**Calcium (Ca) availability to ecosystems: Weathering of limestone,**

**apatite, and Ca-plagioclase (anorthite)**

The weathering of minerals is an integral source of nutrients to biota in all ecosystems and there is a need to understand and quantify the availability of nutrients that can limit plant growth in ecosystems. Having read the Blum et al. study (you have seen that Ca can be a limiting nutrient in nutrient-poor systems—and that it can be difficult to discern which Ca-bearing minerals are weathering in a system with multiple Ca minerals present. In this study you will be quantifying the amount of calcium from each mineral that is can be weathered and available to ecosystems on short time scales (eg. years to decades weathering in a natural ecosystem).

Goal: In this experiment you will (in groups) investigate the availability of Ca during the weathering of from three common calcium minerals: limestone (CaCO3), apatite (Ca5(PO4)3(OH)), and Ca-plagioclase (anorthite, CaAl2Si2O8). We will mimic the weathering of each of these minerals on short time scales (~years to decades) by using 0.1 M nitric acid HNO3 to leach each of these minerals for ~20-24 hrs (similar to methods of the Blum paper you read). This concentration of acid will enable us to investigate the susceptibility of minerals to weathering in natural systems. Specifically, this approach allows us to quantify the amount of calcium through the weathering of each of these minerals in a natural system (where it would be exposed to acids in rain water and organic acids in soil). Importantly, we can then determine if there differences in the availability of calcium from each mineral. The quantification of Ca release from each mineral through this experiment informs you not only about Ca-availability to biota but also about the susceptibility of each mineral to weathering in ecosystems.

**3-day laboratory plan**

**Day 1: set up samples and agitate overnight**

**Day 2: gravity filter samples and dilute for analysis by AA (atomic absorption spectroscopy, with our Science Instructional Technician (SIT))**

**Day 3: run on AA with SIT**

**🡪 Data Analysis (handout) to do on your own**

**Calculations for mineral weathering (please include in your lab notebook)**

-based on the exact mass of each mineral that you weighed out, determine the moles of Ca that would be available if it dissolved completely

-to do this you will need to determine how much a mole of a given mineral weighs.

-on the provided periodic table of elements, find the molar mass for each of the elements in the mineral formula— sum up the masses of each element multiplied by its subscript

-this total should be the mass of one mole of the mineral—based on the mass of the mineral that you put into your sample you can then determine the moles of element that could be available

-based on the molarity of the 0.1M HNO3 acid (M is moles/L) and the volume of the acid in each vial, you can determine the moles of acid present in each vial as well

-if a given mineral strongly interacts with the acid, it is important to determine whether this reaction is limited by the amount of mineral available or the amount of acid available

-In the case of the limestone (for sure) determine the moles of calcium (Ca2+) available in your vial and compare that to the moles of acid (H+) that are also present

-Take a look in Ch. 16 of Grotzinger or use outside resources (including the Blum paper you read) to hypothesize the which mineral will be most and least susceptible to weathering to determine the order that you expect to see in terms of moles of available Ca

P**rocedure for Calcium Determination in Minerals**

**DAY 1**

* Label and pre-weigh 3 vials (in which you will conduct your leaching experiments) for of (1) limestone, (2) apatite, and (c) Ca-plagioclase (anorthite) – make sure to label the vial and its respective cap
* Weigh out (~1.0 g and record the mass) of each of the 3 crushed mineral samples into 3 separate corning vials.
* Add 5mL nitric acid (0.1M) to each vial using a volumetric pipette
* Seal the vial (check the lid to ensure) and them agitate each vial sufficiently to ensure that the acid is interacting with the entire mineral sample
* Put vial on agitator/rotator over night

**DAY 2**

For each of the 3 vials that were agitated you need to conduct the following steps to have them ready for AA analysis in week 8

* Remove vial from rotator and gravity filter contents (Whatman 41) into beaker
  + If turbid, filter again
* Transfer all of the material in the beaker, using small rinse(s) if necessary) beaker contents to 100mL volumetric flask—and then fill to mark with DI water,
* Seal volumetric flask and invert to mix (1st Dilution)
* Transfer 1st dilution sample to a labeled 125 mL bottle
* 2nd dilution of 0.1M nitric acid leach solutions (to dilute down to concentrations possible for analysis on AA)
  + Label and fill 2nd 100mL volumetric flask with ~50mL of DI water
  + Add 2mL of sample solution (1st dilution)
  + Add 1mL of Lanthanum solution (for Ca ionization interferences)
  + Add 1mL of concentrated nitric acid
  + Fill to mark with DI and invert to mix (2nd Dilution)
* Transfer 2nd dilution sample to a labeled 125 mL bottle – this is your sample for analysis

**DAY 3**

* Run diluted samples on AA with SIT
* Using the information for the standard curve (provided when you analyzed your samples with SIT) quantify the Ca concentrations in the diluted and initial leach samples
* Data analysis (**see separate Data analysis handout**)

**Pre-Lab questions (write the answers to these questions in your lab notebook as part of the introduction to this Lab)**

(1) Based on the referenced Blum study, please hypothesize the order in which the 3 minerals you are testing will dissolve under the experimental conditions. Please list them from slowest to fastest and include a brief explanation.

(2) What is the molar mass of each of the 3 minerals (limestone (CaCO3), apatite (Ca5(PO4)3(OH)), and Ca-plagioclase (anorthite, CaAl2Si2O8)) you will be working with? Show your work for each mineral! Your answer can be in X grams/mole.

(For help on how to do this see the bottom of page 1, “**Calculations for mineral weathering (please include in your lab notebook”**).

**References**

Blum, J.D., Klaue, A., Nezat, C.A., Driscoll, C.T., Johnson, C.E., Siccama, T.G. Eagar, C., Fahey, T.J. and Likens, G.E. (2002). Mycorrhizal weathering of apatite as an important Ca source in base-poor forest ecosystems. *Nature* 417, 729-731.

Grotzinger & Jordan (2010). Understanding Earth. W.H. Freeman and Company, ISBN-13 978-1-4292-1951-8.