidation and incipient oxidation of alkaline arsenopyrite-bearing mine tailings, Macraes Mine, New Zealand. Applied Geochemistry, 14 (4): 485-495.

Craw, D., Chappell, D., Reay, A., Walls, D., 2000. Mobilisation and attenuation of arsenic around gold mines, east Otago, New Zealand. New Zealand Journal of Geology & Geophysics, 43 (3): 373-383.

Craw, D., Koons, P.O., Chappell, D., 2002. Arsenic distribution during formation and capping of an oxidised sulphidic minesoil, Macraes Mine, New Zealand. J. Geochem. Explor., 76: 13-29.

Craw, D., Falconer, D., Youngson, J.H., 2003. Environmental arsenopyrite stability and dissolution: theory, experiment, and field observations. Chemical Geology, 199 (1-2): 71-82.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chemical Reviews. 89: 713-764.

Čech, F., Jansa, J., Novák, F., 1976. Kankite, $Fe(AsO_4)_3$ •12 H_2O, a new mineral. Neues Jahrbuch für Mineralogie und Geologie, Monatshefte, 426–436.

Čech, F., Jansa, J., Novák, F., 1978. Zykaite, Fe3+4 (AsO4)3(SO4)(OH)•15H2O, a new mineral. Neues Jahrbuch für Mineralogie und Geologie, Monatshefte, 2: 134–144.

da Silva, E.F, Zhang, C., Pinto, L.S., Patinha, C., Reis, P., 2004: Hazard assessment on arsenic and lead in soils of Castromil gold mining area, Portugal. Applied Geochemistry, 19, 6: 887-898.

Darland, J.E., Inskeep, W.P., 1997. Effects of pH and phosphate competition on the transport of arsenate. Journal of Environmental Quality, 26: 1133–1139.Das D., Chatterjee A., Mandal B.K., Samanta G., Chakraborti D., 1995. Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 2: arsenic concentration in drinking water, hair, nails, urine, skin-scale and liver tissue (biopsy) of the affected people. Analyst, 120: 917-924.

Das, D., Samanta, G., Mandal, B.K., Samanta G., Chakraborti, D., Chanda, B., 1996. Arsenic in groundwater in six districts of West Bengal, India. Environ Geochem Health, 18 (1): 5-16.

Davis, A., Ashenberg, D., 1989. The aqueous geochemistry of the Berkeley Pit, Butte, Montana, USA. Applied Geochemistry, 4: 23–36.

Davis, A., Ruby, M.V., Bloom, M., Schoof, R., Freeman, G., Bergstrom, P.D., 1996. Mineralogic constraints on the bioavailability of arsenic in smelter-impacted soils. Environmental Science & Technology, 30: 392-399.

Davis, C.C., Knocke, W.R., Edwards, M., 2001. Implications of Aqueous Silica Sorption to Iron Hydroxide: Mobilization of Iron Colloids and Interference with Sorption of Arsenate and Humic Substances. Environmental Science & Technology, 35: 2158-2162.

Davis, A., Bellehumeur, T., Hunter, P., Hanna, B., Fennemore, G.G., Moomaw, C., Schoen, S., 2006. The nexus between groundwater modeling, pit lake chemogenesis and ecological risk from arsenic in the Getchell Main Pit, Nevada, U.S.A. Chemical Geology, 228 (1-3): 175-196.

De Brouwere, K., Smolders, E., Merckx, R., 2003. Soil properties affecting solid-liquid distribution of As(V) in soils, European Journal of Soil Science, 55: 165-173.

de Faria, D.L.A., Silva, V., de Oliveira, M.T., 1997. Raman spectroscopy of some iron oxides and oxyhydroxides, Journal of Raman spectroscopy, 28 (11): 873-878.

De Groot, A.C., Peijnenburg, W.J.G.M., van den Hoop, M.A.G.T., Ritsema, R., van Veen, R.P.M., 1998. Heavy Metals in Dutch Field Soils: An Experimental and Theoretical Study on Equilibrium Partitioning. Report No. 607220-001, National Institute of Public Health and the Environment (RIVM), Bilthoven, Netherlands.

Ding, W., Hudson, L.G., Liu, K.J., 2005. Inorganic arsenic compounds cause oxidative damage to DNA and protein by inducing ROS and RNS generation in human keratinocytes. Molecular and Cellutar Biochemistry, 279 (1-2): 105-12.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. Environmental Science & Technology, 37 (18), 4182–4189.

Dixon J.B., White G.N., 1994: Transmission electron microscopy examination of minerals in soils. TSEMJ, 25 (2): 50-53.

Dhoum, R.T., Evans, G.J., 1998. Evaluation of uranium and arsenic retention by soil from low level radioactive waste management site using sequential extraction. Applied Geochemistry, 13 (4): 415-420.

Doi, M., Warren, G., Hodson, M.E., 2005. A preliminary investigation into the use of ochre as a remedial amendment in arsenic-contaminated soils. Applied Geochemistry, 20 (12): 2207-2216.

Dold, B., 2003. Dissolution kinetics of schwertmannite and ferrihydrite in oxidized mine samples and their detection by differential X-ray diffraction (DXRD). Applied Geochemistry, 18 (10): 1531-1540.

Donahue, R., Hendry, M.J., Landine, P., 2000. Distribution of arsenic and nickel in uranium mill tailings, Rabbit Lake, Saskatchewan, Canada. Applied Geochemistry, 15 (8): 1097-1119.

Donahue, R., Hendry, M.J., 2003. Geochemistry of arsenic in uranium mine mill tailings, Saskatchewan, Canada. Applied Geochemistry, 18 (11): 1733-1750.

Dove, P.M., Rimstidt, J.D., 1985. The solubility and stability of scorodite, FeAsO4 . 2H2O. American Mineralogist, 70 (7-8): 838-844.

Drahota, P., Pertold, Z., 2005. Weathering of As-rich rocks in the Čelina-Mokrsko gold district, Bohemian Massif (CZ). In: B. Öhlander (Editor), Securing the Future 2005, Skelleftea. vol. 1: 242-251.

Drahota, P., Pačes, T., Pertold, Z., Mihaljevic, M., Skrivan, P., 2006. Weathering and erosion fluxes of arsenic in watershed mass budgets. Science of the Total Environment, 372 (1): 306-316.

Driessen, P., Deckers, J., Spaargaren, X., Nachtergaele, F., (Editors) 2001. Lecture notes on the major soils of the world. Food and Agriculture Organinization of the United Nations (FAO), Rome, 334 p.

Dudas, M.J., 1987. Accumulation of native arsenic in acid sulphate soils in Alberta. Can. J. Soil Sci., 67: 317-331.

Dudka S., Miller W.P., 1999, Permissible concentrations of arsenic and lead in soils based on risk assessment. Water, Air & Soil Pollution, 113 (1-4): 127-132.

Dunn, P.J., 1982. New data for pitticite and a second occurrence of yukonite at Sterling Hill, New Jersey. Mineralogical Magazine, 46: 261-264.

Dzomback, D.A., Morel, F., 1990. Surface complexation modelling: hydrous ferrioxide. Whiley, New York.

Eggleston, C.M., Ehrhardt, J.J., Stumm, W., 1996. Surface structural controls on pyrite oxidation kineticts: An XPS-UPS, STM, and modeling study. American Mineralogist, 81: 1036-1056.

Ehrlich, H.L., 1996. Beomicrobiology, 3rd ed., 276-286. Marcel Dekker, New York.

Eisler, R., 1988. Arsenic hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish Wildl. Serv. Biol. Rep., 85 (1.12). 92 p.

Eisler, R., 1994. A review of arsenic hazards to plants and animals with emphasis on fishery and wildlife resources. In: Nriagu, J.O. (Ed.), Arsenic in the Environment. Part 2: Human Health and Ecosystem Effects. Vol 27 Advances in Environmental Science and Technology. John Wiley & Sons, Inc, USA, 185–259.

Escobar-Gonzalez, V.L., Monhemius, A.J., 1988. The mineralogy of arsenates relating to arsenic impurity control In Arsenic metallurgy fundamentals and applications. Reddy, R.G., Hendrix, J.L., Queneau, P.B. (eds.) The Minerals, Metals and Materials Society, Warrendale, P.A., USA, p. 405-453.

Ettler, V., Vaněček, A., Mihaljevič, M., Bezdička, P., 2005. Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. Chemosphere, 58: 1449–1459.

Ettler, V., Johan, Z., 2003. Mineralogy of metallic phases in sulphide mattes from primary lead smelting. Comptes Rendus Geosciences, 335 (14): 1005-1012.

Evangelou, V.P., Zhang, Y.L., 1995. A review: Pyrite oxidation mechanisms and acid mine drainage prevention. Critical Rev. Environmental Science & Technology, 25: 141-199.

FAO, 1998. World Reference Base for Soil Resources: World Soil Resources Report. No. 84, FAO, Rome, 88 p.

Farquhar, M.L., Charnock, J.M., Livens, F.R., Vaughan, D.J., 2002. Mechanisms of arsenic uptake from aqueous solution by interaction with goethite, lepidocrocite, mackinawite, and pyrite: An X-ray absorption spectroscopy study. Environmental Science & Technology, 36 (8): 1757-1762.

Fendorf, S.E., Sparks, D.L., Lamble, G.M., Kelley, M.J., 1994. Application of X-ray absorption fine-structure spectroscopy to soils. Soil Science Society of America Journal, 58 (6): 1583-1595.

Fendorf, S., Eick, M.J., Grossl, P., Sparks, D.L., 1997. Arsenate and chromate retention mechanisms on goethite .1. Surface structure. Environmental Science & Technology. 31 (2): 315-320.

Fernandez, M.G.M., Mustin, C., de Donato, P., Barres, O., Marion, P., Berthelin, J., 1995. Occurrences at mineral-bacteria interface during oxidation of arsenopyrite by Thiobacillus ferrooxidans. Biotechnology and Bioengineering, 46 (1): 13-21.

Fernandez, P.G., Linge, H.G., Wadsley, M.W., 1996. Oxidation of arsenopyrite (FeAsS) in acid Part I: Reactivity of arsenopyrite. Journal of Applied Electrochemistry, 26 (6): 575-583.

Fernandez, P.G., Linge, H.G., Willing, M.J., 1996. Oxidation of arsenopyrite (FeAsS) in acid Part II: Stoichiometry and reaction schneme. Journal of Applied Electrochemistry, 26 (6): 585-591.

Fernández, P., Sommer, I., Cram, S., Rosas, I., Gutiérrez, M., 2005. The influence of water-soluble As(III) and As(V) on dehydrogenase activity in soils affected by mine tailings. Science of the Total Environment, 348 (1-3): 231-243.

Fernández-Martínez, A., Cuello, G.J., Román-Ross, G., Turrillas, X., Charlet, L., 2005. Arsenate uptake by gypsum: a neutron diffraction study. Geophysical Research Abstracts, Vol. 7, 3 p.

Ferreira da Silva, E., Zhang, Ch., Pinto, L.S., Patinha, C., Reis, P., 2004. Hazard assessment on arsenic and lead in soils of Castromil gold mining area, Portugal, Applied Geochemistry, 19 (6): 887-898.

Filippi, M., 2001. Research of the anthropogenic arsenic-rich deposit at the Přebuz locality – a second occurrence of kaatialaite in the Czech Republic. Bulletin mineralogicko-petrologického odd. Národního muzea (Praha), 9: 188-190. (in Czech).

Filippi, M., 2004. Oxidation of the arsenic-rich concentrate at the Přebuz abandoned mine (Erzgebirge Mts., CZ): the mineralogical evolution. Science of the Total Environment, 322: 271-282.

Filippi, M., Goliáš, V., Pertold, Z., 2004. Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ). Env. Geol., 45 (5): 716-730.

Filippi, M., Doušová, B., Machovič, V., 2007. Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ). Geoderma. Geoderma, 139 (1-2): 154-170.

Fleet, M.E., MacLean, P.J. and Barbier, J., 1989. Oscillatory-zoned As-bearing pyrite from stratabound and stratiform gold deposits: An indicator of ore fluid evolution. Economic Geology Monograph, 6: 356–362.

Fleet, M.E., Chryssoulis, S.L., MacLean, P.J., Davidson, R. and Weisener, C.G., 1993. Arsenian pyrite from gold deposits: Au and As distribution investigated by SIMS and EMP, and color staining and surface oxidation by XPS and LIMS. The Canadian Mineralogist , 31: 1–17.

Fleet, M.E., Mumin, A.H., 1997. Gold-bearing arsenian pyrite and marcasite from Carlin Trend deposits and laboratory synthesis. American Mineralogist, 82: 182–193.

Flemming, R.L., Salzsauler, K.A., Sherriff, B.L., Sidenko N.V., 2005. Identification of scorodite in fine-grained, high-sulfide, arsenopyrite mine-waste using micro X-ray diffraction (μXRD). The Canadian Mineralogist, 43 (4): 1243-1254.

http://www.cosis.net/abstracts/EGU05/08527/EGU05-J-08527.pdf

Foster, A.L., Brown, Jr., G.E., Tingle, T.N., Parks, G.A., Voigt, D.E., Brantley, S.L., 1997. XAFS determination of As speciation in weathered mine tailings and contaminated soil from California, USA. J Phys IV France 7 C2-815-C2-816.

Foster, A.L., Brown Jr., G.E., Parks, G.A., 1998. Quantitative arsenic speciation in mine tailings using X-ray absorption spectroscopy. American Mineralogist, 83 (5-6): 553-568.

Francesconi, K.A., Kuehnelt, D., 2004. Determination of arsenic species: A critical review of methods and applications, 2000-2003. Analyst, 129: 373-395.

Frank, D., 1998: X-Ray diffractometry. Lab Notes - The Newsletter of the US EPA Region 10 Laboratory. 3, 2. http://yosemite.epa.gov/R10/LAB.NSF/Programs/X-ray+Diff

Frau, F., Ardau, C., 2003. Geochemical controls on arsenic distribution in the Baccu Locci stream catchment (Sardinia, Italy) affected by past mining. Applied Geochemistry ,18: 1373-1386.

Frau, F., Ardau, C., 2004. Mineralogical controls on arsenic mobility in the Baccu Locci stream catchment (Sardinia, Italy) affected by past mining. Mineralogical Magazine, 68 (1): 15-30.

Frau, F., Rossi, A., Ardau, C., Biddau, R., Da Pelo, S., Atzei, D., Licheri, C., Cannas, C., Capitani, G.-C., 2005. Determination of Arsenic Speciation in Complex Environmental Samples by the Combined Use of TEM and XPS. Microchim. Acta, 151: 189–201.

Frost, R.R., Griffin, R.A., 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Science Society of America Journal, 41: 53-57.

Frost, R.L., Kloprogge, J.T., 2003. Raman spectroscopy of some complex arsenate minerals – implications for soil remedation, Spectrochimica Acta A, 59 (12): 2797-2804.

Frost, R.L., Kloprogge, T., Weier, M.L., Martens, W.N., Ding, Z., Edwards, H.G.H., 2003. Raman spectroscopy of selected arsenates – implications for soil remediation. Spectrochimica Acta A, 59 (10): 2241-2246.

Fukushi, K., Sasaki, M., Sato, T., Yanase, N., Amano, H., Ikeda, H., 2003. A natural attenuation of arsenic in drainage from an abandoned arsenic mine dump. Applied Geochemistry, 18 (8): 1267-1278.

Fuller, C.C., Davies, J.A., Waychunas, G.A., 1993. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. Geochimica et Cosmochimica Acta, 57: 2271-2282.

Gao, S., Burau, R.G., 1997. Environmental factors affecting rates of arsine evolution from and mineralization of arsenicals in soil. Journal of Environmental Quality, 26: 753-763.

Garvie, L.A.J., Buseck, P.R., 2004. Unoccupied states of pyrite probed by electron energy-loss spectroscopy (EELS). American Mineralogist, 89 (4): 485-491.

Gasharova, B., Gottlicher, J., Becker, U., 2005. Dissolution at the surface of jarosite: an in situ AFM study. Chemical Geology, 215 (1-4): 499-516.

Ghosh, A.K., Sarkar, D., Bhattacharyya, P., Maurya, U.K., Batak, D.C., 2006. Mineralogical study of some arsenic contaminated soils of West Bengal, India. Geoderma, 136 (1-2): 300–309.

Gieré, R., Sidenko, N.V., Lazareva, E.V., 2003. The role of secondary minerals in controlling the migration of arsenic and metals from high-sulfide wastes (Berikul gold mine, Siberia). Applied Geochemistry, 18 (9): 1347-1359.

Gill, T.E., Gillette, D.A., Niemeyer, T., Winn R.T., 2002. Elemental geochemistry of wind-erodible playa sediments, Owens Lake, California. Nuclear instruments & methods in physics research section B-beam interactions with materials and atoms 189: 209-213.

Gleyzes, C., Tellier, S., Astruc, M., 2002a. In: Ph. Quevauviller (Editor), Methodologies for Soil and Sediment Fractionnation studies, Royal Society of Chemistry, Cambridge, UK, Chapter 4.

Gleyzes, Ch., Tellier, S., Astruc., M., 2002b. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. Trends in Analytical Chemistry, 21 (6-7): 451-467.

Goldberg, S., 1986. Chemical modelling of arsenate adsorption on aluminium and iron oxide minerals. Soil Sci., Soc., Amer., J., 50: 1154-1157.

Goldberg, S., Johnston, C.T., 2001. Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. J. Colloid Interface Sci., 234 (1): 204–216.

Goldberg, S., 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. Soil Science Society of America Journal, 66: 413–421.

Gomez C., Bosecker K., 1999, Leaching heavy metals from contaminated soil by using Thiobacillus ferrooxidans or Thiobacillus thiooxidans, Geomicrobiology Journal, 16 (3): 233-244.

Gräfe, M., Eick, M.J., Grossl, P.R., 2001. Adsorption of arsenate(V) and arsenite(III) on goethite in the presence and absence of dissolved organic carbon. Soil Science Society of America Journal, 65 (6): 1680–1687.

Gräfe, M., Eick, M.J., Grossl, P.R., Saunders, A.M., 2002. Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon. Journal of Environmental Quality, 31 (4): 1115–1123.

Griffiths, P.R., De Haseth, J.A., 1986. Fourier Transform Infrared Spectrometry. Chemical Analysis Series, Vol. 83, Wiley New York, 672 p.

Grygar, T., Šubrt, J., Boháček, J., 1995. Electrochemical dissolution of goethite by abrasive stripping voltammetry, Collection of Czechoslovak Chemical Communications, 60: 950-959.

Grygar, T., 1995. Kinetics of electrochemical reductive dissolution of iron(III) hydroxy-oxides, Collection of Czechoslovak Chemical Communications, 60: 1261-1273.

Grygar, T., 1997. Dissolution of pure and substituted goethites controlled by the surface reaction under conditions of abrasive stripping voltammetry, J. Solid State Electrochem., 1: 77-82.

Grygar, T., van Oorschot, I.H.M., 2002. Voltammetric identification of pedogenic iron oxides in paleosol and loess. Electroanalysis, 14: 339–344.

Guo, X.J., Fujino, Y., Kaneko, S., Wu, K.G., Xia, Y.J., Yoshimura, T., 2001. Arsenic contamination of groundwater and prevalence of arsenical dermatosis in the Hetao plain area, Inner Mongolia, China. Molecular and Cellular Biochemistry, 222: 137–140.

Gupta, S.K., Chen, K.Y., 1978. Arsenic removal by adsorption. J. Water Pollut. Control Fed., 50 (3): 493–506.

Hak, J., 1960. Chemismus löllingitu z Přebuze v Krušných horách. Časopis pro mineralogii a geologii, 5: 104-109. (in Czech).

Hansel, C.M., Benner, S.G., Nico, P., Fendorf, S., 2004. Structural constraints of ferric (hydr)oxides on dissimilatory iron reduction and the fate of Fe(II). Geochimica et Cosmochimica Acta, 68 (15): 3217–3229.

Harrington J.M., Fendorf S.E., Rosenzweig R.F., 1998. Biotic generation of arsenic(III) in metal(loid)-contaminated freshwater lake sediments, Environmental Science & Technology, 32, (16): 2425-2430.

Harris, G.B., Monette, S., 1989. The disposal of arsenical residues. In: Proceedings of Productivity and Technology in the Metallurgical Industries, Cologne, West Germany. September, 17–22.

Harvey, M.C., Schreiber, M.E., Rimstidt, J.D., Griffith, M.M., 2006. Scorodite dissolution kinetics: Implications for arsenic release. Environmental Science & Technology, 40 (21): 6709-6714.

Hattori, K.H., Arai, S., Clarke, D.B., 2002. Selenium, tellurium, arsenic and antimony contents of primary mantle sulfides. Canadian Mineralogist, 40: 637-650.

Haywood, M.G., Riley, J.P., 1976. The spectrophotometric determination of arsenic in sea water, potable water and effluents. Analytica Chimica Acta, 85 (2): 219-230.

Helz, G.R., Tossel, J.A., Charnock, J.M., Pattrick, A.D., Vaughan, D. J., Garner, C.D., 1995. Oligomerization in As(III) sulfide solutions: theoretical constraints and spectroscopic evidence. Geochimica et Cosmochimica Acta, 59 (22), 5491–5604.

Herbel, M., Fendorf, S., 2006. Biogeochemical processes controlling the speciation and transport of arsenic within iron coated sands. Chemical Geology, 228 (1-3): 16-32.

Hill, S.J., Arowolo, T.A., Butler, O.T., Cook, J.M., Cresser, M.S., Harrington, C., Miles, D.L., 2003. Atomic spectrometry update, Environmental analysis. Journal of Analytical Atomic Apectrometry, 18 (2): 170-202.

Hloušek, J., 2000. Současné možnosti sběru minerálů na haldách bývalých dolů rudního pole Jáchymov. Minerál, 8 (3): 252-257. (in Czech).

Hochella, M.F., Moore, J.N., Golla, U., Putnis, A., 1999. A TEM study of samples from acid mine drainage systems: Metal-mineral association with implications for transport. Geochimica et Cosmochimica Acta, 63 (19-20): 3395-3406.

Hochella, M.F., Jr., Moore, J.N., Putnis, C., Putnis, A., Kasama, T., Eberl, D.D., 2005. Direct observation of toxic metal-mineral association from a massive acid mine drainage system: Implications for metal transport and bioavailability. Geochimica et Cosmochimica Acta, 69: 1651-1663.

Hongshao, Z., Stanforth, R., 2001. Competitive adsorption of phosphate on goethite. Environmental Science & Technology, 35: 4753–4757.

Hudson-Edwards, K.A., Schell, Ch., Macklin, M.G., 1999. Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain. Applied Geochemistry, 14 (8): 1015-1030.

Hudson-Edwards, K.A., Houghton, S.L., Osborn, A., 2004. Extraction and analysis of arsenic in soils and sediments. Trends in Analytical Chemistry, 23 (10–11): 745-752.

Chakraborti, D., Rahman, M.M., Paul, K., Chowdhury, U.K., Sengupta, K.K., Lodh, D., Chanda, CJ.R., Saha, K.C., Mukherjee, S.C., 2002. Arsenic calamity in the Indian subcontinent: What lessons have been learned? Talanta, 58 (1): 3-22.

Chappell, W.R., Abernathy, C.O., Cothern, C.R., 1994. Arsenic Exposure and Health. Science and Technology Letters. Northwood, 318 p.

Chappell, W.R., Abernathy, C.O., Calderon, R.L., (eds). 1998. Arsenic exposure and health effects III. Proceedings of the Third International Conference on Arsenic Exposure and Health Effects, San Diego, California, 12-15 July, 1998.

Chappell, D.A., Craw, D., 2002. Geological analogue for circumneutral pH mine tailings: implications for long-term storage, Macraes Mine, Otago, New Zealand. Applied Geochemistry, 17 (8): 1105-1114.

Charlet, L., Bosbach, D., Peretyashko, T., 2002. Natural attenuation of TCE, As, Hg linked to the heterogeneous oxidation of Fe(II): an AFM study. Chemical Geology, 190: 303-319.

Chatterjee, A., Das, D., Mandal, B.K., Chowdhury, T.R., Samanta, G., Chakraborti, D., 1995. Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part I: arsenic species in drinking water and urine of affected people. Analyst, 120: 643-650.

Chen, C.J., Hsu, L.I., Tseng, C.H., Hsueh, Y.M., Chiou, H.Y., 1999. Emerging epidemics of arseniasis in Asia. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects. Elsevier, 113–121.

Chen, M., Ma, L.Q., Harris, W.G., 2002. Arsenic concentrations in Florida surface soils: influence of soil type and properties. Soil Science Society of America Journal, 66 (2): 632–640.

Chunguo, C., Zihui, L., 1988. Chemical speciation and distribution of arsenic in water, suspended solids and sediment of Xiangjiang river, China. Science of the Total Environment, 77: 69-82.

Jacobs, L.W., Syers, J.K., Keeny, D.R., 1970. Arsenic Sorption by Soils. Soil Science Society of America Proceedings, 34: 750-754.

Jalilehvand, F., 2006. http://www.chem.ucalgary.ca/research/groups/faridehj/xas.pdf

Jambor, J.L., 1994. Mineralogy of sulfide-rich tailings and their alteration products. In Environmental Mineralogy of Sulfide Mine-Wastes (J.L. Jambor and D.W. Blowes, eds.). Mineral. Assoc. Can. Short Course Vol. 22: 59-102.

Jambor, J.l., Blowes, D.W., 1998. Theory and applications of mineralogy in environmental studies of sulfide-bearing mine wastes. In Modern Approaches to Ore and Environmental Mineralogy (L.J. Cabri and D.J. Vaughan, eds.) Mineral. Assoc. Can. Short Course Vol. 27: 367-401.

Jambor, J.L., Dutrizac, J.E., Chen, T.T., 2000. Contribution of specific minerals to the neutralization potential in static tests. In proceedings from the Fifth international Conference on Acid Rock Drainage 1. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado, 551-565.

Jambor, J.L., 2003. Mine-waste mineralogy and mineralogical perspectives of acid-base accountings. In Environmental aspects of mine wastes (J.L. Jambor, D.W. Blowes and A.I.M. Ritchie, eds.). Mineral. Assoc. Can. Short Course Vol. 31: 117-146.

Jamieson, H.E., Corriveau, M.C., Parsons, M.B., Koch I., Reimer, K.J., 2006. Mineralogy and bioaccessibility of arsenic-bearing secondary phases in gold mine tailings. Geochimica et Cosmochimica Acta, 70, 18, Supplement 1, 289.

Janatka, J., Morávek, P., 1990. Geochemical exploration in the Jílové Belt: case history of the Čelina deposit, Bohemian Massif, Czechoslovakia. Journal of Geochemical Exploration, 37 (3): 367-384.

Janatka, J., Morávek, P., 1992. Methods of prospection and exploration of Au- deposits. In: Morávek, P., (eds). Gold in the Bohemian Massif. Nakladatelství Českého geologického ústavu, Praha: 187-197 (in Czech).

Jansa, J., 1997. K historii nálezů kaňkitu a zýkaitu u Kutné Hory. Minerál, 5: 342-344. (In Czech).

Jen-How, H., Gunter, I., 2006. Factors affecting arsenic speciation in environmental samples: sample drying and storage. International Journal of Environmental & Analytical Chemistry, 86 (5): 347-358.

Jenkins, R., Snyder, R.L., 1996. Introduction to X-ray Powder Diffractometry. Wiley, New York.

Jílek, V., 1985. Mokrsko – Geomedicínská studie. Final Report, Geofond. Prague. (in Czech).

Johan, Z., 1959. Arsenolamprit – die rhombische Modifikation des Arsens aus Černý Důl (Schwarzenthal) im Riesengebirge. Chemie der Erde, 20: 71-80. (in German).

Johnson, D.B., Roberto, F.F., 1997. Heterotrophic acidophiles and their roles in the bioleaching of sulphide minerals In: Rawlings DE, ed. Biomining: Theory, Microbes and Industrial Processes. Berlin: Springer-Verlag, 259–279.

Jones, C.A., Langner, H.W., Anderson, K., McDermott, T.R., Inskeep, W.P., 2000. Rates of microbially mediated arsenate reduction and solubilization. Soil Science Society of America Journal 64, 600– 608.

Jones, R.A., Nesbitt, H.W., 2002. XPS evidence for Fe and As oxidation states and electronic states in loellingite (FeAs2). American Mineralogist, 87 (11-12): 1692-1698.

Jones, R.A., Koval, S.F., Nesbitt, H.W., 2003. Surface alteration of arsenopyrite (FeAsS) by Thiobacillus ferrooxidans. Geochimica et Cosmochimica Acta, Vol. 67 (5):955–965.

Johnston, R.B., Singer, P.C., 2007. Solubility of symplesite (ferrous arsenate): Implications for reduced groundwaters and other geochemical environments. Soil Science Society of American Journal, 71 (1): 101-107.

Juillot, F., Ildefonse, Ph., Morin, G., Calas, G., de Kersabiec, A.M., Benedetti, M., 1999. Remobilization of arsenic from buried wastes at an industrial site: mineralogical and geochemical control. Applied Geochemistry, 14, 8: 1031-1048.

Jung, M.Ch., Thornton, I., Chonc, H.-T., 2002. Arsenic, Sb and Bi contamination of soils, plants, waters and sediments in the vicinity of the Dalsung Cu–W mine in Korea. The Science of the Total Environment 295: 81–89.

Kabata-Pendias, A., Pendias, H., 2001: Trace elements in soil and Plants, 3rd ed., CRC Press, Boca Raton, 413 p.

Kanel, S.R., Manning, B., Charlet, L., Choi, H., 2005. Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. Environmental Science & Technology, 39 (5): 1291-1298.

Karthe, S., Szargan, R., Suoninen, E., 1993. Oxidation of pyrite surfaces – a photoelectron spectroscopic study. Applied Surface Science, 72 (2): 157-170.

Kavanagh, P.J., Farago, M.E., Thorton, I., Braman, R.S., 1997. Bioavailibility of arsenic in soil and mine waste of the Tamar valley, SW England. Chem. Spec. Bioavail., 9 (3): 77-81.

Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C. Hemond, H.F., 2001. Validation of an Arsenic Sequential Extraction Method for Evaluating Mobility in Sediments. Environmental Science & Technology, 35: 2778-2784.

Kim, M.-J., Nriagu, J., Haack, S., 2000. Carbonate ions and arsenic displacement by groundwater. Environmental Science & Technology, 34 (15) : 3094–3100.

Kirpichtchikova TA, Manceau A, Spadini L, Panfili, F., Marcus, M.A., Jacquet, T., 2006. Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. Geochimica et Cosmochimica Acta, 70 (9): 2163-2190.

Kloprogge, J.T., Duong, L.V., Weier, M., Martens, W.N., 2006. Nondestructive identification of arsenic and cobalt minerals from Cobalt City, Ontario, Canada: Arsenolite, erythrite, and spherocobaltite on pararammelsbergite. Applied Spectroscopy, 60 (11): 1293-1296.

Ko I., Kim J.Y., Kim K.W., 2004. Arsenic speciation and sorption kinetics in the As-hematite-humic acid system. Colloids and Surfaces A: Physicochem. Eng. Aspects., 234: 43-50.

Kořan, J., 1947. Historická zpráva o Božídarském okrsku. MS, Geofond Praha. P 316. (in Czech).

Kosmas, C.S., Curi, N., Bryant, R.B., Franzmeier, D.P., 1984. Characterization of iron oxide minerals by second-derivation visible spectroscopy. Soil Science Society of America Journal, 48: 401-405.

Kratochvíl, F., 1954. Příspěvek k dějinám dolování na cínovec u Přebuzu a Rotavy. Věstník Ústředního Ústavu geologického, 21: 1-54 (in Czech).

Krause, E., Ettel, V.A., 1988. Solubility and Stability of scorodite, FeAsO4.2H2O. New data and further discussion. American Mineralogist. 73 (7-8): 850-854.

Lakshmipathiraj, P., Narasimhan, B.R.V., Prabhakar, S., Raju, G.B., 2006. Adsorption of arsenate on synthetic goethite from aqueous solutions. Journal of Hazardous Materials, 136 (2): 281-287.

Langdon, C.J., Piearce, T.G., Meharg, A.A., Semple, K.T., 2001. Survival and behaviour of the earthworms Lumbricus rubellus and Dendrodrilus rubidus from arsenate-contaminated and non-contaminated sites. Soil Biology & Biochemistry, 33: 1239-1244.

Langdon, C.J., Piearce, T.G., Meharg, A.A., Semple, K.T., 2003. Interactions between earthworms and arsenic in the soil environment: a review. Environmental Pollution, 124 (3): 361-373.

Langmuir, D., Mahoney, J., MacDonald, A., Rowson, J., 1999. Predicting arsenic concentrations in the porewaters of buried uranium mill tailings. Geochimica et Cosmochimica Acta, 63 (19-20): 3379-3394.

Langmuir, D., Mahoney, J., Rowson, J., 2006. Solubility products of amorphous ferric arsenate and crystalline scorodite (FeAsO4 Ć 2H2O) and their application to arsenic behavior in buried mine tailings. Geochimica et Cosmochimica Acta, 70 (12): 2942-2956.

Langner, H.W., Inskeep, W.P., 2000. Microbial reduction of arsenate in the presence of ferrihydrite. Environmental Science & Technology, 34 (15): 3131-3136.

Lazareva, E.V., Pospelova, L.N., 1998. Peculiarities of the initial and secondary distribution of elements in the tailings body. Mineralogical Magazine, 62A: 862-863.

Leblanc, M., Achard, B., Ben Othman, D., Luck, J.M., 1996. Accumulation of arsenic from arsenic mine waters by ferruginous bacterial accretions. Applied Geochemistry, 11: 541-554.

Lee, J.S., Nriagu, J.O., 2003. Arsenic carbonate complexes in aqueous systems. In: Cai, Y., Braids, O.C. (Eds.), Biogeochemistry of Environmentally Important Trace Elements. ACS Symposium Series, vol. 835. American Chemical Society, Washington, DC, 33–41.

Lee, P.-K., Kang, M.-J., Choi, S.-H., Touray, J.-C., 2005. Sulfide oxidation and the natural attenuation of arsenic and trace metals in the waste rocks of the abandoned Seobo tungsten mine, Korea. Applied Geochemistry, 20 (8): 1687-1703.

Leonard, A., 1991. Arsenic. Metals and their compounds in the environment. Weinheim: VCH: 751-772.

Lin, Z., Qvarfort, U., 1996. A study of the Lilla Bredsjoen tailings impoundment in mid-Sweden-a comparison of observations with RATAP model simulations. Applied Geochemistry. 11: 293–298.

Lin, Z., Puls, R.W., 2000. Adsorption, desorption, and oxidation of arsenic affected by clay minerals and aging process. Environmental Geology, 39: 753-759.

Litochleb, J., Veselý, J., 1992. Roudný deposit. In: Morávek, P., (eds). Gold in the Bohemian Massif. Nakl Čes geol ústavu Praha, 112-115. (in Czech).

Liu, J., Zheng, B.S., Aposhian, H.V., Zhou, Y.S., Chen, M.L., Zhang, A.H., Waalkes, M.P., 2002. Chronic arsenic poisoning from burning high-arsenic-containing coal in Guizhou, China. Environmental Health Perspectives, 110: 119–122.

Lombi, E., Sletten, R.S., Wenzel, W.W., 2000. Sequential extracted arsenic from different size fractions of contaminated soils. Water, Air & Soil Pollution, 124 (3-4): 319-332.

Loredo, J., R. Álvarez, R., A. Ordóñez, A., 2005. Release of toxic metals and metalloids from Los Rueldos mercury mine (Asturias, Spain). Science of the Total Environment, 340 (1-3): 247-260.

Lovley, D.R., 1991. Dissimilatory Fe(III) and Mn(IV) reduction. Microbiological Reviews, 55 (2): 259–287.

Lower, S.K., Tadanier, C.J., Hochella, M.F., 2000. Measuring interfacial and adhesion forces between bacteria and mineral surfaces with biological force microscopy. Geochimica Cosmochimica Acta, 64 (8): 3133-3139.

Lower, S.K., Tadanier, C.J., Hochella, M.F., 2001. Dynamics if the mineral-microbe interface: Use of biological force microscopy in biogeochemistry and geomicrobiology. Geomicrobiological Journal, 18: 63-76.

Lumsdon, D.G., Meeussen, J.C.L., Paterson, E., Garden, L.M., Anderson, P., 2001. Use of solid phase characterisation and chemical modelling for assessing the behaviour of arsenic in contaminated soils. Applied Geochemistry, 16 (6): 571-581.

Macklin, M.G., Brewer, P.A., Balteanu, D., Coulthard, T.J., Driga, B., Howard, A.J., Zaharia, S., 2003. The long term fate and environmental significance of contaminant metals released by the January and March 2000 mining tailings dam failures in Maramureş¸ County, upper Tisa Basin, Romania. Applied Geochemistry, 18 (2): 241-257.

Mancur, R.E., Wheeler, J.T., McDermott, T.R., Inskeep, W.P., 2001. Microbial populations associated with the reduction and enhanced mobilization of arsenic in mine tailings. Environmental Science & Technology, 35: 3676– 3682.

Maggs, R., 2000. A review of arsenic in ambient air in the UK. Department of the Environment, Transport and the Regions Scottish Executive, The National Assembly for Wales, unpublished report, 51 p.

Mahoney, J., Langmuir, D., Gosselin, N., Rowson, J., 2005. Arsenic readily released to pore waters from buried mill tailings. Applied Geochemistry, 20 (5): 947-959.

Mains, D., Craw, D., 2005. Composition and mineralogy of historic gold processing residues, east Otago, New Zealand. New Zealand Journal of Geology & Geophysics, 48 (4): 641-647.

Malát, M., 1973. Absorption Inorganic Photometry. Arsenic. Academia, Prague, 511-519. (in Czech).

Mandl, M., Matulová, P., Dočekalová, H., 1992. Migration of arsenic(III) during bacterial oxidation of arsenopyrite in chalcopyrite concentrate by Thiobacillus ferrooxidans. Applied Microbiology and Biotechnology, 38: 429-431.

Manful, G., Verloo, M., Remmerie, B., 1994. The ecochemistry of arsenic in a contaminated soil: a case study. In: Proceedings of Soil Remediation, Paris, Faculté des Sciences Agronomiques, 34-40.

Malmström, M.E., Gleisner, M., Herbert, R.B., 2006. Element discharge from pyritic mine tailings at limited oxygen availability in column experiments. Applied Geochemistry, 21 (1): 184-202.

Malengreau, N., Bedidi, A., Muller, J.P., Herbillon, A.J., 1996. Spectroscopic control of iron oxide dissolution in two ferralitic soils. Eur. J. Soil Sci., 47: 13–20.

Malengreau, N.,Weidler, P.G., Gehring, A.U., 1997. Iron oxides in laterites: a combined mineralogical, magnetic, and diffuse reflectance study. Schweiz. Schweizerische Mineralogische und Petrographische Mitteilungen, 77: 13–20.

Manceau, A., Marcus, M.A., Tamura, N., 2002. Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. In Applications of synchrotron radiation in low-temperature geochemistry and environmental science (P.A. Fenter, M.L., Rivers, N.C., Struchio, S.R., Sutton, eds.), Reviews in Mineralogy & Geochemistry, 49: 341-428.

Manning, B.A., Goldberg, S., 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. Soil Science Society of America Journal, 60 (1): 121–131.

Manning, B.A., Goldberg, S., 1997a. Adsorption and stability of arsenic(III) at the clay mineral-water interface. Environmental Science & Technology, 31: 2005-2011.

Manning, B.A., Goldberg, S., 1997b. Arsenic(III) and arsenic(V) adsorption on three California soils. Soil Sci., 162: 886-895.

Manning, B.A., Fendorf, S.E., Goldberg, S., 1998. Surface Structures and Stability of Arsenic(III) on Goethite: Spectroscopic Evidence for Inner-Sphere Complexes. Environmental Science & Technology, 32: 2383-2388.

Manning, B., 2005. Arsenic Speciation in As(III)- and As(V)-Treated Soil Using XANES Spectroscopy. Microchimica Acta. 151: 181-188.

Marquez, M., Gaspar, J., Bessler, K.E., Magela, G., 2006. Process mineralogy of bacterial oxidized gold ore in Sao Bento Mine (Brasil). Hydrometallurgy, 83 (1-4): 114-123.

Martin, C.J., Al, T.A., Cabri, L.J., 1997. Surface analysis of particles in mine tailings by time-of-flight laser-ionization mass spectrometry (TOF-LIMS). Environmental Geology, 32 (2): 107-113.

Masscheleyn, P.H., R.D. DeLaune, and W.H. Patrick, Jr., 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environmental Science & Technology, 25 (8): 1414-1419.

Matera, V., Le Hécho, I., Laboudigue, A., Thomas, P., Tellier, S., Astruc, M., 2003. A methodological approach for the identification of arsenic bearing phases in polluted soils. Environmental Pollution, 126: 51-64.

Mathieu, C., 1998. Effect of electron-beam/gasinteraction on X-ray microanalysis in the variable pressure SEM. Microchimimica Acta, 15: 295-300.

Matschullat, J., 2000. Arsenic in the geosphere - a review. Science of the Total Environment, 249: 297-312.

Matsubara, S., Miyawaki, R., Shimizu, M., Yamanaka, T., 2001. Pararsenolamprite, a new polymorph of native As, from the Mukuno mine, Oita Prefecture, Japan. Mineralogical Magazine, 65: 807-812.

Mehlich, A., 1985. Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. Comm. Soil Sci. Plant Anal., 15: 1409-1416.

Mermut, A.R., Curtin, D., Rostad, H.P.W., 1985. Micromorphological and submicroscopical features related to pyrite oxidation in a inland marine shale from east central Saskatchewan. Soil Science Society of America Journal, 49: 256-261.

Mikhlin, Y.L., Romanchenko, A.S., Asanov, I.P., 2006. Oxidation of arsenopyrite and deposition of gold on the oxidized surfaces: A scanning probe microscopy, tunneling spectroscopy and XPS study. Geochimica et Cosmochimica Acta, 70: 4874–4888.

Mitchel P., Barr D., 1995, The nature and significance of public exposure to arsenic: a review of its relevance to South West England, Environmental Geochemistry and Health, 17: 57-82.

Mollah M.Y.A., Kesmez M., Cocke D.L., 2004. An X-ray diffraction (XRD) and Fourier transform infrared spectroscopic (FT-IR) investigation of the long-term effect on the solidification/stabilization (S/S) of arsenic(V) in Portland cement type-V. Science of the Total Environment, 325 (1-3): 255-262.

Montperrus, M., Bohari, Y., Bueno, M., Astruc, A., Astruc, M., 2002. Comparison of extraction procedures for arsenic speciation in environmental solid reference materials by high-performance liquid chromatography-hydride generation-atomic fluorescence spectroscopy. Applied Organometallic Chemistry, 16: 347.

Moon, D.H., Dermatas, D., Menounou, N., 2004. Arsenic immobilization by calcium–arsenic precipitates in lime treated soils. Science of the Total Environment, 330 (1-3): 171-185.

Morávek, P., 1995. Gold metallogeny of Central and Western European Variscides. Mineral Deposits. In: Pašava, J., Kříbek, B., Žák, K., (eds). Balkema Rotterdam, 67-70.

Morávek, P., 1996. The Mokrsko gold deposit. In: Morávek, P., (eds). Gold deposits in Bohemia. Czech Geological Survey, Prague 31-56.

Morávek, P., Janatka, P., Pertoldová, J., Straka, J., Ďurišová, J., Pudilová, M., 1989. Mokrsko gold deposit – the largest gold deposit in the Bohemian Massif, Czechoslovakia. Econonomic Geology, Monograph, 6: 252-259. New Haven.

Moretti, G., 1998. Auger parameter and Wagner plot in the characterization of chemical states by X-ray photoelectron spectroscopy: a review. Journal of Electron Spectroscopy and Related Phenomena, 95 (2-3): 95-144.

Morin, G., Lecocq, D., Juillot, F., Calas, G., Ildefonse, Ph., Beline, S., Briois, V., Dillmann, Ph., Chevallier, Ch., Gauthier, Ch., Sole, A., Petit, P.-E., Borensztajl, S., 2002. EXAFS evidence of sorbed arsenic(V) and pharmacosiderite in a soil overlying the Echassières geochemical anomaly, Allier, France. le Bulletin de la Société géologique de France, 173 (3): 21-291.

Morin, G., Juillot, F., Casiot, C., Bruneel, O., Personne, J.C., Leblanc, M., Duquesne, K., Bonnefoy, V., Elbaz-Poulichet, F., 2003. Bacterial formation of tooeleite and mixed Arsenic(III) or Arsenic(V)-Iron(III) gels in the carnoulbs acid mine drainage, France. A XANES, XRD, and SEM study. 37 (9): 1705-1712.

Morin, G., Calas, G., 2006. Arsenic in Soils, Mine Tailings, and Former Industrial Sites. Elements, 2: 97-101.

Munsterman, D., Kerstholt, S., 1996. Sodium polytungstate, a new non-toxic alternative to bromoform in heavy liquid separation. Review of Palaeobotany and Palynology, 91: 417-422.

Murzin, V.V., Semenkin, V.A., Sustavos, S.G., Krinov, D.I., Pikulev, A.I., Milder, O.D., 2003. Mossbauer spectroscopic evidence for nonequivalent sites of iron atoms in gold-bearing arsenopyrite. Geochemistry International. 41 (8): 812-820.

Mutter, G., Eysel, W., Greis, O., Schmetzer, K., 1984. Crystal chemistry of natural and ion-exchanged pharmacosiderites. Neues Jahrbuch für Mineralogie und Geologie, Monatshefte, 4: 183-192.

Mycroft, J.R., Bancroft, G.M., McIntyre, N.S., Lorimer, J.W., Hill, I.R., 1990. Detection of sulphur and polysulphides on electrochemically oxidized pyrite surfaces by X-ray photoelectron spectroscopy and Raman spectroscopy. Journal of Electroanalytical Chemistry, 292: 139-152.

Myneni, S.C.B., Traina, S.J., Waychunas, G.A. and Logan, T.J., 1998. Experimental and Theoretical Vibrational Spectroscopic Evaluation of Arsenate coordination in Aqueous solutions and Solids." Geochimica et Cosmochimica Acta, 62: 3285-3300.

Néel, C., Bril, H., Courtin-Nomade, A., Dutreuil, J.-P., 2003. Factors affecting natural development of soil on 35-year-old sulphide-rich mine tailings. Geoderma, 111: 1-20.

Nesbitt, H.W., Bancroft, G.M., Pratt, A.R., Scaini, M.J., 1995. Oxidation of arsenopyrite by air-saturated, distilled water, and implication for mechanism of oxidation. Geochimica et Cosmochimica Acta, 59 (9): 1773-1786.

Nesbitt, H.W., Muir, I.J., 1998. Oxidation states and speciation of secondary products on pyrite and arsenopyrite reacted with mine waste waters and air. Mineralogy and Petrology, 62: 123-144.

Newman, D.K., Kennedy, E.K., Coates, J.D., Ahmann, D., Ellis, D.J., Lovley, D.R., Morell, F.M.M., 1997. Dissimilatory arsenate and sulfate reduction in Desulfotomaculum auripigmentum sp. nov. Archives of Microbiology, 168 (5), 380–388.

Newman, D.K., Ahmann, D., Morel, F.M.M., 1998. A brief review of microbial arsenate respiration. Geomicrobiology Journal, 15 (4): 255-268.

Ng, J.C., Wang, J., Shraim, A., 2003. A global health problem caused by arsenic from natural sources. Chemosphere, 52: 1353-1359.

Nicholson, R.V., Gillham,, R.W., Cherry, J.A., Reardon, E.J., 1989. Reduction of acid generation in mine tailings through the use of moisture-retaining cover layers as oxygen barriers. Can. Geotech. J., 26: 1-8.

Nickson, R.T., McArthur, J.M,, Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Applied Geochemistry, 15 (4): 403-413.

Nishimura, T., Ito, C.T., Tozawa, K., Robins, R.G., 1985. The calcium-arsenic-water-air system: impurity control and disposal. Proceedings 15th Annual Hydrometallurgical meeting (CIM Vancouver Canada August 1985).

Nordstrom, D.K., Parks, G.A., 1987. Solubility and stability of scorodite (FeAsO4 · 2H2O), Discussion. American Mineralogist, 72 (7-8): 849-851.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. Nature, 333: 134-139.

Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals. Nature, 338: 47-49

Nriagu, J.O., 1994. Arsenic in the Environment, Part I: Cycling and Characterization; Part II: Human Health and Ecosystem Effects. Wiley, New York.

Nriagu, J.O., 2002. Arsenic poisoning through the ages. In: Environmental Chemistry of Arsenic (Frankenberger Jr., W.T. Ed.), 1–26. Marcel Dekker, New York.

O´Day, P.A., 2006. Chemistry and mineralogy of arsenic. Elements, 2: 77-83.

Oliver, M.A., 1997. Soil and human health: a review, Europian Journal of Soil Science, 48: 573-592.

Ona-Nguema, G., Morin, G., Juillot, F., Brown, G.E. JR., Calas, G., 2005. EXAFS analysis of Arsenic(III) sorption onto 2-line ferrihydrite, hematite, goethite, and lepidocrocite under anoxic conditions. Influence of the surface structure. Environmental Science & Technology, 39: 9147-9155.

Ondruš, P., 1993. ZDS – A computer program for analysis of X-ray powder diffraction patterns. Materials Science Forum, 133-136: 297-300 (EPDIC-2, Enchede).

Ondruš, P., 1995. ZDS – software for analysis of x-ray powder diffraction data version 6.01 – user’s guide. Czech Geological Survey, Prague.

Ondruš, P., Veselovský, F., 1995. RECAL – program for quantitative phase analysis of soils based on x-ray diffraction and chemical analyses combination. Bulletin of the Czech Geological Survey, Prague, 70, 2: 93-96

Ondruš, P., Veselovský, F., Hloušek, J., Skála, R., Vavřín, I., Frýda, J., Čejka, J., Gabašová, A., 1997. Secondary minerals of the Jáchymov (Joachimsthal) ore district. Journal of the Czech Geological Society, 42 (4): 3-76.

Ondruš, P., Skála, R., Viti C., Veselovský, F., Novák, F., Jansa, J., 1999. Parascorodite, FeAsO4 center dot 2H(2)O - a new mineral from Kank near Kutna Hora, Czech Republic. American Mineralogist, 84 (9): 1439-1444.

O’Neill, P., 1995. Arsenic. In: Alloway, B.J. (Ed.), Heavy Metals in Soils. Chapman & Hall, Oxford, UK, 105–121.

Ongley, L.K., Sherman, L., Armienta, A., Concilio, A., Salinas, C.F., 2007. Arsenic in the soils of Zimapán, Mexico. Environmental Pollution, 145 (3): 793-799.

Ohnuki, T., Sakamoto, F., Kozai, N., Ozaki, T., Yoshida, T., Narumi, I., Wakai, E., Sakai, T., Francis, A.J., 2004. Mechanisms of arsenic immobilization in a biomat from mine discharge water. Chemical Geology, 212 (3-4): 279-290.

Oremland, R.S., Newman, D.K., Kail, B.W., Stolz, J.F., 2002. Bacterial respiration of arsenate and its significance in the environment. In: J. Frankenberger, W.T. (Ed.), Environmental Chemistry of Arsenic. Marcel Dekker, New York, 273–295.

Oremland, R.S., Stolz, J.F., 2003. The ecology of arsenic. Science, 300: 939–944.

Osborne, F.H., Ehrlich H.L., 1976. Oxidation of arsenite by a soil isolate of alcaligenes. Journal of Applied Bacteriology, 41: 295-305.

Ouvrard, S., de Donato, P., Simonnot, M.O., Begin, S., Ghanbaja, J., Alnot, M., Duval, Y.,B., Lhote, F., Barres, O., SARDIN, M., 2005. Natural manganese oxide: Combined analytical approach for solid characterization and arsenic retention. Geochimica and Cosmochimica Acta, 69 (11): 2715-2724.

Paktunc, D., Dutrizac, J.E., 2003. Characterization of Arsenate-for-Sulfate Substitution in Synthetic Jarosite Using X-Ray Diffraction and X-Ray Absorption Spectroscopy. The Canadian Mineralogist, 41 (4): 905-919.

Paktunc, D., Foster, A., Heald, S., Laflamme, G., 2004. Speciation and characterization of arsenic in gold ores and cyanidation tailings using X-ray absorption spectroscopy. Geochimica et Cosmochimica Acta, 68 (5): 969-983.

Pansu, M., Gautheyrou, J., 2006. Handbook of soil analysis. Springer-Verlag Berlin Heidelberg New York, 974 p.

Papassiopi, N., Stefanakis, M., Kontopoulos, A., 1988. Removal of arsenic from solutions by precipitation as ferric arsenates. In: Reddy, R., Hendrix, J., Queneau P., (eds). Arsenic Metallurgy - Fundamentals and Applications, TMS, Warrendale, 321 – 336.

Papassiopi, N., Vaxevanidou, K., Paspaliaris, I., 2003. Investigating the use of iron reducing bacteria for the removal of arsenic from contaminated soils. Water, Air & Soil Pollution, 3: 81-90.

Paterová, B., Zachariáš, J., Pudilová, M., 2000. Fluid inclusions, stable isotopes and mineralogical constraints on the genesis of Roudný gold-deposit, Czech Republic. Metallogeny 2000: Review and perspectives, Université Henri Poincaré Nancy: 127-128.

Peacor, D.R., Dunn, P.J., 1985. Na-pharmacosiderite, a new analog of pharmacosiderite from Australia and new occurrences of barium-pharmacosiderite. Miner. Rec., 16: 121-124.

Pedersen, H.D., Postma, D., Jakobsen, R., 2006. Release of arsenic associated with the reduction and transformation of iron oxides. Geochimica et Cosmochimica Acta, 70 (16): 4116-4129.

Penrose, W.R., 1974. Arsenic in the marine and aquatic environments: analysis, occurrence, and significance. CRC Critical Reviews in Environmental Control, 4: 465–482.

Pertold, Z., Punčochář, M., 1996. The Kašperské Hory ore district. In: Morávek, P., (eds). Gold deposits in Bohemia. Czech Geological Survey, Prague, pp 79-96.

Peryea, F.J., 1991. Phosphate induced release of arsenic from soils contaminated with lead arsenate. Soil Science Society of America Journal, 155: 1301–1306.

Peters, S.C., Blum, J.D., 2003. The source and transport of arsenic in a bedrock aquifer, New Hampshire, USA, Applied Geochemistry, 18: 1773-1787.

Peterson, P.J., Benson, L.M., porter, E.K., 1979. Biogeochemistry of arsenic on polluted sites in SW England. In: Heavy metals in the environment, London, September 1979, 198-201. CEP Consultants Ltd. Edingurgh.

Peterson, R.C., Grant, A.H., 2005. Dehydration and crystallization reactions of secondary sulfate minerals found in mine waste: in situ powder-diffraction experiments. The Canadian Mineralogist, 43 (4): 1171-1181.

Petrunic, B.M., Al, T.A., 2005. Mineral/water interactions in tailings from a tungsten mine, Mount Pleasant, New Brunswick. Geochimica et Cosmochimica Acta, 69 (10): 2469-2483.

Petrunic, B.M., Al, T.A., Weaver, L., 2006. A transmission electron microscopy analysis of secondary minerals formed in tungsten-mine tailings with an emphasis on arsenopyrite oxidation. Applied Geochemistry, 21 (8): 1259-1273.

Pfeifer, H.-R., Gueye-Girardet, A., Reymond, D., Schlegel, C., Temgoua, E., Hesterberg, D.L., Chou, J.W., 2004. Dispersion of natural arsenic in the Malcantone watershed, Southern Switzerland: field evidence for repeated sorption–desorption and oxidation–reduction processes. Geoderma, 122: 205-234.

Pichler, T., Veizer, J., Hall, G.E.M., 1999. Natural input of arsenic into a coral reef ecosystem by hydrothermal fluids and its removal by Fe(III) oxyhydroxides. Environmental Science & Technology, 33 (9): 1373-1378.

Pichler, T., Hendry, M.J., Hall, G.E.M., 2001. The mineralogy of arsenic in uranium mine tailings at the Rabbit Lake In-pit Facility, northern Saskatchewan, Canada. Environmental Geology, 40 (4-5): 495-506.

Pieczka, A., Golebiowska, B., Franus, W., 1998. Yukonite, a rare Ca-Fe arsenate, from Redziny (Sudetes, Poland). Europian Jornal of Mineralogy, 10: 1367-1370.

Pierrot, R., 1964. Contribution á la mineralogie des arséniates calciques et calcomagnésiens naturels. Bulletin de la Société française de Minéralogie et de Cristallographie, 87: 169-211.

Pierce, M.L., Moore, C.B., 1980. Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution, Environmental Science & Technology, 14 : 214–216.

Pongratz, R., 1998. Arsenic speciation in environmental samples of contaminated soil. Science of the Total Environment, 224 (1-3): 133–141.

Pósfai, M., Buseck, P.R., 1997. Modular structures in sulphides: Sphalerite/wurtzite-, pyrite/marcasite and pyrrhotite-type minerals. 193–235 in: Modular Aspects of Minerals (S. Merlino, editor). EMU Notes in Mineralogy, Vol. 1, Eötvös University Press, Budapest.

Pyatt, F.B., Gilmore, G., Grattan, P.J., Hunt, C.O., McLeren, S., 2000. An imperial legacy? An exploration of the environmental impacts of ancient metal mining and smelting in Southern Jordan. Jornal of Archaeological Science, 27: 771-778.

Raade, G., Mladeck, M.H., Kristiansen, R., Din, V.K., 1984. Kaatialaite, a new ferric arsenate mineral from Finland. American Mineralogist, 69 (3-4): 383-387.

Rajander, J., Harju, L., Lill, J.O., Saarela, K.E., Lindroos, A., Heselius, S.J., 1999. Monitoring of chromium, copper and arsenic in contaminated soils using thick-target PIXE. Nuclear instruments & methods in physics research section B-beam interactions with materials and atoms, 150 (1-4): 510-515.

Ramdor, P., 1980. The ore minerals and their intergrowths (2nd edition) Pergamon Press.

Randall, S.R., Sherman, D.M., Ragnarsdottir, K.V., 2001. Sorption of As(V) on green rust (Fe4(II)Fe2(III)(OH)12SO4 . 3H2O) and lepidocrocite (γ-FeOOH): Surface complexes from EXAFS spectroscopy. Geochimica et Cosmochimica Acta, 65 (7): 1015-1023.

Raposo, J.C., Zuloaga, O., Olazabal, M.A., Madariaga, J.M., 2004. Study of the precipitation equilibria of arsenate anion with calcium and magnesium in sodium perchlorate at 25 °C. Applied Geochemistry, 19 (6): 855-862.

Raudsepp, M., Pani, E., 2003. Application of Rietveld analysis to environmental mineralogy. In Environmental aspects of mine wastes (J.L. Jambor, D.W. Blowes and A.I.M. Ritchie, eds.). Mineral. Assoc. Can. Short Course Vol. 31: 165-180.

Raven, K.P., Jain, A., Loeppert, R.H., 1998. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. Environmental Science & Technology, 32: 344–349.

Redman, A.D., Macalady, D.L., Ahmann, D., 2002. Natural organic matter affects arsenic speciation and adsorption on hematite. Environmental Science & Technology, 36 (13) : 2889–2896.

Regenspurg, S., Peiffer, S., 2005. Arsenate and chromate incorporation in schwertmannite. Applied Geochemistry, 20 (6): 1226-1239.

Reich, M., Becker, U., 2006. First-principles calculations of the thermodynamic mixing properties of arsenic incorporation into pyrite and marcasite. Chemical Geology., 225: 278–290.

Reimann, C., de Caritat, P., 1998. Chemical elements in the environment. Berlin: Springer, 398 p.

Reynolds, J.G., Naylor, D.V., Fendorf, S.E., 1999. Arsenic sorption in phosphate-amended soils during flooding and subsequent aeration. Soil Science Society of America Journal, 63: 1149–1156.

Richardson, S., Vaughan, D.J., 1989. Arsenopyrite: a spectroscopic investigation of altered surfaces. Mineralogical Magazine, 53: 223-229.

Rimstidt, J.D., Vaughan, D.J., 2003. Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. Geochimica et Cosmochimica Acta, 67: 833-880.

Rittle, K.A., Drever, J.I., Colberg, P.J.S., 1995. Precipitation of arsenic during bacterial sulfate reduction. Geomicrobiological Journal, 13 (1): 1–11.

Robins, R.G., 1981. The Solubility of Metal Arsenates. Metallurgical Trans. B, 12: 103-109.

Robins, R.G., Glastras, M.V., 1987. The precipitation of arsenic from aqueous solution in relation to disposal from hydrometallurgical processes. Research and Development in Extractive metallurgy. Aust. Inst. Min. Metall., Adelaide, 223-227.

Roden, E., Zachara, J.M., 1996. Microbial reduction of crystalline iron(III) oxides: influence of oxide surface area and potential for cell growth. Environmental Science & Technology, 30 (5): 1618–1628.

Rochette, E.A., Bostick, B.C., Li, G., Fendorf, S., 2000. Kinetics of arsenate reduction by dissolved sulfide. Environmental Science & Technology, 34 (22): 4714–4720.

Rojík, P., 2000. Historie cínového hornictví v západním Krušnohoří. Sokolovské muzeum, Sokolov, 233 p. (in Czech).

Roman-Ross, G., Cuello, G.J., Turrillas, X., Fernández-Martínez, A., Charlet, L., 2006. Arsenite sorption and co-precipitation with calcite. Chemical Geology, 233 (3-4): 328-336.

Romero, F.M., Armienta, M.A., Villasenor, G., Gonzalez, J.L., 2006. Mineralogical constraints on the mobility of arsenic in tailings from Zimapan, Hidalgo, Mexico. International Journal of Environment and Pollution, 26 (1-3): 23-40.

Romero, F.M., Armienta, M.A., González-Hernández, G., 2007. Solid-phase control on the mobility of potentially toxic elements in an abandoned lead/zinc mine tailings impoundment, Taxco, Mexico. Applied Geochemistry, 22 (1): 109-127.

Roussel, Ch., Néel, C., Bril, H., 2000. Minerals cantrolling arsenic and lead solubility in an abandoned gold mine tailings. Science of the Total Environment, 263: 209-219.

Ryan, C.G., 2004. Ion beam microanalysis in geoscience research. Nuclear instruments & methods in physics research section B-beam interactions with materials and atoms, 219: 534-549.

Sadiq, M., Zaidi, T.H., Attique A., Mian, A.A., 1983. Environmental behavior of arsenic in soils: theoretical. Water, Air & Soil Pollution, 20: 369-377.

Sadiq, M., Alam, I., 1996. Arsenic chemistry in a groundwater aquifer from the eastern province of Saudi Arabia. Water, Air & Soil Pollution, 89: 67-76.

Sadiq M., 1997. Arsenic Chemistry in Soils: An Overview of Thermodynamic Predictions and Field Observations. Water, Air & Soil Pollution, 93 (1-3): 117-136.

Saltikov, C.W., Newman, D.K., 2003. Genetic identification of a respiratory arsenate reductase. Proc. Natl. Acad. Sci. U. S. A., 100 (19), 10983–10988.

Salzsauler, K.A., Sidenko, N.V., Sherriff, L., 2005. Arsenic mobility in alteration products of sulphide-rich, arsenopyrite-bearing mine wastes, Snow Lake, Manitoba, Canada. Applied Geochemistry, 20: 2303-2314.

Sampson, M.I., Phillips, C.V., Ball, A.S., 2000. Investigation of the Attachment of Thiobacillus Ferrooxidans to Mineral Sulfides using Scanning Electron Microscopy Analysis. Minerals Engineering, 13 (6): 643-656.

Sancha, A.M., Castro, M.L., 2001. Arsenic in Latin America: occurrence, exposure, health effects, and remediation. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects. Elsevier, 87–96.

Sánchez-Rodas, D., Gómez-Ariza, J.L., Giráldez, I., Velasco, A., Morales, E., 2005. Arsenic speciation in river and estuarine waters from southwest Spain. Science of the Total Environment, 345: 207-217.

Savage, K.S., Tracy, T.N., O´Day, P.A., Waychunas, G.A., Bird, D.K., 2000. Arsenic speciation in pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne County, California. Applied Geochemistry, 15 (8): 1219-1244.

Savage, K.S., Bird, D.K., O´Day, P.A., 2004. Arsenic speciation in synthetic jarosite. Chemical Geology, 215 (1-4): 473-498.

Serafimovski, I., Karadjova, I.B., Stafilov, T., Tsalev, D.L., 2006. Determination of total arsenic and toxicologically relevant arsenic species in fish by using electrothermal and hydride generation atomic absorption spectrometry. Microchemical Journal, 83 (2): 55-60.

Serna, C.J., Cortina, C.P., Garcia Ramos, J.V., 1986. Infrared and Raman study of alunite-jarosite compounds, Spectrochimica Acta A, 42: 729-734.

Sherman, D.M., Waite, T.D., 1985. Electronic spectra of Fe3+ oxides and oxide hydroxides in the near IR to near UV. American Mineralogist, 70: 1262–1269.

Sherman, D.M., Randall, S.R., 2003. Surface complexation of arsenic(V) to iron(III) (hydr)oxides: Structural mechanism from ab initio molecular geometries and EXAFS Spectroscopy. Geochimica et Cosmochimica Acta, 67 (22): 4223-4230.

Shi, H., Hudson, L.G., Ding, W., Wang, S., Cooper, K.L., Liu, S., Chen, Y., Shi, X., Liu, K.J., 2004. Arsenite causes DNA damage in keratinocytes via generation of hydroxyl radicals. Chem. Res. Toxicol., 17 (7): 871-878.

Shih, Ch.-J., Lin, CH.-F., 2003. Arsenic contaminated site at an abandoned copper smelter plant: waste characterization and solidification/stabilization treatment. Chemosphere, 53: 691-703.

Schaeffer, R., Francesconi, K.A., Kienzl, N., Soeroes, C., Fodor, P., Váradi, L., Raml, R., Goessler, W., Kuehnelt, D., 2006. Arsenic speciation in freshwater organisms from the river Danube in Hungary. Talanta, 69 (4): 856-865.

Schaufuss A.G., Nesbitt H.W., Scaini M.J., Hoechst H., Bancroft M.G., Szargan R., 2000. Reactivity of surface sites on fractured arsenopyrite (FeAsS) toward oxygen. American Mineralogist, 85: 1754–1766.

Scheinost, A.C., Chavernas, A., Barro´n, V., Torrent, J., 1998. Use and limitations of second-derivative diffuse reflectance spectroscopy in the visible to near-infrared range to identify and quantify Fe oxide minerals in soils. Clays Clay Miner., 46: 528–536.

Scheinost, A.C., Schwertmann, U., 1999. Color identification of iron oxides and hydroxysulfates: use and limitations. Soil Science Society of America Journal, 63: 1463–1471.

Schmetzer, K., Medenbach, O., 1986. Kaatialaite from Nieder-beerbach, Odenwald – a second occurrence.- Neues Jahrbuch für Mineralogie und Geologie, Monatshefte, 8: 337-342.

Scholz, F., Meyer, B., 1998. Voltammetry of solid microparticles immobilized on electrode surfaces, in: A.J. Bard, I. Rubinstein (Eds.), Electroanalytical Chemistry - A series of Advances 20, Marcel Dekker, New York, 1-86.

Schulze, D.G., 1981. Identification of soil iron oxide minerals by differential X-ray diffraction. Soil Science Society of America Journal, 45: 437–440.

Schulze, D.G., 1994. Differential x-ray diffraction analysis of soil material. In Quantitative methods in soil mineralogy. SSSA Miscellaneous Publication, 412–429.

Schwertmann, U., Taylor, R.M., 1989. Iron Oxides, Minerals in Soil Environments (2nd edition). SSSA Book Series, vol. 1. Soil Science Society of America, Madison, WI, 379–438.

Sidenko, N.V., Pospelova, L.N., Stolpovskaja, V.N., 1998. Secondary minerals and compounds of toxic elements precipitated from drainage water of Berikul sulphide wastes. Mineralogical Magazine, 62A: 1398-1399.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 17 (5): 517–568.

Smith, E., Naidu, R., Alston, A.M., 1998. Arsenic in the soil environment: a review. Advances in Agronomy, 64: 149–195.

Smith, E., Naidu, R., Alston, A.M., 1999. Chemistry of arsenic in soils: I. Sorption of arsenate and arsenite by four Australian soils. Journal of Environmental Quality, 28: 1719–1726.

Smith, E., Naidu, R., Alston, A.M., 2002. Chemistry of inorganic arsenic in soils: II. Effect of Phosphorus, Sodium, and Calcium on arsenic sorption, Jornal of Environmental Quality, 31: 557-563.

Smith, P.G., Koch, I., Gordon, R.A., Mandoli, D.F., Chapman, B.D., Reimer, K.J., 2005. X-ray absorption near-edge structure analysis of arsenic species for application to biological environmental samples. Environmental Science & Technology, 39 (1): 248-254.

Smith, A.M.L., Dubbin, W.E., Wright, K., Hudson-Edwards, K.A., 2006. Dissolution of lead- and lead–arsenic-jarosites at pH 2 and 8 and 20 °C: Insights from batch experiments. Chemical Geology, 229 (4): 344-361.

Smuda, J., Dold, B., Friese, K., Morgenstern, P., Glaesser, W. 2007. Mineralogical and geochemical study of element mobility at the sulfide-rich Excelsior waste rock dump from the polymetallic Zn-Pb-(Ag-Bi-Cu) deposit, Cerro de Pasco, Peru. Journal of Geochemical Exploration 92 (2-3): 97-110.

Sohrin, Y., Matsui, M., Kawashima, M., Hojo, M., Hasegawa, H., 1997. Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan. Environmental Science & Technology, 31: 2712-2720.

Stefanakis, M., Kontopoulos, A., 1988. Production of environmentally acceptable arsenites-arsenates from solid arsenic trioxide. In: Reddy, R.G., Hendrix, J.L., Queneau, P.B. (Eds.), Arsenic Metallurgy, Fundamentals and Applications. Metall. Soc. Inc., TMS, Warerendale PA, 287–304.

Stolz, J.F., Oremland, R.S., 1999. Bacterial respiration of arsenic and selenium. FEMS Microbiological Review, 23 (5): 615–627.

Strawn, D., Doner, H., Zavarin, M., McHugo, S., 2002. Microscale investigation into the geochemistry of arsenic, selenium, and iron in soil developed in pyritic shale materials. Geoderma, 108: 237-257.

Stöhrer, G., 1991. Arsenic: oportunity for risk assessment, Toxicology, 65: 525-531.

Strunz, H., Nickel, E.H., 2001. Strunz mineralogical tables: chemical-structural mineral classification system, 9th eds. Schweizerbart, Stuttgart: 870 p.

Stumm, W., 1992. Chemistry of the solid-water interface. Wiley, New York. 428 p.

Sun, X., Doner, H.E., 1996. An investigation of arsenate and arsenite bonding structures on goethite by FTIR. Soil Sci. ,161 (12): 865–872.

Sverjensky, D.A., Fukushi, K., 2006. A predictive model (ETLM) for As(III) adsorption and surface speciation on oxides consistent with spectroscopic data. Geochimica et Cosmochimica Acta, 70 (15): 3778-3802.

Swash, P.M., Monhemius, A.J., 1996. The characteristic of calcium arsenate compounds relevant to the disposal of arsenic from industrial processes. Mineral Metals and the Environment II, IMM: 353-361.

Swash, P.M., Monhemius, A.J., 1994. Hydrothermal precipitation from aqueous solutions containing iron (III), arsenate and sulphate. In: Hydrometallurgy `94. Chapman and Hall, New York: 177-190.

Swash, P.M., Monhemius, A.J., 1995. Synthesis, characterisation and solubility testing of solids in the Ca-Fe-AsO_4 system. Sudbury `95 (Mining and the Environment Sudbury Ontario May 28 - June 1 1995) Proceedings: 17-28.

Škvor, V., 1960. Poznámky k petrografii ložiska Přebuz v Krušných horách. Věstník Ústředního Ústavu geologického, 35: 43-54 (in Czech).

Šrein, V., Šťastný, M., Šreinová, B., 1999. Skorodit z Přebuzi. Bulletin mineralogicko-petrologického oddělení Národního muzea (Praha), 7: 218-220. (in Czech).

Šucha, V., Dubiková, m., Cambier, P., Elsass, F., Pernes, M., 2002. Effect of acid mine drainage on the mineralogy of a dystric cambisol. Geoderma. 110: 151-167.

Taggart, M.A., Carlisle, M., Pain, D.J., Williams, R., Osborn, D., Joyson, A., Meharg, A.A., 2004. The distribution of arsenic in soils affected by the Aznalcóllar mine spill, SW Spain. Science of the Total Environment, 323 (1-3): 137-152.

Tamura, N., Celestre, R.S., MacDowell, A.A., Padmore, H.A., Spolenak, R., Valek, B.C., Chang, N.M., Manceau, A., Patel, J.R., 2002. Submicron x-ray diffraction and its applications to problems in materials and environmental science. Review of Scientific Instruments, 73 (3): 1369-1372.

Taylor, D.G., Nenadic, C.M. and Crable, J.V., 1970. Infrared spectra for mineral identification. Amer. Ind. Hyg. Ass., J., 31 (1): 100-108.

Terlecka, E., 2005. Arsenic speciation analysis in water samples: a review of the hyphenated techniques. Environmental Monitoring and Assessment, 107: 259-284.

Thanabalasingam, P., Pickering, W.F., 1986. Arsenic sorption by humic acids. Environmental Pollution, 12: 233-246.

Thornburg, K., Sahai, N., 2004. Arsenic occurrence, mobility, and retardation in sandstone and dolomite formations of the Fox River Valley, eastern Wisconsine. Environmental Science & Technology, 38 (19): 5087-5094.

Tlustoš, P., Gössler, W., Száková, J., Pavlíková, D., Balík, J., 2004. Arsenic compounds in the leaves and roots of radish grown in three soils treated by dimethylarsinic acid. Plant Soil Environ., 50 (12): 540-546.

Tomášek, M., 1990. Soil classification used on soil maps of Czech Republic to a scale 1:50,000. Scientia agriculturae bohemoslovaca. 2: 77-84. (in Czech).

Tse, J.S., 2002. Powder and single diffraction using synchrotron radiation. In Synchrotron Radiation: Earth, Environmental and Materials Sciences Applications (G. Henderson, D.R. Baker, eds.) Mineral. Assoc. Can. Short Course, 30: 46-63.

Tuddenham, W.M., Lyon R.P., 1960. Infrared techniques in the identification and measurement of minerals. Anal. Chem., 32: 1630-1634.

Turpeinen R., Pantsar-Kallio., M., Haggblom M., Kairesalo T., 1999, Influence of microbes on the mobilization, toxicity and biomethylation of arsenic in soil, Science of Total Environment, 236 (1-3): 173-180.

Turpeinen, R., Pantsar-Kallio, M., Kairesalo, T., 2002. Role of microbes in controlling the speciation of arsenic and production of arsines in contaminated soils. Science of Total Environment, 285 (1-3): 133-145.

USEPA, 2001. EPA announces arsenic standard for drinking water of 10 ppb. EPA 815-F-01-010. 31 Oct. 2001. U.S. Gov. Print Office, Washington, D.C.

Utsunomiya, S., Peters, S.C., Blum, J.D., Ewing, R.C., 2003. Nanoscale mineralogy of arsenic in a region of New Hampshire with elevated As-concentrations in the groundwater. American Mineralogist, 88: 1844-1852.

Vahter, M., Li, L., Nermell, B., Rahman, A., El Arifeen, S., Rahman, M., Persson, L.A., Ekström, E.-Ch., 2006. Arsenic, a global public health problem. Toxicology Letters, Volume 164, Supplement 1, 20 September 2006, Page S45

Van der Veen, N.G., Keukens, H.J., Vos, G., 1985. Comparison of ten digestion procedures for the determination of arsenic in soils by hydride - generation atomic absorption spectrometry. Analytica Chimica Acta, 171: 285-291.

van Elteren, J.T., Šlejkovec, Z., Arčon, I., Glass, H.J., 2006. An interdisciplinary physical-chemical approach for characterization of arsenic in a calciner residue dump in Cornwall (UK). Environmental Pollution, 139 (3): 477-488.

Van Geen, A., Robertson, A.P., Leckie, J.O., 1994. Complexation of carbonate species at the geothite surface: implications for adsorption of metal ions in natural waters. Geochimica et Cosmochimica Acta, 58 (9): 2073–2086.

Van Herreweghe, S., Swennen, R., Vandecasteele, C., Cappuyns, V., 2003. Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. Environmental Pollution, 122 (3): 323-342.

van Oorschot, I.H.M., Grygar, T., Dekkers, M.J., 2001. Detection of low concentrations of fine-grained iron oxides by voltammetry of microparticles. Earth Planet. Sci. Lett., 193: 631–642.

Vaughan, D.J., Pattrick, R.A., Wogelius, R.A., 2002. Minerals, metals and molecules: ore and environmental mineralogy in the new millennium. Mineralogical Magazine, 66: 653-676.

Vaughan, D.J., 2006. Arsenic. Elements. 2: 71-75.

Vink, B.W., 1996. Stability of antimony and arsenic compounds in the light of revised and extended Eh-pH diagrams. Chemical Geology. 130 (1-2): 21-30.

Vodyanitskii, Y., N., 2006. Arsenic, Lead, and Zinc Compounds in Contaminated Soils according to EXAFS Spectroscopic Data: A Review. Eurasian Soil Science. 39 (6): 611-621.

Voigt, D.E., Brantley, S.L., Hennet Remy, J.-C. 1996. Chemical fixation of arsenic in contaminated soils. Applied Geochemistry, 11 (5): 633-643.

Wakao N., Koyatsu H., Komai Y., Shimokawara H., Sakurai Y., Shiota H., 1988. Microbial oxidation of arsenite and occurrence of arsenite-oxidizing bacteria in acid mine water from a sulfur-pyrite mine, Geomicrobiology Journal, 6 (1): 11-24.

Walenta, K., 1966. Beiträge zur Kenntnis seltener Arsenatmineralien unter besonderer Berücksitsung von Vorkommen des Schwarzwaldes. Tschermaks Mineralogische und Petrologische Mitteilungen, Wien, 11 (1-2): 121-124.

Walenta, K., 1994. Über den Barium-Pharmakosiderit. Aufschluss, 45: 73-81.

Walker, S.R., Jamieson, H.S., Lanzirotti, A., Andrade, C.F., Hall, G.E.M., 2005. The speciation of arsenic in iron oxides in mine wastes from the Giant gold mine, N.W.T.: application of synchrotron micro-XRD and micro-xanes at the grain scale. The Canadian Mineralogist, 43 (4): 1205-1224.

Walker, F.P., Schreiber, M.E., Rimstidt, J.D., 2006. Kinetics of arsenopyrite oxidative dissolution by oxygen. Geochimica et Cosmochimica Acta, 70 (7): 1668-1676.

Walsh, L.M., Keeney, D.R., 1975. Behaviour and phytotoxicity of inorganic arsenic in soils. In: Arsenical pesticides (E.A., Woolson, ed.). 35-53. Am. Chem. Soc Washington, D.C.

Walsh, L.M., Summer, M.E., Keeney, D.R., 1977. Occurrence and distribution of arsenic in soils and plants. Environmental Health Perspectives, 19: 67-71.

Wang, L.F., Liu, H.D., Lin, F.F., Su, M.Y., Xu, X.F., Sun, X.Z., Aihaidi, Ma, L., Yang, Y., Huang, Z.W., 1993. Endemic arsenism in a village of Xinjiang: epidemiology, clinical and preventive studies for 9 years. Endemic Diseases Bulletin, 8: 71–78.

Wang, S., Mulligan, C.N., 2006. Natural attenuation processes for remediation of arsenic contaminated soils and groundwater. Journal of Hazardous Materials, 138 (3): 459-470.

Warwick, P., Inam, E., Evans, N., 2005. Arsenic´s Interaction with Humic Acid. Environmental Chemistry, 2: 119-124.

Waychunas, G.A., Rea, B.A., Fuller, C.C., and Davis, J.A., 1993. Surface chemistry of ferrihydrite--Part 1--EXAFS studies of the geometry of coprecipitated and adsorbed arsenate: Geochimica et Cosmochimica Acta, 57: 2251-2269.

Weber, P.A., Stewart, W.A., Skinner, W.M., Weisener, C.G., Thomas, J.E., Smart, R.St.C., 2004. Geochemical effects of oxidation products and framboidal pyrite oxidation in acid mine drainage prediction techniques. Applied Geochemistry, 19 (12): 1953-1974.

Wedepohl, K.H., 1991. The composition of the upper Earth's crust and the natural cycles of selected metals. In: Metals and Their Compounds in the Environment (E. Merian, ed.), 3-17. VCH-Verlagsgesellschaft, Weinheim.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta, 59 (7): 1217-1232.

Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Analytica Chimica Acta, 436: 309-323.

Weldon, J.M., MacRae, J.D., 2006. Correlations between arsenic in Maine groundwater and microbial populations as determined by fluorescence in situ hybridization. Chemosphere, 63 (3): 440-448.

Weisener, Ch.G., 2003. Novel spectroscopic techniques to characterize mine waste. In Environmental aspects of mine wastes (J.L. Jambor, D.W. Blowes and A.I.M. Ritchie, eds.). Mineral. Assoc. Can. Short Course Vol. 31: 181-202.

White G.N., Dixon J.B., 1995. Scanning electron microscopy of minerals in soils. TSEM Journal, 26 (1): 9-11.

WHO, 1993. Guidelines for drinking-water quality. Volume 1: Recommendations. Second edition, World Health Organisation, Geneva.

Wilkin, R.T., Wallschlager, D., Ford, R.G., 2003. Speciation of arsenic in sulfidic waters. Geochem. Trans., 4 (1): 1–7.

Villalobos, M., Leckie, J.O., 2001. Surface complexation modeling and FTIR study of carbonate adsorption to goethite. Journal of Colloid and Interface Science, 235 (1): 15-32.

Williams, P.A., 1990. Oxide zone geochemistry. Ellis Horwood: 286 p.

Williams, M., 2001. Arsenic in mine waters: an international study. Environmental Geoogy, 40 (3): 267-278.

Williams, A.G.B., Scheckel, K.G., Tolaymat, T., Impellitteri, Ch.A., 2006. Mineralogy and Characterization of Arsenic, Iron, and Lead in a Mine Waste-Derived Fertilizer. Environmental Science & Technology, 40: 4874-4879.

Williams, A.G.B., Scheckel, K.G., Tolaymat, T., Impellitteri, Ch., 2006. Mineralogy and Characterization of Arsenic, Iron, and Lead in a Mine Waste-Derived Fertilizer. Environmental Science & Technology, 40: 4874-4879.

Violante, A., Pigna, M., 2002. Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil Science Society of America Journal, 66: 1788–1796.

Wilson, G.C., Rucklidge, J.C., Campbell, J.L., Nejedly, Z., Teesdale, W.J., 2002. Applications of PIXE to mineral characterization. Nuclear instruments & methods in physics research section B-beam interactions with materials and atoms, 189: 387-393.

Woolson, E.A., 1977. Fate of arsenicals in different environmental substrates. Environmental Health Perspectives, 19: 73-81.

Xu, H., Allard, B., Grimvall, A., 1988. Influence of pH and organic substance on the adsorption of As(V) on geologic materials. Water, Air & Soil Pollution, 40: 293–305.

Yan-Chu, H., 1994. Arsenic distribution in soils. In: Arsenic in the Environment, Part I: Cycling and Characterization (J.O. Nriagu, ed.), 17-49. Wiley and Sons, New York.

Yu, Y.M., Zhu, Y.X., Williams-Jones, A.E., Gao, Z.M., Li, D.X., 2004. A kinetic study of the oxidation of arsenopyrite in acidic solutions: implications for the environment. Applied Geochemistry, 19 (3): 435-444.

Zachara, J.M., Kukkadapu, R.K., Fredrickson, J.K., Gorby, Y.A., Smith, S.C., 2002. Biomineralization of poorly crystalline Fe(III) oxides by dissimilatory metal reducing bacteria (DMRB). Geomicrobiological Journal, 19 (2) : 179–207.

Zachariáš, J., Frýda, J., Paterový, B., Mihaljevič, M., 2004. Arsenopyrite and As-bearing pyrite from the Roudny deposit, Bohemian Massif. Mineralogical Magazine, 68 (1): 31-46.

Zhang, W., Cai, Y., Tu, C., Mab, L.Q., 2002. Arsenic speciation and distribution in an arsenic hyperaccumulating plant. Science of the Total Environment, 300 : 167–177.

Zhang, W., Singh, P., Paling, E., Delides, S., 2004. Arsenic removal from contaminated water by natural iron ores. Minerals Engineering, 17 (4): 517-524.

Zoubek, V., 1951. Předběžná zpráva o geologickém výzkumu a mapování oblasti karlovarského plutonu. Věstník Ústředního Ústavu geologického, 36: 166-179. (in Czech).

Zobrist, J., Dowdle, P.R., Davis, J.A., Oremland, R.S., 2000. Mobilization of arsenite by dissimilatory reduction of adsorbed arsenate. Environmental Science & Technology, 34: 4747–4753.

Zucchiatti, A., Bouquillon, A., Katona, I., D'Alessandro, A., 2006. The 'della Robbia blue': A case study for the use of cobalt pigments in ceramics during the Italian renaissance. Archeometry, 48: 131-152.

CURRICULUM VITAE of Michal Filippi

Date and place of birth:

February 12, 1974; Louny, Czech Republic

Education and degrees attended:

Masters Degree, Faculty of Science, Charles University Prague, 1997 - 1999

Bachelors Degree, Faculty of Science, Charles University Prague, 1994 - 1997

Secondary education, Gymnasium of Václav Hlavatý, Louny, 1989 - 1993

Professional career:

since 2000: Research worker at the Department of Exogenic Geology and Geochemistry; Institute of Geology, v.v.i., Academy of Science of the Czech Republic, Prague

1997-1999: Assistant at the Department of Geofactors, Institute of Rock Structure and Mechanics, v.v.i., Academy of Science of the Czech Republic, Prague

Selected main projects:

2007-2009: Speciation and mobility of arsenic in the soil – water system in locality affected by historical mining; Czech title: Speciace a mobilita arsenu v systému půda – voda na lokalitě postižené historickou důlní (Grant Agency of the Academy of Sciences of the Czech Republic; leader: M. Filippi, co-leader: P. Drahota.

2005-2007: Evolution and dynamics of the salt karst in Zagros Mts., Iran: Denudation rates, age of karst forms, governing factors; Czech title: Vývoj a rychlosti procesů v solném krasu v pohoří Zagros, Irán: rychlosti enudace, stáří krasových jevů a řídící faktory (Grant Agency of the Academy of Sciences of the Czech Republic); leader: J. Bruthnas, co-leader: M. Filippi.

2000-2002: Elemental mobility in the oxidation zone of mineral deposits in temperate zone climatic conditions of Central Europe; Czech title: Mobilita prvků v oxidační zóně ložisek rud v podmínkách mírného klimatu střední Evropy (Rio Tinto Technology Development, Charles University); leader: Z. Pertold.

Selected workshops:

Experimental methods in X-ray diffraction and neutron structural analyses. June 17–21, 2002, Czech and Slovak Crystallographic Association, Ostravice, Czech Republic.

Mineralogy of the Bohemian Massif and Western Carpathians. May 29–31, 2002, Palacký University, Petrov nad Desnou, Olomouc, Czech Republic.

Accessory minerals. January 17–18, 2001, Masaryk University, Brno, Czech Republic.

SELECTED CONFERENCES:

Arsenic topic

Filippi M.: Concentration of selected arsenate minerals from soils using heavy liquids. *oral presentation*: ***Conference of postgraduate students and young scientist***, April 24–25, 2003, Herlany, Komenský University, Bratislava, Slovakia; abstract in Geovestník, 36 (1), pp. 6, in Mineralia Slovaca, 36 (1), 2004.

Filippi M.: Arsenic mineralogy at the anthropogenic deposit at the Přebuz mine (Bohemian Massif). *oral presentation*: ***Conference of postgraduate students and young scientist***, April 8–9, 2002, Komenský University, Herlany, Bratislava, Slovakia; abstract in Geovestník, 34 (1), pp. 4-5, in Mineralia Slovaca, 34 (1), 2002.

Filippi M.: Changes in arsenic bound and arsenic migration during the weathering of löllingite and arsenopyrite (Case study from the Přebuz arsenic deposit, Krušné hory Mts.). *poster:* ***Czech economic geology at the beginning of the 3rd millennium***, May 20, 2002, Charles university, Prague, Czech Republic.

Filippi M.: Arsenic secondary mineralization in contaminated soils at the Mokrsko locality (Bohemian Massif). *oral presentation*: ***Conference of postgraduate students and young scientist***, April 23–24, 2001, Komenský University, Herlany, Bratislava, Slovakia; abstract in Geovestník, 33 (2), pp. 13, in Mineralia Slovaca, 33 (2), 2001.

Filippi M.: Geochemistry and mineralogy of arsenic in the Quaternary covers of the Mokrsko, Roudný and Kašperské hory deposits. *oral presentation*: ***The 5th student conference***, February 16, 2001, Masaryk university, Brno, Czech Republic.

Other geological topics

Bruthans J., Asadi, N., **Filippi M.**: Salt karts in Iran, longets salt cave in the world. *invited lecture*: ***3th Third ever Persian Gulf cultural tourism symposium***, April 30, 2007, Qeshm free zone area, Shiraz University, Qeshm. Iran.

Filippi M., Bruthans J., Bosák, P., Zare M.: A preliminary note on a various types of chemogenic infillings from halite karst, SE Zagros Mts., Iran. *poster*: ***13th International karstological school***, June 26-29, 2000, Karst Research Institute ZRC SAZU, Postojna. Slovenia.

Bruthans J., **Filippi M.**: Thickness of caprock and other important factors affecting morphogenesis of salt karst. *oral presentation*: ***8th International karstological school***, June 26-29, 2000, Karst Research Institute ZRC SAZU, Postojna. Slovenia.

Bruthans J., **Filippi M.**, Šmíd J.: Thickness of caprock and other important factors affecting morphogenesis of salt karst. *oral presentation and poster*: ***4th Europian congress of speleological expeditions (EXPLO)***, May 29 – May 1, 2000, Profondeville, Belgium.

SELECTED PAPERS (*publication in journal with impact factor):

Arsenic topic

Filippi M.**, Doušová B., Machovič V. (2007): Mineralogical speciation of arsenic in soil above the Mokrsko-west gold deposit, Czech Republic. ***Geoderma, 139 (1-2): 154-170.

Filippi M., Machovič V., Kristek J., Pavlíček R. (2005): Farmakosiderit z Přebuzi.- ***Bull. mineral.- petrolog. Odd. Nár. Muz.*** (Praha) 13: 129-132. Praha.

Filippi M.**, (2004): Oxidation of the arsenic-rich concentrate at the Přebuz abandoned mine (Erzgebirge Mts., CZ): mineralogical evolution. ***Science of the Total Environment, 322, 271-282.

Filippi M.**, Goliáš V., Pertold Z. (2004): Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ). ***Environmental Geology, 45/5, 716-730.

Filippi M., (2001): Výzkum arsenové deponie na lokalitě Přebuz - druhý výskyt kaatialaitu v České Republice. ***Bull. mineral.- petrolog. Odd. Nár. Muz.*** (Praha), 9, 188-190.

Filippi M., Goliáš V., (2001): Studium podmínek stability sekundárních minerálů s arsenem v antropogenních deponiích na ložisku Roudný. ***Bull. mineral.- petrolog. Odd. Nár. Muz.*** (Praha), 9, 190-199.

***Doušová, B., Martaus A., **Filippi M.**, Kloušek D., Švorčíková J., (in review): Stability of arsenic species in soils contaminated naturally and in an anthropogenic manner. *Water, Air and Soil Pollution*.

***Filippi M.**, (in prep): Determination of As-bearing minerals in contaminated soils and mine wastes – a review.

***Drahota P., Rohovec J., Rychlovský P., Červený V., Mihaljevič M., **Filippi M.**, Pertold Z., (in prep). Mineralogical and geochemical controls on arsenic mobility in and around gold deposit: A case study

Other geological topics

Bruthans J., Asadi N., **Filippi M.**, Vilhelm Z., (in press): Erosion rates of salt diapirs surfaces: An important factor for development of morphology of salt diapirs and environmental consequences (Zagros Mts., SE Iran). ***Environmental Geology

Bruthans J., **Filippi M.**, Geršl M., Zare M., Melková J., Pazdur A., Bosák P. (2006): Holocene marine terraces on two salt diapirs in Persian Gulf (Iran): age, depositional history and uplift rates. ***Journal of Quaternary Science. 21, 8: 843-857.

Filippi M., Hyršl J., (2004): Aragonite from Cicov hill in the Czech Republic. ***Mineralogical Record***, 35/2, 137-142.

Filippi M., (2002): Melanoflogit - vzácný polymorf hmoty SiO_2 a jeho druhý výskyt v České republice. ***Bull. mineral.- petrolog. Odd. Nár. Muz.*** (Praha), 10, 120-130.

Filippi M. (2001): Zpráva o výskytu různých morfologických forem aragonitu v Lounském středohoří. ***Bull. mineral.- petrolog. Odd. Nár. Muz.*** (Praha), 9, 76-81.

Bruthans J., Šmíd J., **Filippi M.**, Zeman O., (2000): Thickness of caprock and other important factors affecting morphogenesis of salt karst. ***Acta Carsologica***, 29/2, 51-64.

Bosák P., Bruthans J., **Filippi M.**, Svoboda T., Šmíd J., (1999): Karst and Caves in the Salt Diapirs, SE Zagros Mts., Iran. ***Acta Carsologica***, 28/2, 41-75.

***Bruthans J., **Filippi M.**, Zare M., Adamovič J., Churáčková Z., Vilhelm Z., Asadi N., (in prep). Mature salt karst in the Persian Gulf (Iran): Evolution under diapirs uplift and sea level oscillations. *Geomorphology*

Professional and popular

Filippi M., Bruthans J., Vilhelm Z., Zare M., Asadi N., (2006): La grotte 3N, Iran (6 580 m): le nouveau record du monde de la plus longue cavité dans le sel. ***Spelunca***, 104, 15-18.

Bruthans J., **Filippi M.**, Zare M., Asadi N., Vilhelm Z., (2006): 3N Cave (6580 m): Longest salt cave in the world. ***The NSS news***. National Speleological Society. 64, 9: 10-18.

Filippi M., (2004): Minerály - stavební jednotky Země. - In: Kolektiv, ***Živel Země***, Agentura Koniklec, Praha. 368 pp. (ISBN 80-902606-5-9), 88-93.

Filippi M., (2004): Solný kras. - In: Kolektiv, ***Živel Země***, Agentura Koniklec, Praha. 368 pp. (ISBN 80-902606-5-9), 84-85.

Filippi M., Bruthans J., Vašíček M., (2002): Mineralien aus den Salz-Diapiren von Hormoz, Namakdan und Khurgu, Zagros-Berge, Süd-Iran. ***Mineralien Welt***, 13 (1), 60-72.

Bruthans J., **Filippi M.**, Šmíd J., (2002): Solný kras. ***Vesmír***, roč. 81, 12, 675-682.

Bruthans J., **Filippi M.**, Šmíd J., Palatinus L., (2002): Tří Naháčů and Ghar-e Daneshyu caves - The world´s second and fifth longest salt caves. ***The International Caver,*** 2002, 27-36.

SELECTED UNPUBLISHED REPORTS:

Filippi M. (2002): Annual report by Michal Filippi (2002) In: Pertold Z. (Eds.): Annual Progress Report on the Rio Tinto Technology Development Limited project: Elemental mobility in the oxidation zone of mineral deposits in temperate zone climatic conditions of central Europe - Projects for the academic year October 2001 to September 2002.

Filippi M. (2001): Annual report by Michal Filippi (2001) In Pertold Z. (Eds.): Annual Progress Report on the Rio Tinto Technology Development Limited project: Elemental mobility in the oxidation zone of mineral deposits in temperate zone climatic conditions of central Europe - Projects for the academic year October 2000 to September 2001.

Filippi M. (2001): Arsenic in the oxidation zone at Mokrsko gold deposit, Bohemian Massif (CZ).- Excursion guide for the Mokrsko locality to the SOCRATES – ERASMUS Environmental Geology – Intensive Course, Czech Republic, September 9–25, 2001, Masaryk University Brno (CZ), University of Bristol (UK), University of Freiberg.