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Influence of microorganisms on biotite dissolution: An experimental approach

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Abstract

Microbially assisted dissolution of biotite was studied using four environmentally important species (*Bacillus subtilis*, *Shewanella putrefaciens*, *Streptomyces acisdiscabies*, and *Schizophyllum commune*) incubated for 35 days in batch reactors at slightly alkaline pH conditions (ca. pH 9.5). For comparison we performed a control experiment without biological component. Dissolution was monitored by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of elements (Al, Fe, K, Mg, Mn, Si, and Ti) released into the leach solution. Structural and chemical alterations of biotite were analyzed by a directly evolved gas analysis system (DEGAS) and transmission electron microscopy (TEM) coupled with electron-energy loss spectroscopy (EELS) and energy-dispersive X-ray (EDX) analysis. Our results show that biotite dissolves incongruently with a preferential release of the interlayer cations followed by the octahedral and subsequently the tetrahedral site. Dissolution rates of biotite calculated on the basis of Si release into the solution are similar for abiotic and biotic experiments, on the order of 10^{-13} mol/(m^2 s). However, calculated K release rates as well as Mg/Si and K/Si element ratios show a preferential dissolution of these elements from biotite in the presence of microorganisms. For example, in comparison to the control experiment we observe that *B. subtilis* enhances the Si-normalized Mg and K solute concentrations by about 50%. DEGAS and EDX analyses reveal that the release of K^+ from the interlayer is associated with an uptake of Na^+, H_3O^+, and NH_4^+. These substitutions are strongest for biotite exposed to microorganisms, e.g., in experiments with *B. subtilis* the uptake of NH_4^+ is 6 times higher than in the control experiment. Altogether, these results substantiate the considerable influence of microorganisms on the dissolution of biotite.

Keywords: Mineral dissolution; Weathering; Biotite; *Bacillus subtilis*; *Schizophyllum commune*; *Shewanella putrefaciens*; *Streptomyces acisdiscabies* E13; Batch experiment; TEM; DEGAS

1. Introduction

The weathering of sheet silicates is well known to be related to local and global geochemical cycles and has been extensively studied in both, field and laboratory (White and Brantley, 1995; Brantley, 2003). Particularly,

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biotite as a common primary mineral in a wide range of rock types plays an important role for the bioavailability of inorganic nutrients like K, Mg, and Fe during soil formation and for redox and pH conditions affecting groundwater geochemistry (e.g., Berner and Berner, 1996).

Within the natural (bio-)chemical weathering sequence of sheet silicates, biotite has been early recognized to be least stable (Jackson et al., 1948, 1952). However, the determination of meaningful dissolution rates is complicated for various reasons. On the one hand, rates from the laboratory and field differ commonly by a few orders of magnitude due to the dependency of weathering rates on time. This is because of changes in reactive surface area and secondary mineral formation (e.g., White and Brantley, 2003; Ganor et al., 2005). On the other hand, the experimental setup (e.g., batch versus flow through reactors) can significantly affect the interpretation of mineral dissolution rates (for discussion see Brantley, 2003). Furthermore, microorganisms can influence the mechanism and rate of mineral dissolution in a number of ways, e.g., as a result of the microbial metabolism (energy generation), by the production of organic and inorganic acids, and by the absorption or complexation of desired nutrients (see Barker and Banfield, 1996; Banfield and Welch, 2000 for review). The biogeochemical alteration of biotite has been of long-standing interest in the field of nutrition of plants revealing that the microbially assisted weathering of biotite provides an effective source of potassium (Mortland et al., 1956; Weed et al., 1969; Mojallali and Weed, 1978; Berthelin and Leyval, 1982; Olsson and Wallander, 1998; Calvaruso et al., 2006).

First direct indications that microorganisms could enhance biotite weathering were found by Frankel (1977). Subsequently, Barker et al. (1998) demonstrated that bacteria can accelerate mineral weathering reactions (including biotite) measured by an increase in the elemental release into solution. However, a recent experimental study by Balogh-Brunstad et al. (2008) on biologically stimulated biotite dissolution using an ectomycorrhizal fungus found rates comparable to inorganic weathering.

Here we report microbially assisted biotite dissolution experiments using both bacterial and fungal strains performed in liquid culture batch reactors at 28 °C and at slightly alkaline pH. The focus of this study is to determine relative changes in elemental discharge during biotite dissolution due to different microorganisms which are relevant for soils. Furthermore, the redox state of transition metals in biotite and their fate in relation to microbial activity will be taken into account. Finally, the influence of the culture medium on the dissolution reaction is addressed.

2. Materials and methods

2.1. Starting materials – biotite, biological strains, and culture media

Starting biotite used in dissolution experiments originates from Kragerø, Norway, and was selected from the Mineralogical Collection, Jena. The composition of biotite was determined to be $(K_{0.81}Na_{0.09})(Fe^{2+}_{0.44}Mg_{0.96}Mn_{0.04}Fe^{3+}_{0.65}Al_{0.33}Ti_{0.13})[Al_{1.23}Si_{2.77}O_{10}](OH)_2$ using scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDX). Quantification was based on 10 oxygens, 2 hydroxyl groups, and a ferric to total iron ratio of 0.60 determined by electron-energy loss spectroscopy (EELS) measurements (see Results). A large biotite crystal was grinded in an agate mortar to yield flakes with a particle size of 0.3–300 μm. The particle size was analyzed using a particle size analyzer (LS 13 320, Beckman Coulter, Institute of Geography, Jena). The so-prepared mineral powder was sterilized at 180 °C for 3 h. Multi-point BET (Brunauer, Emmett and Teller)-N_2-specific surface area measurements of the biotite particles (Quantachrome NOVA 2000 at SciTec, University of Applied Sciences, Jena) yielded a surface area of 6.922 m^2/g.

In biologically assisted dissolution experiments we used the bacterial and fungal strains *Bacillus subtilis* subsp. *spizizenii*, *Shewanella putrefacien*s, *Streptomyces acisdiscabies* E13, and *Schizophyllum commune*. *B. subtilis* is arguably one of the best known and most extensively studied Gram-positive bacteria. They are aerobic, endospore-forming, rod-shaped bacteria which are commonly found in soil, water sources and in association with plants (Claus and Berkeley, 1986). The Gram-negative and facultative anaerobic *Sh. putrefaciens* exhibits an enormous diversity of metabolic reactions that are particularly apparent during anaerobic respiration (Venkateswaran et al., 1999). Both strains, *B. subtilis* and *Sh. putrefaciens*, were provided by courtesy of the Hans-Knöll-Institut, Jena. Members of the genus *Streptomyces* are Gram-positive actinobacteria and the species *St. acidiscabies* is a well-known microorganism for low pH soils. *St. acidiscabies* E13 was isolated from soil samples of a heavy metal polluted site at the former uranium mine Wismut in eastern Thuringia, Germany (Amoroso et al., 2000). The eukaryotic, basidiomycete fungus *Sc. commune* is used as a model organism for basidiomycetes and is distributed ubiquitously except Antarctica (see Kothe, 1996 and references therein). The strains *St. acidiscabies* E13 and *Sc. commune* 12–43 used are from the strain collection of Microbial Phythopathology at the University of Jena.

Prior to experimental use, these strains were initially grown in 0.8% nutrient broth (rich in organic nutrients) at 28 °C to exponential/late-exponential growth phase and then harvested by centrifugation at 4000 rpm for 30 min at 4 °C (Megafuge 1.0R, Heraeus Instruments). The cultures were then resuspended and rinsed three times with distilled water to remove any remaining culture medium. Culture media often contain high cation concentrations that could potentially mask the effects of biotite dissolution. To avoid this problem and faciliate an interaction between microorganisms and biotite we have used a freshwater-enriched culture medium that primarily contains N and C required for cell growth. The media (modified from the freshwater enrichment medium from Lovley and Phillips, 1986) were prepared by dissolving sodium