Changes in Zn speciation during soil formation from Zn-rich limestones

Olivier Jacquat a, Andreas Voegelin a,*, Farid Juillot b, Ruben Kretzschmar a

a Institute of Biogeochemistry and Pollutant Dynamics, Department of Environmental Sciences, ETH Zurich, CHN, 8092 Zurich, Switzerland
b Institut de Minéralogie et de Physique des Milieux Condensés, Université Pierre et Marie Curie, Université Paris Diderot, IPGP, UMR-CNRS 7590, Campus Boucicaut, 75015 Paris, France

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Abstract

In order to better understand the long-term speciation and fractionation of Zn in soils, we investigated three soils naturally enriched in Zn (237–864 mg/kg Zn) from the weathering of Zn-rich limestones (40–207 mg/kg Zn) using extended X-ray absorption fine structure (EXAFS) spectroscopy and sequential extractions. The analysis of bulk EXAFS spectra by linear combination fitting (LCF) indicated that Zn in the oolitic limestones was mainly present as Zn-containing calcite (at site Dornach), Zn-containing goethite (Gurnigel) and Zn-containing goethite and sphalerite (Liestal). Correspondingly, extraction of the powdered rocks with 1 M NH4-acetate at pH 6.0 mobilized only minor fractions of Zn from the Gurnigel and Liestal limestones (<30%), but most Zn from the Dornach rock (81%). In the Dornach soil, part of the Zn released from the dissolving limestone was subsequently incorporated into pedogenic hydroxy-interlayered vermiculite (Zn-HIV, ~30%) and Zn-containing kaolinite (~30%) and adsorbed or complexed by soil organic and inorganic components (~40%). The Gurnigel and Liestal soils contained substantial amounts of Zn-containing goethite (~50%) stemming from the parent rock, smaller amounts (~20%) of Zn-containing kaolinite (and possibly Zn-HIV), as well as adsorbed or complexed Zn-species (~30%). In the soil from Liestal, sphalerite was only found in trace amounts, indicating its dissolution during soil formation. In sequential extractions, large percentages of Zn (~55–85%) were extracted in recalcitrant extraction steps, confirming that Zn-HIV, Zn-containing kaolinite and Zn-containing goethite are highly resistant to weathering. These Zn-bearing phases thus represent long-term hosts for Zn in soils over thousands of years. The capability of these phases to immobilize Zn in heavily contaminated soils may however be limited by their uptake capacity (especially HIV and kaolinite) or their abundance in soil.

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1. INTRODUCTION

Zinc is an essential micronutrient for plants and animals. At elevated concentrations, however, Zn may exert toxic effects on plants and microorganisms, thereby leading to a decrease in soil fertility and crop yield (Alloway, 1995). The bioavailability and mobility of Zn in soils depend to a large degree on its chemical form or speciation. Studies on the sorption and speciation of Zn in metal oxide and clay mineral suspensions demonstrated its versatile reactivity and suggested that the formation of layered precipitates such as hydroxides, layered double hydroxides (LDH) or phyllosilicates may be an important sequestration mechanism in contaminated soils at near-neutral to alkaline pH (Ford and Sparks, 2000; Schlegel et al., 2001; Roberts et al., 2003). Spectroscopic studies on the speciation of Zn in soils contaminated over years to decades confirmed the formation and relevance of Zn-phyllosilicate- and Zn-LDH-type precipitates under field conditions (Manceau et al., 2000a; Juillot et al., 2003; Nachtegaal et al., 2005; Panfili et al., 2005; Voegelin et al., 2005b; Kirpichtchikova et al., 2006). In calcareous soils, both Zn-LDH and Zn-phyllosilicate were identified.
with Zn-LDH dominating at higher Zn loadings and extreme Zn levels leading to the formation of hydroxizincite (Jacquat et al., 2008). In contrast, specific sorption of Zn in the Al-hydroxy interlayers of hydroxy-interlayered minerals (HIM) was found to be an important Zn uptake mechanism in (mostly acidic) HIM-containing soils at low to moderate contamination levels (Scheinost et al., 2002; Jacquat et al., 2009a). Thus, several recently identified layered Zn phases are quantitatively relevant in contaminated soils, their occurrence depending on soil pH, the level of Zn contamination, and the abundance of organic and mineral sorbent phases (Jacquat et al., 2009b).

The aforementioned studies showed that Zn-LDH, Zn-phyllosilicates and Zn-HIM may occur in soil environments after years to decades of Zn contamination, but little is still known about the stability of these Zn phases over thousands of years and their impact on the fate of Zn over geologic timescales. Studying the speciation of Zn in pristine soils may provide valuable information about the long-term fate of Zn in a weathering soil environment and also support the optimization of remediation strategies for contaminated soils. Both Zn-HIM and Zn-phyllosilicates (as Zn-kerolite) have been identified in pristine acidic soils (Manceau et al., 2004, 2005; Isaure et al., 2005). In saprolite developed from metamorphic mafic rocks and in weathered Zn-bearing ore deposits, several Zn-rich layered precipitates were identified, including fraipontite (Zn-serpentine), sausonite (Zn-smectite), baileychlore (Zn-chlorite) and zaccaganite (Zn-LDH) (Césaro, 1927; Ross, 1946; Paquet et al., 1986; Rule and Radke, 1988; Merlino and Orlandi, 2001). Supergene alteration of primary Zn-sulfide deposits in limestone may also result in the formation of Zn-hydroxy carbonates and hydroxides in addition to Zn-silicates (Takahashi, 1960).

In this study, we investigated three soils with geologically and climatically different Zn contents which developed over the recent Quaternary period from Zn-rich Jurassic limestones. Our objectives were (i) to determine the chemical forms of Zn in three soil-forming limestone rocks and the associated naturally Zn-enriched soils and (ii) to assess the reactivity of Zn due to changing soil chemical conditions during weathering. The speciation of Zn was determined by bulk- and microfocused EXAFS (μ-EXAFS) spectroscopy. Single and sequential extractions were performed to characterize the reactivity of Zn in the limestone rocks and soil materials.

2. MATERIALS AND METHODS

2.1. Sampling sites

The studied soils are located in the northwestern part of Switzerland and developed from Zn-rich Jurassic limestones of the Jura mountain range. The soils developed since the last glacial maximum (Bourquin et al., 1968; Bitterli-Brunner et al., 1984) and are therefore estimated to be ~10000 years old. At all three sites, the soils were well-drained and unaffected by groundwater.

At soil sampling locations, samples were collected from within a single soil profile. The first soil (DOR) is located 1 km south of the village of Dornach (47° 28’N, 7° 37’E) under forest. Soil samples were collected from five distinct horizons. The soil profile consisted of a 5 cm thick black hemic organic layer with a very thin base of sapric material (Oe), a brown-dark organo-mineral horizon (Ah, 0–7 cm, 10YR 3 3), and two clayey horizons varying in color from light brown (Bw, 7–17 cm, 10YR 4 6) to yellowish brown (BwC, 17–38 cm, 10YR 5 6). The hard saprolitic horizon of oolitic micritic limestone (R) of Oxfordian age (~160 Ma, (Rambeau, 2006)) was sampled at depths of 38–42 cm. The soil profile has previously been described in detail (Desaules et al., 2000; Baize and Sterckeman, 2001) and was classified as Haplic Cambisol according to the World Reference Base for Soil Resources (WRB, 2006).

Both the second (GUR) and third soil (LIE) were classified as Rendzic Leptosol according to the World Reference Base for Soil Resources (WRB, 2006). The soil GUR was sampled on a pasture 2 km east of the pass of la Vue des Alpes (Le Gurnigel, 47° 05’N, 6° 54’E). It had formed on oolitic limestone of late Bajocian age (~168 Ma) and consisted of an organic-rich layer containing limestone particles (Aca, 0–10 cm, 10YR 3 3) covering the unweathered limestone (R, sampled at 10–14 cm depth). The soil LIE was located in a forest on the south–west rolling footslope of the Schleifenberg hill (47° 29’N, 7° 44’E) near Liestal (corresponding to sample “S9” in Quezada-Hinojosa et al., 2009). Both the limestone-rich soil horizon (Aca, 0–8 cm, 10YR 3 3) and the underlying bedrock (R) consisting of oolitic limestone of early Bajocian age (~170 Ma), were sampled.

2.2. Sample preparation and bulk soil properties

The soils sample were air-dried at 25 °C, manually broken into small aggregates, gently homogenized in an agate mortar and sieved to ~2 mm. Powdered samples <50 μm of soil and limestone samples were prepared using a vibratory agate disc mill. The soil pH was measured in 10 mM CaCl2 (at a solution-to-soil ratio(SSR) of 10 mL/g after 30 min equilibration time, single measurements) using a glass electrode. Wax pellets were prepared from the powdered samples (4 g of material and 0.9 g of Licowax®) and analyzed for total element contents by energy-dispersive X-ray fluorescence spectrometry (Spectro X-Lab 2000) using a calibration from the manufacturer for geologic materials (one measurement per sample). Analysis of soil reference materials with certified Zn contents of 509 and 7290 mg/kg returned 513 ± 18 and 7516 ± 44 mg/kg Zn (±standard deviation, n = 14). Total carbon contents (TC) were determined on powdered samples using a CHNS Analyzer (CHNS-32, LECO, 2–4 replicates, relative standard deviation (RSD) ≤ 6%). Total inorganic carbon (TIC) contents were determined by reacting 0.3–0.9 g of soil material with 1 M sulfuric acid (H2SO4) under heating. The evolving CO2 was adsorbed in a Nesbitt bulb containing NaOH-coated sorbent and was quantified gravimetrically (Löeppert and Suárez, 1996) (analyzes in duplicates, standard deviation < 0.6 g/kg TIC). Total organic carbon (TOC) was calculated by subtracting the TIC from the TC content. After pretreatment of the soils with H2O2 for removal of organic matter, the sand content (50–2000 μm) was quantified by wet sieving and the clay content (~2 μm) using the pipette method (Gee and Or, 2002) (single measurements). The silt content (2–50 μm) was calculated as the difference to total soil weight.

2.3. Clay extraction and analysis

The clay size fraction (~2 μm) was isolated by wet sieving and sedimentation following standard procedures (Kimpe, 1993ab). The Mg-saturated clay fraction was freeze-dried for further analysis. K-saturated clay was prepared from Mg-saturated clay by repeated reaction with 1 M KCl followed by washing (Kimpe, 1993). Oriented specimens of Mg- and K-saturated clay were prepared by settling 30 mg clay suspended in water onto glass slides.
(2.5 cm in diameter) and drying at room temperature. Ethylene glycol (EG) and glycerol (Gly) solution was prepared by leaving an oriented Mg-saturated slide on the shelf of an EG- or Gly-solvation. X-ray diffraction (XRD) patterns were recorded from 3° to 72° 2-theta (Cu-K$_\alpha$ radiation, variable slits, 0.02°-steps, 4 step/continuous scan mode, energy-dispersive detector). Oriented mounts of the citrate-extracted clay (HIS) with increasing Zn contents (‘‘Zn-HIS-2.1’’, ‘‘Zn-HIS-4.0’’ and ‘‘Zn-HIS-6.9’’) were recorded from 3 to 37° C (in sequence on same slide). X-ray fluorescence (XRD) patterns were recorded from 3° to 72° 2-theta (Cu-K$_\alpha$ radiation, variable slits, 0.02°-steps, 4 step/continuous scan mode, energy-dispersive detector). Oriented mounts of the citrate-extracted clay fractions (Section 2.9) were analyzed in analogy after Mg-saturation and EG and Gly solvation.

2.4. Reference compounds for EXAFS spectroscopy

For the preparation of the reference samples of Zn coprecipitated with ferrihydrite and goethite, a method for the synthesis of goethite (Schwertmann and Cornell, 1991) was adapted. About 135 mL of 1 M KOH were added to 75 mL of 0.3 M (Fe(NO$_3$)$_3$·9H$_2$O + Zn(NO$_3$)$_2$·4H$_2$O) at a molar Zn/(Zn + Fe) ratio of 0.015. After vigorous stirring, the fresh precipitate was centrifuged and the supernatant decanted. The resulting Zn-containing ferrihydrite (‘‘Zn-ferrihydrite’’) was washed and centrifuged five times with DDI water. Subsequently, the sample was frozen in LN and freeze-dried. In a second vessel, the synthesis was repeated. After dilution in 1.5 L DDI water, the fresh Zn-ferrihydrite precipitate was aged during 67 h at 70°C to achieve transformation to goethite. The suspension was centrifuged and washed five times with 0.2 M oxalic acid in the dark to remove amorphous Fe oxides. The Zn-containing goethite (‘‘Zn-goethite’’) was washed three times with DDI water, frozen in LN and freeze-dried. The structure of Zn-ferrihydrite and Zn-goethite was confirmed by XRD. Final Zn contents determined by XRF spectrometry were 14,000 mg/kg for Zn-ferrihydrite and 16,500 mg/kg for Zn-goethite. Sphalerite (‘‘ZnS’,’’, Alfa Aesar, Nr. 040091), was used without further treatment. Zn-containing calcite (Zn$_{0.00}$Ca$_{0.99}$CO$_3$, ‘‘Zn-calcite’’) was synthesized by reacting 4 g of vaterite with 200 mL of 460 μM ZnCl$_2$ for 5 d (Jacquat et al., 2008). The reference database also included natural and synthetic Zn-containing kaolinite (‘‘nat. Zn-kaolinite’’ and ‘‘syn. Zn-kaolinite’’) with Zn contents of 180 and 270 mg/kg as well as a series of hydroxy-Al interlayered smectites (HIS) with increasing Zn contents (‘‘Zn-AIS-2.1’’, ‘‘Zn-AIS-2.9’’, ‘‘Zn-HIS-4.0’’ and ‘‘Zn-HIS-6.9’’) with Zn contents of 2100, 2900, 4000, and 6900 mg/kg, respectively. These references were discussed in detail in an earlier study (Jacquat et al., 2009a). A series of ZnMg-kerolites with variable Zn and Mg contents included ‘‘Zn-kerolite’’, ‘‘Zn$_{0.8}$Mg$_{0.2}$-kerolite’’, ‘‘Zn$_{0.6}$Mg$_{0.4}$-kerolite’’, ‘‘Zn$_{0.4}$Mg$_{0.6}$-kerolite’’, and ‘‘Zn$_{0.0}$Mg$_{0.94}$-kerolite’’) (Jacquat et al., 2008). References for adsorped and complexed Zn-species included, amongst others, ‘‘Zn-phytate’’, ‘‘Zn-sorbed calcite’’, ‘‘Zn-sorbed ferrihydrite’’, ‘‘low Zn-birnessite’’ and ‘‘Zn-sorbed talc’’ for which details have been provided in earlier studies (Jacquat et al., 2008, 2009b).

2.5. Bulk Zn K-edge EXAFS spectra acquisition

Zinc K-edge EXAFS spectra were measured at the XAS beamline at the Angströmquelle Karlsruhe (ANKA, Karlsruhe, Germany) and the Swiss Norwegian beamline SNBL at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). At both beamlines, the monochromator was calibrated by assigning the first inflection point of the K-edge absorption spectrum of metallic Zn to 9659 eV. Powdered soil and rock samples and reference materials were mixed with polyethylene or Licowax® and pressed into 13-mm pellets for analysis. The pellets were analyzed at room temperature in fluorescence mode using a 5-element (ANKA) or a 13-element (SNBL) Ge solid state detector or in transmission mode (ionization chambers), depending on Zn concentration.

2.6. µ-XRF and µ-EXAFS analyses on soil thin-sections

For µ-XRF and µ-EXAFS analyses, undisturbed soil aggregates from the horizons DOR-BwC, GUR-Aca and LIE-Aca were impregnated with a high purity resin (Epoxi Struers or Araldit 2020) and prepared as polished sections of 50, 150 and 200 μm thickness, respectively. The sections were analyzed at beamline 10.3.2 at the Advanced Light Source (ALS, Berkeley, USA) (Marcus et al., 2004). Soil thin-sections were placed at an angle of 45° to the incident beam and the fluorescence signal was recorded at an angle of 90° using a 7-element Ge solid state detector. The µ-XRF maps were obtained by scanning the samples with step sizes of 20 × 20, 10 × 10, or 5 × 5 μm$^2$ and dwell times of 200 or 100 ms per point at an incident photon energy of 10 keV. For the distribution of Mn in the DOR-BwC horizon, an additional map was collected at an incident photon energy of 7012 eV (100 eV below Fe K-edge). For the other two sections GUR-Aca and LIE-Aca, the Mn K$_\alpha$ intensity was deconvoluted from fluorescence into the Mn channel by subtracting a constant fraction of the recorded Fe signal (determined graphically from the scatter plot of the Mn intensity versus the Fe intensity). Zn K-edge EXAFS spectra were recorded at points of interest (POI) using a beam size between 5 × 5 and 16 × 7 μm$^2$ depending on the size of the relevant feature. The black–white scale of the XRF maps was defined to cover the range between the minimum pixel value (black) and the 99 percentile of all pixel values (white).

2.7. EXAFS data extraction and analysis

EXAFS data extraction was performed using the software code Athena (Ravel and Newville, 2005). All spectra were normalized by fitting a first order polynomial to the pre-edge data (−150 to −30 eV relative to E$_0$) and a second order polynomial to the post-edge region (+150 up to −100 eV before end of spectrum). The energy was converted to photoelectron wave vector units (Å$^{-1}$, k-space) by setting E$_0$ to the first maximum of the first derivative of the absorption edge. EXAFS spectra were extracted by fitting the post-edge data with a cubic spline function using the Autobk algorithm implemented in Athena ($R_{\text{bkg}} = 0.9$ Å, k-weight = 3, spline k-range from 0.5 to 12 Å$^{-1}$).

The soil EXAFS spectra were evaluated by principal component analysis (PCA) and target transform testing (TT) using SIXPack (Webb, 2005). Considering all k$^2$-weighted bulk- and micro-EXAFS spectra (k-range 2–10 Å$^{-1}$), the number of spectral components required to reproduce the entire data set without experimental noise was determined by PCA based on the empirical indicator (IND) function (Malinowski, 1977; Manceau et al., 2003). To identify suitable reference spectra for data analysis by linear combination fitting (LCF), TT was then performed on a large database of reference spectra, which included, among others, synthetic (syn.) and natural (nat.) minerals and precipitates (syn. Zn-kaolinite, nat. Zn-kaolinite, syn. Zn-containing kerolite at various Zn/Mg ratios (pure Zn-kerolite, Zn$_{0.8}$Mg$_{0.2}$-kerolite, Zn$_{0.6}$Mg$_{0.4}$-kerolite, Zn$_{0.4}$Mg$_{0.6}$-kerolite, Zn$_{0.0}$Mg$_{0.94}$-kerolite), Zn-LDH, Zn-lithiophorite), carbonates (Zn-calcite, hydrozincite, smithsonite), Zn incorporated into hydroxy-interlayered smectite (Zn-HIS) at various loadings (Zn-HIS-6.9 (6900 mg/kg Zn), Zn-HIS-4.0 (4000 mg/kg Zn), Zn-HIS-2.9 (2900 mg/kg Zn) and Zn-HIS-2.1 (2100 mg/kg Zn)), and adsorbed/complexed Zn-species (Zn-phytate, Zn-sorbed ferrihydrite, Zn-sorbed calcite, Zn-sorbed goethite, aqueous Zn) (Jacquat et al., 2008, 2009a, 2009b). The empirical SPOIL value (Malinowski, 1978) and the normalized sum of
squared residual (NSSR) of the target transforms (Isaure et al., 2002; Sarret et al., 2004; Pan fili et al., 2005; Kirpichchikova et al., 2006) were used to judge the suitability of reference spectra for LCF.

The spectra of the soil and rock samples were analyzed by linear combination fitting (LCF) using the approach and software developed by Mane ceau and coworkers (Man eau et al., 1996, 2000a). All possible one-component to 4-component fits were optimized by minimizing NSSR (NSSR = \left( \sum_{i}^{k} \left( x_{i} - \sum_{j=1}^{n} a_{ij} \right)^{2} \right)^{1/2} / \sum_{i}^{k} \left( x_{i} - \sum_{j=1}^{n} a_{ij} \right)^{2})\). Starting from the best one-component fit, the best fit with n + 1 components was considered to be significantly better than the best n-component fit, if its NSSR was at least 10% lower than the NSSR of the best n-component fit. The precision of fractions obtained from LCF has previously been estimated to be around 10% of the total Zn (Isaure et al., 2002), but strongly depends on the spectral characteristics of all Zn-species present in the sample (Mane clau et al., 2000a).

2.8. Batch extraction of limestone samples

The calcrete fraction of the limestone samples (R horizons) was dissolved in 1 M NH$_4$-acetate solution buffered at pH 6.0 in order to obtain an estimate for the fraction of Zn contained in carbonates. Ten grams of powdered rock were suspended in 800 mL 1 M NH$_4$-acetate solution. After mixing for 1 h, the suspensions were slowly titrated with about 200 mL 1 M HCl. The exact volume of 1 M HCl needed to dissolve all carbonates was calculated assuming that all Ca in the limestones (determined by XRF spectrometry) was contained in CaCO$_3$. The solution pH remained constant (pH 6.0 ± 0.1) during the entire extraction time. After centrifugation, the supernatants were filtered (0.45 μm, nylon) and acidified with 1% (v/v) 30% HNO$_3$ for subsequent analysis of released Zn by inductively coupled plasma – optical emission spectrometry (ICP-OES, Varian Vista-MPX).

2.9. Extractions of soils and reference compounds

The soil samples were sequentially extracted following the extraction procedure of Zeien and Brüummer (1989). Experimental details have been provided previously (Voegelin et al., 2008). Briefly, each soil was extracted in duplicates (2 g of soil per extraction) according to the following sequence (with hypothetical interpretation according to (Zeien and Brümmer, 1989) in parentheses): Fraction F1: 1 M NH$_4$NO$_3$ (readily soluble and extractable); Fraction F2: 1 M NH$_4$-acetate, pH 6.0 (titrated to pH 6.0 using HCl to dissolve carbonates; mobilizable and CaCO$_3$ bound); Fraction F3: 0.1 M NH$_2$OH-HCl + 1 M NH$_4$-acetate, pH 4.6 (Mn-oxides); Fraction F4: 0.025 M NH$_4$–EDTA, pH 4.6 (bound to organic substances); Fraction F5: 0.2 M NH$_4$-oxalate, pH 3.25 (bound to amorphous and poorly crystalline Fe oxides); Fraction F6: 0.1 M ascorbic acid + 0.2 M NH$_4$–oxalate, pH 3.25 (bound to organic substances); Fraction F5: 0.2 M NH$_4$-oxalate, pH 3.25 (bound to amorphous and poorly crystalline Fe oxides). All extraction steps were performed with a solution-to-soil ratio of 25 mL/g. The solutions from the extraction steps F1–F6 were analyzed by ICP-OES. The residual material after F6 (duplicates pooled, Zr and Ti contents of the residual material after step F6) of the soil samples and the reference Zn-HIS-6.9 spiked into quartz powder. The same extraction was also performed with the pure reference materials Zn-HIS-6.9 and synthetic Zn-kaolinite as well as with the <2 μm size fraction of the soils. The extractions were performed in duplicates using either 50 or 250 mg of material at a solution-to-material ratio of 200 mL/g. The samples were extracted three times in boiling 0.3 M Na-citrate solution adjusted to pH 7.3. The three extracts were quantitatively merged and Zn concentrations analyzed by ICP-OES. The relative standard deviation from duplicate extractions was ≤5%.

3. RESULTS

3.1. Physical and chemical properties and mineralogy of studied soil materials

Physical and chemical properties and Zn contents of the different soil materials are listed in Table 1. Total element contents and molar Zn/element ratios are provided in Table EA1 in the electronic annex. The soil-forming oolitic limestones (horizons R in Table 1), contained between 43 and 207 mg/kg Zn. These concentrations are close to or higher than the 90-percentile level (n = 37) of 48 mg/kg Zn reported for limestones from Switzerland (Tuchschmid, 1995), indicating an elevated Zn content in the limestones from all three locations.

In the DOR soil profile, clay content and pH decreased from the BwC (7.2, 615 g/kg, respectively) to the Ah horizon (5.3, 522 g/kg, respectively), paralleled by an increase in Zn content from 476 mg/kg in the BwC to 783 mg/kg in the Ah horizon. Substantial amounts of Zn (318 mg/kg) were also contained in the acidic Oe horizon. The Aca horizons of the soils GUR and LIE, which were in direct contact with the bedrock, had a neutral pH, a high clay content (>600 g/kg), and high Zn concentrations (864 and 237 mg/kg, respectively). In Switzerland, the upper limits for normal geogenic Zn contents in soils with pH 5.1–6.1, 6.2–6.7 and 6.8–7.6 are 95, 116 and 132 mg/kg, respectively (Keller and Desaulles, 2001). The Zn content of all three soils exceeded these limits by 2–6 times. At Gurnigel and Liestal, significant anthropogenic Zn inputs can be excluded (Wenk et al., 1997; Dubois et al., 2002; Rambeau, 2006). In Dornach, atmospheric emissions of a brass foundry located about one kilometer away have previously been estimated to account for 60–100 mg/kg of the total Zn in cultivated topsoils sampled near the forested sampling location DOR (Baize and Sterckeman, 2001). This anthropogenic Zn input would correspond to ~13% of the total Zn of the DOR-Ah horizon, but would have been further reduced by downward transport in the acidic forest soil profile (in contrast to the cultivated calcareous soils nearby). Furthermore, atmospheric input occurred in the form of readily dissolving ZnO (Voegelin et al., 2005a) and stopped at least 20 years before sample collection. Therefore, anthropogenic Zn input is not expected to have significantly
altered the Zn speciation resulting from geogenic Zn release.

XRD patterns of oriented mounts of the <2 μm size fraction of the soil samples from DOR-BwC, GUR-Aca and LIE-Aca are shown in Fig. 1. The clay mineralogy was dominated by kaolinite, vermiculite, illite and quartz. Goethite was present as a major accessory mineral. The 14.2 Å peak (6.2° 2θ Cu Kα) observed in the air-dried Mg-saturated slides of DOR-BwC and GUR-Aca was partially shifted to higher d-spacings after treatment with ethylene glycol (EG), whereas no shift was observed under glycerol (Gly) solvation. After K-saturation and gentle heat treatment (100 °C), the 14.2 Å peak did not collapse to 10 Å. Instead, it remained expanded and collapsed to ~11.2 Å after heating to 550 °C. These trends indicated that the interlayer space of the 14.2 Å mineral was filled with hydroxyl-polymers (Barnhisel and Bertsch, 1989; Douglas, 1989). Also after the removal of hydroxy-Al interlayers from soil clay minerals by Na-citrate extraction, ethylene glycol (EG) and glycerol (Gly) solvation did not cause a shift of the 14.2 Å peak to higher d-spacings (Fig. EA1), indicating that it originated mainly from hydroxy-interlayered vermiculite (HIV) rather than hydroxy-interlayered smectite (HIS). The 12 Å peak (7.3° 2θ Cu Kα) of the interstratified illite-vermiculite mineral identified in the Mg-saturated slide of LIE-Aca showed similar response to Gly and EG solvation and heat treatment. Thus, like the vermiculite minerals identified in DOR-BwC and GUR-Aca, also the vermiculite minerals of the Mg-saturated slide of LIE-Aca showed similar response to Gly and EG solvation and heat treatment. The Fourier-transformed limestone and the reference spectrum (not shown) compared to a published spectrum of synthetic Zn-containing goethite (Manceau et al., 2000b), for which analysis by shell-fitting indicated Zn substitution for Fe in the goethite structure. In the limestone from LIE (spectrum LIE-R), mainly sphalerite (ZnS) and a minor fraction of Zn-goethite were detected.

The extraction results of the limestone samples were in qualitative agreement with the speciation inferred from EXAFS spectroscopy: From DOR-R, 81% of the total Zn was extracted during carbonate dissolution, in line with EXAFS data showing Zn to mainly substitute for Ca in the calcite structure. In contrast, only minor fractions of the total Zn were extracted from the limestones GUR-R (27%) and LIE-R (17%), suggesting Zn to be contained in residual minerals. The extraction and speciation results were also in line with the higher amounts of Fe and S in the limestones GUR-R and LIE-R relative to DOR-R (Table EA1).

3.3. Principal component analysis and target transform testing

The number of spectral components in the 18 soil EXAFS spectra (5 bulk soil spectra (DOR-Oe, DOR-Ah, DOR-BwC, GUR-Aca, LIE-Aca), 3 spectra from clay fractions (DOR-Ah clay, DOR-BwC clay, GUR-Aca clay) and 10 μ-EXAFS spectra from DOR-BwC (3) GUR-Aca (3) and LIE-Aca (4)) was determined by principal component analysis (PCA). The parameters of the first 8 components from PCA are provided in Table 3. The empirical IND function reached a minimum for the first 5 components, suggesting 5 significant spectral components (Malinowski, 1977), which explained 75% of the total experimental variance.
using these 5 principal components, all soil spectra could be well reproduced (NSSR between 0.01% and 4.8%). Suitable reference spectra for LCF analysis were subsequently identified by target transform testing (TT). Using the 5 principal components from PCA, the empirical SPOIL value was used to classify references as excellent (0–1.5), good (1.5–3.0), fair (3.0–4.5), acceptable (4.5–6.0) and unacceptable (>6.0) (Malinowski, 1978). Results for selected reference spectra are provided in Table 4. Among all tested references, Zn-HIS with intermediate to high Zn loadings (Zn-HIS-2.9, Zn-HIS-4.0, Zn-HIS-6.9) and tetrahedrally coordinated complexed or adsorbed Zn-species (Zn-phytate, Zn-sorbed calcite and Zn-sorbed ferrihydrite) had the lowest SPOIL values and were best reconstructed, as judged from their NSSR (Table 4, Fig. 3). In Zn-HIS with low Zn loadings, Zn is contained in the vacancies of gibbsitic Al-polymers. With increasing Zn-loading of HIS, variance. Using these 5 principal components, all soil spectra could be well reproduced (NSSR between 0.01% and 4.8%). Suitable reference spectra for LCF analysis were subsequently identified by target transform testing (TT). Using the 5 principal components from PCA, the empirical SPOIL value was used to classify references as excellent (0–1.5), good (1.5–3.0), fair (3.0–4.5), acceptable (4.5–6.0) and unacceptable (>6.0) (Malinowski, 1978). Results for selected reference spectra are provided in Table 4. Among all tested references, Zn-HIS with intermediate to high Zn loadings (Zn-HIS-2.9, Zn-HIS-4.0, Zn-HIS-6.9) and tetrahedrally coordinated complexed or adsorbed Zn-species (Zn-phytate, Zn-sorbed calcite and Zn-sorbed ferrihydrite) had the lowest SPOIL values and were best reconstructed, as judged from their NSSR (Table 4, Fig. 3). In Zn-HIS with low Zn loadings, Zn is contained in the vacancies of gibbsitic Al-polymers. With increasing Zn-loading of HIS,
Zn speciation shifts to sites with decreasing Al-coordination and ultimately to exchangeably adsorbed Zn (Jacquat et al., 2009a). Low SPOIL values were also obtained for ZnS, Zn-calcite and Zn-goethite, which were identified in the oolitic limestones. Among the Zn-bearing phyllosilicates in our database, synthetic and natural Zn-kaolinite had the lowest SPOIL values. The reference spectra of the Zn-kaolinites exhibit similarities to the spectra of Zn-HIS with low Zn loadings (Fig. 3). These similarities result from the

Table 3
Results from the principal component analysis of the 8 bulk- and 10 µ-EXAFS spectra collected on soil materials (excluding limestone R horizons).

<table>
<thead>
<tr>
<th>Component</th>
<th>Eigenvalue</th>
<th>Variance</th>
<th>Cum. Var.</th>
<th>IND</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>134.6</td>
<td>0.385</td>
<td>0.385</td>
<td>0.0600</td>
</tr>
<tr>
<td>2</td>
<td>45.2</td>
<td>0.129</td>
<td>0.514</td>
<td>0.0542</td>
</tr>
<tr>
<td>3</td>
<td>36.0</td>
<td>0.103</td>
<td>0.617</td>
<td>0.0485</td>
</tr>
<tr>
<td>4</td>
<td>28.5</td>
<td>0.081</td>
<td>0.699</td>
<td>0.0425</td>
</tr>
<tr>
<td>5</td>
<td>17.5</td>
<td>0.049</td>
<td>0.749</td>
<td>0.0423</td>
</tr>
<tr>
<td>6</td>
<td>11.2</td>
<td>0.031</td>
<td>0.781</td>
<td>0.0466</td>
</tr>
<tr>
<td>7</td>
<td>10.3</td>
<td>0.029</td>
<td>0.810</td>
<td>0.0519</td>
</tr>
<tr>
<td>8</td>
<td>9.67</td>
<td>0.027</td>
<td>0.838</td>
<td>0.0584</td>
</tr>
</tbody>
</table>

a Cumulative variance.
b Indicator function.

Table 4
Results from target transform testing of reference spectra based on the 5 principal components obtained by PCA of the 17 soil EXAFS spectra. Spectra are arranged by increasing SPOIL value. All listed references except pure Zn-kerolite and Zn-LDH were included in the LCF analysis.

<table>
<thead>
<tr>
<th>References</th>
<th>SPOIL</th>
<th>NSSR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-HIS-6.9</td>
<td>0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Zn-phytate</td>
<td>1.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Zn-sorbed calcite</td>
<td>1.2</td>
<td>6.2</td>
</tr>
<tr>
<td>Zn-HIS-4.0</td>
<td>1.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Zn-HIS-2.9</td>
<td>1.4</td>
<td>3.9</td>
</tr>
<tr>
<td>syn. Zn-kaolinite</td>
<td>1.4</td>
<td>3.8</td>
</tr>
<tr>
<td>Zn-sorbed ferrihydrate</td>
<td>1.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Zn-HIS-2.1</td>
<td>1.6</td>
<td>5.6</td>
</tr>
<tr>
<td>nat. Zn-kaolinite</td>
<td>2.0</td>
<td>4.8</td>
</tr>
<tr>
<td>ZnS</td>
<td>2.0</td>
<td>8.8</td>
</tr>
<tr>
<td>Low Zn-birnessite</td>
<td>2.1</td>
<td>15.7</td>
</tr>
<tr>
<td>Zn-calcite</td>
<td>2.3</td>
<td>15.2</td>
</tr>
<tr>
<td>Aqueous Zn</td>
<td>2.6</td>
<td>4.3</td>
</tr>
<tr>
<td>Zn-goethite</td>
<td>3.0</td>
<td>9.9</td>
</tr>
<tr>
<td>Zn-lithiophorite</td>
<td>3.2</td>
<td>13.0</td>
</tr>
<tr>
<td>Zn0.06Mg0.94-kerolite</td>
<td>3.3</td>
<td>7.2</td>
</tr>
<tr>
<td>Zn0.34Mg0.66-kerolite</td>
<td>4.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Zn-ferrihydrite</td>
<td>4.6</td>
<td>36.2</td>
</tr>
<tr>
<td>Zn-sorbed goethite</td>
<td>4.8</td>
<td>11.9</td>
</tr>
<tr>
<td>Zn-sorbed talc</td>
<td>5.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Zn0.6Mg0.4-kerolite</td>
<td>5.3</td>
<td>23.5</td>
</tr>
<tr>
<td>Zn0.8Mg0.2-kerolite</td>
<td>5.8</td>
<td>41.7</td>
</tr>
<tr>
<td>Zn-kerolite</td>
<td>6.4</td>
<td>50.8</td>
</tr>
<tr>
<td>Zn-LDH</td>
<td>6.9</td>
<td>24.4</td>
</tr>
</tbody>
</table>

Spoil: 0–1.5 excellent, 1.5–3 good, 3–4.5 fair, 4.5–6 acceptable, >6 unacceptable reference (Malinowski, 1978).

Fig. 3. Zn K-edge EXAFS spectra of selected Zn reference compounds (solid lines) and respective target transforms (dotted lines, Table 4) calculated with the first 5 components from the principal component analysis of 17 soil EXAFS spectra (Table 3).
predominant Zn incorporation into the vacancies of the dioctahedral sheets of kaolinite, resembling the local coordination of Zn in the vacancies of gibbsitic Al-polymers of HIS. Spectral differences between Zn-kaolinite and low-Zn-HIS result from the backscattering contributions from the tetrahedral sheets of kaolinite as well as from potential partial Zn substitution of Zn for Al in the dioctahedral sheets of Zn-kaolinite (Jacquat et al., 2009a). Also in Zn-lithiophorite, considered a fair reference based on its SPOIL value, Zn is contained in the vacancies of gibbsitic sheets. The SPOIL values of ZnMg-kerolites were much higher and increased with increasing Zn content, paralleled by an increase in the NSSR of the respective target transforms. In ZnMg-kerolites, Zn is contained in trioctahedral sheets. At low Zn/Mg ratio, Zn is mainly surrounded by second-shell Mg, resulting in a similar local coordination as in low Zn-HIS and Zn-kaolinite (Jacquat et al., 2009a). Differences however result from the EXAFS contributions of the two adjacent tetrahedral Si sheets. With increasing Zn content, the spectral features are changing significantly due to the formation of Zn-rich trioctahedral sheets with substantial backscattering contributions from second-shell Zn. The target transform of Zn adsorbed to the edges of talc (Zn-sorbed talc) had an acceptable SPOIL value and a lower NSSR than Zn-rich kerolites. SPOIL values above 6 suggested that Zn-LDH and pure Zn-kerolite were not relevant in the studied soil materials. In Zn-LDH, Zn is contained in trioctahedral sheets containing Zn and Al, but lacks spectral contributions from tetrahedral sheets as in ZnMg-kerolites. The SPOIL values of phases containing Zn in octahedral sheets thus indicated a clear preference for Zn-HIS and Zn-kaolinites, whereas Zn incorporation into Zn-rich trioctahedral sheets did not seem to be a dominant structural feature in the studied soils.

In adsorbed and complexed Zn-species, the first-shell Zn-O signal may dominate the shape of the EXAFS spectrum due to a low number of second-neighbor atoms, the presence of weak low-Z backscatterers, or due to destructive interference of the EXAFS of different types of second-neighbor atoms. As a consequence, the EXAFS spectra of adsorbed or complexed species with the same type of first-shell coordination (tetrahedral or octahedral) may be difficult to distinguish in soil spectra with several spectral contributions (Jacquat et al., 2008). In LCF, we therefore only referred to tetrahedrally coordinated sorbed Zn (‘‘sorbed IVZn,” reference spectra Zn-phytate, Zn-sorbed calcite, Zn-sorbed ferrihydrite, and low Zn-birnessite) and octahedrally coordinated sorbed Zn (‘‘sorbed VIZn,” reference spectra Zn-sorbed goethite, aqueous Zn, and Zn-sorbed talc), indicating the reference used in the best LCF in Tables 5–7.

### 3.4. Speciation of Zn in the soil samples

For each studied soil, the dominant Zn-species were determined by bulk EXAFS spectroscopy. To better delineate the types of Zn-species present in the soils, we also analyzed the Zn speciation in selected clay-size isolates by bulk EXAFS as well as the distribution and speciation of Zn in soil thin-sections using µ-XRF and µ-EXAFS spectroscopy.

#### 3.4.1. Soil DOR

The distribution of Zn, Fe and Mn in a thin-section of undisturbed material from the DOR-BwC horizon is shown in Fig. 4. Zn occurs diffusively distributed in the clayey matrix and concentrated in localized Zn-rich spots. The distribution of Zn was closely related to the distribution of Fe, but not to that of Mn. µ-EXAFS spectra collected on selected KO (Fig. 4) as well as bulk EXAFS spectra from all soil horizons are shown in Fig. 5. LCF parameters are provided in Table 5.

In a localized Zn-rich spot next to a calcite grain and lacking correlation with Fe or Mn (DOR-BwC-3),

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Zn-HIS (%)</th>
<th>nat. Zn-kaolinite (%)</th>
<th>Zn-calcite (%)</th>
<th>Sorbed VIZn (%)</th>
<th>Sorbed IVZn (%)</th>
<th>Sum (%)</th>
<th>NSSR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOR-Oe</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>55</td>
<td>56</td>
<td>111</td>
<td>5.0</td>
</tr>
<tr>
<td>DOR-Ah Fit A</td>
<td>56</td>
<td>–</td>
<td>–</td>
<td>45</td>
<td>–</td>
<td>99</td>
<td>4.5</td>
</tr>
<tr>
<td>Fit B</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>61</td>
<td>–</td>
<td>91</td>
<td>7.4</td>
</tr>
<tr>
<td>Fit C</td>
<td>53</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>44</td>
<td>100</td>
<td>4.5</td>
</tr>
<tr>
<td>DOR-Ah-clay</td>
<td>49</td>
<td>22</td>
<td>–</td>
<td>32</td>
<td>–</td>
<td>103</td>
<td>2.4</td>
</tr>
<tr>
<td>DOR-BwC Fit A</td>
<td>57</td>
<td>–</td>
<td>–</td>
<td>47</td>
<td>–</td>
<td>104</td>
<td>4.8</td>
</tr>
<tr>
<td>Fit B</td>
<td>–</td>
<td>55</td>
<td>–</td>
<td>–</td>
<td>43</td>
<td>98</td>
<td>4.9</td>
</tr>
<tr>
<td>Fit C</td>
<td>32</td>
<td>30</td>
<td>–</td>
<td>39</td>
<td>–</td>
<td>101</td>
<td>3.7</td>
</tr>
<tr>
<td>DOR-BwC-clay</td>
<td>32</td>
<td>35</td>
<td>–</td>
<td>34</td>
<td>–</td>
<td>101</td>
<td>2.7</td>
</tr>
<tr>
<td>DOR-BwC-1</td>
<td>40</td>
<td>22</td>
<td>–</td>
<td>36</td>
<td>–</td>
<td>98</td>
<td>6.6</td>
</tr>
<tr>
<td>DOR-BwC-2</td>
<td>42</td>
<td>15</td>
<td>–</td>
<td>44</td>
<td>–</td>
<td>101</td>
<td>6.4</td>
</tr>
<tr>
<td>DOR-BwC-3</td>
<td>–</td>
<td>–</td>
<td>82</td>
<td>–</td>
<td>34</td>
<td>116</td>
<td>17.1</td>
</tr>
</tbody>
</table>

a Zn-HIS-6.9.  
b Zn-HIS-4.0.  
c Zn-HIS-2.9.  
d Zn-HIS-2.1.  
e Aqueous Zn.  
f Zn-sorbed ferrihydrite.  
g Zn-sorbed calcite.

Table 5  
Linear combination fits of the bulk and µ-EXAFS of the DOR-Oe, DOR-Ah, DOR-BwC.
Zn-calcite was identified. The two \( \mu \)-EXAFS spectra recorded within the clayey matrix of the soil (DOR-BwC-1 and DOR-BwC-2) were nearly identical to the EXAFS spectra from the clay fraction and the bulk soil of the BwC and Ah horizons (Fig. 5). This indicated that the Zn speciation in the bulk soil was dominated by Zn associated with minerals in the clay size fraction. In all these spectra, the first EXAFS oscillation was split at 3.8 Å/\( C_0 \), similar to Zn-HIS and Zn-kaolinite reference spectra (Fig. 3).

For DOR-BwC, a better two-component fit was achieved.

Table 6
Linear combination fits of the bulk and \( \mu \)-EXAFS of GUR-Aca.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Zn-goethite (%)</th>
<th>nat. Zn-kaolinite (%)</th>
<th>Sorbed ( ^{VI} )Zn (%)</th>
<th>Sorbed ( ^{IV} )Zn (%)</th>
<th>Sum (%)</th>
<th>NSSR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GUR1A-Aca</td>
<td>49</td>
<td>16</td>
<td>27( ^a )</td>
<td>–</td>
<td>92</td>
<td>5.3</td>
</tr>
<tr>
<td>GUR1A-Aca-clay</td>
<td>30</td>
<td>13</td>
<td>36( ^b )</td>
<td>16( ^c )</td>
<td>95</td>
<td>4.1</td>
</tr>
<tr>
<td>GUR1A-Aca-1</td>
<td>53</td>
<td>–</td>
<td>35( ^b )</td>
<td>12( ^d )</td>
<td>100</td>
<td>7.0</td>
</tr>
<tr>
<td>GUR1A-Aca-2</td>
<td>55</td>
<td>17</td>
<td>–</td>
<td>24( ^d )</td>
<td>96</td>
<td>6.8</td>
</tr>
<tr>
<td>GUR1A-Aca-3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>40( ^f ) + 54( ^f )</td>
<td>94</td>
<td>8.9</td>
</tr>
</tbody>
</table>

\( ^a \) Zn-sorbed goethite.
\( ^b \) Aqueous Zn.
\( ^c \) Zn-phytate.
\( ^d \) Zn-sorbed calcite.
\( ^f \) Zn-sorbed ferrihydrite.

Table 7
Linear combination fits of the bulk and \( \mu \)-EXAFS of LIE-Aca.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Zn-goethite (%)</th>
<th>ZnS (%)</th>
<th>nat. Zn-kaolinite (%)</th>
<th>Sorbed ( ^{VI} )Zn (%)</th>
<th>Sorbed ( ^{IV} )Zn (%)</th>
<th>Sum (%)</th>
<th>NSSR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIE-Aca</td>
<td>58</td>
<td>–</td>
<td>18</td>
<td>–</td>
<td>–</td>
<td>101</td>
<td>6.1</td>
</tr>
<tr>
<td>LIE-Aca-1</td>
<td>–</td>
<td>106</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>106</td>
<td>10.6</td>
</tr>
<tr>
<td>LIE-Aca-2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>23( ^a )</td>
<td>75( ^b )</td>
<td>98</td>
<td>7.0</td>
</tr>
<tr>
<td>LIE-Aca-3</td>
<td>45</td>
<td>–</td>
<td>21</td>
<td>–</td>
<td>–</td>
<td>33( ^b )</td>
<td>99</td>
</tr>
<tr>
<td>LIE-Aca-4</td>
<td>23</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>71( ^f )</td>
<td>94</td>
<td>7.5</td>
</tr>
</tbody>
</table>

\( ^a \) Aqueous Zn.
\( ^b \) Zn-sorbed ferrihydrite.
\( ^f \) Zn-sorbed calcite.

Fig. 4. Light microscope image of a thin-section from soil DOR-BwC and corresponding \( \mu \)-XRF maps for Zn, Fe and Mn. The mapped area is 3000 \( \times \) 2000 \( \mu \)m\(^2\) (20 \( \times \) 20 \( \mu \)m\(^2\) resolution, 200 ms dwell time).
with Zn-HIS-4.0 and aqueous Zn (Fig. 5, DOR-BwC Fit A) than with nat. Zn-kaolinite and aqueous Zn. However, addition of Zn-kaolinite in a three-component fit caused a substantial decrease in the NSSR (Table 5). The lower NSSR was reflected in a visually improved fit in the $r$-range 3–4.5 Å in Fourier transformed spectrum (Fig. 6). Since this region is sensitive to contributions from next-nearest Si in phyllosilicates (Manceau and Calas, 1986; Schlegel et al., 2001) which are absent in Zn-HIM (Scheinost et al., 2002; Schlegel and Manceau, 2007; Jacquat et al., 2009a), the improved LCF strongly suggested that Zn-kaolinite was present in the sample DOR-BwC in addition to Zn-HIM. The Zn-HIS and Zn-kaolinite reference spectra were also present in the best LCF of the EXAFS spectra from the clay size fraction of the Ah and BwC horizons (DOR-Ah-clay, DOR-BwC-clay) as well as the two $\mu$-EXAFS spectra recorded on the soil matrix (BOR-BwC-1, DOR-BwC-2), with similar improvements in $r$-space as reported for DOR-BwC (Fig. 6, Table 5). In best LCF fits, natural Zn-kaolinite was always preferred over synthetic Zn-kaolinite. In contrast, adding Zn-kaolinite to the LCF of the DOR-Ah EXAFS spectrum did not result in spectral improvements of the fit or a decrease in NSSR (Fig. 6, Table 5).

3.4.2. Soil GUR

The light microscope image of a thin-section from the Aca horizon of soil GUR and corresponding Zn, Fe and Mn distribution maps are shown in Fig. 7. The Zn distribution indicated localized Zn and Fe rich zones and Zn at lower concentrations associated with FeMn-concretions and the clayey matrix. Bulk and $\mu$-EXAFS spectra and corresponding LCF spectra of the bulk soil (GUR-Aca), the clay size fraction (GUR-Aca-clay) and 3 POI on the soil thin-section (GUR-Aca-1 to GUR-Aca-3) are shown in Fig. 8. LCF parameters are provided in Table 6. The $\mu$-EXAFS spectrum recorded within a FeMn concretion (GUR-Aca-3) exhibited a splitting at 6 Å/C0, as observed more intensively for birnessite with low Zn surface coverage (Manceau et al., 2002). Correspondingly, the LCF indicated mainly Zn sorbed to birnessite and ferrihydrite (Table 6). On the other hand, the $\mu$-EXAFS spectrum collected in the Fe-rich zone (GUR-Aca-1) closely resembled the bulk soil spectrum having an asymmetric first oscillation maximum at 3.8 Å−1. Such spectral features were also present in the spectra of the clay fraction (GUR-Aca-clay) and
clayey soil matrix (GUR-Aca-2), although less pronounced (Fig. 8). LCF on these spectra indicated Zn-goethite to be a major Zn-species in the soil, in agreement with the LCF analysis of the limestone spectrum showing Zn-goethite to be the dominant Zn-species (Fig. 2, Table 2). For some of the soil EXAFS spectra, LCF also indicated minor fractions of nat. Zn-kaolinite (always yielding better fits than syn. Zn-kaolinite or Zn-HIS).

3.4.3. Soil LIE

Distribution maps of Zn, Fe and Mn in a thin-section from the Aca horizon of soil LIE are shown in Fig. 9. The μ-EXAFS spectra from 4 POI on this thin-section and the EXAFS spectrum of the bulk soil are shown in Fig. 10. Similar to the Aca horizon of soil GUR, the distribution of Zn resembled the distribution of Fe and the μ-EXAFS spectrum of POI 3 (LIE-Aca-3) and the bulk soil spectrum were best fitted with Zn-goethite and minor contributions of nat. Zn-kaolinite and sorbed Zn. At POI 1 locally high Zn levels were not correlated with either Fe or Mn, and the respective μ-EXAFS spectrum (LIE-Aca-1) closely matched the spectrum of ZnS, the dominant Zn-species in the corresponding limestone rock (Fig. 2, Table 2). In contrast, the spectra LIE-Aca-2 and LIE-Aca-4 did not exhibit pronounced high frequency features and LCF returned high fractions of tetrahedrally coordinated adsorbed Zn.

3.5. Sequential extraction

In order to investigate the relation between Zn speciation and Zn fractionation, the geogenically Zn-rich soils and selected Zn reference compounds in pure form or spiked into quartz powder or non-calcareous soil were sequentially extracted. Sequential extraction results are presented in Fig. 11. Zn-ferrihydrite spiked in quartz powder was mainly extracted in F5, which is intended to remove poorly crystalline iron oxides (Zieen and Brümmer, 1989). However, the acidic (pH 3.25) 0.2 M ammonium oxalate ([NH₄]₂C₂O₄) solution used in F5 not only selectively dissolved Zn-ferrihydrite but also mobilized a substantial fraction of ZnS spiked into quartz. Most Zn from Zn-goethite spiked into quartz was extracted in the fraction F6, which is assumed to dissolve crystalline iron oxides (Zieen and Brümmer, 1989). Most Zn from Zn-HIS-6.9 spiked into quartz was extracted in the fraction F6, which is assumed to dissolve crystalline iron oxides (Zieen and Brümmer, 1989). Most Zn from Zn-HIS-6.9 spiked into quartz was extracted in the fraction F6, which is assumed to dissolve crystalline iron oxides (Zieen and Brümmer, 1989). Most Zn from Zn-HIS-6.9 spiked into quartz was extracted in the fraction F6, which is assumed to dissolve crystalline iron oxides (Zieen and Brümmer, 1989). Most Zn from Zn-HIS-6.9 spiked into quartz was extracted in the fraction F6, which is assumed to dissolve crystalline iron oxides (Zieen and Brümmer, 1989). Most Zn from Zn-HIS-6.9 spiked into quartz was extracted in the fraction F6, which is assumed to dissolve crystalline iron oxides (Zieen and Brümmer, 1989).
demonstrating substantial readsorption or reprecipitation of Zn during sequential soil extraction. The extraction of pure Zn-HIS-6.9 and pure synthetic Zn-kaolinite with Na-citrate (Jacquat et al., 2009a) confirmed the selectivity of this extraction for hydroxy-Al polymers, mobilizing 78% of the Zn from Zn-HIS-6.9 but only 15% of the Zn from Zn-kaolinite (not shown in Fig. 11).

In the DOR soils, the percentage of mobile and readily mobilisable Zn (fractions F1 + F2) decreased with increasing soil pH, i.e. increasing horizon depth. In parallel, the amount of Zn found in the last fraction (F7) increased from the Ah (47%) to the BwC horizon (77%), indicating a gradual shift to highly stable forms of Zn with depth. In all three soil horizons, additional Na-citrate extraction of the sequentially extracted samples (after step F6) mobilized similar fractions of the total Zn (~20%). The results from the sequential extraction of the Aca horizons from GUR and LIE were nearly identical. Almost all Zn (~80% of total Zn) was extracted in the last two fractions (F6 + F7), indicating that Zn was associated with highly recalcitrant phases. From all soils, only minor fractions of Zn were extracted in F3 designed for the dissolution of Mn-oxides (Zeien and Brümmer, 1989) and shown to extract birnessite and lithiophorite (Jacquat et al., 2009a).

4. DISCUSSION

4.1. Origin and speciation of Zn in the studied limestones

The three oolitic limestones investigated in this work had elevated Zn contents (43–207 mg/kg). High Zn (and Cd) contents in Jurassic limestones of the Jura mountain range may result from atmospheric fallouts due to volcanic activities (Rambeau, 2006) or post-sedimentation processes, i.e., hydrothermalism linked to tectonic extension (Efimenko et al., 2008). Regarding the first possibility, phases of volcanism have been identified for the Jurassic period (Jeans et al., 2000; Pankhurst et al., 2000). Rambeau (2006) suggested that variations in atmospheric metal input (occasional events) and in depositional environment strongly influence Zn and Cd enrichments in oolitic limestones. Elevated input of organic matter (due to enhanced productivity) into the sediments at the carbonate platform margin may have led to reducing conditions and formation of metal sulfides, whereas in lagoon environments, co-precipitation and micronization may have favored metal incorporation into carbonate phases (Rambeau, 2006). The detection of Zn-calcite in the lagoonal oolitic limestone DOR-R, Zn-goethite in the oolitic barrier limestone...
GUR-R, and occurrence of Zn-goethite and sphalerite in the platform margin limestone LIE-R are in qualitative agreement with this model.

During the Bajocian/Bathonian and Oxfordian, intense hydrothermal activity due to the reactivation of basement structures led to the mineralization of veins, alteration of minerals and illitization in Jurassic sediments of the Jura mountain range, the nearby Black Forest and the Vosges (Wetzel et al., 2003). In the Black Forest, hydrothermal Pb-Zn quartz-fluorite deposits containing sphalerite were dated to the Eocene-Oligocene (Von Gehlen, 1987; Schwinn et al., 2006). Even though mineralization veins were not observed in the limestones investigated here, the occurrence of sphalerite in the limestone LIE-R and in other limestones of the Jura mountain range (Efimenko et al., 2008) may also be linked to hydrothermal events. Following this hypothesis, the presence of Zn-containing goethite in the limestones LIE-R and GUR-R and of Zn-calcite in DOR-R could result from the oxidative transformation of hydrothermal sphalerite in contact with meteoric waters. Differences in rock permeability related to differences in rock facies (e.g., micritic versus sparitic matrix in DOR-R and GUR-R, respectively) could cause the spatial heterogeneity of metal enrichments observed in the Jura mountain range (Efimenko et al., 2008) and the formation of different Zn-species. More detailed chemical and stratigraphical analyses of the respective geological formations will be needed to evaluate the importance of different enrichment pathways and their influence on Zn speciation in limestones of the Jura mountain range.

4.2. Fate of geogenic Zn-species during soil formation

During limestone weathering and soil formation, the identified geogenic Zn-species showed different behavior.
At Gurnigel and Liestal, the elevated Zn concentrations observed in the soils were to a large extent due to the inheritance of Zn-goethite from the limestone. This interpretation was based on the EXAFS analyses indicating Zn-goethite to be a major Zn-species in the bedrock and sequential extraction data showing Zn-goethite to be highly resistant to acidifying conditions, and thus to pedogenic weathering. The formation of Zn-goethite from the weathering of Zn–Fe spinel has previously been observed in pristine and contaminated soils (Manceau et al., 2000a,c; Isäure et al., 2005). However, Zn-goethite in soil GUR and LIE did not form pedogenically but originated from the dissolution of the underlying limestone rock containing Zn-goethite. Based on Zn-goethite fractions from LCF (Table 2) and total Zn and Fe contents of the limestones from LIE and GUR (Table EA1), the Zn contents in goethite from the LIE and GUR limestones were estimated to be 2000 and 13,600 mg/kg, respectively. This closely compares to estimated Zn contents of 2000 and 9000 mg/kg Zn in goethite from the respective soil horizons LIE-Aca and GUR-Aca (based on LCF results from Tables 6 and 7 and the amounts of Zn and Fe extracted in the fraction F6 of the sequential extraction procedure). Even though sphalerite represented the major Zn-species in the limestone from Liestal, it was only detected in traces in the LIE soil, reflecting the oxidation of sulfides in the aerobic soil environment. Both at Gurnigel and Liestal, the molar ratios Zn/Al, Zn/Si, Zn/Ti and Zn/Fe of the limestone and the corresponding soil were of the same order of magnitude (Table EA1), suggesting limited Zn leaching during soil formation. This can be attributed to the inheritance of geogenic Zn-goethite which resisted transformation during weathering and soil formation as well as to the neutral soil pH of GUR and LIE, which limited the leaching of Zn released from geogenic Zn-species.

The relation between Zn-rich limestones and elevated Zn concentrations in soils of the Jura mountain range has previously been reported (Baize and Sterckeman, 2001; Dubois et al., 2002). These authors suggested that the wide spatial variability of Cd (and Zn) contents observed in soils resulted from variations in the metal concentrations of the underlying rocks. Our results show that not only the Zn content but also the chemical forms of Zn in the limestone rock and the chemical properties (pH, TIC) of the above-lying soil strongly influence soil Zn contents.

4.3. Pedogenic Zn-species

Our EXAFS analyses indicated that Zn released from the dissolution of geogenic Zn-species and retained in the soils was sequestered into Zn-HIM and/or Zn-kaolinite as well as into adsorbed and/or complexed Zn-species. Regarding sorbed and complexed forms of Zn, the LCF results (Tables 5–7) were in line with our earlier observation on contaminated soils that increasing soil pH resulted in a shift from octahedrally coordinated to tetrahedrally coordinated sorbed/complexed Zn, which we explained by a decrease in the fraction of exchangeably bound Zn (which is octahedrally coordinated) (Jacquart et al., 2009a). In the following, the formation of Zn-HIM and Zn-kaolinite and the potential for a geogenic origin of these species as well as the relevance of other layered Zn-bearing precipitates will be further discussed.

The LCF analysis of the EXAFS spectra from soil DOR indicated the occurrence of Zn-HIM (Table 5). Since only HIV but no HIS was identified by the XRD analysis (Fig. 1, Figs. EA1 and EA2), the fitted Zn-HIS fractions likely corresponded to Zn-HIV. According to Pochon (1978), HIM in soils of the Jura mountain range have developed from weathered geogenic chlorite and are indicative of post-Würmian (<10,000 years) pedogenesis. Furthermore, the trends in Zn-HIS references used in best LCF were in line with an enhanced Zn loading of HIS with higher soil Zn content and lower pH (from the BwC to the Ah horizon), advocating against a geogenic origin of Zn-HIV. Thus, Zn-HIV in soil DOR likely formed via the release of Zn from dissolving geogenic Zn-calcite and subsequent incorporation into pedogenic HIV during soil formation. Similar incorporation of Cu into pedogenic HIV has previously been reported in soils developed from Cu-rich schists (Ildefonse et al., 1986). Zn-HIM has previously been identified in pristine (Manceau et al., 2004, 2005) and contaminated soils (Jacquot et al., 2009a, 2009b; Scheinost et al., 2002) and may represent a dominant Zn-species in (mostly acidic) HIM-containing soils, though its capacity for Zn uptake is limited (Jacquat et al., 2009a).

The identification of Zn-kaolinite in all three studied soils was based on EXAFS analysis by LCF (Fig. 6, Table 5). In soil DOR, the best LCF of the EXAFS spectra from the BwC horizon consistently included Zn-kaolinite, whereas this species was only included in the best LCF to the EXFAS spectrum from the clay fraction of the Ah horizon, but not the bulk soil (Table 5, Fig. 6). At the same time, the residual fraction F7 decreased from 77% of the total Zn in DOR-BwC to 47% in DOR-Ah, mostly due to a decrease of the non-citrate-extractable residual fraction (Fig. 11). Considering that the citrate extraction effectively extracts Zn-HIM but only a small fraction of Zn-kaolinite (Jacquot et al., 2009a), the trends strongly supported the presence of Zn-kaolinite in soil DOR and its higher fraction in the BwC horizon, which had a higher soil pH than the Ah horizon (whose lower soil pH likely favored the formation of Zn-HIV). Furthermore, XRD analysis showed that kaolinite was one of the major minerals in the clay size fraction of soil DOR (Fig. 1, Figs. EA1 and EA2), which represented ~60% of the total soil weight (Table 1). For the soils GUR and LIE, LCF of the bulk EXAFS spectra indicated a minor fraction (~20%) of Zn-kaolinite (Tables 6 and 7). XRD confirmed the presence of kaolinite in the respective soil clay fractions, but also indicated the occurrence of HIV (Fig. 1, Figs. EA1 and EA2). The observation that the best LCF of soils GUR and LIE with near-neutral pH (Table 1) included Zn-kaolinite and not Zn-HIS was in line with the speciation trend in soil DOR, which suggested higher pH to promote formation of Zn-kaolinite rather than Zn-HIV (Tables 1 and 5). For soil GUR (but not LIE), the presence of ~20% Zn-kaolinite did not agree with the complete citrate-extractability of the residual fraction F7 (Fig. 11), which pointed to the formation of mainly Zn-HIV rather than Zn-kaolinite. Considering the rela-
tively small fraction of Zn-kaolinite obtained from LCF (Table 6), this discrepancy may be due to limitations in differentiating Zn-kaolinite and Zn-HIV (with similar spectral characteristics, Fig. 3) when co-occurring and accounting for a low fraction of total Zn, as well as to the limited selectivity and quantitative accuracy of concentration determination in soil extracts and the soil matrix. Thus, we interpret the EXAFS, XRD, and extraction results for soil GUR and LIE to indicate that ~20% of the total Zn was contained in mostly Zn-kaolinite and possibly a minor fraction of Zn-HIV.

Earlier studies on the speciation of Zn in pristine soils identified Zn-HIM and Zn-containing trioctahedral phyllosilicates (Manceau et al., 2004, 2005), but the occurrence of Zn-containing dioctahedral phyllosilicates, i.e. Zn-kaolinite, as a relevant soil Zn-species has not been reported before. In previous work, we postulated that Zn-kaolinite was present in the clay size fraction of a slightly contaminated soil (Jacquat et al., 2009a). This soil also developed from limestone of the Jura mountain range, but was additionally contaminated by aqueous Zn from corroding power line towers. In the geogenically Zn-rich soils studied here, Zn-kaolinite may have formed during pedogenesis or may have been inherited from the limestone, since traces of kaolinite were detected by XRD in the insoluble limestone residuals (data not shown). Considering the Zn contents of the studied soils, the fractions of Zn-kaolinite obtained by LCF, and assuming the soil clay fraction to contain 25% kaolinite, the Zn content of Zn-kaolinite was estimated to at most ~1000 mg/kg. This concentration compares to Zn contents of 180 and 270 mg/kg for the natural and synthetic Zn-kaolinites used as EXAFS references (Jacquat et al., 2009a). Assuming all Al in the limestone DOR-R (Table EA1) to be contained in kaolinite and considering a maximum content of 1000 mg/kg Zn in kaolinite, at most 1% of the total Zn in DOR-R could have been present as Zn-kaolinite. This fraction would have been too small for detection by EXAFS spectroscopy. Considering that the Zn/Al ratio in DOR-R was ~60–100 times higher than in the respective soil samples (Table EA1), our data do not allow to definitely exclude the possibility that Zn-kaolinite in soil DOR resulted from the residual enrichment of geogenic Zn-kaolinite already present in the limestone rock. However, in the soils GUR and LIE, a geogenic origin of Zn-kaolinite seems unlikely, since only sphalerite and/or Zn-goethite were detected in the limestones and similar molar ratios of Zn relative to Al, Si, Ti and Fe were found for the rock and corresponding soil samples (Table EA1), excluding substantial loss of Zn during soil formation. Furthermore, percolating waters from soils of the Jura mountain range have previously been shown to be oversaturated with respect to kaolinite (Pochon, 1978). Thus, our data support the interpretation that Zn-kaolinite in the soils GUR and LIE, and most likely also DOR, was of pedogenic origin.

In a previous study on the speciation of Zn in soils that had been contaminated over periods of years to decades with aqueous Zn from corroding powerline towers, we found Zn-LDH and to a minor extent trioctahedral Zn-phyllosilicates to be important Zn-species (Jacquat et al., 2009b). These phases were previously identified in a series of soils contaminated by different forms of Zn, including smelter and foundry emissions or dredged sediments (Juillot et al., 2003; Manceau et al., 2000a; Nachtegaal et al., 2005; Panfili et al., 2005; Voegelin et al., 2005b; Kirpichtchikova et al., 2006). Factors favoring the formation of these phases were higher soil pH and higher Zn concentrations (Jacquat et al., 2008, 2009b). In the current study, we did not detect these species in the soils GUR and LIE with near-neutral pH. This may be due to relatively low Zn levels compared to the previously studied heavily contaminated soils, but may also reflect the limited long-term stability of these phases in the soil environment (Voegelin et al., 2002; Voegelin and Kretzschmar, 2005; Jacquat et al., 2008). As reported by Paquet et al. (1986), trioctahedral Zn-rich smectites from ore deposits are unstable upon weathering and evolve to dioctahedral smectites with low Zn contents and finally to Zn-kaolinite and Zn-containing Fe (hydr)oxides. Consequently, the Zn-kaolinite and Zn-goethite, which we identified in ~10,000 years old soils, are expected to be stable long-term hosts for Zn in oxic soils. However, the potential of these phases for the immobilization of large amounts of Zn introduced into contaminated soils is determined by their abundance and Zn uptake capacity, the latter likely being limited in the case of Zn-kaolinite.

5. CONCLUSIONS

The speciation of Zn in naturally Zn-rich soils strongly depends on soil properties and the chemical forms of Zn present in the parent material. Zn in soils developed from the weathering of Zn-rich rocks is either linked to the inheritance of resistant Zn-bearing minerals or dissolution of primary Zn minerals and subsequent redistribution of Zn into pedogenic phases. Zn-containing goethite occurring in Zn-rich limestone is a highly resistant phase, causing its enrichment during limestone dissolution and soil formation. In contrast, sphalerite and Zn-calcite dissolve during pedogenesis. The released Zn may either be leached from the soil or be incorporated into Zn-bearing HIM or kaolinite, which we identified in soils developed over ~10,000 years of soil formation. Thus, Zn-goethite as well as Zn-HIM and Zn-kaolinite are highly resistant in the soil weathering environment and may act as long-term hosts for Zn. In highly contaminated soils, however, the low abundance (especially goethite) and/or the low capacity for Zn uptake (especially HIM and kaolinite) may limit the relevance of these phases for the immobilization of high Zn inputs.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.05.069.

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