

Accurate multidisciplinary identification of nanophase iron minerals in simulated pedogenic environment

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We have begun an inter-disciplinary investigation (solid state chemistry, low temperature magnetism, Mössbauer effect and microbiology) to test chemical reactivity and environmental controls in simulated pedogenic transformations of nanophase (1-100 nm) iron oxyhydroxides and oxides of controlled size, crystallinity and impurity, in the presence or absence of iron-reducing bacteria (IRB). Pedogenic nanophase magnetite/maghemite end-products found in modern and ancient soils developed over loess (windblown silt deposits) parent materials in temperate climates are currently assumed to be proxies of annual rainfall (alone). We are testing and calibrating this abiotic model as well as comparing it with IRB-mediated magnetite formation since the latter (microbial type and concentration) could represent length of summer season and hence provide a new parameter, seasonality, for numerical climate model benchmarks.

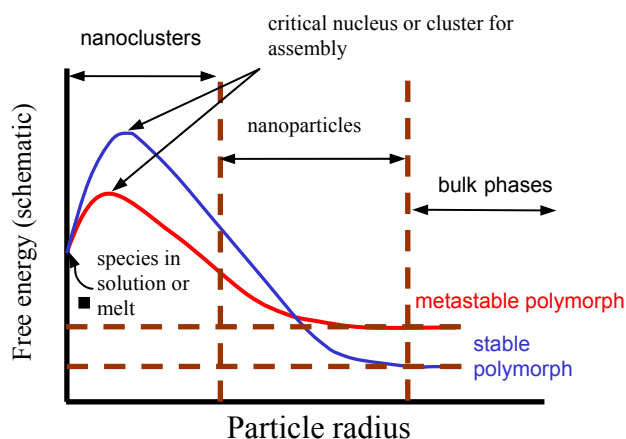
Our research to date has led to a comparison of known synthesis techniques to produce monodisperse ferrihydrite (Fh) of different crystallinity, nanogoethite (Gt) and magnetite (Mt). High resolution transmission electron microscopy (HRTEM), x-ray absorption fine structure (XAFS) and Mössbauer spectra were used for sample characterization. Magnetometry and Mössbauer spectra at low temperatures (to 2.5K) and high field (to 5Tesla) have allowed cross-checked grain-size determinations. These two latter methods, used in conjunction, have proven to be rapid and reliable tools for granulometry, and for discovery of oriented aggregation in grain growth, adsorbed species on the surface and for core/shell distinction in these nanophase materials. Examples of data from iron oxyhydroxide precursors and their microbial conversion product of nanophase magnetite will be presented.

Nanoparticle-mediated processes and the Ostwald step rule

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There is increasing recognition that many processes which involve crystallization or phase separation do not occur by classical nucleation and growth but rather by the aggregation of pre-existing nanoparticles of 2-3 nm size. Such particles may, because of a competition between the energetics of polymorphism and surface energetics, have structures of phases which are metastable when coarse-grained. Furthermore, within a given composition, it appears generally true that the more metastable a structure in the bulk, the lower its surface energy. The classical Ostwald step rule observes that, during crystallization, a series of metastable phases is often visited on the way down to the final appearance of the most stable crystals. As the figure shows, the correlation between metastability and decreasing surface energy may offer a rationalization of the Ostwald step rule. Nanoparticles of metastable phases may be more stable thermodynamically, as well as having lower energy barriers and smaller critical nuclei, than nanoparticles of the final stable phase. The crossover in stability between polymorphs may occur at much larger particle sizes than the "critical nucleus" for crystallization.



Antiferromagnetic nanoparticles

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Nanoparticles of antiferromagnetic materials such as α -Fe₂O₃ (hematite), α -FeOOH (goethite) and ferrihydrite, commonly found in geological environments, have attracted limited attention in magnetic studies, because the sublattice magnetizations are aligned antiparallel such that the particles may have negligible magnetic moments. A number of studies have, however, revealed that antiferromagnetic nanoparticles have a wealth of fascinating magnetic properties, e.g. a magnetization due to uncompensated spins with implications for their rock magnetic signature [1]. Recently we proposed that the thermal energy may excite the magnetic structure of antiferromagnetic nanoparticles such that a thermoinduced magnetic moment occurs [2]. This is a novel type of nanomagnetism where the magnetization increases with temperature. At room temperature the thermoinduced magnetic moment can be similar in magnitude to that originating from uncompensated spins. Magnetic dipole interactions between antiferromagnetic nanoparticles can be considered negligible [3-5] despite magnetic moments from e.g. uncompensated spins, but strong exchange interactions can be established between surface atoms of neighboring particles by drying aqueous suspensions of particles [3-5]. This interparticle exchange interaction significantly influences the properties of the individual particles [3-5] e.g. it suppresses superparamagnetic relaxation. In samples with strong interactions, there is a tendency for oriented attachment of the particles [4]. It is possible that exchange interaction can act as a driving force for the attachment. The agglomeration process is reversible, in the sense that ultrasonic treatment or grinding can separate the particles and reinduce fast superparamagnetic relaxation without reducing particle sizes [4,6]. Thus the nanoscopic coupling between particles is sensitive to simple macroscopic treatments. The results stress that the properties of nanoparticles, in addition to differing from bulk properties, have to be described in terms of interactions.

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In situ observation of thermodynamic size effects on melting of natural gold nanoparticles

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Thermodynamic and quantum size effects, i.e. the change in physical and electronic properties as size is decreased to the nanoscale, are widely documented for synthetic nanomaterials. However, there is little information on how natural nanocrystalline materials behave under a wide range of geological temperatures. In order to evaluate size effects on melting of metal nanoparticles, we have performed controlled heating experiments of natural gold nanoparticles in As-rich pyrite (formed at ~150-200°C) under HAADF-STEM observation.

In-situ heating in the TEM revealed no changes in the initial size distribution until ~350°C, where the smallest nanoparticles (<2 nm) start to melt. The most dramatic changes in nanoparticle size and distribution occur between 400-500°C; nanoparticles with diameters <2 nm melt completely at ~440°C, while at temperatures above 500°C, only nanoparticles >8 nm in size are stable. Computer-aided HAADF image analysis of size distributions as a function of temperature reveal that the initial average diameter (~4 nm) of Au nanoparticles is constant until ~350°C, above which it starts to increase gradually. The increase in average size is coupled with a significant decrease in the number of nanoparticles as temperature is raised above 400°C. At 600°C, the upper temperature bound of the experiment, only 3 nanoparticles (~25 nm) have survived, replacing the initial 115 of average size ~4 nm. During heating, larger nanoparticles (~9 nm) grow at the expense of the smaller ones (<2 nm) although no coalescence is observed.

Analytical results reveal that a significant fraction of the initial size distribution of Au nanoparticles (~2-8 nm) is unstable at temperatures above ~350°C, confirming thermodynamic size effects on melting in natural samples. As a result, the preservation of metallic gold nanoparticles in the geologic record is size-dependent, and restricted to lower temperature (<400°C) hydrothermal systems.

Reactivity of iron oxyhydroxide nanoparticles with heavy metals as a function of particle size

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Nanoparticles of inorganic mineral phases are widespread in aqueous environmental systems and can play a significant role in the natural cycling of heavy metals and semi-metals. In particular, iron oxyhydroxides are present in many natural environments as dispersed and/or aggregated nanoparticles covering a wide range of sizes. However, the effects of particle size on heavy metal uptake, especially during nanoparticle aggregation and growth, are not well understood yet hold significant implications for contaminant sequestration and mobility.

To study the effects of particle size on metal uptake, a series of iron oxyhydroxide batches ranging from 5-80 nm in average diameter was synthesized using a rapid microwave technique followed by aging in suspension at 90°C. Selected iron oxyhydroxide nanoparticle suspensions of 5, 25, and 75 nm in effective diameter were then exposed at pH 6 to 0.5 mM concentrations of As(V), Cu(II), Hg(II), and Zn(II), metal(loid) contaminants frequently associated with acid mine drainage systems.

EXAFS spectroscopy of the resulting solids shows that while metal speciation on the 25- and 75-nm particles is identical (suggesting direct inner-sphere bonding), uptake to the 5-nm particles displays slightly longer (0.1-0.3 Å) second-neighbor metal-iron distances. This suggests distortion and/or disordering of the Fe(O,OH)₆ octahedra which comprise the structure of iron oxyhydroxides. It is also consistent with the oblong morphology and greater degree of surface curvature observed in the 5-nm particles through TEM microscopy, with particles becoming more tabular/acicular as particle size increases (25-, 75-nm).

Macroscopic uptake curves were generated using the same nanoparticle batches and metal contaminants over a concentration range of 5-1000 µM. Results show that the smallest particles exhibit greater overall uptake (due to higher surface areas) yet have reduced surface loadings (expressed in µmol/m²) relative to larger particles. Thus there are observable differences in both the extent and mode of metal uptake onto iron oxyhydroxides which appear to be largely dependent on size and morphology at the nanoscale.

Nanoscience meets geochemistry: Size-dependent reactivity of hematite

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Geological materials at the nanoscale, typically considered to be approximately 1-100 nm, are extremely common. Nanoscience explores how the properties of nanoscale materials change as a function of size. Consequences of these size-dependent property changes for the geochemical reactivity of nanoscale materials in the environment remain almost entirely unexplored. Results will be presented involving the size-dependent reactivity of synthetic (7 nm, 9 nm, and 40 nm average diameter), commercial (NANOCAT 3 nm, MACH-1, Inc.), and natural (150-250 nm ground fraction) hematite and hematite-like materials. In this study, the reactivities of these particles is tracked using heterogeneous manganese oxidation rates and photochemical reactivity. Dramatic size-dependent reactivity is observed and rationalized in both systems.

Initial rates of heterogeneous manganese oxidation on synthetic 7 nm, 9 nm, and 40 nm hematite in the presence of oxygen decrease by approximately 1-2 orders of magnitude as the average particle diameter increases, when normalized to surface area. This size-dependent rate change is hypothesized to result from changes in metal coordination environment and surface chemistry.

In additional experiments, photochemical release of ferrous iron has been measured experimentally upon UV illumination in pH 4.0 oxalate (0.005 M) solutions. Surface area normalized release of ferrous iron from synthetic 40 nm and natural ground 150-250 nm hematite are very similar. Release was approximately two orders of magnitude greater for 3 nm NANOCAT material and approximately one order of magnitude greater for 7 nm and 9 nm synthetic hematite. Previous researchers have found photochemical reduction of bulk hematite to be relatively inefficient; electron-hole pairs recombine after an average diffusive length of a few nanometers. As the dimensions of the particles approach this length, trapping of electrons at the particle surface (as Fe²⁺) is expected to compete significantly with recombination.

Reactivity of ferrihydrite nanoparticles prepared with and without added carbonate, arsenate, and other oxoanions

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Iron oxides and oxyhydroxides are common and important materials in the environment. These materials commonly occur as nanoparticles in the 3-10 nm size range and strongly impact the biogeochemical cycle of iron and other species at the Earth's surface. Surface-area normalized rates of reduction of ferrihydrite nanoparticles using hydroquinone in batch experiments enables comparisons of reactivity as a function of preparation conditions. We have used this system to characterize the reactivity of several different ferrihydrite samples. In general, ferrihydrite was synthesized by precipitation from homogeneous solution. Surprisingly, ferrihydrite nanoparticles prepared using sodium bicarbonate are substantially more reactive than ferrihydrite nanoparticles prepared using sodium hydroxide. Furthermore, the reactivity of microwave-heat treated ferrihydrite nanoparticles (after the method of Knight and Sylva, 1974) is greater than untreated ferrihydrite nanoparticles. Ferrihydrite nanoparticles prepared by coprecipitation with sodium arsenate are substantially more reactive than ferrihydrite nanoparticles that are equilibrated in solutions containing sodium arsenate, and both arsenate containing samples are substantially less reactive than arsenate-free ferrihydrite nanoparticles.

The structural chemistry of hydroxyl moieties in ferric polymers

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Introduction and Objectives

Ferric (oxy)hydroxy polymers are ubiquitous in surface environments and play an important role in several geochemical processes. They are short-lived intermediates produced as aqueous Fe(III) hydrolyzes to form stable crystalline Fe(III)-(oxy)hydroxides. Our goal is to examine the short range order in ferric polymers, the chemical variables that influence their structure and formation, and the relationship between structure and reactivity.

The bridging and terminal hydroxyls in ferric polymers hold the key to their reactivity in the environment. Because it is highly sensitive to small changes in hydroxyl coordination, infrared (IR) spectroscopy was used to interpret the structure of hydroxyls in ferric polymers based on well characterized crystalline Fe(III)-(oxy)hydroxides.

Discussion of Results

Our investigation focused on the hydroxyl stretching and bending vibrations and their variations as a function of pH, ligand type, and reaction time. Since ripening of ferric polymers into nano-crystalline, and ultimately into macro-crystalline phases, is slower at room temperatures, initial studies were conducted at elevated temperatures (50-90°C).

Freshly prepared ferric polymers from the hydrolysis of Fe(III) in the pH range of 3-7.5 exhibited a broad band around 900 cm⁻¹, corresponding to the Fe-OH bending vibrations. In time (0-144 hrs), this band gradually evolved into two distinct bands centered around 900 and 800 cm⁻¹, similar to those observed for goethite. Ferric polymers aged in the presence of NO₃⁻ and Cl⁻ exhibited the greatest maturation rate at high pH. Conversely, the presence of SO₄²⁻ not only accelerated polymer aging relative to the NO₃⁻ and Cl⁻ systems, but also maximized the maturation rate at low pH. Ligand concentration associated with the polymers also changed with gel maturation. A mechanistic explanation for this disparity will be the focus of future research.

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Computational subcolloidal mineralogy

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Computation is now well established as a primary means of discovering and *understanding* chemical reactivity in aqueous and interfacial systems. Progress has not moved as quickly in the Earth sciences as it has in molecular biology because low-temperature Earth materials are so difficult to characterize. An important aspect of nano-Earth science is that while “small” is not necessarily different, “small” may be more precisely characterized. Recent advances in research on nanometer-sized aqueous poly(hydr)oxocations provide a particularly well defined path toward understanding surface reactivity in aqueous oxide systems. It has been possible to crystallize such ions as salts and determine their structure with single-crystal x-ray diffraction. These salts may then be redissolved in solution while preserving the complex ion for reactivity studies.

These ions can form an unusually tight link with computer simulation. This synergy is discussed in two case studies. The first of these involves water and hydroxide ligand exchange reactions in the ϵ -(Al, Ga, Ge)Al₁₂ “Keggin” ion system. We find that the exchange mechanism is highly cooperative and not at all similar to mechanisms derived from the studies of octahedral substitution in aquo ions, which are often used in conceptualization of ligand exchange processes on oxide surfaces. For example, activation volume-mechanism relationships are completely opposite to those known for aquo ions. The second case study involves “*in silico*” acidometric titrations of model poly(hydr)oxocations in aqueous solutions. Here the reactivity of the Keggin $MO_4(OH)_{24}(H_2O)_{12}^{7+}$ structure is contrasted against that of the larger $M_{30}O_8(OH)_{56}(H_2O)_{26}^{18+}$ structure. The M_{30} structure has six triply-bridging hydroxide functional groups which might be expected to make the M_{30} ion more acidic than the M_{13} ion. The enhanced acidity of the M_{30} ion is indeed predicted by the model, but the contributing functional groups are unexpected and do not correlate at all with gas-phase acidity.

Controls of step length and direction on crystal solubility

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Solubility’s direction dependence is a fundamental property of anisotropic materials. For example, thermodynamics dictates that chemical potential necessary to maintain the growth of an individual crystal differs amongst faces that have different surface energies. This leads to the conclusion that multiple solubilities exist on anisotropic crystals where faces unrelated by any symmetry operations are present. Consider a step in the i^{th} direction, the direction-dependent solubility can be expressed by

$$\ln K_i = \ln K_{sp} + (2M_w/3RT\rho)[\gamma_i/l] \quad (1)$$

where K_i and K_{sp} are step solubility and standard state solubility product, M_w and ρ are molecular weight and density, γ_i the surface energy of the step riser, l the step length, and RT have their usual thermodynamic meaning. Eq. (1) states that K_i is always greater than K_{sp} . However, a closer examination of the $\ln(K_i/K_{sp}) \sim l$ relationship reveals that all direction-dependent solubility converges to K_{sp} when l is infinitely large (in reality, a length of a few μm is sufficient). While this warrants the rationality of approximating solubility by K_{sp} in traditional studies of crystal growth and dissolution for larger crystals, it implies that direction-dependence cannot be ignored when dealing with nano-crystal growth/dissolution. In situ AFM experiments conducted on the cleavage face of calcite show that the $\langle \overline{441} \rangle \pm$ steps indeed exhibit direction and length dependent behaviour at nm to sub- μm scales. Whereas advance is observed in steps of μm -lengths in both directions at near equilibrium conditions defined by K_{sp} , nano steps (10-100 nm) do not grow until the solution saturation is up to 50% higher than that defined by K_{sp} . Furthermore, simultaneous growth and dissolution at the two directions are observed in a narrow range of saturation, providing a direct proof for the existence of direction dependent solubility in calcite.

Nanogeochemistry: Geochemical reactions in nanopores

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Nanopores are ubiquitous in porous geologic media and constitute an integral part of total porosity of rocks. Existing data indicate that the contribution of nanopores to the total surface area in geologic materials can be very high, probably over 90 percents. To clarify the effect of nanopore confinement, acid-base titration and metal adsorption experiments were performed on both nanoporous alumina and alumina particles under various chemical conditions. The experiments have demonstrated that the nano-scale confinement has a significant effect, most likely via the overlap of the electric double layer, on ion sorption onto nanopore surfaces. Under the same chemical conditions, the surface charge per mass on nanoporous alumina was as much as 45 times higher than that on alumina particles. The nanopore confinement leads to a shift of ion sorption edges and enhances ion sorption on nanopore surfaces for both cations and anions. As a result, trace elements in natural systems tend to be preferentially enriched in nanopores. This effect cannot be adequately modeled by existing surface complexation models. To understand the state of water in nanopores, the experiment of water adsorption under various relative-humidity conditions were performed in combination with H magic-angle spinning nuclear magnetic resonance (MAS NMR) and Fourier transform infrared (FTIR) spectroscopic analyses. The experimental results show that water molecules in nanopores form more rigid structures than those in bulk solutions. The observed nanopore confinement effects will shed a light on many important geochemical phenomena.

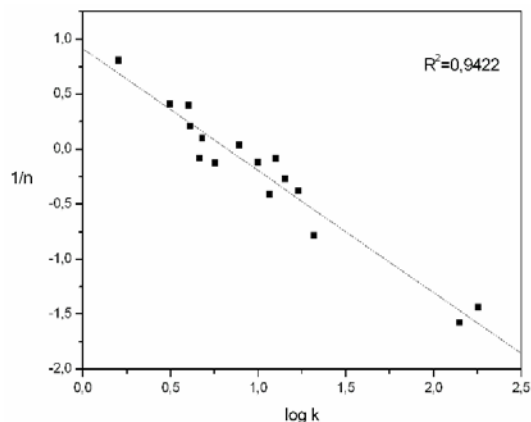
Relationship between Freundlich equation constants for zinc sorption on nanocrystalline calcite

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The solid state properties of nanocrystalline particles obtained by high-energy milling with a high surface area has led recently to their utilization as reactive minerals and heavy metal sorbents [1]. The nanoparticles have been shown to possess a much greater number of defect sites per unit surface area, which are believed to be responsible for the observed chemistry [2,3]. The aim of this work was to examine the sorption behaviour of zinc ions on calcite whose solid state properties were modified by high-energy milling. Freundlich equation has been applied for the description of sorption process. A good relationship has been found between the Freundlich equation constants $\log k$ and $1/n$ for zinc sorption on 16 samples of nanocrystalline calcite modified by high-energy milling (Fig.1).

Figure 1 Freundlich isotherm



The different solutes applied for the adsorption on one sample of carbon described in paper [4] and the different calcites (as for origin and solid state properties) applied for the adsorption of one solute (zinc ions) in our work has led to the same character of relationship between constants of Freundlich equation which demonstrates its universal character.

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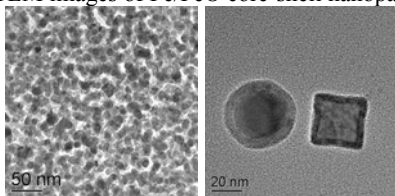
Iron-iron oxide core shell nanoparticles for contaminant underground water treatment

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Metallic iron chemically reduces contaminants such as chlorinated hydrocarbons for underground water cleanup. The use of nano-sized particles of iron is of interest because of enhanced possibilities for distribution, a high rate of reactivity and the possibility enhancing environmentally friendly reaction paths. An oxide shell or other protective layer plays an important role along with the metallic iron core in chemical reactions. Examination of the chemical properties of monodispersed metallic iron nanoparticles with a well-defined clean oxide shells is important to understand the chemistry of nanoparticles. However, production of these particles by conventional methods is difficult. Therefore, we are using a cluster deposition system, which prepare the iron nanoparticles and iron-iron oxide core shell nanoparticles at room temperature by a method that is a combination of high-pressure sputtering and aggregation techniques. The outer oxide layer acts as a passivation layer of these particles, preventing further oxidation of the cores upon continued exposure to the atmosphere. Size of the iron-iron oxide core-shell nanoparticles can be varied with the rate of He and Ar gas flow, the chamber pressure, the sputtering power and the growth distance. These films are characterized by XPS, XRD, HRTEM and voltametry measurements.

Fig. 1 TEM images of Fe/FeO core-shell nanoparticles



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Thermodynamics of high temperature iron oxide nanoparticles obtained by laser pyrolysis

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Pure and uniform γ -Fe₂O₃ nanoparticles particles between 2 and 15 nm have been prepared at high temperature by a continuous process based on ethylene sensitised laser pyrolysis of gaseous Fe(CO)₅ in an oxidizing atmosphere, suggesting that γ -Fe₂O₃, rather than α -Fe₂O₃, is the thermodynamically stable phase for ultra small iron oxide particles.

The samples were characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer-Emmet-Teller gas adsorption (BET), thermogravimetric analysis (TG), elemental analysis and Mössbauer spectroscopy. The thermodynamic properties of the iron oxide samples were determined by transposed temperature drop calorimetry and high temperature drop solution calorimetry using sodium molybdate solvent at 700° C.

The crystal structure of the iron oxide ultra fine particles potentially depends not only on the particle size, but also on the thermal history of the particle formation. In order to explore the effect of the thermal history of the particles, the thermodynamic properties of the obtained materials were compared with the properties of γ -Fe₂O₃ nanoparticles obtained by chemical solution techniques.

Migration of geogas-carrying gold nanoparticles in Quaternary sediments

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The ascending geogas from the Earth's interior can capture nanoparticles from the ores during passing through ore bodies and deliver them to the surface. Hidden ore bodies may be detected by examining the geogas-carrying nanoparticles in the top of Quaternary sediments [1]. In this study, we investigated the migration behaviors of gold nanoparticles in the Quaternary sediments by means of indoor simulation experiments and field tracer tests. The gold nanoparticles at 20 nm were used in the study. The indoor simulation experiments were designed in which the ascending gas flows with gold nanoparticles flowed through the sediments. The field tracer tests were performed in Shuntian town, Heyuan county, northeast Guangdong Province, China. The gold nanoparticles were laid at the bottom of the sediments and the tests ran for five months. The samples of both the indoor simulation experiments and the field tracer tests, including sediments and particles collected from the gas in the sediments, were analysed by means of instrumental nuclear activation analysis (INAA) and transmission electron microscopy (TEM). The results show that: 1 In the geogas, gold nanoparticles migrate by absorbing on the surface of other particles, or in the form of groups; 2 The gold nanoparticles in the geogas are absorbed by kaolinites, illites, montmorillonites, hematites, goethites, gibbsites, etc., during passing the Quaternary sediments; 3 Gold nanoparticles exist in both gas and solid phases of the Quaternary sediments, and their distribution between the two phases is related to mineral compositions and pHs of the Quaternary sediments.

Acknowledgement

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Effects of cobalt on oxide film formation on manganese carbonate

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The fate and the transport of metal contaminants in natural waters are linked with manganese oxide coatings. In the current work, cobalt adsorption and co-precipitation with manganese oxides on manganese carbonate is studied by atomic force microscopy at circumneutral pH. We also investigate how the cobalt ion affects the dissolution of manganese oxide film and MnCO_3 .

In the presence of $\text{O}_2(\text{aq})$, crystallization begins as islands that expand laterally to grow into a film across the surface. The islands have flat tops and are rhombohedral with a uniform thickness of 2.4 nm in the absence of added $\text{Co}^{2+}(\text{aq})$. In contrast, a multilayer structure with apparently unrestrained z-directional growth forms in the presence of $\text{Co}^{2+}(\text{aq})$. The net macroscopic dissolution rate slows by a factor of two in the presence of $\text{Co}^{2+}(\text{aq})$. The normally rhombohedral shape of the dissolution pits of MnCO_3 is distorted in the presence of cobalt, and $\text{Co}^{2+}(\text{aq})$ preferably associates with the obtuse steps. Cobalt also affects the dissolution rate of the Mn oxide film. Dissolution of the Mn oxide layer is observed simultaneous to the formation of a second oxide film. The observations are explained by the parallel oxidation of $\text{Co}^{2+}(\text{aq})$ and reduction of $\text{Mn}^{\text{III/IV}}$ on the surface. Under this model, a $\text{Mn}_x\text{Co}_y\text{O}_z$ composition is suggested for the second oxide film. The cobalt adsorption rate ($\text{mol m}^{-2} \text{s}^{-1}$) on the surface increases with the initial $[\text{Co}^{2+}](\text{aq})$ and with increasing Mn oxide film coverage.

The timing of cobalt addition affects film growth. When no $\text{Co}^{2+}(\text{aq})$ is added initially, rhombohedral Mn oxide islands nucleate by heterogeneous oxidation on the MnCO_3 substrate and film growth continues until the entire surface is covered. Adding $\text{Co}^{2+}(\text{aq})$ disrupts growth of the Mn oxide film and results in the formation of a second $\text{Mn}_x\text{Co}_y\text{O}_z$ phase. When $\text{Co}^{2+}(\text{aq})$ is added at the beginning of the experiment, growth of the $\text{Mn}_x\text{Co}_y\text{O}_z$ phase is predominant, and no evidence of the Mn oxide film is observed.

Direct microscopic observations of the interactions of cobalt with manganese oxide coatings provide new mechanistic insights that are important in the quantitative modeling of the fate and the transport of toxic metals in the environment.

Reduction of halogenated groundwater contaminants by nano-sized magnetite

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Introduction

Permeable reactive barriers have been shown to be a viable technology for remediation of halogenated solvent contaminated groundwaters. When the zero-valent iron used in these barriers corrodes under anoxic conditions, the corrosion film that forms at the iron-water interface is often composed of nanocrystalline corrosion products such as magnetite (Fe_3O_4). This magnetite has the potential to participate in the reduction of halogenated contaminants. The ubiquity and small size of nanoscale magnetite makes this a potentially important reactive phase in granular iron systems. Many nanosized materials exhibit reactivities that differ significantly from larger sized bulk particles. The objective of this study was to quantify the reactivity of nanoscale magnetite particles under anoxic conditions towards halogenated solvents and to determine if a relationship exists between reactivity and particle size.

Experimental

Monodisperse suspensions of Fe_3O_4 were synthesized under anoxic conditions. Several batches of magnetite were synthesized under different solution conditions (pH, ionic strength, co-solutes) such that precise control of particle size was possible. Batch reactors of buffered magnetite (both nanosized as well as bulk magnetite) were spiked with halogenated solvents (carbon tetrachloride, trichloroethene) and monitored over periods of one week.

Results and Discussion

The reduction of halogenated solvents occurred more rapidly when exposed to nanoparticulate (10-20 nm diameter) magnetite as compared to "bulk" magnetite particles (>100 nm). In addition, daughter products were more fully reduced by nanoparticulate magnetite than by bulk magnetite.

This presentation will address the relationship between magnetite particle size and halogenated contaminant reduction capability. Additionally, this presentation will discuss the effects of oxidation on particle aggregation in nano-sized magnetite suspensions.

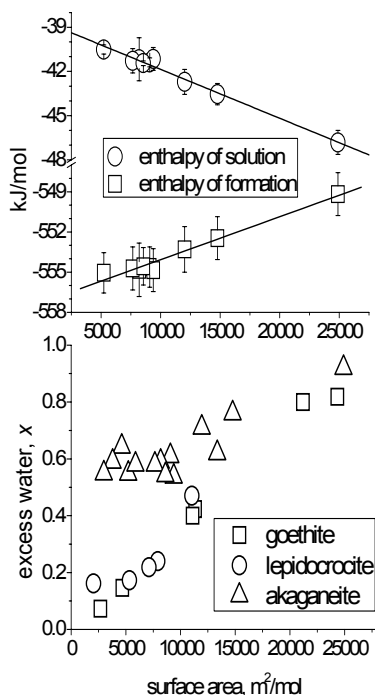
Thermochemistry of bulk and nano akaganeite

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Enthalpy of formation of akaganeite, $\beta\text{-FeOOH}$, as a function of particle size is reported for the first time. Fourteen samples with the particle size range of 5-100 nm and surface area 30-280 m^2/g were prepared. Characterisation was performed using XRD, FTIR, BET, TEM, SEM and TGA. Solution enthalpy in hydrochloric acid at room temperature and in sodium molybdate at 700 °C was measured. Refinement of XRD data showed that at higher surface areas akaganeite has a monoclinic polymorph. Calorimetric data were corrected for excess water assuming this loosely adsorbed water has the same energetics as bulk liquid water. The plot of enthalpy of solution for monoclinic akaganeite vs surface area (see figure) gives a surface enthalpy of $0.33 \pm 0.05 \text{ J/m}^2$ and enthalpy of formation of bulk akaganeite of $-557.3 \pm 1.2 \text{ kJ/mol}$. Although surface energy of akaganeite is found to be lower than for lepidocrocite $\gamma\text{-FeOOH}$ and goethite $\alpha\text{-FeOOH}$, the amount of adsorbed water is higher

especially for lower surface areas (see figure). The reason is probably the tunnel structure of akaganeite, with excess water accumulating in the tunnels. Preliminary calorimetric data showed that the surface energy of akaganeites with lower surface areas (and probably a different polymorph) is higher, but additional work is required. The energetics of adsorbed water on the akaganeite surface is also under investigation.



Nano-crystalline osbornite from Carbonados: Spectroscopic studies

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Carbonado has been recognised as a polycrystalline aggregate of diamond since 1840 and was mined as a placer mineral in Sincoro County in Brazil. Carbonado has been recovered only from alluvial deposits in Brazil and the Central African Republic (CAR). The origin of the unusual type of polycrystalline diamond is not yet understood. In order to understand the origin of this exotic diamond aggregates, we have carried out powder-X-ray diffraction, Nuclear Magnetic Resonance and FT-IR, and TEM studies on the carbonados from Brazil as well as CAR. While our data on the chemical and trace elements analyses agree with the earlier data, there is a minor difference in the observation of presence minor minerals. We have identified few grains of osbornite (TiN) with 50 to 100 nm size, and presence of lonsdaleite- a high – pressure polymorph of diamond. The presence of these two minerals has been independently and unambiguously confirmed by XRD. The NMR spectrum also show a shock-induced broadening of the diamond line centred at 34.8 ppm which is more than the chemical shift 34.5ppm of pure diamond crystal. Our observation of presence of osbornite in carbonado shows the possible extraterrestrial origin of carbonado, as this mineral is known to exist only in enstatite chondrites and achondrites.

Incorporation of guest-molecules into natural zeolite mordenite

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Microporous materials such as zeolites are more and more applied for the design of advanced nano-materials, e.g. miniaturized electronic devices. They are also a group of minerals with geologic and environmental importance. Despite kinetic and spectroscopic studies of guest incorporation, little is known about the exact positions, geometrical arrangement and disorder phenomena of encapsulated guest-compounds.

Large synthetic mordenite single-crystals of good quality and suitable morphology were used for incorporation of semiconductor material (selenium) and organic dye molecules (thionin blue ($C_{12}H_9N_3S^+$), methylene blue ($C_{16}H_{18}N_3S^+$)). Single-crystal X-ray diffraction experiments were performed with a conventional in-house X-ray source as well as using synchrotron radiation at the Swiss Norwegian Beamline at ESRF, France. Complementary methods such as polarization and fluorescence microscopy were applied to analyze the orientation of the dye molecule transition dipole-moment.

Guest-molecule arrangement in all three guest-host systems is highly influenced by electrostatic interaction with the mordenite framework and the present extraframework occupants (Na^+ , H_2O). Elemental Se in mordenite builds chains, which show a highly variable geometrical arrangement and differ clearly from the regular chain geometry as occurring in elemental, trigonal selenium. The dye molecules show distinct occupational disorder along the channel axis and prefer an inclined arrangement within the channel cross-section resulting in short CH...O and NH...O contacts to the framework.

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Genesis and mineralogical characteristics of hematite in loess-paleosol sequences of China

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Hematite is an important iron oxide mineral in loess-paleosol sequences of China, and it is benefit reconstruction of paleoclimate of Chinese inner terrene investigation and understanding mineral characteristics, forming process of hematite as well as relationship with other iron oxides and containing iron minerals. For example if we know on grain size distribution, exactly quantitative testing of hematite will be obtain by diffuse reflectance spectroscopy. Employed optic microscopy, X ray diffraction, scanning electron microscopy, high resolution transmission microscopy for original samples and magnetic extracted samples, obtaining results as follows:

There are four kinds of mechanisms for hematite occurring in loess-paleosol sequences of China during pedogenic. (1) Weathering from containing iron silicate, example for chlorite, etc, which released free iron ion, hydrolyzed, and dehydration; (2) Oxidation from magnetite which is micrometers and wind dust origin; (3)Phase transformation from wind dust goethite to hematite by topomorphology; (4) Hematite forming on the edge of maghemite. The hematite forming from the first mechanism is the best important occurrence and size from several to tens nanometers, irregular morphology, low crystallinity, as well as characteristic mesoporous because of dehydration from iron hydroxide (example for ferrihydrite), which results in redness in paleosol.

Acknowledgements

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Mechanical, chemical, magnetic, transport, and electronic properties changes at the nanometer scale

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Systems (such as materials, minerals, and fluids) at nanometer scale behave differently from their bulk systems. Nanoscience and nanotechnology are making big progress now because it is possible to purposefully manipulate materials and theoretically simulate / compute the properties of small systems at nano-scale. Deformation mechanisms for nanocrystalline metals will be dominated by twinning, grain boundary sliding, wide stacking faults, and partial dislocation emission from grain boundaries. Brittle oxide minerals will behave like elastic when their sizes reach the nanometer scale. Reactivity and stability of nanocrystals needs to be modified according to their crystal sizes, shapes, and textures. Geochemical reactions in nanopores and nanotube environments will be greatly different from those in bulk solution systems because of electric double layer overlap and water property changes (such as activity and dielectric constant). Especially the change in dielectric constant of water will modify Born solvation energies of ions, which will affect many aspects of geochemical processes, such as chemical weathering, ore deposit formation, replacement reactions, and fate of toxic metals in ground water aquifer. Nanocrystalline and nano-structured magnetite and maghemite that are superparamagnetic will enhance magnetic susceptibility of rocks and sediments dramatically. Darcy's law for the transport behaviour of water in nanoporous media will deviate. The band gap between valence band and conduction band of nano-crystalline semiconductor minerals (such as CdS, and CdSe) and materials will be a function of their crystal dimensions. The electron densities of states of nanocrystalline semiconductors will be greatly different from their bulk system. This property has been used in many opto-electronic materials and devices.

Acknowledgement

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