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Beryllium desorption from minerals and organic ligands over time

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ABSTRACT

Beryllium isotopes sorbed to sediments have provided useful tools in the field of geochronology and geomorphology over the last few decades. The use of beryllium isotopes relies on the premise that beryllium sorbed to sediments is unaltered over large timescales. Changes in the environmental chemistry, either in-situ or en route from soil to fluvial system, to the ocean, can cause beryllium desorption and may preclude some beryllium isotopic applications.

Four mechanisms were tested to determine the relative desorption potential of beryllium including a reduction in pH, an increase in ionic strength (NaCl) and complexation by soluble organic (malonic acid) and inorganic species (NaF). To assess the relative effect of each mechanism on beryllium desorption from both organic and mineral fractions, we prepared separate solutions of beryllium bound to minerals and organic compounds and measured beryllium concentrations in solution before and after each chemical perturbation. We conclude a reduction in pH resulted in the greatest amount of desorption among the four treatments, removing 97% and 75% of sorbed beryllium from illite and montmorillonite, respectively, and none from the organic ligands tested. The addition of malonic acid and increasing the ionic strength also resulted in desorption from montmorillonite. Although increasing the ionic strength did remove 32% and 8.4% of beryllium from montmorillonite and sulfonate, respectively, the presence of sodium significantly enhanced sorption to illite. The addition of NaF did not result in any beryllium desorption. Our results demonstrate that various chemical processes can promote the exchange of beryllium between solid and dissolved phases, the extent to which depends on the composition of the system.

We also related differences in beryllium desorption behavior to complexation mechanisms driving retention among organic and mineral species. We estimate inner sphere complexation is the predominant sorption mechanism among the organic ligands tested due to the minimal amounts of desorption and the large stability constants previously reported in the literature. Additionally, we found that different complexation processes are involved in beryllium sorption to illite versus montmorillonite. Because beryllium desorbed from montmorillonite due to changes in pH, ionic strength and organic acid complexation, we hypothesize that a portion of beryllium-montmorillonite associations involve outer sphere processes, driven by weaker electrostatic attractions. However, beryllium exhibited a unique relationship with illite in that sorption not only involves inner sphere processes but also physical inclusion within collapsed interlayer spaces.

1. Introduction

In the past few decades, beryllium isotopes have been used in the field of geomorphology and geochronology to determine the residence time of sediments in landscapes ranging from several weeks to millions of years (Granger et al., 2013; Wallbrink and Murray, 1996; Willenbring and von Blanckenburg, 2010a, 2010b). These methods use concentrations of beryllium isotopes sorbed to sediments and often rely on the assumption that these concentrations are unchanged over such large timescales. However various biotic and abiotic processes could influence beryllium's behavior in soils and aquatic environments. As sediment is transported, undergoing various cycles of erosion and deposition, beryllium sorbed to these particles is exposed to a variety of different chemical environments and is susceptible to transformations along the path from source to sink. For example, marine core sediments used to measure $^{10}Be/^{9}Be$ ratios for estimating total denudation in a landscape can experience a salinity gradient during their transport from fresh to saline waters. Such changes in the ionic strength could result in competition for sorption sites and subsequent desorption of beryllium. Additionally, within a single soil profile, in-situ processes like plant and microbial production of chelating organic acids can stimulate beryllium mobilization altering its natural distribution with depth. Beryllium desorption poses a problem for the environmental scientist and the geomorphologist, both of whom rely on the retention of beryllium to sediment to prevent the contamination of ground water, preserve a landscape's erosional signature and for tracking particle movement. Therefore, although the sorption behavior of beryllium is important to understand, it is equally important to consider processes that cause desorption.

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In this study, we investigate four major processes known to stimulate metal desorption including a reduction in pH, an increase in the ionic strength and complexation by soluble organic and inorganic species. A decrease in pH reduces available sorption sites encouraging the exchange of sorbed cations for protons. Increasing the ionic strength also enhances competition between cations for reactive sites on the surfaces of particles, resulting in desorption of ions previously bound to the surface. Additionally, low molecular weight organic acids (LMWOA) that are excreted by biota are capable of chelating cationic species like beryllium, mobilizing them into the soil solution (Qin et al., 2004; Vanhees et al., 1999; Vranova et al., 2013). Examples of such acids include oxalic, malonic, succinic and other dicarboxylic acids. In addition to organic ligands, beryllium is also complexed by inorganic species such as fluoride. Previous studies determined that dissolved, unsorbed beryllium concentrations were dependent on the amount of fluoride in fresh water systems and that the presence of fluoride can increase the mobility of beryllium (Vesely et al., 1989; Vesely et al., 2002; Krám et al., 1998).

Although these chemical perturbations are intended to provide us with a greater understanding of processes driving beryllium desorption, the relative rate and extent of desorption can also provide information relating to the complexation mechanisms driving retention among the organic ligands and mineral tested. Sorption processes can be characterized as specific or non-specific. Non-specific sorption, or outer sphere complexation, involves the electrostatic interactions of hydrated metal ions with sorption site ligands. Considering these interactions are driven simply by differences in charge, there is less specificity with regard to ligand type. Conversely, specific sorption, also referred to as inner sphere complexation, involves an actual chemical reaction between the metal and sorption site. The term ‘specific’ refers to the thermodynamic preference of a metal ion to form a covalent bond with particular ligands. Considering specific, inner sphere complexation involves the formation of chemical bonds, it produces a stronger metal-ligand association compared to outer sphere complexation. These inner sphere complexation mechanisms are therefore more resistant to chemical disturbances that affect electrostatic interactions between metal and ligand like changes in ionic strength or pH. It is important to note that both inner and outer sphere processes occur simultaneously, although one mechanism can be more predominant depending on the nature of the sorbent, sorbate and the chemical environment (Catalano et al., 2008). Typically, X-ray absorbance spectroscopy is used to assess the dominant complexation mechanism driving metal retention among sorbents. However, beryllium's transparency to X-rays complicates the use of such techniques. Therefore, the use of desorption experiments to assess the ease of beryllium removal from organic and mineral sorbents can be used to estimate sorption types, with outer sphere complexation allowing for greater desorption at faster rates. We can use this knowledge to estimate how beryllium chemically associates with specific organic ligands and minerals.

Understanding how the four chemical treatments affect the equilibrium of beryllium between sorbed and dissolved phases is central in understanding not only the potential for beryllium desorption and mobilization but the complexation mechanisms driving retention among organic and mineral sorbents. The goals of this paper are to 1) establish the relative effect of each chemical perturbation on beryllium desorption, 2) to determine their relative effect on beryllium desorption from organic ligands versus mineral sorbents and 3) to indirectly estimate how sorption mechanisms differ among organic ligands and minerals by observing their responses to various chemical treatments .

2. Materials and methods

2.1. Sorption of beryllium to sorbent materials

In order to test the ability of different processes to desorb beryllium, we initially needed to sorb beryllium to organic and inorganic sorbents. We selected two clay minerals to represent the mineral fraction and two organic compounds to represent the organic matter fraction of soils. We chose to use separate, model materials in order to identify how different chemical perturbations affect the retention of beryllium by either mineral or organic fractions. By observing their individual behaviors we are able to better approximate the extent each chemical perturbation has on a natural soil depending on its organic or clay mineral content. Using model materials also removes any uncertainty that results from the complex and heterogeneous nature of using an actual soil sample and can allow us to better elucidate differences in the desorption behavior of beryllium between organic and inorganic soil materials.

We selected mineral and organic materials based on their ability to complex beryllium as determined from previous experiments (Boschi and Willenbring, 2016). Of the minerals tested, illite and montmorillonite exhibited the greatest amount of beryllium sorption. We obtained these minerals through Ward science (Rochester, NY, USA) and confirmed their mineralogical purity using X-ray diffraction (XRD). The samples were ground using a disc mill and rinsed with a weakly acidic HCl (Fisher Scientific, Pittsburgh, PA, USA) solution and ultrapure Millipore (Billerica, MA, USA) water to remove impurities. The minerals were then wet sieved and dried in an oven overnight. The <20 μm fraction was collected for use in this experiment. A Beckman-Coulter Particle Size Analyzer (Miami, FL, USA) was used to determine the proportion of each mineral sample that was smaller than 0.45 μm to ensure the filter removed mineral particles from solution. It was determined that $<0.5\%$ of the sample was smaller than 0.45 μm. As an additional precaution in order to ensure particles were not escaping through the filter, all mineral samples were centrifuged at the appropriate speed and time interval prior to filtration to ensure the $>99.5\%$ of particles were excluded from the filtrate.

Similarly to the mineral samples, we selected phosphonic and sulfonic acid bearing compounds because they formed the most stable complexes with beryllium relative to other organic compounds tested in previous experiments (Boschi and Willenbring, 2016). Octadecylphosphonic acid (Sigma Aldrich, St. Louis, MO, USA), a large insoluble alkane and toluenesulfonic acid bound to a polystyrene resin (30–60 mesh size) (Alfa Aesar, Ward Hill, MA, USA) were selected to represent a phosphonate and sulfonate group respectively. These compounds were selected so that they could be easily separated from solution by filtration using a 0.45 μm filter. By selecting organic ligands and minerals with larger stability constants relative to other materials, our results will provide a conservative estimate of beryllium desorption.

We prepared individual, 50 mL organic compound and mineral solutions at a concentration of 250 mg L^{-1}. It is important to note that for organic compounds 250 mg L^{-1} represents the concentration of the active functional group, not the entire organic molecule because the ratio of functional group to organic compound mass varies for either compound. For example, 250 mg L^{-1} phosphonate (PO_3) was prepared rather than 250 mg L^{-1} of octadecylphosphonic acid ($C_{18}H_{39}O_3P$). However, for the mineral samples, 250 mg L^{-1} represents the concentration of the bulk mineral.

We spiked each sorbent solution with beryllium, which we prepared using a beryllium ICP standard (BDH, Lutterworth, UK). The concentration of beryllium in each sample solution was 1 mg L^{-1}, which was intended for sorption onto each sorbent material to mimic its average abundance in soils and sediments (Taylor et al., 2003; US DHHS, 2002). Each beryllium-sorbent solution was prepared in ultrapure Millipore water and initially adjusted to a pH of 6 using NaOH (Fisher Scientific) to ensure maximum sorption of beryllium to each sorbent material. We could not exceed a pH of 6 considering the dependence of beryllium speciation on pH. At a concentration of 1 mg L^{-1}, beryllium is present as a divalent cation at low (<6.5) and high (>11) pH's and as insoluble $Be(OH)_2$ in-between. For example at a pH of 7, 79% of $Be(OH)_2$ is removed from the solution via filtration with a 0.45 μm filter (Boschi