



## Fungal biomineralization of montmorillonite and goethite to short-range-ordered minerals

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Received 25 November 2015; accepted in revised form 10 July 2016; available online 16 July 2016

### Abstract

Highly reactive nano-scale minerals, e.g., short-range-ordered minerals (SROs) and other nanoparticles, play an important role in soil carbon (C) retention. Yet, the mechanisms that govern biomineralization from bulk minerals to highly reactive nano-scale minerals remain largely unexplored, which critically hinders our efforts toward managing nano-scale minerals for soil C retention. Here we report the results from a study that explores structural changes during *Aspergillus fumigatus* Z5 transformation of montmorillonite and goethite to SROs. We examined the morphology and structure of nano-scale minerals, using high-resolution transmission electron microscopy, time-resolved solid-state <sup>27</sup>Al and <sup>29</sup>Si NMR, and Fe K-edge X-ray absorption fine structure spectroscopy combined with two dimensional correlation spectroscopy (2D COS) analysis. Our results showed that after a 48-h cultivation of montmorillonite and goethite with Z5, new biogenic intracellular and extracellular reactive nano-scale minerals with a size of 3–5 nm became abundant. Analysis of 2D COS further suggested that montmorillonite and goethite were the precursors of the dominant biogenic nano-scale minerals. Carbon 1s near edge X-ray absorption fine structure (NEXAFS) spectra and their deconvolution results demonstrated that during fungus Z5 growth, carboxylic C (288.4–289.1 eV) was the dominant organic group, accounting for approximately 34% and 59% in the medium and aggregates, respectively. This result suggested that high percentage of the production of organic acids during the growth of Z5 was the driving factor for structural changes during biomineralization. This is, to the best of our knowledge, the first report of the structural characterization of nano-scale minerals by 2D COS, highlighting its potential to elucidate biomineralization pathways and thus identify the precursors of nano-scale minerals.

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**Keywords:** Biomineralization; Fungi; High-resolution transmission electron microscopy; Montmorillonite; Short-range-ordered minerals; Two dimensional correlation spectroscopy

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## 1. INTRODUCTION

Biomining is an important environmental process that drives the formation of secondary minerals in soils (Baumgartner et al., 2013; Wei et al., 2013). The secondary minerals, including allophone, imogolite, ferrihydrite, and other nano-scale minerals, comprise the most reactive mineral components of soils (Torn et al., 1997; Masiello et al., 2004; Hochella et al., 2008). The former is often called short-range-ordered minerals (SROs) that are meta-stable nanocrystals, form from the weathering of framework silicates and ferromagnesian minerals, and exist only in nano scale (Hochella et al., 2008; Kramer et al., 2012). Meanwhile, they possess structural defects and have high specific surface area ( $\sim 700\text{--}1500\text{ m}^2\text{ g}^{-1}$ ) (Torn et al., 1997; Rasmussen et al., 2006), charge density, surface reactivity, and bioavailability for organisms (Torn et al., 1997; Aiken et al., 2011). Most importantly, the SROs play essential roles in binding and preserving soil organic carbon (SOC). The formed SROs can bind up to 6-fold more SOC than their bulk minerals (Rasmussen et al., 2006) and had a positive relationship with SOC (Torn et al., 1997). Also, Lalonde et al. (2012) quantitatively demonstrated that  $21.5 \pm 8.6\%$  of the organic carbon was directly bound to reactive Fe minerals. Under favorable conditions, SOC bound to SROs can persist for much longer ( $\sim 250,000$  yrs) than that bound to bulk minerals ( $\sim 500$  yrs) (Yu et al., 2012).

Previous long-term fertilization experiments have revealed that the applications of organic amendments can significantly increase the levels of soil SROs (Yu et al., 2012; Zhang et al., 2013; Wen et al., 2014a,b; Wu et al., 2014), which may provide unique opportunities to manage soil SROs and further benefit soil C sequestration. The mechanisms through which organic amendments affect the formation of SROs are poorly understood, but it is generally believed that the biomineralization process plays a primary role (Lian et al., 2008; Wiesner et al., 2011; Baumgartner et al., 2013; Fdez-Gubieda et al., 2013; Wei et al., 2013).

Fungi can significantly contribute to biomineralization through physical and biochemical mechanisms, e.g., through the excretion of  $\text{H}^+$ ,  $\text{CO}_2$ , organic acids, and other metabolites (Sterfvinger, 2000; Wei et al., 2012, 2013). Among fungi, many *Aspergillus fumigatus* strains are ubiquitous in soils and have been suggested to possess potential geoactive properties (Daghino et al., 2008; Lian et al., 2008). They can solubilize metals, including Ca, Mg, and Zn, from certain minerals (Castro et al., 2000; Lian et al., 2008; Wei et al., 2013). Montmorillonite is the most reactive clay mineral in soils, and it possesses high permanent negative charges and cation-exchange capacity (i.e.,  $90\text{--}127\text{ cmol kg}^{-1}$ ) (Gupta and Bhattacharyya, 2006; Proust et al., 2013). Another important mineral is goethite ( $\alpha\text{-FeOOH}$ ), the dominant iron oxyhydroxide phase in soil (Liu et al., 2013b; Chen et al., 2014). Whether the interactions between *A. fumigatus* strains and montmorillonite or goethite commonly occur during biomineralization remains unclear. Also, despite recent advances in the understanding of the morphology (Lian et al., 2008; Wei et al., 2012, 2013)

and the identification of new biogenic minerals (Wei et al., 2012; Zhang et al., 2012), little is known about the detailed structural changes that occur during the formation of biogenic SROs. These knowledge gaps critically limit our capacity to manage the formation of SROs in soil.

Nano-scale particles are difficult to be detected by conventional techniques such as scanning electronic microscopy (SEM) and X-ray diffraction (XRD) (Baker et al., 2010; Wei et al., 2012, 2013). Recently, high-resolution transmission electron microscopy (HRTEM), extended X-ray absorption fine structure (EXAFS), and nuclear magnetic resonance (NMR) spectroscopy have been used to investigate the morphology and quantification of biominerals (Chan et al., 2004; Fomina et al., 2007; Mitsunobu et al., 2012; Fdez-Gubieda et al., 2013). However, overlapping spectral features often limit their applications because of the extreme heterogeneity of mineral constituents (Yu et al., 2011). Two-dimensional correlation spectroscopy (2D COS) can help resolve the overlapped peak issue by distributing spectral intensity trends within a data set collected as a function of the perturbation sequence (e.g., time, temperature) over a second dimension (Yu et al., 2011; Li et al., 2013). Moreover, it can probe the specific sequence of spectral intensity changes (Yu et al., 2011), providing a unique approach for identifying precursors of new biogenic minerals and characterizing the structural changes during biomineralization. More importantly, 2D COS can be used to explore the so-called heterospectral correlation, i.e., correlations among bands from two different types of spectroscopy (e.g., NMR and EXAFS). This type of heterospectral correlation is very useful for investigating the structural and physical properties of materials and identifying the origin of neofomed minerals under a particular external perturbation (Noda and Ozaki, 2005). For example, Choi et al. (2003) employed X-ray absorption (XAS)/Raman heterospectral analysis for the study of the electrochemical reaction mechanism of lithium with CoO (Choi et al., 2003).

In this study, the objective were (i) to characterize structural changes during the formation of biogenic minerals from both montmorillonite and goethite by *A. fumigatus* Z5 using 2D COS and (ii) to identify the morphology and the diffraction pattern of new biominerals by HRTEM combined with fast Fourier transform (FFT) analyses. SEM and X-ray microanalysis was performed on the same regions to obtain semi-quantitative information of the element composition. The 2D COS analysis was combined with solid-state  $^{27}\text{Al}$  and  $^{29}\text{Si}$  NMR and Fe K-edge EXAFS spectroscopies to record the structural changes of Al, Si, and Fe. Carbon 1s near edge X-ray absorption fine structure (NEXAFS) spectroscopy was used to examine organic C composition.

## 2. MATERIALS AND METHODS

### 2.1. Cultivation experiments

*A. fumigatus* Z5, our experimental fungi, were originally provided by Dr. Dongyang Liu (Liu et al., 2013a), Nanjing Agricultural University. All experiments were performed at

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