



Composition and molecular scale structure of nanophases formed by precipitation of biotite weathering products

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Abstract

Because of their large surface area and reactivity, nanometric-size soil mineral phases have a high potential for soil organic matter stabilization, contaminant sorption or soil aggregation. In the literature, Fe and Al phases have been the main targets of batch-synthesized nanomineral studies while nano-aluminosilicates (Al and Si phases) have been mainly studied in Andic soils. In the present work, we synthesized secondary nanophases of Fe, Al and Si. To simulate a system as close as possible to soil conditions, we conducted laboratory simulations of the processes of (1) biotite alteration in acidic conditions producing a Al Si Fe Mg K leachate solution and (2) the following neoformation of secondary nanophases by titrating the leachate solution to pH 4.2, 5 and 7. The morphology of the nanophases, their size, crystallinity and chemistry were characterized by TEM-EDX on single particles and their local atomic structure by EXAFS (Extended X-ray Absorption Fine Structure) at the Fe absorption K-edge. The main nanophases formed were amorphous particles 10–60 nm in size whose composition (dominated by Fe and Si) was strongly controlled by the pH conditions at the end of the titration. At pH 4.2 and pH 7, the structure of the nanophases was dominated by the polymerization of Fe, which was hindered by Al, Si, Mg and K. Conversely, at pH 5, the polymerization of Fe was counteracted by precipitation of high amounts of Si. The synthesized nanophases were estimated to be rather analogous to nanophases formed in natural biotite-bearing soils. Because of their small size and potential high surface reactivity, the adsorption capacities of these nanophases with respect to the OM should be revisited in the framework of soil C storage.

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1. INTRODUCTION

Because of their large surface area, large percentage of surface atoms with unbalanced charge and large number of surface functional groups per unit of mass, nanometric-size mineral phases have a high potential for soil organic matter stabilization (Qafoku, 2010; Levard

et al., 2012), contaminant adsorption, (Levard et al., 2009) or soil aggregation (Asano and Wagai, 2014). These natural nanoparticles (NPs) may occur either as ùmineral NPsý (defined as minerals that can also exist in larger sizes) or as ùnanomineralsý (defined as minerals that only exist at the nanometric scale) (Hochella et al., 2008).

In surface environments, Fe and Al systems have been the main subjects of previous studies due to soil observations (Kaiser and Guggenberger, 2000) as well as due to the poor solubility of Fe and Al species in most soil pH

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and redox conditions (pH above ≈ 2 for Fe in oxidative conditions and pH above ≈ 5 for Al). However nanominerals other than Al and Fe oxy-hydroxides are known to form in surface systems, one of the best known examples being the Al and Si imogolite/allophane phases (Torn et al., 1997; Basile-Doelsch et al., 2005; Basile-Doelsch et al., 2007; de Junet et al., 2013; Basile-Doelsch et al., 2015).

Released by the continuous alteration of the primary minerals, Al, Si, Fe, etc. can form nanominerals at the surface of the primary mineral or at a distance from the initial altered surfaces. Direct formation of nanophases by the weathering of rock material has been described in oxic waters (Faimon, 2003; Zänker et al., 2006). In presence of organic matter, these newly formed nanophases can complex the organic compounds and stabilize them for extended periods of time. The conceptual model proposed by Basile-Doelsch et al. (2015) represents this mechanism. To validate the model, it is necessary to show that (1) the products of the alteration of primary minerals are likely to form nanophases and (2) these nanophases complex the OM. In this paper, we focus on step (1). We characterized the chemical nature and the structure of the nanophases formed from the elements resulting from the alteration of a primary mineral in the absence of OM. For this purpose, we considered biotite as a common soil primary mineral able to provide a complex combination of elements (Fe, Al, Si, Mg and K) via weathering.

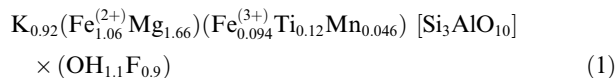
The formation of nanophases from a solution requires a polymerizing step by hydrolysis of metallic cations like Fe or Al (Manceau and Drits, 1993; Rose et al., 1997; Doelsch et al., 2000). In oxic conditions and at pH higher than 3–4, Fe^{3+} for instance, is known to be insoluble and reactive (Dousma and Debruyne, 1976; Byrne et al., 2000; Rose and Waite, 2003). Polymerization steps start from elementary monomeric building blocks such as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ octahedron and are accomplished via intramolecular condensation that initially involves deprotonation (Combes et al., 1989; Rose et al., 1997). Formation of small clusters via edge and double corner sharing between Fe octahedra is all included in the initial stage of “nucleation” which is followed by later stages of growth and aggregation (Wells, 1984; Rose et al., 1997). Polymerization routes have also been found for Al, with the formation of a transient Al_{13} polymer (Bottero et al., 1980). It has been shown that Si can strongly impair the polymerization stages in both elements (Lartiges et al., 1997; Doelsch et al., 2000).

Our experimental protocol combined a weathering step that provided a complex solution of Fe, Si, Al, K and Mg cations, followed by the polymerization of nanophases in a range of pH corresponding to soil conditions (pH 4.2, 5 and 7). The atomic structures of the nanophases were determined by Fe k-edge EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy and size, shape, crystallinity and chemical composition by TEM-EDX. Three main questions are raised in this paper: (1) Does the proposed experimental protocol make it possible to obtain nanophases? (2) Are the polymerized nanophases homogeneous or of variable chemical composition? (3) Are the nanophases obtained representative of phases that can form in soils?

2. MATERIALS AND METHODS

2.1. Experimental protocol

The biotite studied comes from Bancroft, Ontario Canada (Ward Science) (Turpault and Trotignon, 1994):



Biotite was mechanically ground ($< 50 \mu\text{m}$) in a zirconium oxide ‘ball mill’ setup, washed, sieved with ultra pure water and dried at 40°C .

Dissolution step: 33 g of $< 50 \mu\text{m}$ biotite particles were placed in 1L of pH = 2 HNO_3 solution (solid:liquid ratio of 1:30). After 29 days, the dissolved species were separated from non-weathered biotite particles using Tangential Filtration flow (TFF) (Spectrum Labs) at a cut-off size of 10 kD (pore size of $\sim 2 \text{nm}$). The filtered solution is hereafter referred to as ‘leachate solution’. Concentrations of dissolved species in the leachate solution were monitored with an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Horiba Jobin-Yvon “Ultima C”, Longjumeau, France). The measurement uncertainty was $< 10\%$. The preliminary experimental setup that contributed to the design of the above dissolution protocol is detailed in supplementary information (Fig. A1 and Table A1).

Polymerization step: Nanophases were precipitated by increasing the pH of the leachate solution. The initial pH (2) was raised by adding 0.2 N NaOH (Sigma Aldrich) at a constant rate of $70 \mu\text{L}/\text{min}$ (785 DMP Titrino). Pyrex beakers and stir bars were used. Three final pH values were targeted: 4.2, 5 and 7. To determine the target pH values, a preliminary titration curve of the leachate solution was performed (Fig. A2). The slope of this curve changed at pH 4.2 and 5. The variations in slope pointed to changes in the nature of the hydrolyzing system, inferring correlative changes in the nature and/or structure of the polymerized phases. At pH 7, the addition of NaOH no longer had an effect on polymerisation. The durations of titration were 1.4, 1.5 and 1.67 h at pH 4.2, 5 and 7 respectively. When the target pH was reached, a 1 ml aliquot of sample was collected for TEM-EDX analyses and the remaining solution was ultra-centrifuged at 80,000 rpm for 2 h to separate precipitated nanophases from the dissolved species. The settled particles were freeze-dried for EXAFS analyses. The whole experimental protocol is summarized in Fig. A3.

2.2. TEM images and analyses

Images were obtained and chemical analyses of nanophases were performed using a transmission electron microscope coupled with an EDX analyzer (JEOL JEM 2011 TEM). For each sample, EDX analyses were performed on a set of around 40 nanophases of different sizes. The parameters were 50,000X magnification, an angular tilt of 20° toward the detector, energy range of 40 keV, and corrected counting time of 30 s. A constant beam density

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