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Abstract.

^{10}Be (half life = 1.39×10^6 years) is a cosmogenic radionuclide (Korschinek et al. 2010). Meteoric ^{10}Be ($^{10}\text{Be}_{\text{met}}$) is generated in the atmosphere and deposited on surfaces (Lal and Peters 1967). Despite its use as a tracer of surface processes, there are observations that $^{10}\text{Be}_{\text{met}}$ can remobilize (Graly et al. 2010). In contrast, in situ ^{10}Be ($^{10}\text{Be}_{\text{is}}$) forms inside mineral grains and is not susceptible to remobilization (Bierman 1994). However, analyzing $^{10}\text{Be}_{\text{is}}$ is time-consuming, expensive, and only possible where sand-size grains of quartz are available. The stable isotope ^9Be is present in grain coatings and may have similar reactivity to $^{10}\text{Be}_{\text{met}}$. If so, the $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratio of a sample remains fixed, even if remobilization occurs (Von Blanckenburg et al. 2012). I will use several extraction techniques to understand the distribution of ^9Be in samples that have already been analyzed for $^{10}\text{Be}_{\text{met}}$ and $^{10}\text{Be}_{\text{is}}$. By removing the entire grain coating, I can calculate $^{10}\text{Be}_{\text{is}}$.

$^{10}\text{Be}_{\text{met}}/^{9}\text{Be}$ ratio should only be influenced by erosion rate, $^{10}\text{Be}_{\text{met}}$ deposition rate, and radioactive decay (Vesil et al. 2002).

This project proposes to extract sequentially ^{9}Be from soils and sediments in order to quantify the amount and distribution of ^{9}Be in grain coatings and mineral matrixes. I will also do a total extraction of ^{9}Be held in grain coatings in order to calculate the $^{10}\text{Be}_{\text{met}}/^{9}\text{Be}$ ratio and by comparison to existing data, determine whether it is a useful proxy for the erosion rate of drainage basins.

Beryllium can exist on sediment and soil grains in several species, which are either adsorbed to the surface of grains (exchangeable), adsorbed into the structure of mineral phases (oxy-hydroxides, carbonates, silicate minerals), or complexed with organic material. Tessier et al. (1979) outline a sequential extraction procedure that partitions particulate trace metals in to five fractions: exchangeable, bound to carbonate, bound to Fe-Mn oxides, bound to organic matter, and residual. Wittmann et al. (2012) optimized the Tessier et al. (1979) procedure specifically for Be extraction from fluvial sediments. I will further optimize this sequential extraction method for soils, fluvial sediments, and lake core sediments. Analyzing the quantity of ^{9}Be in each of the sequential extraction fractions will allow for: 1. better understanding the mechanisms of pedogenesis that allow Be to be mobile in natural systems and 2. better understanding of which fractions (or combinations of fractions) contain ^{9}Be concentrations that, when used to normalize $^{10}\text{Be}_{\text{met}}$ data, correlate to previously measured $^{10}\text{Be}_{\text{is}}$ soil profiles and $^{10}\text{Be}_{\text{is}}$ -derived erosion rates.

Background.

Natural distribution of Be. Beryllium has three naturally occurring isotopes – ^{10}Be with a half-life of 1.39×10^6 yrs (Korschinek et al. 2010), ^7Be with a half-life of 53 days, and ^9Be , the only stable isotope and the only isotope with greater than trace concentrations. ^{10}Be has proven very useful for applications in geomorphology and climatology. Greater than 99% of the ^{10}Be in natural systems is formed in the atmosphere when neutrons (secondary cosmic rays) react with nitrogen or oxygen (Gosse and Phillips 2001). After production, this $^{10}\text{Be}_{\text{met}}$ adheres to aerosols in the atmosphere and is deposited onto the landscape, where, because of its affinity to solids, it accumulates in soils and on sediments (Lal and Peters 1967, Pavich et al. 1986, Monaghan et al. 1986). However, because $^{10}\text{Be}_{\text{met}}$ only adheres to the surface of grains, it is subject to redistribution (or in extremely weathered environments, removal) *via* eluvial and illuvial processes that are independent of physical erosive processes (Figure 1; Takahashi et al. 1998, Graly et al. 2010, Bacon et al. 2012). ^{10}Be is also formed inside mineral grains from interactions between cosmic rays and ^{16}O atoms (Nishiizumi et al. 1986). This $^{10}\text{Be}_{\text{is}}$ accounts for less than 1% of the total ^{10}Be and has been shown to reflect basin-scale erosion rates (Granger et al. 1996, Bierman and Steig 1996) and the erosion rate of outcrops (Nishiizumi et al. 1986, Bierman et al. 2002, Bierman and Nichols 2004).

Nearly all Be in soils and sediment is the stable isotope ^9Be (Willenbring and von Blanckenburg 2009, Wittmann et al. 2012). Beryllium concentrations generally range from 1-15 ppm in upper crust materials, but an initiative by the US Department of Health and Human Services to document trace element concentrations in surficial materials found that ^9Be concentrations of soils (average US concentration of 0.6 ppm), surface water (average US

concentration of 0.24 ppm), and air (average US concentration of 0.03 ng/m³) are much lower than bedrock (Smith et al. 2002). Determining the distribution of ⁹Be in grain coatings by sequential extraction will help understand the reactivity of this trace metal.

Variables that influence Be phase and mobility in grain coatings. Solid-state materials are most reactive at their exposed surfaces, where electronic imbalances encourage red-ox chemical reactions. As a result, smaller grains with a high surface to volume ratio will have the highest capacity to sorb red-ox active metals such as Be (Zumdahl and Zumdahl 2010). Many studies (Graly et al. 2010, Bacon et al. 2012, Reusser and Bierman 2010) show

the soluble ion Al^{3+} (Bacon et al. 2012, Figure 3). This Al^{3+} is free to compete with other metals for exchange sites, potentially becoming the principal sorbate on negatively charged surfaces (called the exchangeable phase of the grain coating). Acidic conditions thus encourage Be^{2+} to desorb from the exchangeable phase of the sediment (Willenbring et al. 2009).

Above pH 5, organic ligands can remain deprotonated and able to form organometallic complexes with available cations. Organic-rich soils in strongly acidic to neutral conditions can decrease Be mobility by sequestering Be in organometallic Be^{2+} complexes that have a strong affinity for positively charged Fe-oxy-hydroxides, Al hydroxides, and clay minerals (Willenbring et al. 2009). Further, Taskahashi et al. (1998) found that in soils with pH between 3 and 11, nearly all Be takes the form of the hydroxylated species ($\text{Be}(\text{OH})_x^{-n}$); see Figure 4. Similar to Be^{2+} organic complexes, $\text{Be}(\text{OH})_x^{-n}$ humate complexes readily adsorb onto positively charged crystalline oxide or amorphous oxy-hydrate surfaces. Consequently, Takahashi et al. (1998) observed that when dissolved Be^{2+} (pH 7.5) was mixed with humic acids in the presence of kaolinite, over 70% of Be was adsorbed to the kaolinite in the form of hydroxylated Be humate complexes. This research indicates that if significant concentrations of humic acid are present, Be will remain adsorbed to the crystalline oxide or amorphous oxy-hydrate surfaces, even at low pH.

⁹Be dynamics in the biosphere – a closed system? Although studies of rock, soil, water, and aerosols indicate that significant amounts of ⁹Be are unlikely to be added or removed from the soil column (and can thus be considered a closed system on the millennial timescales used to study pedogenesis and erosion), the degree to which Be cycles through the biosphere is not well constrained (Kabata-Pendias and Szteke 2015, Vesel et al. 2002). The similar reactivity of Be and other common biologically relevant elements such as Mg, Ca, and Al has been used to

In these settings, precautions will be necessary to either measure or remove the coal component of samples.

Initial Sample Selection. The first phase of this project will analyze a set of fluvial sands from the Susquehanna River Watershed ($^{10}\text{Be}_{\text{met}}$ and $^{10}\text{Be}_{\text{is}}$ sample pairs), a set of acidic peat soil samples along a depth profile in Scotland ($^{10}\text{Be}_{\text{met}}$ and $^{10}\text{Be}_{\text{is}}$ sample pairs), and a set of homogenized varve samples from a series of stratigraphic sections in the Connecticut River Valley (10 samples, only measured for $^{10}\text{Be}_{\text{met}}$) (Reusser and Bierman 2010, DeJong et al. 2012, Fulop et al. 2015). The varve samples can be sub-divided into two sets, one that was accumulated relatively distal to the retreating ice sheet, and another that was accumulated proximal to the ice sheet. The proglacial lake sediment data sets contrast conditions of incipient soil formation several thousand years after glaciation with a more barren, recently glaciated landscape. These soil, sand, and varve samples have been selectedmet

sequential extraction. These samples will provide more data to support conclusions drawn in the first phase of the project, and will cover a gradient of climates and tectonic regimes (see Table 1. for a list and description of sample locations.) Providing data that shows how $^{10}\text{Be}_{\text{met}}/{}^9\text{Be}$ ratios behave across climates and tectonic regimes will test the validity of using $^{10}\text{Be}_{\text{met}}/{}^9\text{Be}$ ratios as an erosion rate proxy in more extreme end members of erosion and climactic environments.

Hypothesis. Relatively few studies of ${}^9\text{Be}$ sequential extractions from soils and sediments have been performed (Barg et al. 1997, Bacon et al. 2012, Wittmann et al. 2012), so it is difficult to predict which fractions of sequential Be extraction will have the highest ${}^9\text{Be}$ concentrations. Barg et al. (1997) and Wittmann et al. (2012) show that Be accumulates in organic-rich and clay-rich layers of soils. I therefore hypothesize that the sequential extraction fractions that selectively dissolve organic and exchangeable phases will liberate the largest quantity of Be. However, in samples with significant amounts of humic acids, I hypothesize that the crystalline oxide and amorphous oxide-bound fractions will contain significant amount of ${}^9\text{Be}$ (Taskahashi et al. 1998). Because the total grain coating is extracted for $^{10}\text{Be}_{\text{met}}$ analysis, I hypothesize that the ${}^9\text{Be}$ from the total grain coating will result in the most meaningful relationship between ${}^9\text{Be}$, $^{10}\text{Be}_{\text{met}}$, and long-term erosion rates. I hypothesize that there will be an increased concentration of ${}^9\text{Be}$ in grain coatings in the distal glacial lake sediments than the proximal sediments because ${}^9\text{Be}$ will have become more mobile during pedogenesis in the time after glaciation.

Many published reports show results that indicate the $^{10}\text{Be}_{\text{met}}/{}^9\text{Be}$ ratio normalizes $^{10}\text{Be}_{\text{met}}$ data to account for grain size effects, $^{10}\text{Be}_{\text{met}}$ remobilizing and/or $^{10}\text{Be}_{\text{met}}$ leaching (Merrill et al. 1959, Barg et al. 1997, Bacon et al. 2012, Conyers 2014, Von Blanckenburg et al. 2012, Wittmann et al. 2010, Willenbring and von Blanckenburg 2010). Because publications indicate that $^{10}\text{Be}_{\text{met}}/{}^9\text{Be}$ ratios could be meaningful indicators of erosion, I hypothesize that a $^{10}\text{Be}_{\text{met}}/{}^9\text{Be}$

ratio that includes the total ^9Be in the outside coating of grains will correlate with erosion rates calculated using $^{10}\text{Be}_{\text{is}}$ data.

Methods.

The initial methods for ^9Be sequential extraction will be adapted from of the sequential extraction published by Wittmann et al. (2012) (see Figure 5. for reagents and targeted fractions). Before running the sequential extraction, I will measure the average grain size for each sample set to ensure that the samples have all been powdered to a similar size. Each sample will result in five fractions that will be analyzed for ^9Be concentration on the UVM Geology Department's JY Horiba Optima Ion Coupled Plasma-Optical Emission Spectrometer (ICP-OES). In addition to the sequential extraction, I will use a mineral acid (HCl or HNO_3) to remove the total grain coating. This will allow me to measure the total ^9Be in the coating that should be liberated during the sequential extraction. Because $^{10}\text{Be}_{\text{met}}$ data are derived from total fusion of grains, the ^9Be in the total grain coating will be most likely to correlate with $^{10}\text{Be}_{\text{met}}$ and $^{10}\text{Be}_{\text{is}}$. I will monitor the silicate concentration of the supernatant in these extractions during measurements on the ICP-OES to ensure that the reagent is not attacking mineral grains.

To test the hypothesis that $^{10}\text{Be}_{\text{met}}$ measurements made in sediment and soil can accurately reflect rates of landscape denudation if native ^9Be is also measured, statistical tests such as ordinary least squares (a simple regression) will be used. Regressions will also be used to assess the influence of climate and tectonic regime on $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratios.

Research Plan.

1. Refine a selective sequential extraction procedure for ^9Be that can be used for soil and sediment samples and a total grain coating extraction method that will not attack the mineral

matrix.

2. Measure ^9Be in the extracted fractions and calculate $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratios for soil and sediment samples in which $^{10}\text{Be}_{\text{is}}$ and $^{10}\text{Be}_{\text{met}}$ have already been measured.

3. Compare $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratios to previously measured $^{10}\text{Be}_{\text{is}}$ data to determine what (if any) systematic variations exist.

4. Compare $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratios and the distribution of ^9Be to climate or tectonic regimes to determine what (if any) correlation exists.

Implications. This project combines measurements of $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratios, $^{10}\text{Be}_{\text{met}}$ and ^9Be to better understand the meaning of $^{10}\text{Be}_{\text{met}}$ data. If the hypothesis that native ^9Be chemically behaves similarly to meteoric ^{10}Be in weathering and pedogenic reactions is true, the $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratio could in theory be used to normalize the $^{10}\text{Be}_{\text{met}}$ nuclide inventory to account for weathering effects.

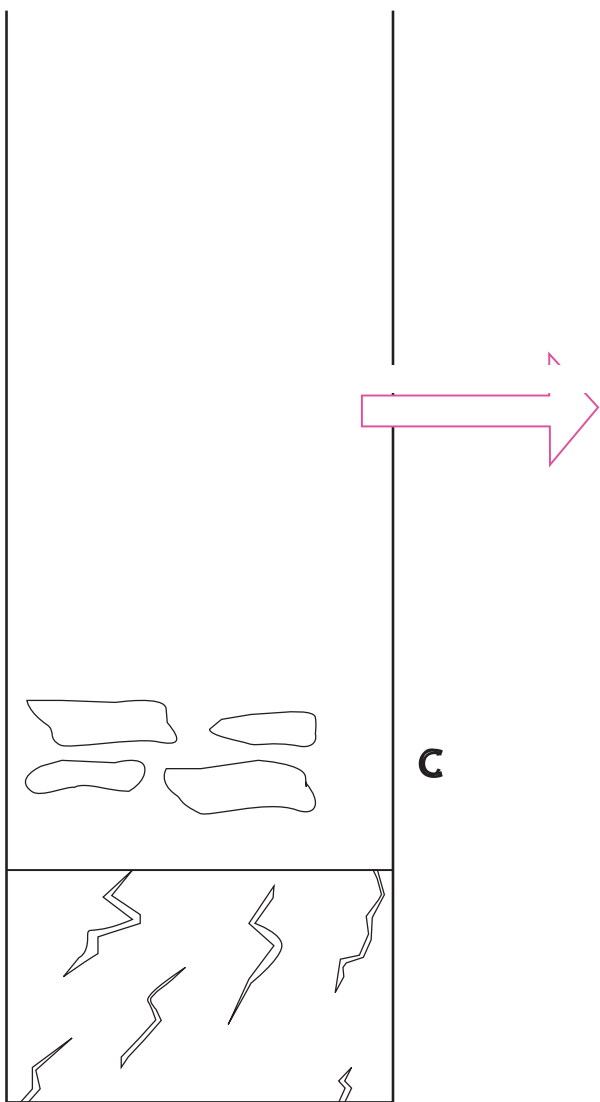
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Korschinek G., A. Bergmaier, T.

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Sequential Extractions Method (modified from Wittmann et al. 2012)

Sample

Exchangeable

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