

Chimia 51 (1997) 884–892
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ISSN 0009–4293

Characterization of Environmental Solids and Surfaces

Stephan J. Hug^{a)}*, Annette Johnson^{b)}, Gabriela Friedl^{c)},
Thomas Lichtensteiger^{b)}, Hasan Belevi^{b)}, and Michael Sturm^{d)}

Abstract. The characterization of the solid phase is one of the first steps in the study of any of the myriad of environmental reactions that involve solids and solid-liquid interfaces. Environmental solids range from relatively pure and crystalline phases to heterogeneous and multiphase particle aggregates whose characterization requires a combination of a number of analytical methods and methodologies. The first section of this paper gives a cross section of general strategies used in different departments at EAWAG for the characterization of field samples of both natural and anthropogenic origin. The morphological characterization and the determination of the chemical composition is described in respect to the properties of anthropogenic solids. As an example, the long-term behavior of incinerator bottom ash is discussed in a case study. A second section gives two examples of molecular level studies on environmental solids: application of Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy for the characterization of poorly crystallized manganese lake particles in the context of the genesis of lake sediments, and *in situ* Atomic Force Microscopy (AFM) and Fourier Transform Infrared (FTIR) studies on synthetic goethite particles during the oxidation of Fe^{II} and the reduction of Cr^{VI}.

Introduction

The surface of the earth ($5 \cdot 10^8 \text{ km}^2$) contains an estimated 10^{12} km^2 of mineral-water interfaces. These surfaces are constantly being renewed and changed in a biogeochemical cycling of elements between rocks, water, atmosphere, and biota. With industrialization, the fraction of material fluxes caused by human activities (anthropogenic fluxes) has reached similar proportions to the natural turnover. Large amounts of natural solids are consumed, processed, and returned to the environment in various forms. This has led to the contamination of natural solids and surfaces in soils and sediments as well as to the production of large amounts of potentially hazardous solid waste materials. Contamination of soils and sediments

has a direct and long-term impact on water quality. Human water use relies to a large extent on water purification by infiltration through soils, sediments, and rocks whose surfaces adsorb, retain, and incorporate pollutants. However, contaminated solids can also release hazardous compounds, particularly when solids dissolve, and small suspended particles (colloids) can transport pollutants over large distances. To be able to protect future water resources, processes in solids and on interfaces must be understood more completely than is currently the case. Given the complexity of natural solids and surfaces, this is a difficult task which ultimately requires an understanding of at least some of the key processes on a molecular level. To identify and to study these key processes requires complementary field and laboratory studies on different levels of complexity and detail. A first and indispensable step in these studies is a characterization of the solid phases and of their surfaces. While the characterization of the bulk structure of pure crystalline solids down to exact nuclear coordinates is possible, the characterization of poorly crystallized samples to the same level of detail is often impossible. Environmental samples usually consist of many components and phas-

es, all with an internal order from amorphous to various degrees of crystallinity. A meaningful characterization has to occur in the context of the environmental question of interest. This paper gives a brief cross section of methodologies used at EAWAG.

General Methodology for the Characterization of Solids in Soils, Sediments, and Rocks of Natural and Anthropogenic Origin

Morphology

Natural or anthropogenic sediments and rocks hold abundant environmental information. In order to use this potential, it is necessary to determine sources, texture, structure, and chemical composition of these solids. Morphological investigations focus on the macroscopic and microscopic characteristics of particles and of particle associations and provide information about the composition and origin of a sample. This information provides the framework to understand the biogeochemical processes that are involved in the formation and interaction of solids. For example, the texture and structure of lake sediments reveal information about transport mechanisms and diagenetic processes, which are essential to understand lake ecosystems. In anthropogenic sediments, it is important to know how particles are constituted and associated with respect to their origin and genesis in order to be able to understand the future behavior in deposits. The more precise this knowledge is, the better are the preconditions for optimizing the properties of anthropogenic deposits with respect to potential hazards and their potential use as future resources [1]. Thus, geological and petrological investigations are an integral part of studies which aim to understand and influence the processes controlling environmental and anthropogenic systems.

Commonly, morphological investigations already begin during field work:

- Macroscopic identification of lithological facies
- Definition of medium- to macro-scale structures, tectonic position, sedimentary deposition
- Determination of *in situ* parameters (e.g. climatic or engineering parameters).

Representative subsamples are then measured in subsequent laboratory work. This includes the determination of solid density, porosity, grain sizes, mineralogical and chemical composition. Various techniques, both, simple/low-cost meth-

*Correspondence: Dr. S.J. Hug
EAWAG

Überlandstrasse 131
CH-8600 Dübendorf

^{a)} Department of Chemistry

^{b)} Department of Resource and Waste Management

^{c)} Department of Biogeochemistry

^{d)} Department of Environmental Physics

ods and complex/highly sophisticated procedures can be used to complete these investigations. A list of important methods is given in *Table 1*.

Solid Density/Porosity

Simple techniques, such as determination of wet and dry sample weights, and simple pycnometer measurements are sufficient for these parameters.

Grain-Size Analysis

Many techniques can be applied to determine the different size parameters. Sieving and settling techniques are the more simple methods. The more advanced techniques include analyses with automated instruments, such as Sedigraph, Coulter Counter, Flow Field Diffraction, Laser-light scattering and others (see also *Table 1*).

Optical Microscopy

Optical or petrographic microscopy of solids is a common method in earth and material sciences. Diascopic (transmitted light) and episcopic (reflected light) polarizing microscopes are important tools in solid investigations. One of the main advantages of microscopic investigations is that the existing framework and thus the particles or even the particle distribution are not disturbed. Environmental investigations often deal with unconsolidated or poorly consolidated sediments or highly

porous materials. Often, initial impregnation and embedding in transparent resins is necessary, after which thin sections, peels, and slices can be analyzed.

A thin section of an embedded sample of conventional Municipal Solid Waste Incinerator (MSWI) bottom ash is shown in *Fig. 1, a* (diascopic). *Fig. 1, b* (episcopic) shows a polished section of an embedded sample from an advanced high-temperature waste treatment plant.

Within these samples, all particles are in their original context and their shape and the spatial relationship to each other allows the distinction between relevant and nonrelevant particles with respect to the thermal treatment process. This provides preliminary information on process efficiency as well as on the future behavior in an environmental compartment. In the MSWI sample shown in *Fig. 1, a*, mixed particles are aggregated with molten products generated in the grate system. After cooling, the molten zones consist of a glassy matrix with needle-like silicate crystals, dendritic oxide crystals (typical for rapid solidification), and various inclusions (mainly iron, black color). The glassy matrix is very unstable under landfill conditions. During alteration, the glassy phases hydrate and decompose. As a consequence, secondary gels are deposited in the pore spaces [3][5]. The obvious advantage of advanced high-temperature treatment (*Fig. 1, b*) is the separation and

the homogeneity of the products and the potential for the reuse of the silicates and the metals [2][3].

By using special techniques to study fabrics and textures (geometrical relationship among particles), and mineralogy (phases and phase associations), information about the sequence of events that lead to the formation of a specimen can be extracted (petrogenesis). Some of these techniques are quantitative, many are qualitative and descriptive. Quantification can be elaborated statistically and in combination with other methods and approaches.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

Complementary to optical microscopy, solids, interfaces, and pore fillings can be examined by SEM. Sediment and rock analysis with SEM has become a widely used and convenient technique applied in various environmental studies and investigations. SEM offers the advantage of greater depth of focus and much higher resolution (magnification) than optical microscopy. *Fig. 1, c* shows an SEM example for anthropogenic sediments.

The high depth of focus compared to optical microscopy is clearly apparent. An example how SEM/EDS techniques are used to determine the influence of entrophication of lake sediments is given in *Fig. 2, a and b*. Instruments equipped with

Table 1. List of Analytical Methods

No.	Analytical Method	Information	Spatial range/ resolution
1	Particle-size analysis – Flow Field Diffraction (FFD) – Sedigraph – Coulter Counter – Laser-Light Scattering, Photoncorrelation	– size distribution, separation – size distribution – size distribution – size distribution	0.5–100 µm 0.5–100 µm 0.5–100 mm 3 nm –5 µm
2	Optical microscopy	morphology, heterogeneity particle size, color, polarization properties	µm–cm
3	Transmission Electron Microscopy (TEM) Scanning Electron Microscopy (SEM)	morphology, heterogeneity particle size	1 nm–cm 10 nm–cm
4	SEM with Energy Dispersive Spectroscopy (EDS)	elemental composition	> 1 µm
5	Scanning Tunneling Microscopy Atomic Force Microscopy (AMF/STM)	surface structure/topography, atomic scale, <i>in situ</i> studies	> 0.2 nm
6	X-Ray Diffraction (XRD)	crystal structure (extended periodic structures)	mm (depending on sample preparation/beam diameter)
7	Extended X-Ray Absorption Fine Structure (EXAFS)	identification of solid local bulk and surface structures, <i>in situ</i> studies	mm (depending on sample preparation/beam diameter)
8	Fourier Transform Infrared Spectroscopy (FTIR)	solid identification, local bulk and surface structure, <i>in situ</i> studies	mm (depending on sample preparation/beam diameter)
9	Atomic Absorption Spectroscopy (AA) Inductively Coupled Mass- and Atomic Emission Spectroscopy (ICP-MS and ICP-AES)	elemental composition	

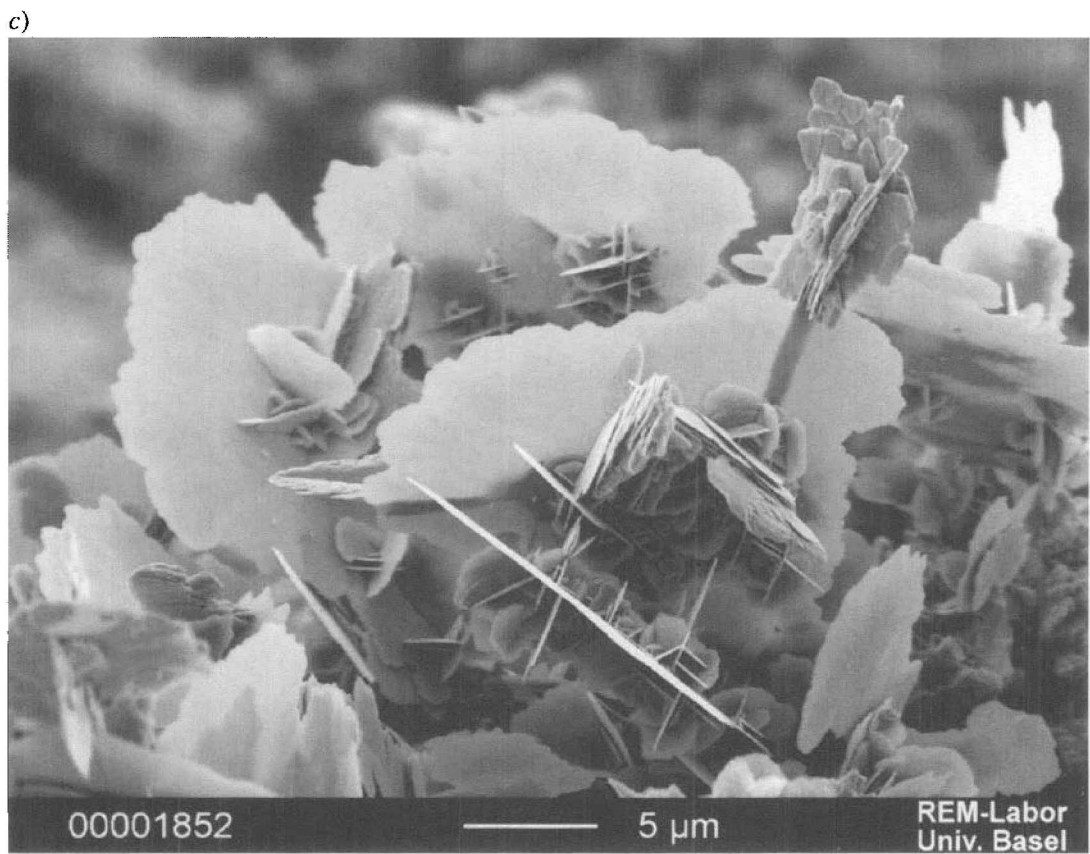
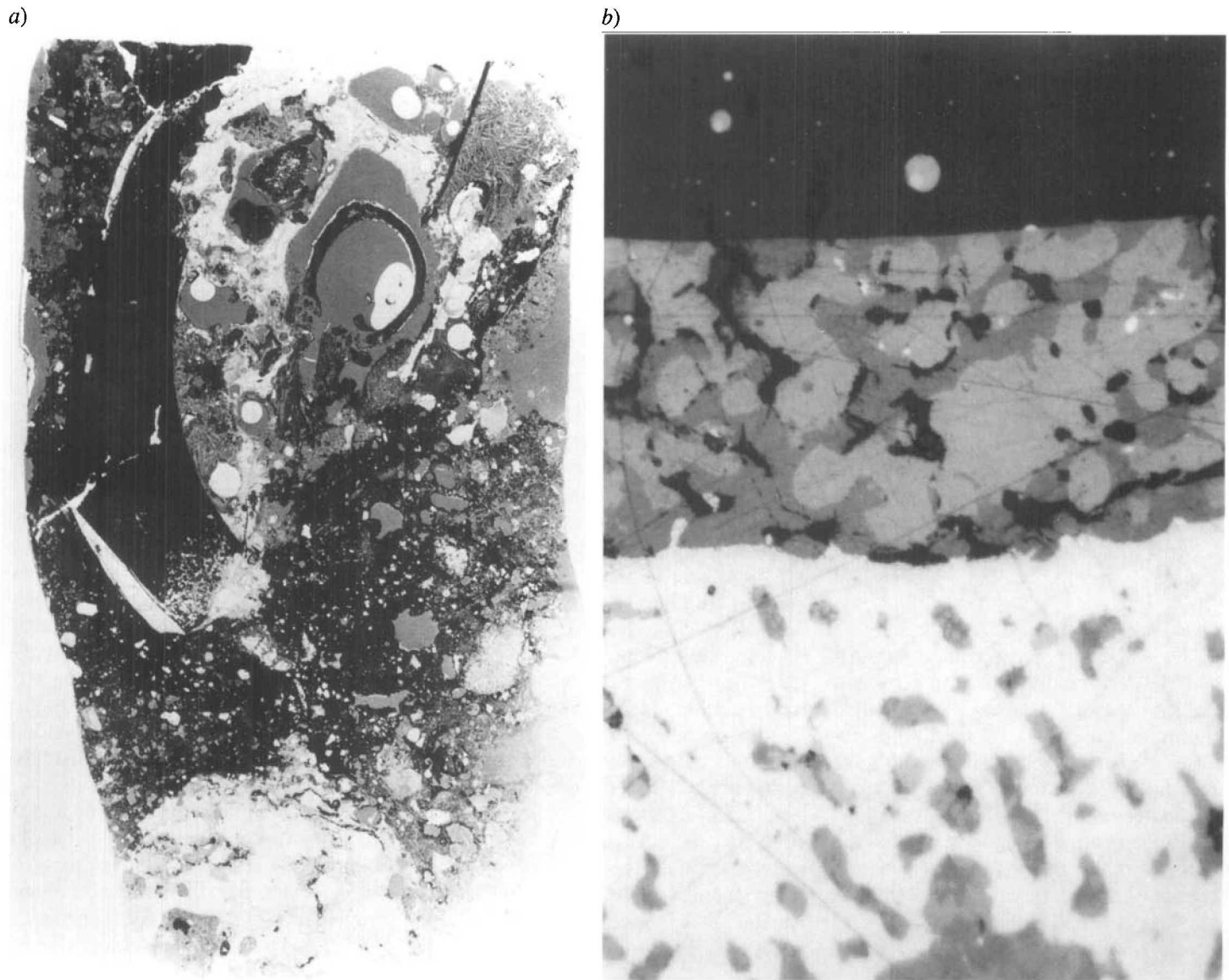


Fig. 1. a) A thin section of MSWI bottom ash showing a porous and heterogeneous assemblage of minerals, molten phases, and inclusions typical for grate systems (width of the picture 30 mm). b) An episcopic picture of the interface silicate/iron-copper-metal melt from a high-temperature MSWI treatment plant (width of the picture 0.2 mm). Normally only silicate and metal melts are formed. In this case the sulfur content of the system is large and a third layer is formed. Layers in order of their densities: above: silicate glass (dark) with settling metal droplets; in the middle: matte (Fe-Cu-sulfide; brown, violet); below: metal structure (white) with sulfides (brown, violet) [2]. c) A SEM image of a MSWI bottom-ash surface: CuS crystallization as a local temporary product of alteration during storage [3]. Overall oxidizing conditions result in sulfide oxidation in the long-term [4].

dispersive X-ray analysis system (EDS) are able to perform an elemental analysis of micron-sized regions by locally stimulating X-ray emission, whose spectra reveals the elemental composition. With high-resolution image analysis, modern software, and user-defined data bases, modern SEM/EDS instruments are able to analyze single particles, thin sections, coated surfaces, and fresh rock planes. These techniques reveal a large amount of relevant information about rock samples, unconsolidated sediment samples, and about individual particles.

X-Ray Powder Diffraction

X-Ray diffraction (XRD) is the most widely used method to determine the mineral structure and composition in solids [6]. At EAWAG, XRD is used in collaboration with ETHZ, or samples are characterized by XRD/SEM, and specific surface area at the Laboratorium für Elektronenmikroskopie at the University of Bern. Depending on the research objective and the solid composition, it is possible that the sample must be separated and the different fractions analyzed for components. Methods may include magnetic separation, as in the case of MSWI bottom ashes [7][8], density separation, or size fractionation techniques. Where the location of substances such as heavy metals is of interest, additional methods such as optical microscopy, PIXE, or SEM/EDAX are applied.

Chemical Composition

The first step undertaken is to determine the elemental content. Some analytical methods can be applied directly to a solid. However, most routine quantitative analytical measurements are performed on solutions. Typical procedures for the dissolution (digestion) of solid samples and subsequent analytical methods for the analysis of the solutions are listed in Table 2 [9].

The selection and preparation of a solid sample for analysis is an essential step. Drying (freeze-drying or heating) and sieving procedures are usually necessary, whereby care must be taken to minimize chemical changes. Procedures have to be adapted to the sample characteristics and the aim of the study. The elemental characterization requires a combination of analytical techniques, adopted for maximum recoveries and detection ranges and optimized for each sample type [9].

The next step in the characterization of a solid is the determination of the species of the constituents which are pertinent to the reactivity of the solid material. To-

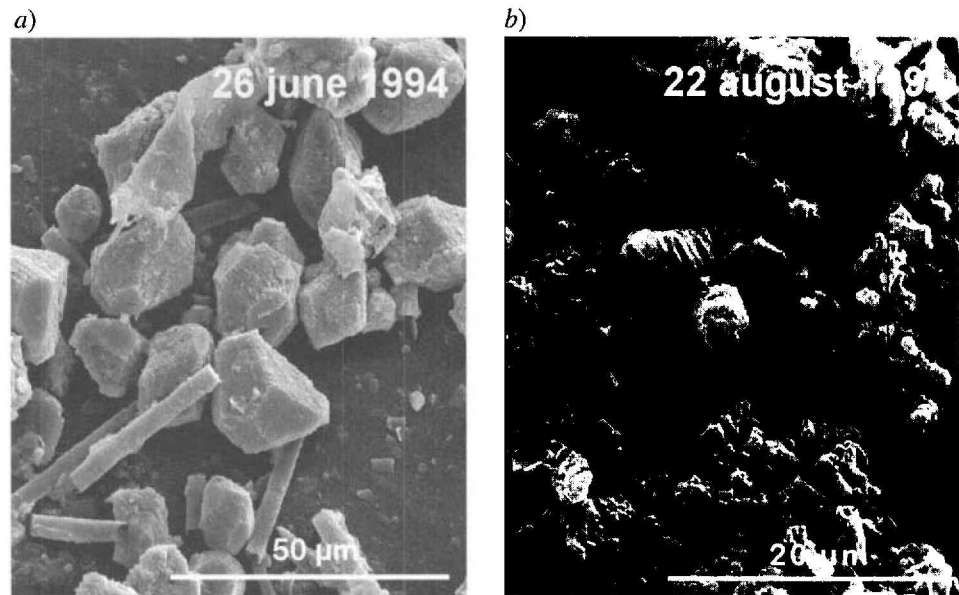


Fig. 2. a) SEM image of large diameter idiomorph calcite crystals (up to 50 µm), which occur regularly during early spring and summer in a lake. b) As the summer proceeds, calcite crystals become distinctly smaller and subcrystalline (diameters of < 5 µm). Determination of particle sizes of calcites allows the reconstruction of the trophic history of a lake system or artificial reservoir.

Table 2. Analytical Techniques to Determine the Elemental Content of Solid Samples

Wet digestion and extraction techniques:

- 1 Open system with Aqua Regia
- 2 Microwave digestion with a mixture of HF, HCl, HNO₃ and H₃BO₃
- 3 Digestion with sodium peroxide in a closed combustion system
- 4 Digestion in hot sodium hydroxide
- 5 Extraction with water
- 6 Dry ashing

Determination of element concentrations in solutions:

- 7 AAS, ICP-AES, ICP-MS, ion chromatography, potentiometry with ion-selective electrodes, colorimetry by flow injection analysis, polarography

Other methods

- 8 Wavelength-dispersive X-ray fluorescence spectrometry
- 9 Oxidation/reduction and subsequent gas chromatography for total carbon, nitrogen, and sulfur determination
- 10 Acidification of the sample and analysis of CO₂ by coulometry

Table 3. Element Concentrations in a MSWI Bottom-Ash Sample

Element	Concentration	
	Average [g/kg dry matter]	Standard deviation [g/kg dry matter]
TC	21	0.7
TIC	7.4	0.1
TOC	13.4	0.7
N	0.41	0.04
F	0.35	0.02
Na	27	1.7
Mg	17	0.3
Al	52	1.1
Si	198	1
P	3.4	0.1
S	1.4	0.3
Cl	3.7	0.2
K	8.9	0.3
Ca	130	1.4
Ti	7.2	0.14
Cr	1.5	0.06
Mn	1.0	0.02
Fe	85	1.1
Ni	0.26	0.01
Cu	2.4	0.25
Zn	2.8	0.06
Pb	1.6	0.1
Sn,Mo,Cd,Co,Hg	< 0.10	0.02

TC: Total carbon, TIC: Total inorganic carbon, TOC: Total organic carbon

gether with an understanding of the morphology and the origin of the material, the following step is to make hypotheses as to the most probable constituents. These are then tested in a combination of analytical techniques and experiments. The combination of methods selected will always be associated with the research objective. The following two examples of investigations on the long-term behavior of bottom ash should serve as illustrations.

Case Study: Characterization of Municipal Solid Waste Incinerator (MSWI) Bottom Ash

a) Elemental Composition

Table 3 shows an example of the element concentrations in an MSWI bottom ash sample (< 0.5-mm fraction dried at 40°) [10]. The major components (> 95%) of MSWI bottom ash are Si, Ca, Al, Fe, Na, Mg, K, and C. These components strongly affect the properties and provide insights into incinerator processes [10] and long-term geochemical behavior [11] [12] associated with the production and landfilling of these ashes. In order to gain an understanding of these processes, a high degree of accuracy with respect to the chemical composition is essential. The relative standard deviation ranges from less than 1% for Si to ca. 24% for S. The high precision of silicon concentration determination is achieved by an XRF calibration method that has been developed

specially for bottom ash [9]. Sulfur concentrations cannot be determined with high precision, since metal sulfides cannot be always completely oxidized by the CNS analyzer used.

b) The Chemical Speciation of Organic Carbon

In order to investigate the processes in MSWIs in which organic materials are involved and to understand the long-term behavior of MSWI bottom ash in mono-fills, the speciation of carbon in the bottom ash needs to be known [9][13][14]. The first step is a pyrolysis/oxidation which is designed to differentiate between organic carbon, elemental carbon, and inorganic carbon. The organic carbon fraction is further characterized by extraction with water and dichloromethane. The extractable organic carbon is analyzed by several methods including ion-exclusion chromatography, ion-pair chromatography, size-exclusion chromatography, infrared spectroscopy. The non-extractable organic carbon is investigated by pyrolysis – gas chromatography – mass spectrometry. The four fractions of total organic carbon in a bottom-ash sample are shown in Fig. 3.

c) The Buffer Capacity of MSWI Bottom Ash

Wet-chemical investigations are often important for the characterization of heterogeneous materials, particularly when

an understanding of water-rock interactions is to be achieved. One such example is the problem of the long-term mobility of heavy-metal cations in MSWI bottom ash [15]. Mobility in recent ashes is relatively low because of the basic pH values of leachate solutions, caused by mineral components in the solid phase which buffer solution pH through dissolution. In this context, buffer capacity is operationally defined as the sum of the buffering components expressed in milliequivalents of

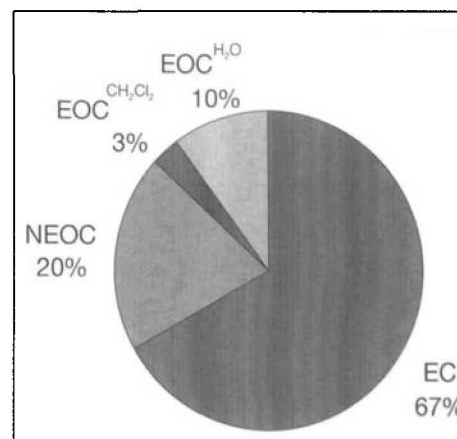


Fig. 3. Organic carbon fractions in a bottom-ash sample. About two thirds of the total organic carbon consist of elemental carbon (soot). Non-extractable organic carbon partly consists of organic polymers. The water extract consists of low molecular and polar substances, such as aliphatic and aromatic acids. The dichloromethane extract contains mostly unpolar aliphatic species.

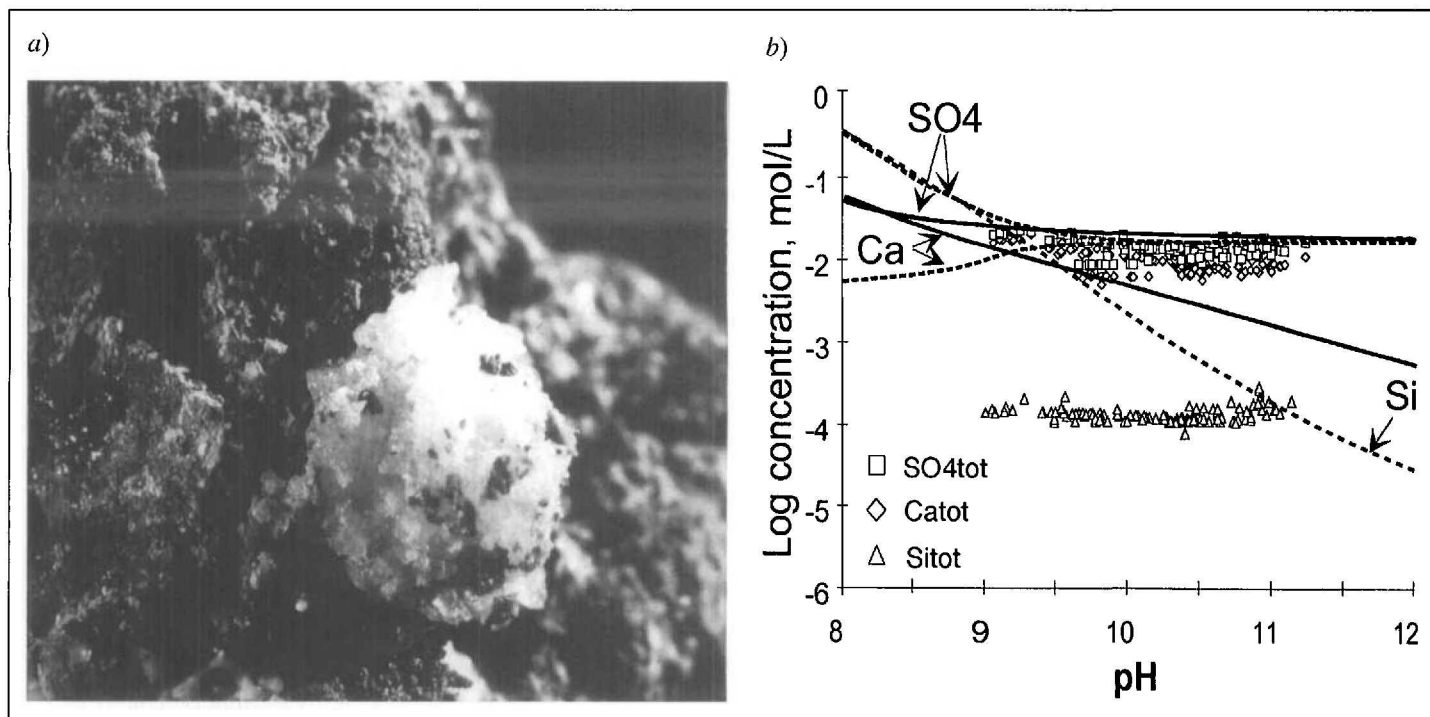


Fig. 4. a) Photograph of a gel sampled at Landfill Lostorf, AG, Switzerland. The gel contains ettringite, gypsum, and gibbsite. b) Total concentrations of Ca, Si, and SO₄ plotted as a function of pH. The solid and the dashed lines represent the maximum solubilities in equilibrium with ettringite and a Ca silicate hydrate gel (1:1)/CaSO₄ mixture, respectively. Ettringite appears to represent the field data solubility best. Ettringite: 3Ca(OH)₂·3CaSO₄·2Al(OH)₃·14H₂O, Ca silicate hydrate (1:1): Ca(OH)₂·H₄SiO₄·yH₂O [16].

protons per weight of the solid phase required to reach pH 7.5 in a stirred suspension. Leaching experiments in the laboratory have indicated that the Ca minerals are responsible for the buffering effect. With respect to the long-term behavior and the leaching of heavy metals, it is important that the Ca minerals be determined and their reactivity be assessed.

Equilibrium calculations suggest that a number of cement minerals could be controlling leachate composition, namely ettringite, Ca silicate hydrate, and others. This is illustrated in Fig. 4. Indeed, secondary mineral formation has been observed in landfilled ashes and cement minerals have been identified [4]. These results suggest that cement minerals are buffering the leachates in recent deposits. It is probable that such minerals are carbonated within a number of years and that CaCO_3 forms and replaces the cement minerals as the dominant buffer with time. This has been observed in MSWI bottom-ash samples from aged deposits [12]. Alternative weathering products are aluminosilicates, though the evidence for this is scant. Zevenbergen *et al.* [17] observed the formation of anorthite in aged deposits. With a knowledge of the geochemical behavior of MSWI bottom-ash minerals and the most probable aging processes it will become possible to develop our concepts of the risk associated with ash and cemented ash residues.

Molecular Level Structure Studies of Lake Particles and Mineral Oxide Surfaces

Studies of Lake Particles with EXAFS Spectroscopy

Among emerging spectroscopic methods that have recently been developed, EXAFS (Extended X-Ray Absorption Fine Structure) spectroscopy is one of the few methods capable of providing direct structural information on the short-range order of amorphous natural colloids. EXAFS can also be used to study sorption phenomena including formation of surface complexes, heterogeneous nucleation coprecipitation, and solid-state diffusion. Structural studies of environmental particles face two major difficulties: Autigenic particles formed in low-temperature environments are often poorly crystallized and, therefore, X-ray amorphous and they are usually finely dispersed so that concentrations can be quite low. Synchrotron radiation-based EXAFS has opened a new area for the examination of environmental particles [18][19]. With a number of studies

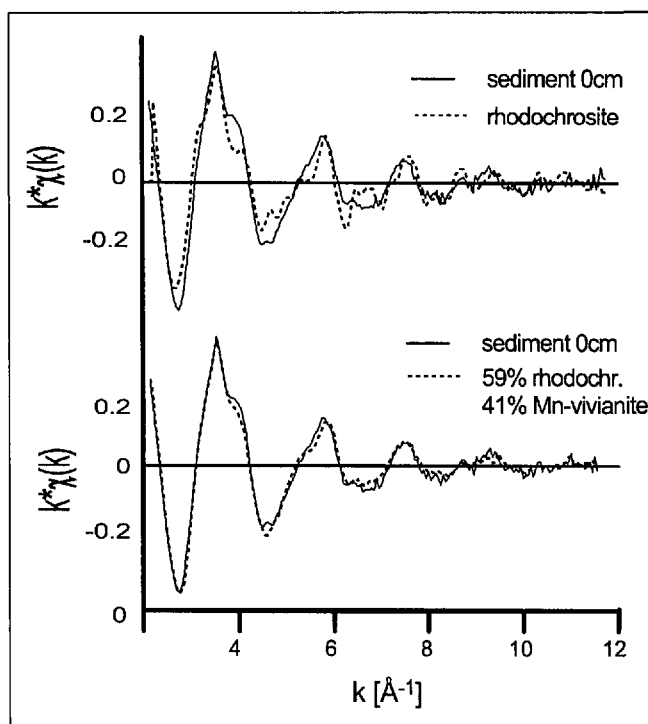


Fig. 5. Mn-EXAFS spectrum of a sediment sample superposed with a rhodochrosite spectrum and a combined spectrum of rhodochrosite and Mn-containing vivianite. Higher frequencies present in the rhodochrosite spectrum are smeared out in sediment samples, which suggest a loss of long-range order or the occurrence of an additional Mn-bearing phase. The latter is supported by the excellent agreement between the sample spectrum and the combined spectrum [18–22][24–26].

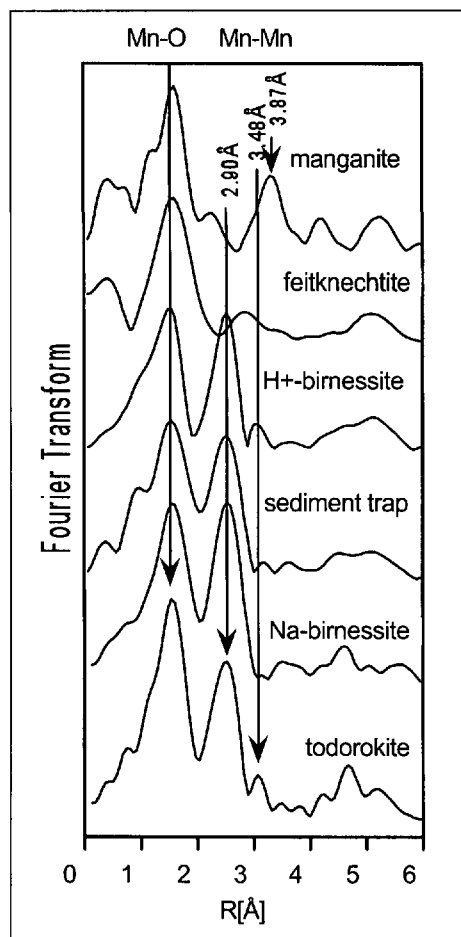


Fig. 6. RDFs of various Mn^{IV} oxides and Mn^{III} hydroxides are compared with the RDF of a sediment trap sample. The RDF of feitknechtite shows a weak and broad Mn-Mn contribution, which differs in shape, height, and slightly in the position from the contribution found in the sediment trap sample. Manganite differs from the trapped sample by a weak contribution at a distance of 2.85 Å and an intense contribution at large distance. The sample is similar to various Mn^{IV} minerals. Best agreement in R and N exists with H^+ -birnessite.

on model compounds in the past ten years, it is now possible to apply this technique to natural systems [20].

EXAFS spectra are obtained by measuring the X-ray absorption or fluorescence as a function of wavelength. The spectral scan is performed in the vicinity

of an X-ray absorption edge of a chosen target element. It is, therefore, an element specific, bulk sensitive, and nondestructive method. The distance and the number and in some cases the nature of atoms in the vicinity of the X-ray absorber can be determined. Environmental particles of

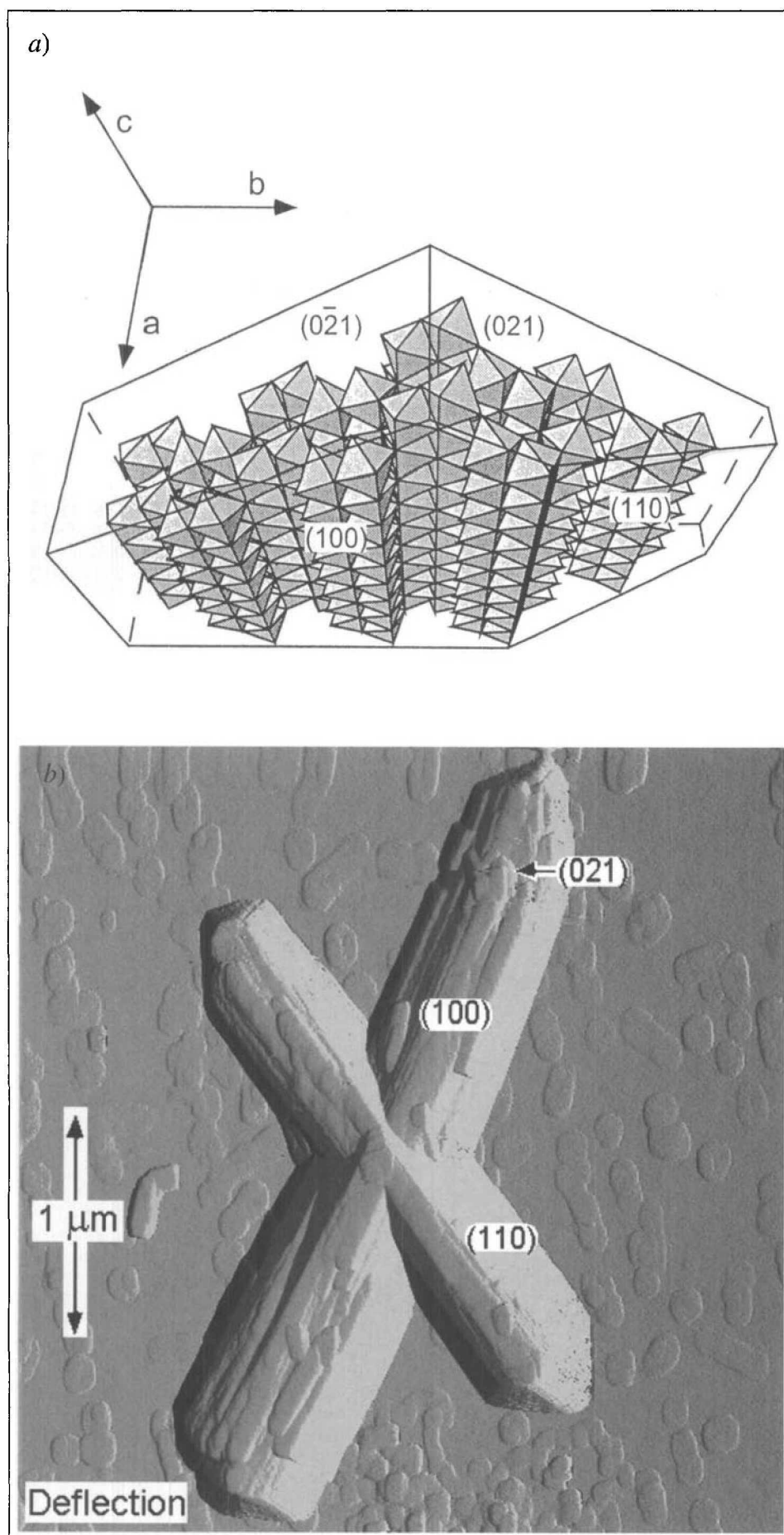


Fig. 7. a) Coordination octahedra model of a slice of goethite confined by crystal faces which are typically observed in small goethite particles. The 'empty' double rows are occupied by H^+ ions (not shown). b) A micrometer-sized goethite crystal, immobilized on a glass slide and imaged with the AFM in air. The X-shaped crystal is twinned on the (021) planes. The stepped (100) faces on the top of the crystal, as well as (110) and (021) faces confining the sides, are clearly visible. The steps on (100) faces are bounded by (021) faces with steps heights from 2–200 nm.

ten contain a variety of elements as a result of coprecipitation, adsorption, substitution, or diffusion phenomena. Through the atomic selectivity, information can be obtained on the way foreign elements are trapped by host particles. EXAFS is a bulk technique and yields averaged structural parameters if the element of interest is present in more than one phase.

The Formation of Mn Minerals in Eutrophic Lakes

Transformations of manganese minerals in the aquatic environment play an important role in many processes, such as scavenging of heavy metals by highly reactive surfaces or in microbial respiration. However, little is known about the structure of metastable species formed in oxic environments during the oxidation of Mn^{2+} ions and in reducing conditions during the formation of Mn^{II} -carbonate or -sulfide minerals.

For a long time, hydrous ferric and manganese oxides were thought to be amorphous in their highest disordered state since their XRD patterns display only two broad bands at about 2.5 Å and 1.5 Å. The XRD curves for all these compounds result from the small size of their coherent scattering domain. EXAFS spectroscopy yields structural information on a molecular scale (5 Å) in 'X-ray amorphous' minerals. The EXAFS studies conducted at EAWAG use a fingerprint approach, whereby the spectra of natural samples are compared with reference spectra of well-known compounds, or structural parameters obtained from fitting procedures are compared with those of reference minerals [21–23].

The refined EXAFS spectrum obtained from surface sediments from lake Sempach, an eutrophic lake with anoxic sediment, is shown in Fig. 5. The spectrum has been found to be similar to two reference spectra: rhodochrosite ($MnCO_3$) and Mn-containing vivianite ($(Mn,Fe)_3(PO_4)_2$). By linear combination of $MnCO_3$ and vivianite, the best fit with the sediment spectrum yields rhodochrosite as the main component (55–60%) together with vivianite (with 40–45%). Note the excellent agreement.

The Fourier transformation of EXAFS spectra yields the radial distribution function (RDF) with the position of the peaks corresponding to the interatomic distances and the amplitude to the number of neighbors. The RDF of a sediment trap sample from lake Sempach is similar to various Mn^{IV} minerals (Fig. 6) but differs clearly from Mn^{III} hydroxides such as manganite or feitknechtite. The main dif-

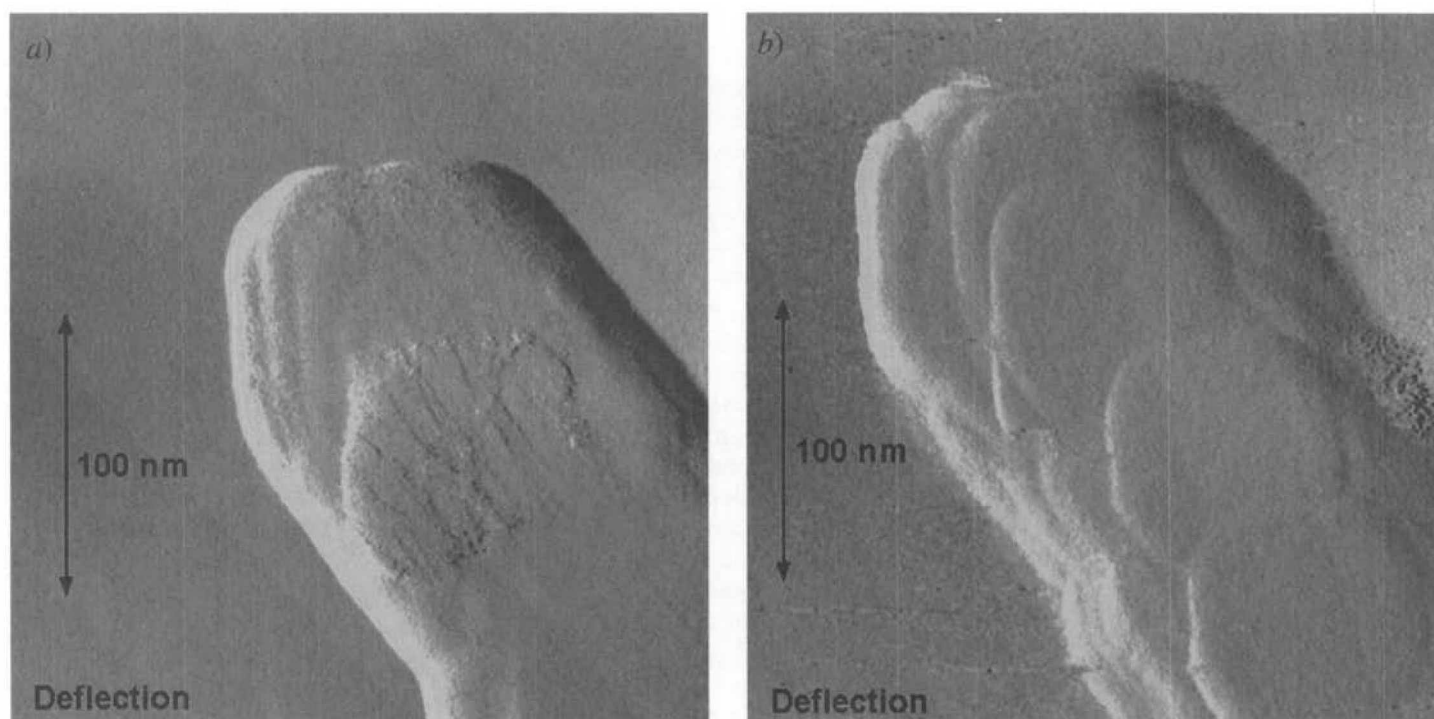


Fig. 8. Part of an ca. 200 nm long goethite crystal, imaged in aqueous solution. The left image (a) was measured before, the right image (b) 2 h after addition of $50 \mu\text{M Cr}^{\text{VI}}$ and $125 \mu\text{M Fe}^{\text{II}}$ at pH 4.8. The oxidation of Fe^{II} by Cr^{VI} leads to formation solid Fe^{III} and Cr^{III} phases which grow on the goethite surface and form new layers and steps. Thus, the new phase appears to be crystalline, probably a Cr^{III} -substituted goethite.

ferences between the Mn^{IV} -oxides arise from the relative intensity of the second and third peak in the RDFs, which yield information about Mn-Mn pairings. The presence of a third peak in the RDF of the sample excludes Na-birnessite as possible dominant phase. Todorokite and H^+ birnessite are the remaining possibilities. However, the analysis of the third peak yields for the sample a significant lower number of next nearest Mn neighbors than todorokite. Best agreement in R and N exists with H^+ -birnessite.

Recently, the same approach has been applied to follow the formation of Fe^{II} sulfide minerals. Amorphous FeS is a metastable precursor to the formation of mackinawite and pyrite. The current EXAFS studies at EAWAG are conducted in cooperation with the research group of environmental geochemistry of University Joseph Fourier, Grenoble.

AFM/STM and FTIR Studies of Surface Structures and Reactions on Mineral Oxide Surfaces

A characterization of the surface structure of small particles on a crystal unit cell and atomic scale is essential for a molecular understanding of surface properties and surface processes. An assessment of the average properties of surface sites has been made possible by surface complexation models developed by Schindler and Stumm [27], introducing the concept of

specific chemical interactions of adsorbents with surface sites (formation of inner-sphere surface complexes in addition to electrostatic interactions). It was assumed that properties of different types of sites on the same crystal surface are averaged ('mean field approach'), or that existing differences can be accounted for by adjustable model parameters. Recent models make an attempt to specifically account for multiple sites on different crystal faces (e.g. the multisite complexation model [28]). To develop these models in a constrained manner, properties of a mineral oxide surface such as the relative contributions of the confining crystal faces and their topography (steps, kinks, defects, dislocations) must be known.

Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) are new techniques which can image surfaces down to molecular dimensions. While SEM and TEM require high-vacuum environments, STM and AFM can image surfaces without pretreatment under environmental conditions (air, humidity, aqueous phase). A more complete description of AFM and STM is given in [29] and references therein. Briefly, both STM and AFM instruments build an image by scanning a sharp tip line by line over a surface. STM measures an electrical tunnel current between tip and sample and thus requires conductive samples. While some mineral oxides possess band

gaps sufficiently narrow to allow imaging by STM, others, such as iron (hydr)oxides have to be considered as nonconductors. In these cases, AFM is the method of choice. In AFM, the tip is usually approached to the surface until direct contact between tip and sample causes a strong repulsion between the electron clouds of surface and tip atoms. The upward deflection of the elastic cantilever on which the tip is mounted is measured with a fine laser beam.

Two techniques are usually used to image mineral surfaces. *i)* Larger crystals are cleaved and flat regions are imaged. This technique was used in several studies at EAWAG, e.g. in the oxidation of pyrite [30], dissolution of calcite [31], adsorption of Cr^{III} [32] and of sulfate on hematite [33]. *ii)* Nanometer- to micrometer-sized particles are immobilized on a flat carrier surface (e.g. a glass slides). Even though sharp features of particles must be interpreted with care, flat regions are usually present and angles can be measured to identify crystal faces and the identity of nanometer-sized crystals. Flat areas can be imaged to a resolution of typically 2 nm or better. On this scale, growth steps, dislocations, corrosion pits, and other surface features can be observed *in situ* during chemical reactions, providing mechanistic information about surface processes such as precipitation, crystal growth and dissolution.

In collaboration with *Dr. Peter Weidler* (Institute for Terrestrial Ecology/ ETHZ) micron- and nanometer-sized goethite particles have been imaged at EAWAG. Several studies in different groups at EAWAG are conducted with synthetic goethite with the aim of understanding surface reactions in soils and sediments, where iron minerals play an important role in the adsorption and transformation of pollutants. Different goethite preparations often show differences in reactivities that furthermore change in the course of a reaction. From a crystallographic point of view, one would expect different reactivities on different crystal faces. In reactions where solid phases are formed (*e.g.* during the oxidation of Fe^{II} at higher pH values), surfaces could change by crystal growth or by precipitation of amorphous phases. AFM images reveal the relative abundances of different crystal faces and changes during chemical reactions. *Fig. 7, a* shows a model of a slice of the goethite structure confined by crystal faces which are typical for goethite crystals next to a goethite particle imaged with the AFM in air (*Fig 7, b*). On the (100) face, growth steps consisting of {021} faces, down to one unit cell height, can be recognized. *Fig. 8* shows two *in situ* images of smaller goethite particles in aqueous solution before addition and 2 h after addition of Cr^{VI} and Fe^{II} . The formation of new confined layers and sharp steps indicates that the newly formed phase, a mixed $\text{Cr}^{\text{III}}\text{-Fe}^{\text{III}}$ phase, is mostly crystalline. In a similar study, it was found that during Fe^{II} oxidation by O_2 , new Fe^{III} phase is formed more quickly on the (100) than on the (110) face, a process that changes the relative abundance of (100) and (110) surface areas [34].

IR spectroscopy is another powerful and often complementary tool for the study of processes in the bulk phase and on the surface of mineral particles. With special techniques such as Attenuated Total Reflection (ATR)-FTIR [35], the formation or dissolution of solid phases can be followed *in situ*. FTIR measurements on goethite exposed to Fe^{II} solutions containing dissolved O_2 or Cr^{VI} , respectively, showed that the typical lattice in-plane $\delta\text{-O-H}$ and out-of-plane $\gamma\text{-O-H}$ bending vibrations at 891 cm^{-1} and 793 cm^{-1} increased with the formation of Fe^{III} . This confirms the interpretation of the AFM study that the new solid phase formed is at least partially crystalline goethite or Cr^{III} substituted goethite, respectively. Complementary information is often obtained by applying several independent methods (*e.g.* the combination of FTIR and STM has helped to understand sulfate adsorption [33]).

Conclusions

A detailed characterization of heterogeneous, multiphase environmental field samples down to atomic and molecular dimensions would constitute an extremely complex, demanding, and even impossible task. However, a meaningful partial characterization in the context of relevant environmental processes is often sufficient to gain information about the importance of a wide range of solid and surface properties. A combination of modern analytical methods coupled with computer-aided analysis and data banks facilitates the overall morphological and chemical characterization of complex environmental field samples. Once the key properties and processes are identified, they are studied in more detail on separated phases or on analogous solid phases prepared in laboratory. Advances in the last decade, most notably of EXAFS and of STM/AFM, have made detailed, atomic level structure studies under environmental conditions possible. With a combination of field and laboratory studies, important aspects of heterogeneous environmental reactions are being unraveled. Many studies in this direction already contribute directly to solutions for current problems, *e.g.* in the assessments of pollutant transformation rates in surface and subsurface aqueous environments and in improved remediation procedures for contaminated soils and aquifers. In a long term, a molecular level understanding is the key for advances in environmental technologies, *e.g.* soil and sediment remediation, water purification, and sustainable soil and water management.

Received: September 25, 1997

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