ESS 461: Cosmic Ray Exposure Dating

Cosmogenic Nuclide Lab - 413 Johnson Hall

This lab will provide hands-on experience of a geochronological technique. Lectures can't convey all of the technicalities involved in the laboratory work that goes into an age determination. It's easy to write formulae that describe how some chemical or isotopic concentration N changes with time. Here we will discover what goes into measuring N.

The object of the lab is to date the moraine boulders that we collected on Fidalgo Island. To do so, we will measure a cosmic-ray-produced isotope – ¹⁰Be. The build-up of ¹⁰Be will allow us to calculate their *exposure ages*. From our geological examination of the site, and what's already known about the deglaciation history of Puget Sound, we think these rocks were deposited underwater as the ice sheet retreated, and then emerged as isostatic rebound raised the sea floor. If so, we might expect to see an older age for the higher-altitude sample (044-GPT), than for the sample slightly lower on the hillside (043-GPT). The age we get for the higher boulders is a *minimum age* for deglaciation of Fidalgo Island.

The accumulation of ¹⁰Be in rock surfaces exposed to cosmic rays depends on time. The longer a surface is exposed, the more ¹⁰Be grows in. If we know the production rate of the isotope, we can calculate the "exposure age", using the relationship:

$$N_{Be-10} = (P/\lambda) (1 - e^{-\lambda t})$$

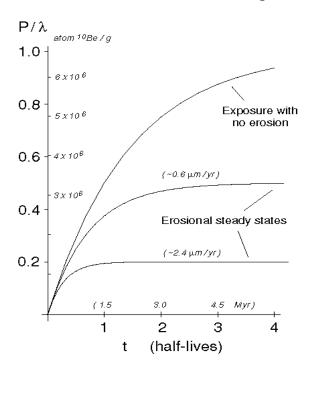
Here *N* is the concentration of the isotope (in atoms per gram of the target material – quartz), *P* is the rate of ¹⁰Be production (in atoms/g/yr), λ is the decay constant of ¹⁰Be, which is a long-lived radioisotope, and *t* is the exposure age. The production rate, *P*, is derived from a combination of theory and *calibration* measurements made on surfaces of known age.

We may need to take the effect of erosion into account when calculating the exposure time of the samples. Erosion reduces the rate of cosmogenic isotope accumulation, because erosion continuously uncovers rock that has been shielded from cosmic rays beneath the rock surface. The faster the erosion rate, the greater the amount of rock stripped away during the exposure period, and the lower the final isotopic concentration. Note – this effect can actually be used to measure erosion rates (as opposed to exposure ages). Once a surface has been eroding steadily for long enough to have lost 3-5 m of rock, the ¹⁰Be concentration reaches a constant level (a "steady state"), from which the erosion rate ε can be determined:

$$N_{Be-10} = \frac{P}{\left(\lambda + \frac{\rho\varepsilon}{\Lambda}\right)}$$

Here, ρ is the rock density, and Λ is the "attenuation length" for ¹⁰Be production beneath the rock surface, in the unusual units of length of g/cm² (length in cm x density in g/cm³).

Note that a measured cosmogenic isotope concentration can be interpreted in terms of *either* an exposure age, or an erosion rate. A careful geomorphic assessment is required to decide which is the correct interpretation.



— P is a complicated parameter which depends on the altitude and latitude of the sample site, the sample thickness, and the presence of any features such as mountains surrounding the sample site that obstruct the incoming cosmic ray flux. We will discuss this further in class and determine the production rate for each sample.

— $\lambda = 5.00 \times 10^{-7} \text{ yr}^{-1}$; after ¹⁰Be has been produced, it is radioactive, and has a half-life of 1.39 Myr.

— The samples for this project are cobbles of granite. We will assume a rock density of 2.7 g/cm³, and an attenuation length of 150 g/cm^2 .

Our task in the first half of the lab, however, is to measure N in each of the samples.

Note that these are real samples, of unknown age. Measurements on nearby boulders in 2008 gave exposure ages of 12-13 kyr, but the samples we're working on this year have not been analysed before. They are likely to be similar in age, and this makes sense based on simple geomorphic observations: The rock surfaces are fairly fresh and unaltered, with less than 1 cm of "roughness" between crystals. This suggests that they haven't been heavily eroded since exposure began. Likewise, because they're largely unweathered, we can be fairly sure that they haven't been re-cycled from an older glacial deposit, where they might have been previously exposed to cosmic rays. (In that case, we would obtain an erroneously *old* age). The samples come from boulders sitting stably on flat bedrock shelves; each weighs a ton or more, so it seems unlikely that they've rolled or changed orientation relative to incoming cosmic rays since deposition. Finally, remember that these boulders were raised out of the ocean by isostatic uplift, so they would have had to pass through the intertidal zone on the way. If they began life buried in glacial till, which seems quite possible (remember the outcrop in Burrows

Bay), the surrounding sediment may have taken some time to be washed away by wave action as they emerged. They're unlikely to have remained buried in till long after emergence – which would *lower* their ¹⁰Be concentrations, but this possibility may result in *exposure ages* which underestimate their *emergence ages*.



On the next page is a flow-chart summarising the tasks from sample collection to isotopic analysis. This is on the class website at:

http://faculty.washington.edu/stn/ess_461/research_project.shtml

A full description of the laboratory method can be downloaded (as a .pdf file) from a link on the Cosmogenic Nuclide Lab chemistry web page:

http://depts.washington.edu/cosmolab/chem.html

The document itself is called: Al-26_Be-10.pdf . I'll bring some copies to the lab which you can consult as we work through the procedure.

Collect sample: Record altitude, latitude, horizon obstructions	
Trim and crush sample: Record thickness	
Mineral separation using dense liquids	Flowchart of ¹⁰ Be & ²⁶ Al extraction from quartz for
Clean up quartz (dilute HF). Removes meteoric ¹⁰ Be, reduces aluminum concentration	exposure dating and erosion measurements
Weigh sample (~10 g clean quartz)	
Add pure ^g Be carrier (~250 μg)	
Dissolve sample in HF (~2 days)	
Weigh, homogenize and remove duplicate Measure [Al] by ICP. Calculate subsamples for [Al] measurement [Al] in quartz sample	
Evaporate SiF4. Convert residual F ⁻ salts to Cl ⁻ for anion exchange.	
Anion exchange (in 6M HCl) to remove Fe(III), Elute Al + Be + Ti.	
Evaporate HCI. Convert residual CI ⁻ salts to SO ₄ ²⁻ for cation exchange.	
Cation separation. Elute TiO.H ₂ O in 0.25 M H ₂ SO ₄ . Separate and elute Be in 1.2M HCI. Elute Al in 3M HCI.	
Evaporate HCI → pure BeCl ₂ Evapor	rate HCI \rightarrow pure Al chloride
Redissolve. Precipitate Be(OH) ₂ Red	issolve. Precipitate Al(OH) ₃
Bake at 800° \rightarrow ~750 µg BeO E	Bake at >800° \rightarrow 1-3 mg Al ₂ O ₃
Mix with Nb powder. Pack into cathode.	Mix with Ag powder. Pack into cathode.
Measure ¹⁰ Be/ ⁹ Be. (Accelerator Mass Spectrometry) Measure ²⁶ Al/ ²⁷ Al.	

We'll start today from pure quartz samples, prepared over the last two weeks by crushing the rocks, and a sequence of mineral separation procedures. Some of this is described on the class web pages. Take some time out to examine the transformation from raw material to pure quartz. Compare pure quartz samples to their parent rock material - can you spot the quartz grains among the original rock fragments? Examine the different colors of quartz (bonus question - what causes the differences?). Check out some of the pure K-feldspar and heavy mineral splits separated from bulk rock samples

using heavy liquids. Pick up a bottle of heavy liquid (lithium meta-tungstate, density ca. 2.6 - 2.8 g/cm^3). [Careful - this costs about \$200 for a 250 mL bottle!].

Procedure (We'll try to get through as many steps as possible during the lab period. Where possible, I'll ask for volunteers to carry out the various steps described below.)

Sample weighing:

Select one of the pure quartz samples. It has been analysed for Al, Fe and Ti. Record the ppm concentration values from the sample bag.

- Tare a clean 250 mL FEP teflon (bottle + solid lid) to at least 3 decimal places. Record the bottle number and its tare weight.
- Transfer the sample to the bottle with a <u>clean</u>, <u>non-reagent</u> spatula. If possible, move the sample grains all the way into the bottle and tip them directly on to the base. Run the bottle and sample bag through the high-voltage gate to minimise static build-up. It is important to stop grains from jumping to the neck, especially onto the outer screw thread. *Don't pour directly from a plastic sample bag*. Inevitably, some grains will charge and cling to the bottle walls. No problem, as long as they are inside. Cap the bottle.

Re-weigh the bottle. Subtract the tare to determine the sample weight.

Using dilute (1%) HNO₃ from the wash bottle, wash sample grains down and away from the bottle mouth. Add just enough acid to fully wet the sample grains in the bottom of the bottle. Take care not to touch the spout on the sample container.

Carrier addition:

- Take the current Be carrier bottle and record the concentration. We will use a very pure "carrier" solution made from a beryl crystal mined well below the Earth's surface. This ensures that it has the lowest possible concentration of cosmic-ray-produced ¹⁰Be. As best we can measure it, the ratio of ¹⁰Be/⁹Be in this solution is $\sim 2 \pm 2 \times 10^{-16}$. Invert it a few times to mix the solution thoroughly. Be sure drops of condensation around the lid are taken up and mixed in. Weigh it. Record the initial weight.
- Load the 0 1 mL Gilson pipette with a clean tip. Adjust it to deliver carrier containing ~250 µg Be (i.e. ~0.5 mL). Be sure the tip does not touch anything while handling the pipette. If it does, discard it and take another. DON'T RISK CONTAMINATING THE CARRIER.

Open the sample bottle.

Tare the balance to zero. Remove the carrier bottle, open it and pipette carrier solution into the sample bottle. Eject the carrier smoothly, being sure not to leave a drop in the tip. Don't allow the tip to touch the sample bottle. Recap the carrier bottle and re-weigh it. The balance will read the weight removed. Record the weight. Calculate the weight of Be added, in micrograms. Work deftly, but not hurriedly, while the carrier bottle is open. Everyone's work depends on the integrity of the carrier. Don't leave it open to evaporate any longer than necessary. Don't contaminate it with labware that has come into contact with sample material. Mix it well before use. Store it properly after use.

At the end of each session, record the final weight of the carrier bottle for cross-comparison next time it is used. Check the cap is screwed on firmly.

Enter all of the data (bottle numbers, tare, sample and carrier weights) in the log-sheet.

Dissolution: (Because of the danger of hydrofluoric acid (HF), John or Joy will do this step)

In the fume hood, wearing gloves ...

For each sample ...

Uncap the sample bottle and store the solid cap in a clean plastic bag.

- Using a plastic measuring cylinder marked for clean acids, add 5 mL of AR grade HF for each gram of quartz.
- Re-cap the bottle tightly with a vented (drilled) cap. Match each bottle with its corresponding drilled cap. <u>Check that the bottle is not sealed, so that fumes can escape and pressure won't build up</u> (squeeze it gently). Beware if the sample is fine-grained - the reaction may proceed fast and the bottle may get quite hot. If it does, be prepared to cool it down by sitting it in a large beaker of cold water. Don't swirl the bottle at first - the initial reaction doesn't need any encouragement. <u>Never</u> shake the bottle.
- Once the reaction has subsided (usually a few hours), the bottles can be placed on a hotplate set to its lowest setting. They only need very gentle warming to ensure dissolution in 24-48 hrs. From this point on, they should be swirled occasionally to mix up the dense layer of H₂SiF₆ which forms over the quartz grains. Wear gloves when handling the bottles, and beware of droplets of acid condensed on the lid, which can be pushed through the vent hole if you squeeze the bottle while handling it.

The quartz should disappear within 24-48 hrs, leaving a clear solution of H_2SiF_6 . There may be a few tiny insoluble grains (usually zircon (Zr_2SiO_4) or ilmenite (FeTiO₃) left after the quartz has dissolved.

We will proceed with "splitting" the solutions for Al analysis, and drying them to expel Si and recover the Al and Be fluorides (along with unwanted Fe, Ti, Ca, Na, K, Mg, etc), next week.