

# In situ transformations of fine lead oxide particles in different soils

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*Lead oxides particles can either be covered rapidly by a weathering crust of secondary minerals or can remain virtually unchanged over 18 months depending on the soil type.*

## Abstract

We present a field application of a new in situ technique to analyze phase transformations of fine lead oxide particles (50–100 µm) in different soils directly in the field over 18 months. After the first month of exposure to a calcareous sand we found newly precipitated secondary mineral phases on the lead oxide. The samples exposed to two loamy soils (Dystric Cambisol and Luvisol) showed only very few traces of new phases. We identified the new phases as mainly lead-hydroxy carbonates (hydrocerussite). Whereas the results confirm the transformation of lead phases to lead carbonates in calcareous soil, they also show that an easily soluble phase such as PbO may persist in soils virtually unweathered for more than one year. The formation of a weathering crust is therefore not necessarily needed for preservation of easily soluble phases. The use of experimental in situ methods is thus giving new information on contaminant mineral behavior under field conditions.  
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## 1. Introduction

Transformations of mineral phases are important natural geological and pedological processes in rock weathering and soil formation. They can also be rate limiting in the release of toxic metals from anthropogenic particles' emissions distributed into the environment or in the immobilization into more stable phases. Particulate contaminants (e.g. sulfide minerals) released from mining and tailing heaps are prone to phase transformations because of the different environmental conditions between the place they were formed (anaerobic) and the earth surface (aerobic) where they are deposited during mining (Callander, 2004) resulting in acid mine drainage generation. Metal smelters can release significant amounts of metal oxide particles (Ripley et al., 1996) into the atmosphere resulting in widespread contamination (Sobanska et al., 1999). Soils and sediments generally are the ultimate sinks of such emissions.

The pathways and rates of mineral transformation processes in the environment are subject to large uncertainties (Casey et al., 1993; Swoboda-Colberg and Drever, 1993), although a rich database on thermodynamics of mineral phases and their transformation reactions is available. The reason is that due to the complexity of soil and sediment environments it is difficult to simulate field conditions in the laboratory and even more difficult to adequately capture all relevant processes and factors in model calculations (Strömberg and Banwart, 1994).

Therefore it is crucial for the study of the kinetics of mineral transformations in the environment to have methods by which these processes can be studied under conditions as they occur in real soils and sediments (Schnoor, 1990; White and Brantley, 2003). Several types of in situ methods have been used for this purpose. The reactions of soil forming minerals were studied in situ by means of incorporating mineral particles into soils and recover them after selected reaction times (Augusto et al., 2001; Rogers et al., 1998). Ranger et al. (1991) examined the weathering of vermiculites by incorporating small bags of polyamide with 20 µm mesh size

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filled with these minerals for various time periods into selected soil sites. This bag method was also used to study the mineral transformations in mine affected soils over time (Monterroso and Mañas, 1998) and to study the physico-chemical alteration of minerals in soils associated with changes in the vegetation (Hatton et al., 1987).

Another in situ approach was to incorporate samples of minerals directly into soil and to recover them for analysis by means of a density fractionation (Cotter-Howells, 1993; Tsaplina, 1996). This technique has the disadvantage of disturbing the soil structure as the test particles are mixed into the soil. Moreover the direct contact of the reacted test material with chemicals in the sample preparation step (Cotter-Howells, 1993) could alter, damage or remove newly formed mineral phases.

A new method to study the in situ reactions of particulate materials was developed and described recently (Birkefeld et al., 2005a,b). This method uses small polymer supports as carrier material onto which the minerals of interest are fixed with a thin layer of epoxy resin. The coated polymer plates are then inserted into soils, sediments or other environmental systems. Not only is it easy to insert these samples into soil and to achieve good soil contact with minimum disturbance, but it is also easy to recover the samples. In addition the method provides the possibility to identify individual mineral sample grains as well as analyze microscopic changes on the minerals. The method is suitable for particle sizes of down to 20 µm diameter. Previously the method has been used to investigate the dissolution of heavy metal containing particles in an acidic forest soil (Birkefeld et al., 2006). It was possible to analyze the mineral behavior over time in this specific soil environment revealing obvious dissolution features on some of the mineral grains. The dissolution rates measured in situ in the forest soil with this method were compared to rates measured in the laboratory in different media using the same technique. Dissolution rates were found to be faster in the field than in the laboratory under similar conditions of exposure.

For this study lead oxide particles were selected because lead compounds are well characterized and several studies reported the environmental behavior of lead phases in soils (Cao et al., 2003a; Corsi and Landim, 2002; Hardison et al., 2004; Jorgensen and Willems, 1987; Martinez and Motto, 2000). Davis et al. (1993) described the occurrence of lead oxide particles in mine wastes and mine waste contaminated soils and discussed the importance of the mineralogical form (species) of lead controlling the potential bioavailability of this heavy metal. Lead phases occur in different forms (e.g. PbO, PbSO<sub>4</sub>, PbS, PbCO<sub>3</sub>, Pb(OH)<sub>2</sub>, Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH) in soil environments (Davis et al., 1993). Lead oxides and lead sulfides are typical primary minerals found in ore bodies or deposits (Davis et al., 1993), whereas metallic lead can be found in soils affected by mining and smelting activities (Lottermoser, 2003) or in shooting ranges (Lin et al., 1995). Under aerobic conditions these phases are unstable and subsequently transformed into secondary lead phases like lead carbonates, lead phosphates, lead sulfates or lead oxides (Ruby et al., 1994) depending on factors such as pH, anions, DOC, or water

content (Bataillard et al., 2003; Essington et al., 2004; Lin et al., 1995).

The objective of this study was to analyze phase transformation reactions of fine mineral particles under field conditions with the new in situ technique. Under the given physico-chemical soil properties we expected to see the formation of lead carbonates or lead phosphates directly on the mineral grains. We used small lead oxide particles incorporated in different circumneutral soils for a time span of up to 18 months applying the new in situ method of Birkefeld et al. (2005a,b) which does not need special sample treatment prior to the analysis by microanalytical methods.

## 2. Methods and materials

### 2.1. Sample preparation

Particle supports were made from polymethylmethacrylate (PMMA) polymer (Plexiglas<sup>®</sup>/Acrylite<sup>®</sup>). Pre-cut plates of 2 cm × 2 cm were weighed at 0.0001 g accuracy by means of an analytical balance (Mettler Toledo AT 261, Switzerland). The mass of each plate was carved into its backside. Then the plates were covered with a thin adhesive film of a two-component epoxy resin (Bisphenol A resin – Suter, Switzerland) using a micro-foam paint roll. For this purpose, a set of 10 weighed and marked supports was placed in two rows in a frame holder.

Lead oxide particles were obtained from a commercial manufacturer (Penaroya Oxide, Germany). The lead oxide particles consisted of a mixture of the two PbO polymorphs massicot and litharge (XRD analysis, D4 Endeavor Bruker, Germany). Particle sizes ranged from 20 to 100 µm in diameter. There were only minor elemental impurities in the lead oxide particles (Na 3.5%, Mg 0.65%, Al 0.14%, K 0.05%, Ca 0.03%, Fe 0.02%).

The particles were applied onto the support surfaces by using a downsized copy of a commercially available dust spray gun. The spray gun was held perpendicular at a distance of 1.5 m to the supports. Gentle moving of the dust spray gun during application (30 s) provided a relatively homogenous material cover on the supports. For a more detailed description of sample preparation and field application of the method, the reader is referred to Birkefeld et al. (2005b).

### 2.2. Pre-experimental analysis

After hardening of the epoxy resin (12 h) each polymer plate was analyzed by energy dispersive X-ray fluorescence analysis (XRF) (Spectro X-Lab 2000, Germany) to establish the elemental composition of the mineral particles fixed to the supports. Stereomicroscopy was used to assess the coating quality. A custom calibration was made for the mineral type used to convert the XRF counts into concentrations (mg Pb/plate). For the calibration a sample set with different particle concentrations was first analyzed by XRF and afterwards completely dissolved and analyzed by AAS (Varian SpectraAA 220, Australia). Fig. 1 shows a lead oxide particle glued onto the sample support, ready for incubation.

### 2.3. Soils and sample incubation

Three field sites in the vicinity of Zürich, Switzerland, were chosen for this study. They are characterized by different soils, a Luvisol topsoil (non-calcareous loam; pH 6.4), a Dystric Cambisol topsoil (loam; pH 7.5) and a Pleistocene calcareous sand (pH 8.0). The carbonate content in the soils ranged from 0.3% to 35% (Table 1). The mean annual temperature of the field sites was 10.2 °C and the mean annual precipitation was 1100 mm (Bosshard, 2004). The carbonate content of the soils was determined by gas-volumetric analysis (Page et al., 1982), the soil organic matter content by the Walkley–Black method (Page et al., 1982), the grain size distribution by sedimentation after destruction of organic matter. The pH was measured in 0.01 M CaCl<sub>2</sub> at a solid:solution ratio of 1:2.

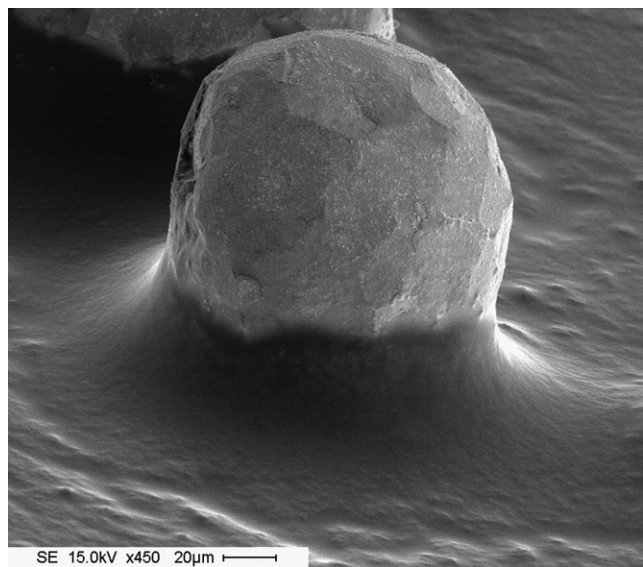


Fig. 1. SEM microphotograph of lead oxide particles attached to a polymer support. The minerals are arranged as a single layer on the support surface, ensuring optimal contact of each grain to the soil during incubation.

The polymer supports were inserted into the soils by means of a small lancet made of stainless steel (3 cm width; 0.5 cm thickness; 40 cm length). The lancet was gently pushed into the topsoil down to a depth of 15 cm and bent forward to open a small slit. A coated sample was then introduced into this slit and the coated face was pressed against the soil. A small nylon thread attached to the non-coated side of the support was left protruding from the buried sample to the soil surface in order to facilitate locating the sample for later recovery. For recovery the samples were dug out, put in small labeled polyethylene bags to preserve the soil moisture and transferred to the laboratory. Exposure times were varied from 2 up to 18 months with sampling intervals between 1 and 6 months. Eight supports were incubated in the calcareous sand, seven in the non-calcareous loam and three in the loam.

#### 2.4. Sample analysis

In the laboratory the recovered samples were immersed in demineralized water for about 5 min in order to soften and detach adhering soil. Particles still remaining after this procedure were removed carefully using a soft brush. The cleaned samples were left to dry over night under ambient room conditions. After drying, all samples were checked for damages under a stereomicroscope (Zeiss Stemi 2000, Germany). Metal concentrations of the recovered samples were analyzed by XRF spectroscopy.

Scanning electron microscopy (SEM) was used to identify changes in the surfaces of the mineral particles on the recovered samples using a CamScan CS44 instrument (Obducat CamScan, Sweden) with an attached energy

Table 1  
Properties of the used soils

Soil	Dystric Cambisol	Luvisol	Pleistocene sand
Soil label	Loam	Non-calcareous loam	Calcareous sand
pH (in 0.01 M CaCl <sub>2</sub> )	7.5	6.4	8.0
Carbonate content (%)	7.2	>0.3	35.1
Organic matter content (%)	3.1	1.5	0.1
Grain size distribution (Clay–silt–sand) (%)	25–40–35	15–49–36	5–7–88

dispersive X-ray (EDX) probe (EDAX Econ, USA) for elemental spot and small area analysis ( $\sim 3\text{--}5\ \mu\text{m}^3$ ). The SEM-EDX analysis was performed with 15 kV accelerating voltage using a secondary electron detector for imaging and the EDX probe for X-ray fluorescence analysis. The basic settings are denoted in the SEM photographs as well. One sample from the non-calcareous loam was analyzed using a Quanta 600 (FEI, USA) environmental scanning electron microscope (ESEM) with attached EDX probe (EDAX Econ, USA).

Micro-Raman spectroscopy was carried out on a Jobin Yvon Horiba LabRam HR (Jobin Yvon, France) spectrometer with attached reflected light microscope. The sample analysis was performed in confocal mode with a 514 nm Ar-Laser at 30 mW power (10/50 $\times$  working objective magnification). Spectra of expected lead phases (lead carbonate, -hydroxycarbonate, -nitrate, -sulfate, -phosphate) were recorded and added to the existing Raman spectra database. The reference compounds were obtained from commercial chemical suppliers (Merck, Switzerland; Fluka, Switzerland).

Samples which showed newly formed mineral phases under the SEM were also analyzed by X-ray powder diffraction (XRD) analysis. Diffractograms were generated on an XRD system (D4 Endeavor Bruker, Germany) in spinning sample mode to increase the orientation randomness (Pecharsky and Zavalij, 2003). The PDF-2 database of the International Centre for Diffraction Data (ICDD) was used for the identification of spectra. All compounds, which were added to the Raman database were also analyzed by XRD and integrated into the search and match routine of the XRD evaluation software (Bruker Diffrac<sup>plus</sup>, Germany).

### 3. Results

#### 3.1. Field results

Fig. 2 shows that the concentration of lead on the support (determined by XRF) did not change to any significant degree over the 18 months of incubation in none of the three soils (in mg/plate, normalized to the initial concentration). Each data-point represents an individual sample recorded after the respective incubation time. This means that transformation into new solid phases may have occurred, but with no detectable loss due to dissolution and leaching.

The original PbO surface was smooth (Fig. 1). The SEM microphotographs of the incubated samples show obvious signs that new phases had formed in all three soils. Significant amounts of precipitates were detected already after 2 months on the supports and as well on the PbO mineral surfaces of the samples incubated in the calcareous sand (Fig. 3). The lead oxide grains showed little change though indicating that

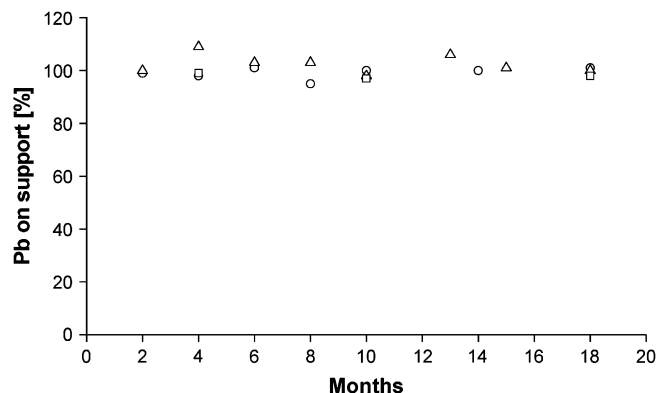


Fig. 2. Mass of lead on the supports (determined by XRF) after incubation of PbO in calcareous sand ( $\Delta$ ), loam ( $\square$ ) and non-calcareous loam ( $\circ$ ) in percent of the initial amount.

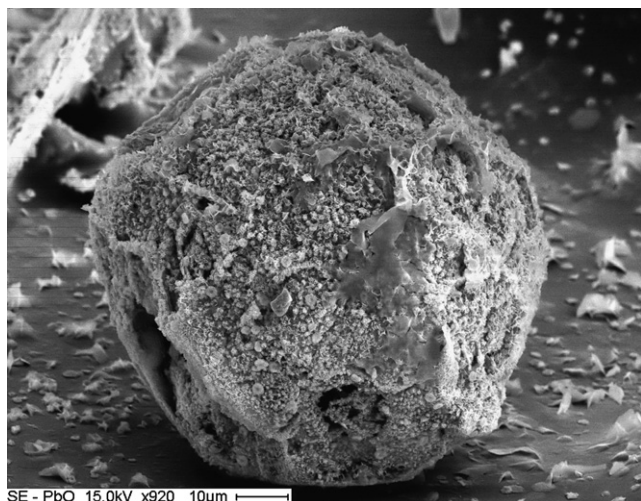


Fig. 3. SEM microphotograph of an individual lead oxide particle after incubation in a calcareous sand for 10 months. Newly formed mineral phases can clearly be seen on the grain surface and on the support surface.

only a very small fraction had been transformed. The new mineral precipitates predominantly show a tabular hexagonal form and are mostly grouped in patches on the mineral surfaces, and on the calcareous sand samples, in the spaces between the grains. The spatial distribution of new mineral phases indicates that dissolution and phase transformation had occurred all over the sample surfaces.

The samples incubated in the two loam soils showed much less formation of new phases on and between the sample particles than in the calcareous sand (Figs. 4 and 5). Changes in surface morphology are limited to a few spots on particles incubated in the calcareous loam (see inset in Fig. 4). These changes consisted of small cavities in which precipitates of secondary phases were visible. These visible cavities are most probably generated by etching parts of the thin surface layer of the initial lead oxide particle which has a “cellular” structure caused by its manufacturing process. The remaining particle surface is partially covered by fine-grained mineral phases. The samples incubated in the non-calcareous loam showed the least signs of transformation and were almost unaltered (Fig. 5). Very small patches of newly formed minerals can be found at the bottom of the grains (see inset in Fig. 5).

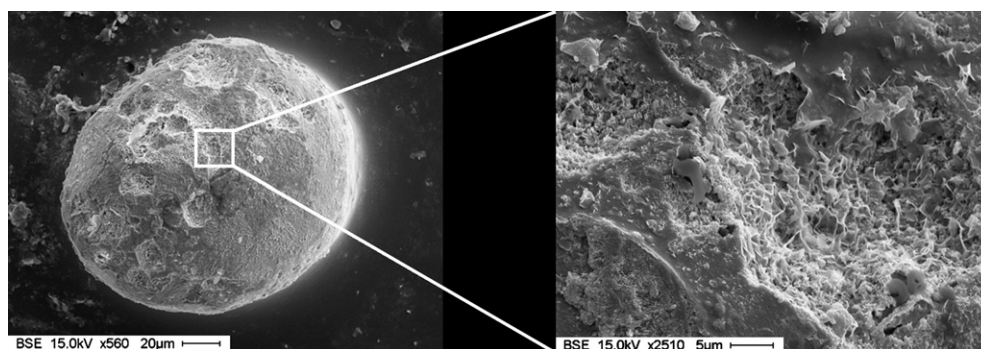


Fig. 4. SEM microphotograph of a lead oxide particle after incubation in the loam soil for 10 months. Small patches of new mineral phases can be seen in the enlarged cavity that resulted from weathering during that period.

### 3.2. Identification of phases

Energy dispersive point analysis in combination with SEM revealed that the new phases consisted primarily of oxygen, carbon, and lead. Fig. 6 shows the example of an EDX spectrum taken from a sample in which a new phase had formed in an intergranular area on the support surface so that no background signal from the original PbO could interfere. The silicon and potassium peaks most likely originated from minor residues of the soil matrix.

Micro-Raman analysis clearly showed the difference between the initial PbO and the secondary precipitates. Fig. 7 shows the disappearance of the initial lead oxide peak and the formation of a new peak in the  $1050\text{ cm}^{-1}$  area in the Raman spectra taken from samples which had been incubated in the calcareous sand. The initial lead oxide phase shows only peaks in the  $300\text{--}400\text{ cm}^{-1}$  region, whereas the new phases show peaks all over the scan, but with dominant peaks in the range from  $1050$  to  $1100\text{ cm}^{-1}$ , i.e. close to the sample peak. The peaks in the latter region are typical for lead carbonates (Frost et al., 2003). The inset in Fig. 7 shows a magnification of the spectrum around  $1050\text{ cm}^{-1}$  of the samples compared to the spectra of cerussite and hydrocerussite. The comparison suggests that the new mineral phase was predominantly hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ). Moreover, the peak in the  $680\text{ cm}^{-1}$  area indicates the presence also of a minor cerussite ( $\text{PbCO}_3$ ) phase. Black et al. (1995) reported similar Raman spectra for cerussite and hydrocerussite prepared from pure chemicals in the laboratory. The formation of these lead carbonates must have occurred quite rapidly, because they are already formed in the first samples after 2 months of incubation. The Raman signals of the samples recovered from the two loam soils were not strong enough to analyze secondary phases.

Bulk XRD analysis on samples recovered from the calcareous soil revealed the occurrence of hydrocerussite, cerussite, litharge and massicot (data not shown). Litharge and massicot are the two polymorphs representing the primary mineral phases introduced into the soil with the samples, hydrocerussite and cerussite the secondary, new mineral phases that formed on the lead oxide particles during the incubation. Using XRD, the two lead carbonate phases were identified

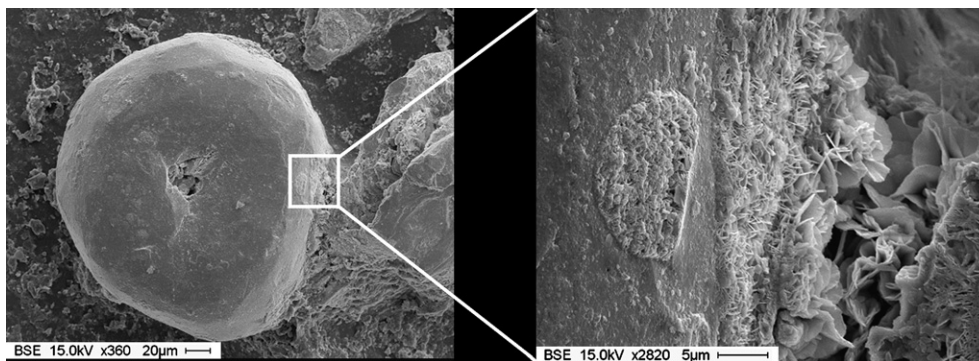


Fig. 5. SEM microphotograph of a PbO particle after 10 months reaction time in the non-calcareous loam soil. A slight precipitation of a secondary phase can be seen on the mineral surface. The visible cavity in the PbO grain on the left hand side picture resulted from the lead oxide manufacturing process.

also on the samples recovered from the two loam soils, although they were present in traces only.

Fig. 8 shows a comparison of XRD scans on the hydrocerussite main peak ( $34^\circ 2\theta$ ) of individual samples recovered from the test soils normalized by the initial amount of mineral mass. This plot shows semiquantitatively the development of hydrocerussite over the incubation time. A rapid formation of hydrocerussite within 2 months is evident and no significant changes occurred over the whole experimental period of 18 months.

An additional EDX scan on a sample recovered from the non-calcareous loam revealed the presence of carbon, oxygen and traces of phosphorus (Fig. 9). The XRD and the Raman analysis did not show any trace of a phosphorous-containing phase due to the much higher detection limit of these methods.

#### 4. Discussion

The results show that our method allows to expose fine particles for up to 18 months to in situ weathering conditions in field soils and to recover them afterwards for analysis. A loss of particles due to detachment from the supports was negligible and the method can give quantitative information on the dissolution of the particles (Birkefeld et al., 2005a). Furthermore, we were able to obtain microanalytical information on the mineral phases that formed during incubation in soil. Because disturbance of the soils where the samples were incubated was minimal and because of the direct and close contact of the samples with the surrounding soil, we can assume the conditions of weathering were representative for undisturbed soils and do not represent an artificial situation.

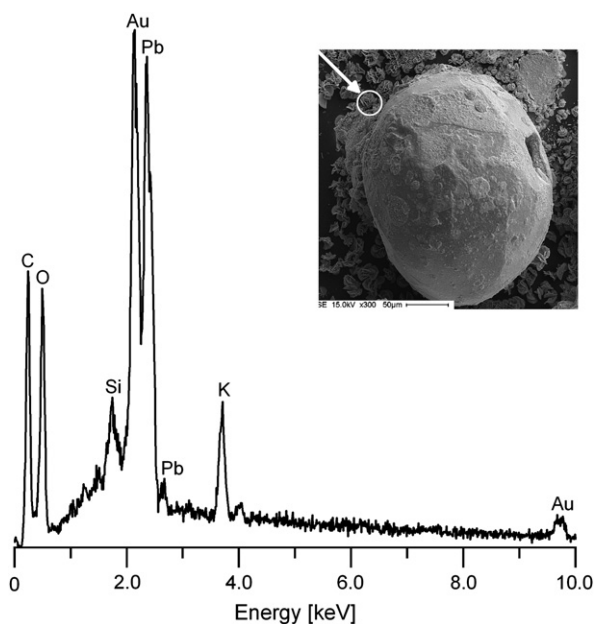


Fig. 6. ESEM-EDX small area scan (white circle in the inset picture) of a precipitate next to a PbO particle after recovery from incubation in the calcareous sand.

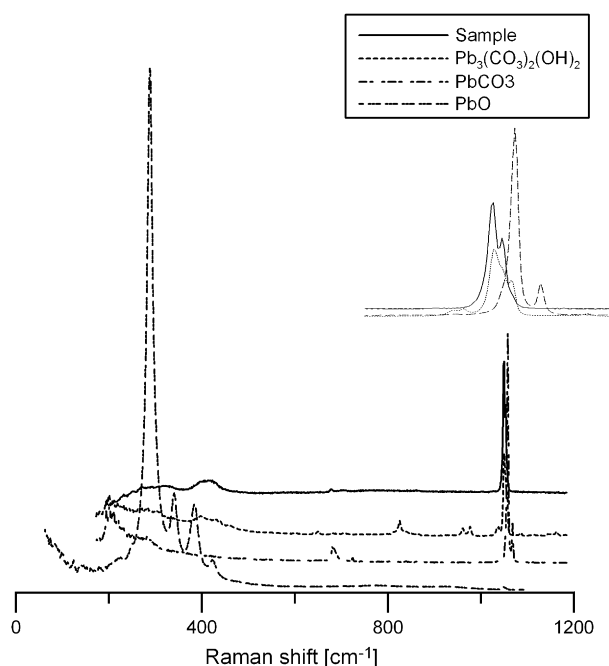


Fig. 7. Raman spectra of a lead oxide sample recovered from incubation in the calcareous sand. The graph shows the sample spectrum, the initial PbO mineral spectrum and two spectra of possible new lead phases. The inset graph is a magnification of the scan in the region from 1000 to 1100  $\text{cm}^{-1}$ .

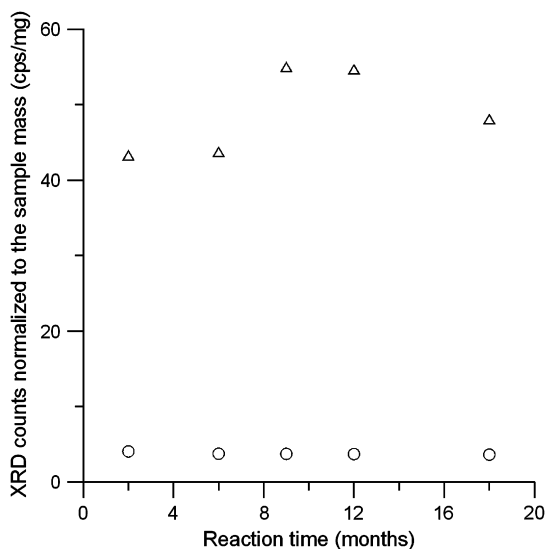


Fig. 8. Development of the hydrocerussite main peak over time on lead oxide samples (XRD analysis).  $\Delta$  – Samples recovered from the calcareous sand and  $\circ$  – samples from the non-calcareous loam.

The great advantage of the method is that the reactions of fine mineral particles (20–100  $\mu\text{m}$   $\varnothing$ ) can be directly studied. So far analysis of in situ reacted particles has been restricted to larger particles that can be separated from the soil matrix (White et al., 1996).

The lead content of the samples remained relatively stable over the whole experimental time and no net-dissolution was observed. PbO is very soluble around neutral pH and complete dissolution or phase transformation into more stable phases would be expected. Dissolution of PbO in an acidic forest soil (pH 3.6) has indeed been observed (Birkefeld et al., 2006). The formation of a weathering crust of less soluble

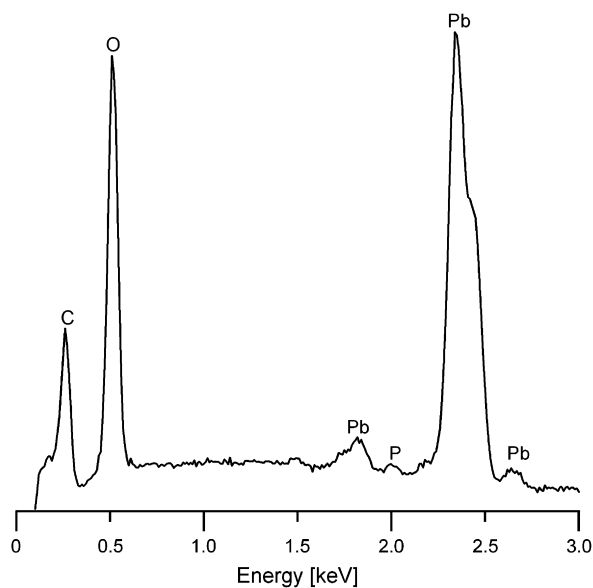


Fig. 9. ESEM-EDX analysis on the mineral surface of a PbO particle after recovery from the loam soil.

minerals is the most likely cause of the inhibited or slowed down dissolution in the studied soils.

Cao et al. (2003b) reported a similar stability behavior of lead bullet weathering crusts in neutral and alkaline soils. The crusts predominantly consisted of lead carbonates. According to Cao et al. (2003b) they are stable in the range of pH 6–10. Souvent and Pirc (2001) investigated corrosion products of soils contaminated with metallic lead and found protective layers of lead carbonate covering the initial lead particles. Also Gamsjäger et al. (1984) observed cerussite precipitation on calcite mineral grain surfaces under similar conditions and concluded that the lead carbonate phase formed a protective layer over the more soluble lead oxide phase, controlling the kinetics of further dissolution. Lead pipes buried in soils for millennia were found to be protected against further phase changes by a crust of lead carbonates (Essington et al., 2004).

The SEM microphotographs of the recorded samples showed clear signs of newly formed precipitates already at the earliest sampling after 2 months incubation. The results of the various methods applied to analyze the precipitates all agree in the conclusion that the latter primarily consisted of hydrocerussite and traces of cerussite. These findings also are in good agreement with results of previous investigations of lead phases and lead oxide weathering in neutral and carbonatic soils (Graedel, 1994; Jorgensen and Willems, 1987; Martinetto et al., 2002; Ryan et al., 2001). The relatively fast kinetics of carbonate formation is also in agreement with the results of Hardison et al. (2004) who reported lead carbonate formation on lead or lead oxide in an alkaline soil within weeks. A prediction if either cerussite or hydrocerussite will be formed cannot be done with accuracy as the thermodynamic data is still of an ambiguous nature (Essington et al., 2004). Mercy et al. (1998) reported that in soils paragenesis of cerussite and hydrocerussite can occur due to the  $\text{CO}_2$  partial pressure equilibrium between both minerals ( $\sim 10^{-4}$  atm) which is close to the atmospheric  $\text{CO}_2$  partial pressure ( $10^{-3.5}$  atm).

The samples exposed to the non-calcareous loam showed only minor traces of lead carbonate phases on an otherwise almost unaltered surface. Traces of phosphate have been found by ESEM-EDX point scan analysis on the particle surface. Formation of lead phosphate (pyromorphite) would be an explanation for the presence of phosphate on the surface. Essington et al. (2004), however, concluded according to their speciation calculations that in calcareous soils usually lead carbonate phases will control lead solubility in the long run, even in the presence of significant phosphate concentrations. The lack of visible lead phosphate formation may have been due to interference of organic substances. Lang and Kaupenjohann (2003) found that lead phosphate precipitates did not increase in size beyond finely dispersed colloids in the presence of dissolved soil organic carbon. Also Buatier et al. (2001) found only poorly crystallized lead phosphate phases in soils under similar conditions. If lead phosphate precipitates did form they were too small to be visible in the SEM microphotographs. So it is possible that lead phosphates were formed in the non-calcareous

loam soil, though to a much smaller extent than lead carbonates. The fine layer of lead phosphate efficiently protected the soluble PbO from further dissolution. Also adsorbed phosphate which would not be visible was found to inhibit the dissolution of minerals (Stumm, 1997).

The results using the new in situ method show that field experiments are needed to establish the phases formed under natural conditions. The easily soluble lead oxide proved to be quite stable in these soils under field conditions with minimal surface alterations in the non-calcareous loam. This shows that not only visible weathering crusts are able to inhibit further alterations of the surface of easily soluble minerals. Such experiments may help to improve our understanding of phase transformation reaction in soils leading to meta-stable phases or increase our knowledge about the kinetics of the transformation reactions.

## 5. Conclusions

The study shows the potential of the new incubation method to analyze the phase transformation of fine mineral particles under in situ conditions in the field, if combined with mineralogical and geochemical methods for the analysis of the recovered samples in the laboratory. Lead oxide particles incubated in a calcareous sand were covered by a crust of lead carbonate within 2 months. The crust protected the lead oxide particles efficiently against further weathering. Formation of lead carbonate phases was much less in the two loam soils. The easily soluble lead oxide proved to be quite stable in these soils under field conditions with minimal surface alterations in the non-calcareous loam. The use of experimental in situ methods is thus giving new information on contaminant mineral behavior under field conditions.

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