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Experimental dissolution vs. transformation of micas under acidic soil conditions: Clues from boron isotopes

A. Voinot[a,b,*], D. Lemarchand[a], C. Collignon[b], M. Granet[a], F. Chabaux[a], M.-P. Turpault[b]

[a] *Laboratoire d'Hydrogéologie et de Géochimie de Strasbourg (CNRS), F-67084 Strasbourg, France*
[b] *Unité de Recherche Biogéochimie des Ecosystèmes Forestiers (INRA), F-54280 Champenoux, France*

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Abstract

Minerals in soils evolve through contact with water and other weathering agents (protons, organic acids and ligands) from the atmosphere or released by the surrounding vegetation and associated fauna. Determining the respective contribution of these agents to weathering budgets and the mechanisms by which they interact with soil minerals is a key step toward obtaining refined models of soil development, plant/mineral interactions and, ultimately, soil sustainability.

To test the influence of different chemical agents on the processes of mica weathering (dissolution and transformation), we conducted a series of laboratory flow-through experiments on biotite using three chemical groups of reactants found in forest soils: protons (HCl), organic acids (citric acid) and ligands (siderophores). These experiments were performed at two different pH values (pH 3 and pH 4.5) for 37 days at 20 °C. Biotite was chosen as a test-mineral because it is reactive with acids and water and because it is commonly found in granite soils. To investigate the weathering reactions, the chemical and isotopic compositions of B ($\delta^{11}B$) and the concentrations of predominant cation (Si, Al, Mg, K and Fe) were monitored in the outflowing solutions. The choice of B as a proxy for weathering processes is based on the fact that B is located in different crystallographic sites in biotite (interlayers and structural sites, named I- and S-sites, respectively). We observed a large $\delta^{11}B$ contrast between these sites ($\Delta^{11}B_{S\text{–}I\ sites}$~80‰), which allows for a precise quantification of the respective contribution of I- and S-sites to B released during biotite weathering.

The individual reaction rates for these crystallographic sites were inferred from the B chemical and isotopic compositions of the outflowing solutions. A comparison with the major elements reveals that B is preferentially released to solution under all tested experimental conditions (up to 4 times more), particularly in the presence of siderophores. A major finding of the present work is that the dissolution of $\delta^{11}B$ is shown to be highly dependent on the nature of the weathering agent: the presence of citric acid leads to a near-stoichiometric contribution of I- and S-sites to dissolved B, whereas the presence of siderophores results in an almost exclusive release of B from the I-sites, which indicates a mineral transformation without significant dissolution. The presence of HCl leads to an intermediate situation that shows a higher B reactivity from the I-sites than from the S-sites, indicating that biotite minerals transform faster than they dissolve. Because the dissolution reactions imply the destruction of the mineral structure, whereas transformation reactions are non-destructive, assessing the proportions in which minerals evolve by dissolution and transformation reactions has important implications for predicting plant/mineral interactions and soil sustainability.

1. INTRODUCTION

Micas are common minerals in plutonic and metamorphic rocks. Like clay minerals, micas belong to the

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[*] Corresponding author at: Laboratoire d'Hydrogéologie et de Géochimie de Strasbourg (CNRS), F-67084 Strasbourg, France.
E-mail addresses: alexandre.voinot@etu.unistra.fr, voinot@geol.queensu.ca (A. Voinot).

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phyllosilicate mineral series and exhibit an alternation of crystalline sites (S-sites) consisting of tetrahedral and octahedral layers (T- and O-sites, respectively), separated by interlayer spaces (I-sites). In soils, this particular structure causes phyllosilicate minerals to be subject to a variety of possible chemical reactions that differentially involve the crystallographic sites: the transformation into other phyllosilicates (corresponding to a preferential reactivity of I-sites) or the dissolution of the bulk mineral (stoichiometric dissolution of both I- and S-sites). The nature and intensity of these reactions depend on the ambient conditions: climate, hydrology, water chemistry, and bedrock mineralogy, as well as on the presence and type of vegetation cover (e.g., Hatton et al., 1987; Fichter et al., 1998; Bronger, 2007; Mareschal et al., 2011). Additionally, some major cations required for plant growth (K, Mg, and Fe) are abundant in micas, either in the structure or in interlayer sites (Augusto et al., 2001), which makes these minerals a potential source of nutrients for plants (e.g., Berner and Berner, 1996; Turpault et al., 1996; Andrist-Rangel et al., 2006; Barré et al., 2007, 2008). Finally, the chemical fluxes in soils are highly impacted by the biological cycle and result from complex and coupled interactions of organic compounds and silicates (Kelly et al., 1998; Ganor et al., 2009 and references therein). Among other possible sources of nutrients for plants (atmosphere and dead biomass), the dissolution and transformation of soil minerals play a key role in the sustainability of soils over long time scales (e.g., Brantley and White, 2009). Therefore, deciphering the mechanisms by which nutrients are released from soil minerals and made available for plants has important implications for understanding and predicting plant/mineral interactions.

In laboratory experiments, the concentrations of major elements are suitable for tracing biotite dissolution (Si or Al) or transformation (K or Ca) rates under controlled conditions using salts (Gilkes et al. (1973); Robert and Pedro, 1973), acids (Acker and Bricker, 1992; Turpault and Trotignon, 1994) and bases (Samson et al., 2005). Very acidic or basic pH conditions lead to high dissolution rates, whereas salts at near-neutral pH lead to high transformation rates. Isotope geochemistry has helped to distinguish the source effects from the process effects and thus has contributed significantly to insights into the mechanisms of the weathering of silicate and, more particularly, of phyllosilicates. According to numerous studies, the interlayer and structure sites show distinct Sr isotopic ratios in weathered biotite and phlogopite, which demonstrates an exchange between the fluid and the phyllosilicate interlayer cations (e.g., Clauer and Chaudhuri, 1995; Taylor et al., 2000). A significant Fe isotopic fractionation is caused by the different weathering rates of Fe-bearing sites during biotite and chlorite weathering (Kiczka et al., 2010) but is also dependent on the fluid chemistry, as shown by the influence of ligands, and the redox state of the reacting solution (Brantley et al., 2004; Wiederhold et al., 2006). The investigation of Li isotope fractionation during experimental precipitation of smectite (Vigier et al., 2008), during diagenetic transformation of interstratified illite–smectite minerals (Williams and Hervig, 2005), during weathering of volcanic glasses (Verney-Carron et al., 2011) and along a soil profile (Lemarchand et al., 2010) all indicate the significant potential of Li for tracing mineral transformation and dissolution reactions.

Here, we argue that boron (B) likewise has suitable chemical properties for providing innovative information on mica weathering mechanisms. In silicate minerals, B is expected substitute for Si within tetrahedrons (T-sites), and there is no clear evidence of the presence of B in octahedrons (O-sites) (Williams and Hervig, 2005; Hålenius et al., 2010, and references therein). B is also trapped in the interlayers (Williams et al., 2001) and adsorbed on the surface of the mineral as either boric acid (H_3BO_3) or borate ion ($B(OH)_4^-$), forming bidendate complexes with adjacent –OH groups (Keren and Mezuman, 1981; Lemarchand et al., 2005). This latter chemical property directly links the concentration of adsorbed B to the concentration of dissolved B through a pH-dependent partition coefficient (Palmer et al., 1987; Lemarchand and Gaillardet, 2006). Moreover, previous studies of the B isotope distribution in physillosilicates have emphasized great differences between crystallographic sites: the I-sites are significantly enriched in ^{11}B compared to the adjacent T-sites (Williams et al., 2001; Williams and Hervig, 2005). B isotopes can therefore help to quantify the differential intra-crystalline reaction rates by independently recording the reactivity of the various sites. Finally, two recent studies have demonstrated a large B isotopic fractionation between granitic soil particles (approximately $-26‰$) and the surrounding soil solutions (approximately $+15‰$) (Cividini et al., 2010; Lemarchand et al., 2012). These results indicate that the release of B during the weathering of soil minerals is either associated with a large isotopic fractionation or controlled by an isotopically heavy B-pool in soil that is yet to be identified.

In the present work, we experimentally investigate the potential of B isotopes to trace transformation and dissolution reactions in biotite. For this purpose, we first determine the isotopic composition and concentration of the B-bearing crystallographic sites (S-sites, I-sites and surface) within the test-biotite. Then, we monitor the evolution of B isotopes during flow-through weathering experiments in which biotite minerals are placed in contact with solutions that contain different altering agents chosen to mimic those present in forest soils (protons, organic acid and siderophores). The B isotope budget is then compared to that of other major elements and is used to assess the reaction rates of each of the B-bearing sites.

2. EXPERIMENTAL SETUP

2.1. Mineral samples and preparation

The test-mineral chosen for this study is a biotite collected in Bancroft (Ontario, Canada), which has a well-known chemical composition of (Si_3Al_1) $(Fe^{3+}_{0.12}$ $Fe^{2+}_{0.61}$ $Mg_{2.06}$ $Mn_{0.02}$ $Ti_{0.13})$ $K_{0.88}$ $Na_{0.06}$ O_{10} $(OH_{0.98}$, $F_{1.02})$ (Calvaruso et al., 2006) and which has already been used in numerous published works (Gilkes et al. (1973); Acker and Bricker, 1992; Turpault and Trotignon, 1994). The biotite crystals range in size from 5 to 10 cm. The edges of the mineral sheets were cut off with scissors to remove potential oxides and hydroxides. The calcite inclusions were separated from the