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The effect of pH, organic ligand chemistry and mineralogy on the sorption of beryllium over time

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Environmental context. Beryllium is a toxic environmental contaminant but has many industrial and scientific applications. Our work explores the effects of soil composition on beryllium retention, focussing on organic matter, mineralogy and pH and concludes that phosphorus and sulfur oxides in addition to soil acidity are strong controls on beryllium mobility. These results aid in future predictions regarding the fate of beryllium in the environment.

Abstract. Understanding the chemical controls on beryllium sorption is fundamental when assessing its mobility as a pollutant and interpreting its concentration as a geochemical tracer of erosion, weathering and landscape surface stability. In order to evaluate the interactions of beryllium with soil- and aquatic-related materials, we selected model organic compounds and minerals to perform sorption experiments. The retention of beryllium by each of these compounds and minerals was evaluated over a pH range of 3–6 and at various equilibration times to determine which conditions allowed the greatest retention of beryllium. We conclude that most beryllium sorption occurred within 24 h for both organic and mineral materials. However, equilibration required longer periods of time and was dependent on the solution pH and sorbent material. The pH exhibited a strong control on beryllium sorption with distribution coefficient (K_d) values increasing non-linearly with increasing pH. A system with a pH of 6 is likely to retain 79–2270 % more beryllium than the same system at a pH of 4. Phosphonate retained the greatest amount of beryllium, with K_d values 2–30× greater than all other materials tested at a pH of 6. Therefore, soils containing larger amounts of phosphorus-bearing minerals could result in greater retention of beryllium relative to phosphorus-limited soils. Overall, soil composition, with an emphasis on phosphorus oxide content and pH, is an important property to consider when evaluating the capacity of a system to retain beryllium.

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Introduction

Currently, two very different scientific communities generate beryllium research: environmental geochemistry and inorganic and medicinal chemistry. In the field of environmental geochemistry, beryllium isotopes have been used in the last 25 years as a tool in geochronology and geomorphology for a range of applications from assessing chemical weathering fluxes from continents to understanding the age and stability of topsoils.^[1–4] Such isotopes including ‘meteoric’ cosmogenic ^{10}Be and ^7Be are produced from high-energy spallation reactions involving oxygen and nitrogen in the atmosphere. ^{10}Be and ^7Be fall onto the Earth’s surface through wet or dry deposition, adsorbing onto surface sediments, and can be used to understand sediment redistribution. The concentration of ^7Be (half-life $t_{1/2} = 53.1$ days) and ^{10}Be ($t_{1/2} = 1.39$ Ma) scales with the residence time of sediments in a landscape.^[5] In addition to cosmogenic ^{10}Be and ^7Be , recent work indicates ^9Be leached from mineral lattices during weathering processes moves through a landscape adsorbed to soil particles and in solution.^[4,6] As such, the flux of ^9Be from rivers is indicative of the weathering extent of soils within the catchment. When deposited in ocean sediment along with ^{10}Be , these concentrations of ^9Be are thought to record the silicate

weathering history of Earth.^[4] Natural conditions that cause beryllium mobilisation or preferential sorption, thus biasing its concentration, would complicate the interpretation of these measurements. A better understanding of the chemical controls affecting the environmental behaviour of beryllium is fundamental.

Such information is also essential because of beryllium’s toxicity and potential as an environmental contaminant. Beryllium qualifies as a Class A carcinogen – the highest ranking issued by the US Environmental Protection Agency relating to carcinogenicity.^[7] Anthropogenic sources of beryllium include beryllium ore processing and the combustion of fossil fuels – principally coal, which accounts for 99 % of anthropogenic beryllium emissions into the atmosphere and 93 % of total atmospheric beryllium levels.^[8,9] Wet and dry deposition processes deliver atmospheric beryllium to surface soils and water systems.^[10] After deposition, beryllium could potentially be leached from particles in acidic environments and mobilised into the soil profile and possibly into the ground water. In addition to atmospheric emissions, wastewaters from industries including metal manufacturing, electric power generation, paint and ink formulation, coal mining and other sources can contain beryllium up to or possibly exceeding 5 mg L^{-1} , or

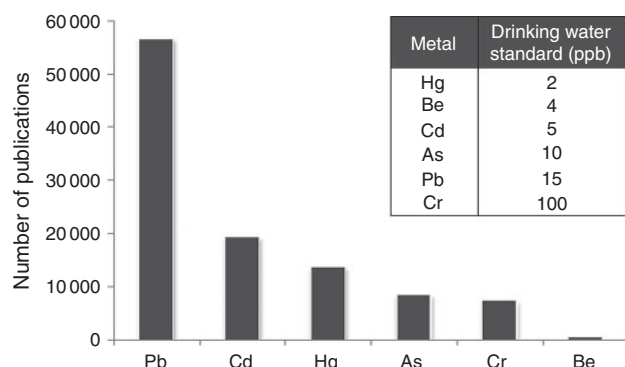


Fig. 1. The number of environmentally related papers published on various heavy metals and their respective drinking water standards as established by the US Environmental Protection Agency (EPA).

1250 times the drinking water standard.^[11] The behaviour of beryllium and beryllium compounds in soil and water systems proximal to anthropogenic sources provides a cause for environmental concern. Unfortunately, unlike other heavy metals, there is a paucity of data regarding the behaviour of beryllium in the environment despite its toxicity as evidenced by its low drinking-water standard (Fig. 1).^[12] Therefore, further investigation into its environmental behaviour is needed.

Both fields of environmental geochemistry and inorganic and medicinal chemistry contribute a unique perspective on beryllium and if merged, could provide a more complete understanding of beryllium's behaviour in soils and aquatic environments. In the field of geochemistry, most studies report observations relating to beryllium in the environment or in the presence of natural materials used to simulate environmental conditions. Several review papers have been published and summarise these findings.^[5,7,13,14]

Although some of these studies report the sorption of beryllium among specific minerals to demonstrate the effect of mineralogy on beryllium retention, none incorporate individual organic ligands into their research design. Additionally, there is a lack of consensus in the geochemical literature regarding the role of organic matter in the retention of beryllium. A study of the geochemical availability of beryllium in lake and river surface sediments did not show significant correlation between organic matter content and beryllium concentration.^[15] A global meta-analysis investigating the relationship between meteoric ¹⁰Be concentrations and the physical and chemical properties of soils found no correlation between ¹⁰Be and the organic matter concentrations in soils. It has also been reported that the presence of organic matter did not significantly affect beryllium retention to specific minerals.^[16] However, other studies have concluded that both humic and fulvic acids were able to form stable complexes with beryllium and influenced its speciation and sorption to minerals.^[17,18] In fact, it has been shown that the organic fraction of lake sediments contains ~100× more ¹⁰Be atoms per gram than the bulk sediment.^[19] The inconsistency in available data has spurred a debate regarding the distribution of beryllium between organic and inorganic phases in the environment. Understanding the relative strength of organoberyllium complexes with ligands like carbonate, sulfate and phosphate and the relative strength of various beryllium–mineral associations can help resolve inconsistencies between data sets and aid in predictions regarding the fate of beryllium in different environments.

Conversely, work published in the field of inorganic and medicinal chemistry discusses the aqueous coordination chemistry of beryllium, particularly the strength of various beryllium–ligand complexes, for medicinal applications related to the toxicity of beryllium.^[20–25] Many of these studies report the stability constants for various inorganic and organic beryllium complexes. Unfortunately, no single study examined the various ligands and biomolecules expected to exist in natural organic matter and soils with varying acidity and time. Therefore, there is a need to examine such ligands in addition to selected minerals under the same environmental conditions to determine their relative strength in complexing beryllium.

In the present study, we merged these two areas of science and used both approaches by applying chemical principles to environmental materials to understand the behaviour of beryllium in soils and aquatic systems. We performed fundamental experiments to determine how the chemical composition of materials including minerals, organic ligands mimicking organic matter and pH affect the strength of beryllium sorption and under what time scales equilibrium is established between solid and solution phases. Our goals were to (1) determine the relative strength of beryllium sorption among organic ligands and minerals; (2) to estimate the difference in the degree of sorption with pH; and (3) to determine the time scales over which equilibrium occurs between dissolved and sorbed beryllium. With a better understanding of the conditions and materials that affect the sorption of beryllium, we can make predictions regarding the behaviour of beryllium in various soil and aquatic systems for the application of geomorphologic techniques and assessment of its risk as an environmental contaminant.

Experimental

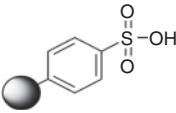
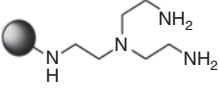
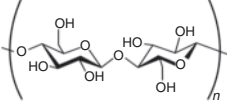
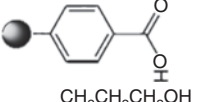
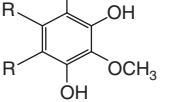

Organic compound selection and preparation

We selected organic compounds on the basis of their environmental availability and individual chemical properties to determine how those properties affect their ability to sorb beryllium. For example, organic molecules containing carboxylic acids are presumed drivers for metal retention in soil organic matter. In order to test whether or not carboxylic acids and other functional groups are responsible for beryllium retention, we selected organic compounds containing a single functional group of interest. These functional groups include (i) an alcohol, (ii) a carboxylic acid, (iii) an amine, (iv) a sulfonate, and (v) a phosphonate. We also used graphite (Acros, Ceel, Belgium) as a control because it contains no functionalities that would allow an electrostatic interaction with beryllium.

In order to calculate the proportion of sorbed beryllium, we used a 0.45- μ m filter (Pall Life Sciences, Port Washington, NY, USA) to separate non-bound beryllium from beryllium sorbed to the surfaces of the selected materials. All of these compounds with the exclusion of graphite contain polar functionalities, thus making them water soluble. Therefore, the organic compounds used were either insoluble or exceeding 0.45 μ m in size so that they could be easily separated through filtration. For example, we selected polystyrene-bound compounds when available with a mesh rating that exceeded 0.45 μ m so they could be easily removed through filtration. Benzoic acid (Alfa Aesar, Ward Hill, MA, USA), tris(2-aminoethyl)amine (Sigma–Aldrich, St Louis, MO, USA) and toluenesulfonic acid (Alfa Aesar) bound to a polystyrene resin were selected to represent a carboxylic acid, amine and sulfonate group respectively (Table 1). We chose octadecylphosphonic acid (Sigma–Aldrich), a large

Table 1. Structural formulas for each model organic compound

The grey circles represent the polystyrene backbone for compounds that were resin-bound. There is no defined structure for lignin; however, it is believed to consist of aromatic rings and alcohol functionalities

| | | |
|--------------------------|---|--|
| Toluenesulfonic acid |  | $\text{R}-\text{S}(=\text{O})_2-\text{O}^-$ |
| Octadecylphosphonic acid | $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$ | $\text{R}-\text{P}(=\text{O})(\text{O}^-)_2$ |
| Tris(2-aminoethyl)amine |  | $\text{R}-\text{N}(\text{H})_3$ |
| Benzoic acid |  | $\text{R}-\text{C}(=\text{O})-\text{O}^-$ |
| Cellulose |  | $\text{R}-\text{O}^-$ |
| Lignin |  | $\text{R}-\text{O}^-$ |
| Graphite |  | None (control) |

insoluble alkane, to represent a phosphonate group. Phosphonate was used as an analogue for phosphate, the more abundant form of phosphorus in the environment. The complexation of beryllium by these two ligands is very similar.^[20,26] Similarly, sulfonate was used as a representative for sulfate. We also selected cellulose (Sigma–Aldrich) and lignin (Tokyo Chemical Industry Co., Tokyo, Japan) because they are the most abundant biopolymers, are insoluble and contain numerous alcohol functional groups.

Mineral selection and preparation

We also selected mineral samples to determine if mineralogy affects the retention of beryllium in soils. We chose (i) illite, (ii) montmorillonite, (iii) kaolinite, and (iv) goethite because of their great abundance in many soils. These minerals were acquired through Ward's Science (Rochester, NY, USA). Each sample's mineralogical purity was verified using X-ray diffraction (XRD) analysis. The samples were then ground using a disc mill. Each sample was rinsed with weakly acidic HCl (Fisher Scientific, Pittsburgh, PA, USA) solution to remove any impurities, then rinsed with ultrapure Millipore (Billerica, MA, USA) water. The ground mineral samples were wet-sieved and dried in an oven overnight. The <20- μm fraction was collected for use in the present experiment. Prior to experimentation, a Beckman–Coulter particle size analyser (Miami, FL, USA) was used to determine the proportion of each mineral's <20- μm fraction that was smaller than 0.45 μm to ensure the filter would be able to remove mineral particles from solution. We found that

~99.5% of particles were greater than 0.45 μm in size for all mineral samples. As an additional precaution, all mineral samples were centrifuged with the appropriate speed and time interval before filtration to ensure >99.5% of particles were excluded from solution.

Solution preparation

We prepared individual organic compound and mineral solutions at a concentration of 250 mg L^{-1} . We selected a sorbent concentration of 250 ppm to ensure the sorbent was in excess over the beryllium concentration and would not limit the extent of beryllium sorption. It is important to note that for organic compounds, 250 mg L^{-1} represents the concentration of the active functional group, not the organic molecule because the ratio of functional group to organic compound mass varies from compound to compound. For example, 250 mg L^{-1} phosphonate (PO_3) was prepared rather than 250 mg L^{-1} of octadecylphosphonic acid ($\text{C}_{18}\text{H}_{39}\text{O}_3\text{P}$). Maintaining the same concentration of the active functional group ensures consistent comparison of each beryllium–ligand complex. However, with regard to the mineral samples, 250 mg L^{-1} represents the concentration of the bulk mineral, not the concentration of active binding sites, which unfortunately restricts direct comparison of organic and mineral results. We selected a solution concentration of 1 mg L^{-1} $\text{Be}_{(\text{aq})}^{2+}$ prepared using a beryllium ICP standard (BDH, Lutterworth, UK) because this magnitude falls in the range of natural, dissolved concentrations of beryllium, which can be as high as ~100 ppb in surface waters and can exceed 5 mg L^{-1} in wastewaters.^[13] This concentration also ensures our ability to resolve small changes in sorbed beryllium amounts. Considering 1 ppm is greater than beryllium's natural abundance in the environment, we used *Hyperquad Simulation and Speciation* software (Protonic Software, Hanau, Germany) to model the effect of beryllium concentration on its speciation and ligand complex formation. We selected ligands similar to those used in the present experimental study to model beryllium complex formation at different beryllium concentrations using previously determined stability constants published in Alderighi et al.^[21] Beryllium hydrolysis and ligand complexation were modelled using 1-ppm and 0.1-ppb beryllium. The results will be discussed in the *Results from modelling concentration effects* section.

We prepared each organic compound and mineral solution in triplicate at a pH of 3, 4, 5 and 6 and for each of four different time intervals. The solution pH was adjusted using dilute HCl (Fisher Scientific) and NaOH (Fisher Scientific). An explanation as to why these pH values were selected is provided below in the *Blank spike filtration results* section. Therefore, a total of forty-eight 50-mL solutions were prepared for each compound for a total of 528 individual mineral and organic compound solutions. Each sample was prepared in a solution of 0.1 M KCl (Sigma–Aldrich). This was done to maintain constant ionic strength so that the abundance of ions in solution capable of interacting with beryllium, potentially restricting its interaction with the sorbent, was not variable with pH. The solutions were placed on a roller table to allow constant but gentle mixing of the material and $\text{Be}_{(\text{aq})}^{2+}$ solution.

Blank spike sample preparation

To ensure the $\text{Be}_{(\text{aq})}^{2+}$ in solution was not adhering to the surfaces of the sample containers or removed during filtration, blank spike solutions containing 1 mg L^{-1} beryllium were carried

through the same procedure as the samples. Beryllium precipitates at approximately neutral pH at the concentrations used and it was important to determine if the 0.45- μm filter would remove unbound, precipitated $\text{Be}(\text{OH})_2$ in solution. We prepared two sets of solutions containing 1 mg L^{-1} beryllium in 0.1 M KCl for a pH range of 2–12 with each pH solution prepared in triplicate; a total of 60 solutions were prepared. We examined this range to determine under what pH conditions the use of filtration would be suitable for the separation of bound and unbound beryllium remaining in solution. One set of the duplicate solutions was filtered through a 0.45- μm filter and the other set was not. Both the filtered and non-filtered solutions were analysed to determine the amount of $\text{Be}_{(\text{aq})}^{2+}$ remaining in solution.

Analysis

The pH was monitored throughout the duration of the experiment and before sampling to ensure there were no fluctuations. The change in pH did not exceed ± 0.1 pH units. Samples were collected after 1, 7, 14 and 120 days. At the time of sampling, we filtered each solution through a 0.45- μm Pall GHP Acrodisc filter made of polypropylene to ensure low binding potential. Whatman glass-fibre filters (GE Healthcare Bio-Sciences, Pittsburgh, PA, USA) retained $\sim 2\%$ of beryllium from a blank spike solution and were therefore excluded. We analysed the filtered solutions using an inductively coupled plasma–optical emission spectrophotometer (ICP-OES) (Spectro, Mahwah, NJ, USA) to determine the concentration of unbound beryllium remaining in solution.

Results and discussion

Beryllium speciation

Blank spike filtration results

The blank spike filtration data indicated that a 0.45- μm filter is capable of removing most of the precipitated $\text{Be}(\text{OH})_2$ at certain pH values. $\text{Be}(\text{OH})_2$ precipitates at a pH of ~ 7 , resulting in the removal of 79% of beryllium from the solution (Fig. 2). In addition, there is increased removal of beryllium with increasing pH; almost 100% of the beryllium was filtered from solutions with a pH of 9 and 10. The filtration of beryllium agrees with its speciation under these conditions. Beryllium is expected to exist as insoluble $\text{Be}(\text{OH})_2$ in solutions with a pH of ~ 7 to 12 when its concentration is 1 mg L^{-1} . The speciation of beryllium, and thus the pH at which $\text{Be}(\text{OH})_2$ is formed, is dependent on the concentration of beryllium in solution. Therefore, it is strongly encouraged when using filtration that blank spike solutions be prepared using the same solution matrix, pH range and concentration of metal as expected in the samples to determine if the filter restricts precipitated metal oxide or hydroxide.

Unfortunately, this result affects the pH range for which we were able to study the behaviour of beryllium. Non-bound $\text{Be}(\text{OH})_2$ would be removed under neutral conditions and mistakenly calculated as beryllium sorbed by either the mineral or organic material. Thus, the pH range used in this investigation was 3–6. These pH values are most relevant to soil chemistry while also ensuring accurate use of filtration to differentiate between bound and non-bound beryllium.

Results from modelling concentration effects

After modelling various ligands in aqueous solutions ranging in pH from 2 to 7 and with different beryllium concentrations,

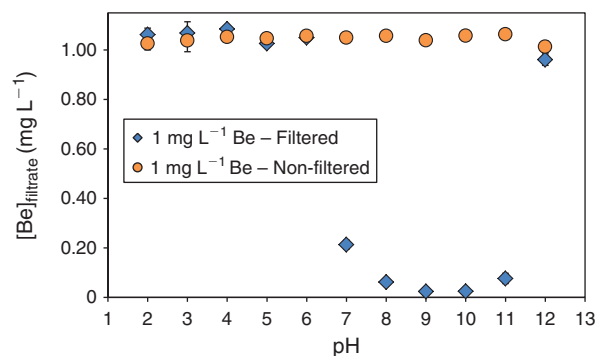


Fig. 2. The concentration of beryllium remaining in solution after filtration using a 0.45- μm filter as a function of pH for a solution containing 1 mg L^{-1} $\text{Be}_{(\text{aq})}^{2+}$. A non-filtered solution containing 1 mg L^{-1} Be was used as a control. (Note: error bars were included for all data points. However, for some of the data the error bars are smaller than the markers so are not visible.)

we conclude that beryllium concentration has minimal effect on beryllium complexation under the conditions studied. For each beryllium–ligand system we modelled, beryllium speciation as a function of pH for a system containing 0.1 ppb was similar to a system containing 1 ppm beryllium. Although the beryllium concentration affects the pH at which it precipitates as a hydroxide, considering $\text{Be}(\text{OH})_2$ does not form until a pH of 7 under our experimental conditions, the beryllium–ligand complexes tested in the present study were not in competition with hydroxide formation. This would become even less of a concern at natural beryllium concentrations, where $\text{Be}(\text{OH})_2$ is formed at even higher pH. At natural concentrations, beryllium could remain complexed by a ligand over a greater pH range, under even more basic conditions but the relative abundance of beryllium–ligand species would not differ significantly from the same system containing 1 ppm beryllium at the pH range studied. Therefore, the relative order of ligand preference is maintained at lower, natural beryllium concentrations under our experimental conditions and the pH range studied.

Distribution coefficient calculations

It should be noted that in the current study, the term ‘sorption’ can refer to any of three possible mechanisms including adsorption, absorption or complexation. We report the extent of beryllium sorption among the various organic ligands and minerals as the distribution coefficient (K_d). The K_d represents the ratio of sorbed beryllium normalised by the sorbent concentration, to non-sorbed beryllium at equilibrium (Eqn 1):

$$K_d = S/C \quad (1)$$

where K_d is reported in units of millilitres per gram, where S represents the concentration of sorbed beryllium normalised by the concentration of sorbent and C represents the concentration of non-sorbed beryllium remaining in solution.

In order to calculate the amount of sorbed beryllium, we calculated the difference between the initial concentration of beryllium and the concentration of beryllium remaining in solution at the time of sampling. However, rather than using an initial concentration of 1 mg L^{-1} of beryllium in solution, we calculated its activity. Although the use of a 0.1 M KCl matrix normalised the ionic strength of solutions with differing pH, the abundance of potassium and chloride ions affects the ability of beryllium to form associations with the sorbent material.

Therefore, we accounted for beryllium's reduced chemical potential by calculating its effective concentration, or activity, in solution. In order to calculate activity (a), the concentration of beryllium in solution (c) is multiplied by an activity coefficient (γ) (Eqn 2).

$$a = c\gamma \quad (2)$$

We derived the activity coefficient from the extended Debye–Hückel Equation where A and B are constants, I represents the ionic strength, α represents the ionic radius and z represents the ionic charge (Eqn 3):

$$\log \gamma = -\frac{Az^2I^{0.5}}{1 + B\alpha I^{0.5}} \quad (3)$$

where $A = 0.51$, $B = 0.00328 \text{ pm}^{-1}$, $I = 0.10 \text{ M}$, $z = 2$ and $\alpha = 35 \text{ pm}$.

Applying the activity coefficient 0.239, the effective concentration of beryllium in solution, as represented by C in the K_d equation, was adjusted for each sample to account for the reduced ability of beryllium to interact with the sorbent due to the ionic strength of the solution. These corrected values were used to calculate the K_d .

Beryllium sorption as a function of pH

Organic compound results

The distribution coefficients reported for most organic ligands demonstrate a clear dependence on solution pH (Fig. 3). With the exception of graphite, cellulose and benzoic acid, which showed very little to no retention of beryllium, there is a positive correlation between the amount of beryllium sorbed and the pH: as pH increases, more beryllium is retained. This relationship is non-linear and is unique for each organic ligand. For example, K_d values reported for phosphonate and sulfonate differed significantly from pH 3 to 6 relative to the other organic ligands like lignin and the trisamine group in tris(2-aminoethyl) amine (henceforth referred to as 'trisamine'), which exhibited a smaller increase in K_d with increasing pH.

Overall, pH exhibits a significant control on beryllium retention and is an important variable to consider when comparing beryllium concentrations in differing environments because it can have an effect on the amount of beryllium complexed by organic matter. Table 2 reports the percentage increase in the amount of retained beryllium from a pH of 4 to 6 after 14 days for each organic compound. (Note: a pH of 4 was used to calculate percentage change rather than 3 because soil with a pH of 4 is more common.) The combined results for the organic compounds indicate a sorbent–solution mixture with a pH of 6 is capable of retaining 79–475 % more beryllium than the same mixture with a pH of 4. Lignin and trisamine exhibit the greatest percentage increase in the amount of sorbed beryllium, retaining 350 and 475 % more beryllium at a pH of 6 respectively. Phosphonate and sulfonate also demonstrate a significant percentage increase in sorbed beryllium of 86 and 98 % respectively. Although having larger K_d values, sulfonate and phosphonate exhibit a smaller percentage increase in the amount of complexed beryllium relative to lignin and trisamine because they are able to complex beryllium more effectively over the entire pH range studied. Cellulose, benzoic acid and graphite exhibited smaller percentage increases relative to lignin and trisamine because they provided little retention of beryllium at any pH.

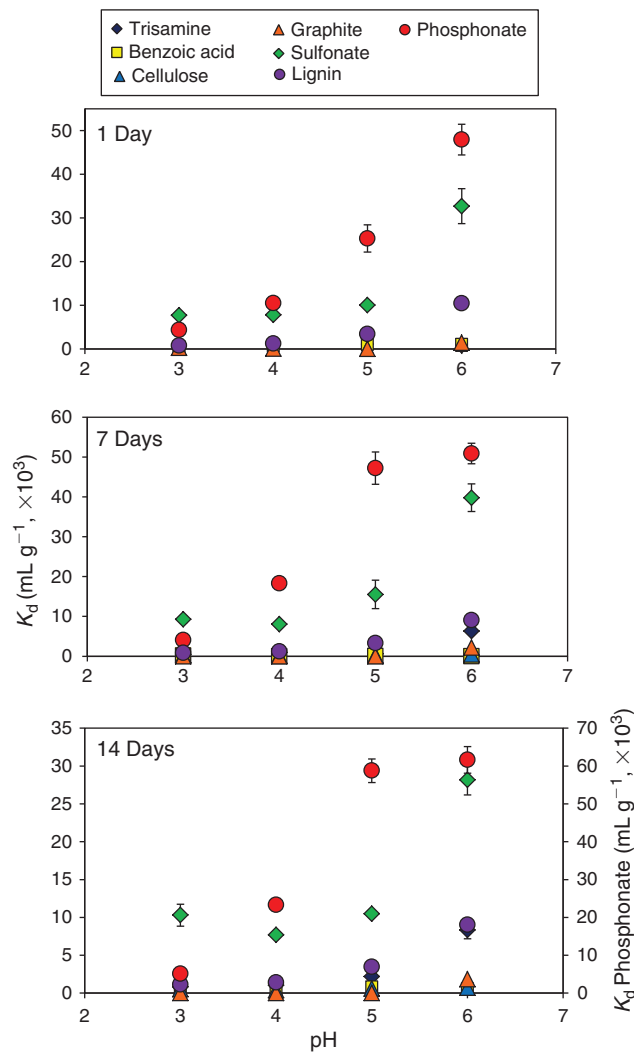


Fig. 3. Distribution coefficient for Be for each model organic compound expressed as a function of pH after 1, 7 and 14 days.

Table 2. The percentage increase in the amount of retained beryllium from a pH of 4 to a pH of 6 after 14 days for selected organic compounds

| | |
|--------------|-------|
| Cellulose | 79 % |
| Phosphonate | 86 % |
| Sulfonate | 98 % |
| Benzoic acid | 105 % |
| Lignin | 350 % |
| Trisamine | 475 % |

We expect this behaviour in view of each ligand's charge dependence on the pH. Acid dissociation constants, represented as K_a , approximate the availability of each ligand to attract and form an association with beryllium as a function of pH (Table 3). These values describe the extent of protonation at any pH and thus the charge on the active functional group. The pK_a represents the pH at which half of the acidic functional groups are deprotonated, making them more capable of complexing metals. With increasing pH, more acidic functional groups become

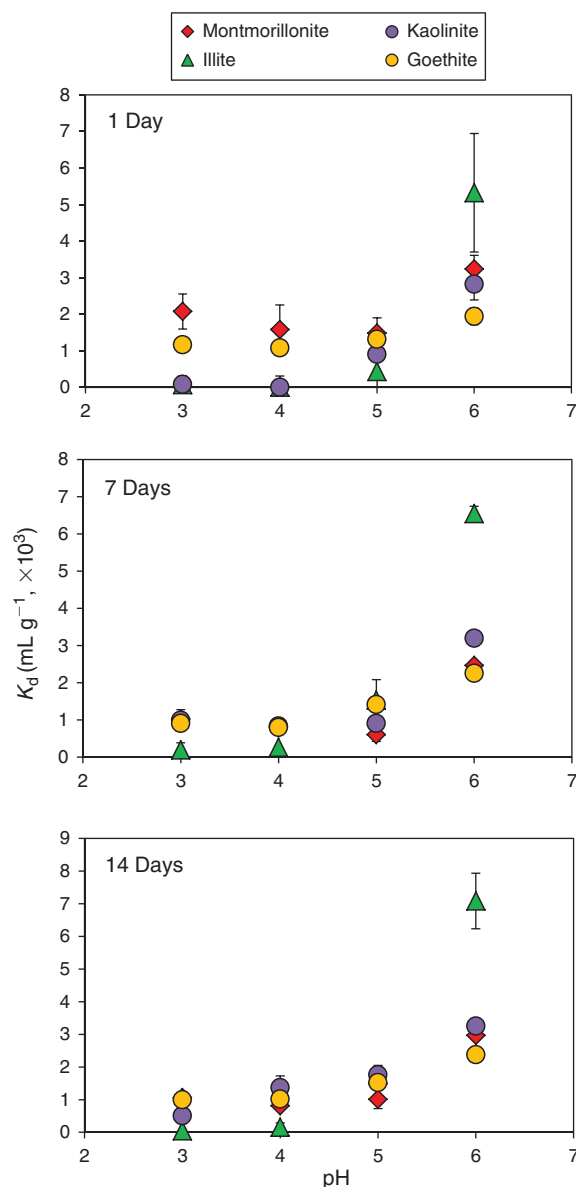
Table 3. List of the model organic compounds, the functional groups they represent and their associated pK_a values

| Compound | Functional group | Approximate pK_a |
|--------------------------|---|--------------------|
| Toluenesulfonic acid | $-\text{SO}_3\text{H}, \text{SO}_3^-$ | -2.8 |
| Octadecylphosphonic acid | $-\text{PO}_3\text{H}_2, \text{PO}_3\text{H}^-, \text{PO}_3^{2-}$ | 2.6, 8.5 |
| Benzoic acid | $-\text{CO}_2\text{H}, \text{CO}_2^-$ | 4.2 |
| Lignin | $-\text{OH}, \text{O}^-, \text{CO}_2\text{H}, \text{CO}_2^-$ | 6.0–11 |
| tris(2-Aminoethyl)amine | $-\text{NH}_3^+, \text{NH}_2$ | 8.6 |
| Cellulose | $-\text{OH}, \text{O}^-$ | 15 |
| Graphite | $-\text{C}=\text{C}$ | 43 |

deprotonated, explaining the increase in sorption and K_d values. Beryllium exhibited strong retention in the presence of toluenesulfonic acid and octadecylphosphonic acid, representing the sulfonate and phosphonate functional groups respectively. Their low pK_a values indicate that most of the organic species in solution were deprotonated and negatively charged at the pH values used, thus allowing a stronger attraction of beryllium. Toluenesulfonic acid has a lower pK_a , and more readily complexes beryllium at a pH of 3 compared with octadecylphosphonic acid, which has a slightly higher pK_a . However, above a pH of 3, octadecylphosphonic acid complexes larger amounts of beryllium relative to toluenesulfonic acid and the other organic ligands. This reflects the chemical nature of the phosphonate–beryllium complex and will be further discussed in the *Beryllium sorption as a function of organic matter composition* section.

The K_d values for trisamine are significantly lower (Fig. 3). Considering the pK_a value for trisamine is 8.5, the extent to which the primary amine groups are deprotonated is minimal even at a pH of 6. Therefore, there is a large difference in the amount of beryllium retained by trisamine at a pH of 6 versus a pH of 4. According to the Henderson–Hasselbalch equation, $\sim 0.28\%$ of the amine groups would be deprotonated at a pH of 6, rendering a lone electron pair available for complexation compared with 0.0028% at a pH of 4. Thus at a pH of 6, 0.28% or 750 ppb of the total amine groups would be available for complexation. Beryllium typically assumes a four-coordinate, tetrahedral geometry. Therefore, we assume that beryllium is coordinated by a single trisamine molecule, owing to steric hindrance, and two water molecules. Assuming it is thermodynamically favourable for both primary amines to chelate a single beryllium, we could approximate the amount of complexed beryllium to be 344 ppb, applying a 2:1 amine/beryllium ratio. We observed that 340 ppb of beryllium was retained by trisamine after 14 days at a pH of 6, which is very close to the estimated value. Lignin behaves similarly to trisamine in that its pK_a value falls within the pH range studied and therefore with increasing pH, there is an increase in the amount of retention.

The smaller K_d values reported for cellulose can also be explained by its pK_a value. Within the pH range of interest, the hydroxyl groups of cellulose are protonated, providing little attraction towards beryllium. Although the pK_a value for benzoic acid suggests we should observe greater K_d values, we see very little retention. This indicates that in some instances the chemical nature of the ligand provides an additional control on beryllium complexation other than pH. This effect will be further discussed in the following section.

**Fig. 4.** Distribution coefficient for Be for each model mineral expressed as a function of pH after 1, 7 and 14 days.

Mineral results

Similar to the trends observed in organoberyllium complexation, K_d values representing beryllium–mineral associations show a non-linear increase with increasing pH (Fig. 4). Beryllium–illite mixtures exhibited the greatest change in K_d with increasing pH whereas goethite demonstrated the smallest variation. The percentage increase in sorbed beryllium from a pH of 4 to 6 was also evaluated for each mineral (Table 4). The combined results for all minerals demonstrate that a mineral–solution mixture with a pH of 6 is capable of retaining 121–2270% more beryllium than the same mixture with a pH of 4. Illite exhibited the largest percentage increase, 2270%, in the amount of complexed beryllium between a pH of 4 and 6.

Similarly to pK_a values, the pH of zero point charge, pH_{zpc} , can be used to determine the overall surface charge of a mineral at a given pH (Table 5). The pH_{zpc} accurately predicts that beryllium would form the weakest association with goethite relative to the other minerals. At the pH values of interest, the

Table 4. The percentage increase in the amount of retained beryllium from a pH of 4 to a pH of 6 after 14 days for selected minerals

| Mineral | Percentage increase in Be |
|-----------------|---------------------------|
| Goethite | 121 |
| Kaolinite | 120 |
| Montmorillonite | 223 |
| Illite | 2270 |

Table 5. Minerals and their corresponding cation exchange capacities (CEC) (meq 100 g⁻¹) and pH of zero point charge (pH_{ZPC})^[36]

| Mineral | CEC | pH _{ZPC} |
|-----------------|--------|-------------------|
| Goethite | 4–100 | 7.8 |
| Kaolinite | 3–15 | 4.6 |
| Montmorillonite | 80–120 | 2.5 |
| Illite | 20–50 | 3.2 |

overall surface charge is predominantly positive. However, the pH_{ZPC} and the estimated cation exchange capacity still fail to explain the overall trend in sorbed amounts of beryllium. These values suggest that montmorillonite should exhibit the greatest amount of sorbed beryllium. Instead, illite was the strongest mineral sorbent under our experimental conditions. We hypothesise that the abundance of ions in solution could result in increased interlayer spacing, preferentially affecting the illite mineral, allowing increased penetration of beryllium ions. Additionally, this could be a result of particle aggregation occurring predominantly within the montmorillonite samples, resulting in reduced surface area and effective surface charge available for sorption. We are further investigating this result.

There is a significant increase in the amount of beryllium retained by each mineral species with increasing pH and overall, these differences in sorption from a pH of 4 to 6 are greater than those observed for the organic compounds. This indicates that changes in pH have a greater effect on the ability of minerals to sorb beryllium than the organic compounds evaluated in the present study. Again, this suggests the importance of considering pH when evaluating the sorption potential of a system and the behaviour of beryllium.

These results have implications specifically for the geomorphologic community using beryllium isotopes to compare denudation in areas with differing environmental conditions. For example, if we were using beryllium isotopes to assess total denudation within a highly weathered landscape, we might expect less beryllium to accumulate in the soil over time owing to reduced soil pH and sorption capacity. Chemical weathering leaches calcium and magnesium, typically lowering soil buffering capacity and ultimately reducing soil pH. Acidic environments would also reduce the ability of organic matter to complex beryllium. Therefore, more weathered, acidic soils may have reduced sorption capabilities, thus unfavourably affecting the results of geomorphologic investigations using beryllium isotopes.

Considerations for Be complexation as a hydroxide

As stated previously, the sorptive behaviour of beryllium could not be determined above a pH of 6 because at a

concentration of 1 ppm, beryllium exists as an insoluble hydroxide, which would be removed by filtration. Although our filtration method limited our ability to study beryllium under these conditions, it is worth noting the various inorganic chemistry papers that do report beryllium–ligand interactions at approximately neutral pH values. Many of these studies utilise ⁹Be nuclear magnetic resonance (NMR) and potentiometry to characterise beryllium–ligand complexation with varying pH. An excellent review paper produced by Alderighi et al.^[21] concluded that most beryllium–ligand complexes are not thermodynamically stable enough to compete with hydrolysis and the eventual precipitation of Be(OH)₂.^[21] In fact, both enthalpy and entropy favour the hydrolysis of beryllium and aggregate formation, with thermodynamic favourability increasing as each additional hydroxyl bridge is formed.^[21,27] Only few ligands are capable of competing with hydrolysis. Of the monodentate ligands reviewed (not including sulfonates), only fluoride and phosphonates can compete with water for Be²⁺.^[21] Dihydroxyaromatic and hydroxylcarboxylic bidentate ligands are also capable of forming complexes that are stable enough to suppress the formation of Be(OH)₂. Additional research is needed to better understand the behaviour of beryllium hydroxide under environmental conditions and is the focus of our future work.

Beryllium sorption as a function of organic matter composition

Although helpful in determining the charge of each organic compound as a function of pH, the pK_a values do not fully explain the difference in the degree of complexation. For example, although phosphonic and sulfonic acids have similar acidities, phosphonic acid exhibited K_d values two times greater than sulfonic acid. Benzoic acid showed very little retention of beryllium despite being negatively charged at a pH of 5 and 6. In addition to benzoic acid, cellulose and graphite also exhibited little to no retention of beryllium. We expected little sorption of beryllium on graphite. However, cellulose and benzoic acid contain oxygen-containing functionalities that could form stable interactions with beryllium. Although beryllium's electronegativity and charge-to-size ratio allow it to form stable interactions with hard donors like oxygen, as predicted by hard acid–base theory, the oxygen-containing hydroxyl groups in cellulose and carboxylic acid group in benzoic acid do not complex beryllium at the pH values studied. Thus, the chemical nature of the organic ligand provides additional control on beryllium sorption and can be further explained using beryllium coordination chemistry.

Previous research in this area reveals weak associations between beryllium and monocarboxylic acid groups like those in benzoic acid.^[21] Most monodentate ligands, both organic and inorganic, do not form stable complexes with beryllium in aqueous conditions.^[28] However, beryllium does form stable complexes with dicarboxylic, dihydroxyaromatic and hydroxylcarboxylic ligands, all of which are bidentate ligands capable of chelation (Fig. 5). The chelation effect provides added stability to a complex by lessening the reduction in entropy that typically accompanies complexation with multiple ligands. Monodentate ligands like the monocarboxylic acid in benzoic acid are not capable of chelation, which explains their weak coordination with beryllium. Although cellulose contains multiple hydroxyl groups, they are sterically hindered from chelating beryllium. Combined with their poor acidity as evidenced by their large pK_a, we also observe little retention of beryllium by

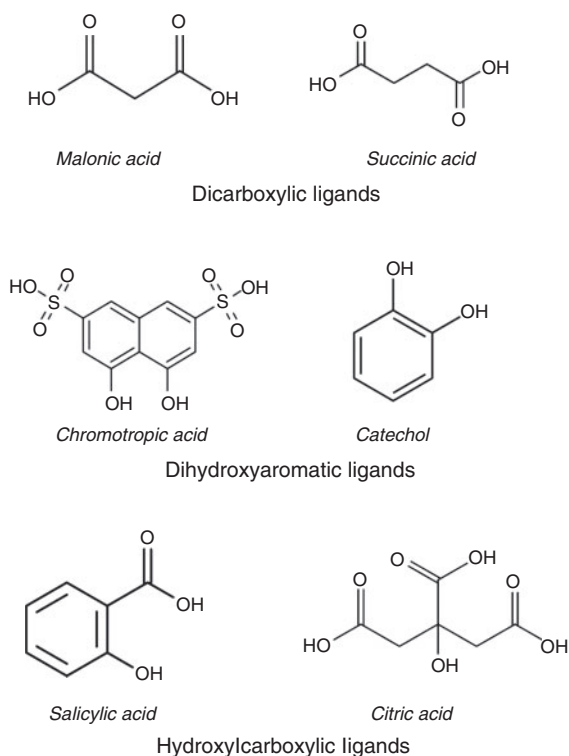


Fig. 5. Structural formulas of examples of dicarboxylic, dihydroxyaromatic and hydroxycarboxylic ligands.

cellulose. Conversely, lignin contains aromatic hydroxyl groups resembling a polymer of catechol. Its aromaticity enhances the acidity of the hydroxyl groups, providing lower pK_a values. This would explain its enhanced retention over cellulose. Lignin complexation with beryllium resulted in K_d values almost 10 times greater than cellulose and benzoic acid.

Even though oxygen donors form the most stable interactions with beryllium, nitrogen coordination can occur as well. Although weak, it has been shown that the amino group in amino acids are capable of complexing beryllium. These compounds have been studied extensively because of their potential involvement in beryllium retention in the body, specifically in identifying the mechanism and cause for beryllium's toxicity. The trisamine compound used in the present study provided greater retention than benzoic acid and cellulose, exhibiting K_d values similar to lignin. This greater retention may be a result of beryllium chelation by the two primary amine groups, which would provide enhanced retention over a single primary amine, like those found in amino acids and proteins that contribute to organic matter content.

Of all the ligands, beryllium appeared to bind most efficiently with phosphonic acid. Beryllium's enhanced affinity for complexation with phosphonic acid even over sulfonic acid can be explained by examining the thermodynamics of each system. Owing to its large charge-to-size ratio, beryllium is capable of polarising and strongly orienting water molecules around it.^[29] However, owing to their lower charge-to-size ratio, sulfonate groups are less capable of ordering surrounding water molecules. These differences in hydration entropies provide a weaker metal–ligand association between sulfonate and beryllium relative to phosphonate.^[29]

There are several studies that have investigated the unique relationship between beryllium and phosphonate and phosphate

ligands. It has been discovered that their strong associations are due to the fact that they are both able to displace the highly arranged water ligands surrounding beryllium and form stable complexes.^[20,21] The interaction between beryllium and phosphonate is so favourable that it provides more stability than that gained through chelation. In fact, a study by Alderighi et al.,^[20] reports a larger formation constant for methylphosphonic acid, a monodentate ligand, when complexed with beryllium than for malonic acid, which actually chelates beryllium to produce a sterically desired six-membered ring.^[20] Interestingly, phosphonate groups are even capable of complexing beryllium without being fully deprotonated. Diphosphonic acid, which contains two phosphonic acid groups capable of chelation, provides even greater stability, having a formation constant two times greater than that reported for malonic acid complexes.^[20]

It is important to assess the abundance and availability of phosphates and phosphonates in soils of interest owing to their strong ability to complex beryllium. Phosphonates are much less abundant in soils but their biosynthesis is more common than previously believed.^[30] They are of growing interest in environmental science and play an important role in the global phosphorus cycle. Both phosphonates and phosphates are capable of strongly binding to the surfaces of minerals and organic material.^[31] In addition, phosphates are sequestered by biota and held in organic forms. Therefore, very little phosphorus exists in the soil solution. Its accessibility is greatly dependent on pH, with peak availability occurring at pH ~6–7.5.^[32] Above a pH of 7.5, it forms complexes with calcium and below a pH of 6, it complexes with aluminium and iron. Aluminium and iron phosphates are insoluble in water and calcium phosphates are only partially soluble. Therefore, depending on the environmental conditions and soil composition, phosphorus oxides can greatly affect the mobility of beryllium and should especially be considered in areas affected by agricultural activity where phosphate-containing fertiliser is frequently applied.

Beryllium sorption as a function of mineral composition

Similarly to the organic ligand results, mineralogical composition also influences the amount of sorbed beryllium. Illite exhibited the largest beryllium K_d values relative to the other minerals. Although it was expected for montmorillonite to provide the greatest amount of surface charge to form electrostatic associations with beryllium, illite was capable of sorbing almost twice the amount at a pH of 6. Our results are supported by the findings of You et al. who performed similar sorption experiments using ⁷Be and various minerals including montmorillonite, kaolinite and illite.^[16] Their results also demonstrated larger K_d values for illite than montmorillonite (Table 6). The K_d values reported by You et al. were two orders of magnitude greater than the values reported in the present study.^[16] However, their experiment was conducted at a higher pH and lower ionic strength, both of which favour greater sorption of beryllium.

Iron and manganese oxides are important minerals when evaluating the sorption potential of the soil. Because of their large surface area and surface charge, Fe and Mn oxides have long been evaluated for their ability to sorb heavy metals in the soil.^[33] Our observation is that at the pH values studied, goethite sorbed smaller amounts of beryllium relative to the other aluminosilicate minerals. As previously discussed, part of goethite's reduced sorption is due to its pH_{zpc} . However, other studies have also found that beryllium is more highly associated

Table 6. K_d values reported by You et al.^[16] and the present study
I represents ionic strength and [S] represents the solid concentration

| Mineral | Study parameters | |
|-----------------|--|------------------------------|
| | You et al. ^[16] | Present study |
| | pH = 7.8 | pH = 6 |
| | <i>I</i> = ~0.05 M | <i>I</i> = 0.1 M |
| | [S] = ~200 mg L ⁻¹ | [S] = 250 mg L ⁻¹ |
| | K_d values (mL g ⁻¹ , × 10 ³) | |
| Illite | 220 | 5.32 |
| Montmorillonite | 210 | 3.23 |
| Kaolinite | 160 | 2.82 |

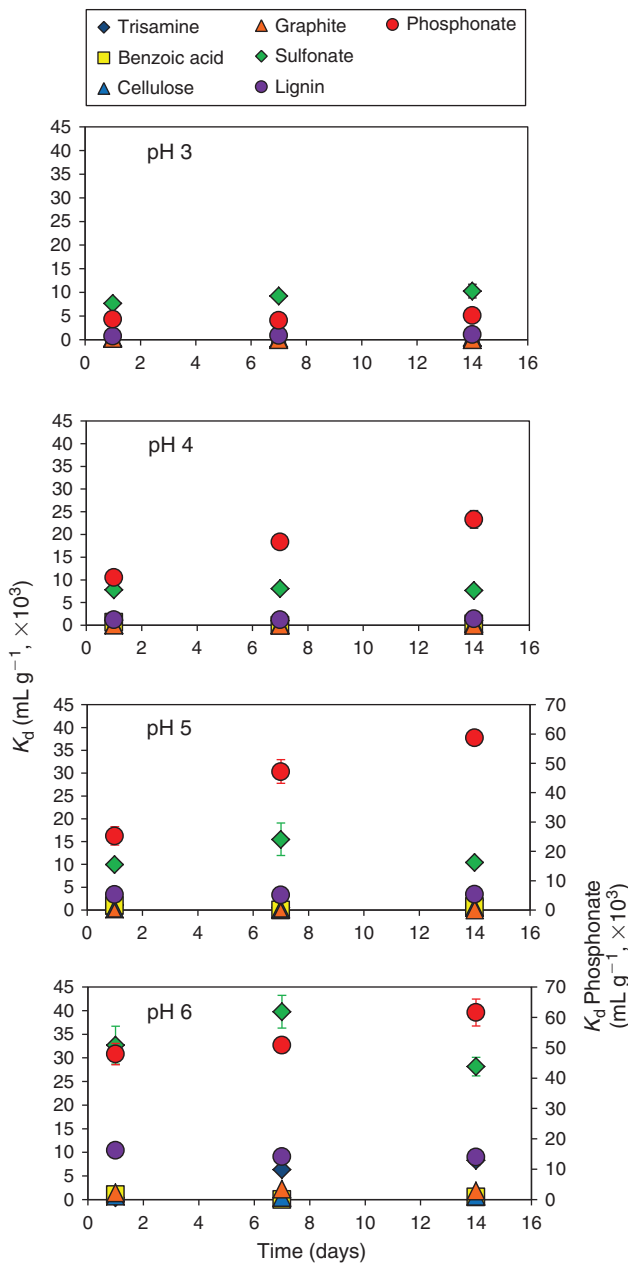


Fig. 6. Distribution coefficient for each organic compound expressed as a function of time for solutions with a pH of 3, 4, 5 and 6.

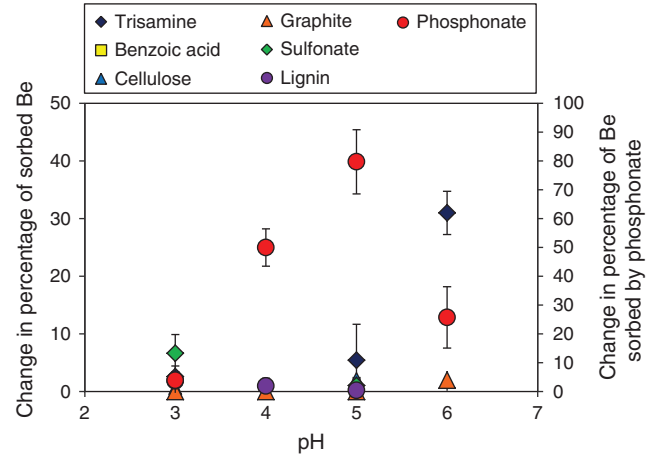


Fig. 7. The change in the percentage of total beryllium retained by each organic compound between 1 and 14 days.

with aluminosilicates than iron oxides in river sediments.^[15] Lum and Gammon found that gentle acid leaching of beryllium showed no significant correlation with iron but a strong correlation ($R^2 = 0.79$) with aluminium. They concluded that beryllium is more highly correlated with aluminosilicate phases similarly to copper, molybdenum and vanadium whereas cadmium, zinc, cobalt, lead, chromium, nickel, manganese and phosphorus were more highly associated with iron oxides.

Beryllium sorption as a function of time

The sorption of beryllium was evaluated at different time intervals to determine how quickly beryllium complexation occurred. The rate at which beryllium is sorbed to the surface of particles is very important because it affects the degree of beryllium mobility. The faster it is able to form interactions with soil material, the more quickly it is removed from the soil solution, preventing its movement through the soil column. Beryllium sorption for each organic compound and mineral was examined after 1, 7, 14 and 120 days. Unfortunately without the use of buffers, the pH could not be controlled over the 120-day time interval. Although the drift in pH was slight, causing samples with an original pH of 5 and 6 to increase in alkalinity, it was indiscernible if sorption amounts were attributable to the removal of Be(OH)₂, known to form above a pH of 6. Therefore, these results were omitted. However, we can still derive useful information from the sorption data reported for 1, 7 and 14 days.

Organic compounds

We reviewed the K_d values at each time interval and pH and observed for most compounds, there was little change in the amount of beryllium absorbed, with some exceptions (Fig. 6). To better understand the overall change in beryllium concentration over time, we calculated the difference in the percentage of beryllium sorbed between 1 and 14 days as a function of pH for each organic compound (Fig. 7). Although it is accepted that beryllium sorption occurs very rapidly, it appears that for some of the organic compounds, it required 14 days or more to establish equilibrium for a given pH. Therefore, the time required to reach equilibrium is dependent on the pH of the solution as well as the nature of the organic compound. We can classify the behaviour of the organic compounds into three categories. The first category includes compounds that exhibit little change in the amount of beryllium retained over the 14-day

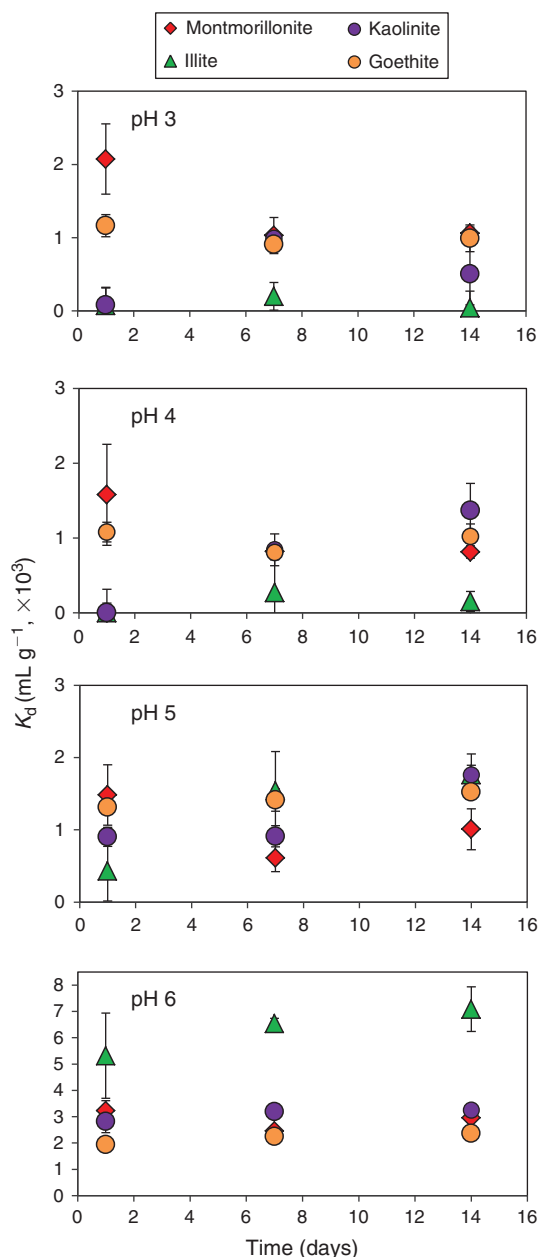


Fig. 8. Distribution coefficient for each mineral expressed as a function of time for solutions with a pH of 3, 4, 5 and 6.

time period because they provided little to no retention of beryllium overall. This category includes graphite, cellulose and benzoic acid. The second category consists of compounds that readily establish equilibrium after 1 day regardless of solution pH. There is no change in the amount of beryllium sorbed by lignin after 1, 7 and 14 days, indicating beryllium readily establishes equilibrium with lignin. The third category includes compounds that at certain pH values continue to sorb beryllium after 14 days had passed. These compounds include trisamine and phosphonate. Both phosphonate– and trisamine–beryllium complexation rates were dependent on the pH. For trisamine, the greater the pH, the greater the amount of time required to reach equilibrium. Even after 14 days, trisamine continued to sorb increasing amounts of beryllium when the solution pH was 5 or 6. For example, 31 % more beryllium was retained by trisamine over the entire 2-week time period relative

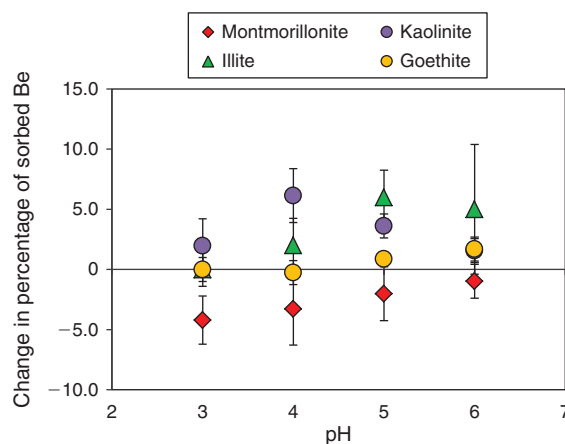


Fig. 9. The change in the percentage of total beryllium retained by each organic compound between 1 and 14 days.

to the first 24 h. Phosphonate exhibited similar behaviour at pH 4–6. After 2 weeks, phosphonate complexed 50, 80 and 26 % more beryllium at a pH of 4, 5 and 6 respectively relative to the first 24 h. The ionic strength of the solution may reduce the rate of beryllium complexation by impeding beryllium's ability form strong hydrogen bonds with the active functional groups on these ligands.^[34]

Sulfonate exhibits unique behaviour, particularly at a pH of 5 and 6, in that the concentration of beryllium fluctuates with time (Fig. 6). It appears that the concentration of sulfonate-bound beryllium increases up to 7 days and then decreases after. More resolved time intervals would be needed to further understand the behaviour of beryllium–sulfonate complexation with time. Overall, the ligands that are capable of sorbing beryllium, including lignin, trisamine, sulfonate and phosphonate, appear to sorb the majority of beryllium in ~24 h, with some ligands continuing to sorb beryllium after 14 days had passed.

Mineral results

Similarly to the organic compound results, beryllium readily sorbed to each of the minerals, exhibiting retention in less than 1 day but requiring longer time periods to reach equilibrium. We also observed that like the organic compounds, the pH affected the rate of sorption of beryllium to certain minerals. For example, beryllium sorption more readily approached equilibrium with montmorillonite, kaolinite and goethite at a pH of 6 and with illite at a pH of 3 (Fig. 8). Goethite was the only mineral unaffected by pH, exhibiting little change in the K_d constant over time, which reflects its higher pH_{zpc} . For minerals other than goethite, depending on the pH, the concentration of sorbed beryllium was changing even after 14 days had passed. Although the difference in the percentage of sorbed beryllium between 1 and 14 days was small overall (under 6%), it indicated that equilibrium was not established after 14 days (Fig. 9).

Similar equilibration times were reported by You et al. for beryllium sorption to montmorillonite and kaolinite.^[16] After ~12–20 days, there was negligible change in the amount of beryllium sorbed by either mineral. Rates of sorption onto biotite and albite as reported by Aldahan et al. also revealed equilibration times on the scale of days; the concentration of beryllium remaining in solution appeared constant after ~4–10 days.^[35] The faster equilibration times reported by Aldahan et al. can be explained by the significantly lower ionic

strength of their prepared solutions because they did not maintain a constant ionic strength for solutions of differing pH.^[35]

We also observed a reduction in beryllium K_d values associated with montmorillonite over time, which increased with decreasing pH (Fig. 9). To ensure the increase in beryllium concentration in solution was not due to mineral dissolution, we monitored changes in major ion concentrations in solution using ICP-OES, and determined that dissolution was not occurring. Therefore, we believe the reduction in beryllium K_d values over time could be attributed to beryllium desorption under acidic conditions or a result of the mineral's behaviour at lower pH values causing reduced sorption capacity.

Conclusions

Overall, we conclude that pH exhibits a strong control on beryllium retention among the mineral and organic compounds. The increased amount of sorbed beryllium at a pH of 6 relative to the same system at a pH of 4 is significant (79–2270 %) and should be considered when evaluating the potential for sorption of beryllium in the environment. With increasing pH, K_d values increased non-linearly for both organic ligands and minerals. The composition of organic matter also affects the extent of beryllium complexation and retention. Phosphonates and sulfonates exhibited the largest K_d values of all materials tested, indicating they could be a major driving force in beryllium sequestration in soils and aquatic environments. Not only are the K_d values associated with phosphonate large, phosphonate continues to complex beryllium over the 14-day time span. Thus, sulfur and phosphorus oxide abundances may be important variables to consider when estimating the sorption potential of soils. Lignin, an abundant biopolymer and component of natural organic matter, was also associated with large K_d values. Beryllium retention also varied depending on mineral composition, with illite exhibiting the highest sorption of those measured. For both organic and mineral materials, sorption occurred within 24 h. However, longer periods of time were required for equilibration to occur between beryllium and the sorbent. Equilibration time was dependent on the solution pH and sorbent material. Overall, soil pH, mineralogy and organic matter composition, with a specific emphasis on phosphorus and sulfur oxides, are important properties to consider when evaluating the capacity of a system to retain beryllium and when comparing beryllium concentrations in different environments.

Safety considerations

The inhalation of beryllium compounds can result in serious illness. Inhalation of beryllium compounds causes a potentially fatal pulmonary condition known as berylliosis, which leads to chronic granulomatous disease. All beryllium-containing compounds should be handled in a fume hood and with the proper respiratory equipment, such as a properly rated mask. Beryllium exposure to the skin should also be avoided through the use of gloves.

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