

ESS 461 Cosmic Ray Exposure Dating (II)

Cosmogenic Isotope Lab – 413 Johnson Hall

Last week we weighed out quartz samples and dissolved them to produce homogenous solutions. Today we will see how to extract Al and Be from those solutions. Several intermediate steps — removing sub-samples for Al analysis, drying the HF solutions to expel Si (as gaseous SiF_4), and Fe removal by anion exchange, were completed over the past week. In preparation for today's procedures, the samples, which now contain Al, Be and Ti with subsidiary amounts of Ca, Na, Mg and K, have been reduced into a drop of concentrated sulfuric acid. This has been reacted with a drop of hydrogen peroxide solution to raise the oxidation state of Ti to 4+, converting it to the amber-colored peroxy-titanium cation complex ($\text{TiO} \cdot \text{H}_2\text{O}^{2+}$).

Today we will separate Al and Be from the residues, using *ion exchange chromatography*. The full procedure actually requires two successive ion exchange separations. The first, which we have already completed, removes Fe by *adsorbing* it onto an *anion exchange resin*. Al, Be, Ti and other metals (cations) are not adsorbed by the resin, and have been recovered for the next stage of the separation. In the second step, Be and Al are separated from the remaining metals by *cation exchange* — the metals are adsorbed onto a *cation exchange resin* and then selectively released by washing the resin with different mixtures of acids. The *ion exchange resins* consist of tiny polystyrene beads coated with organic compounds that have a strong binding affinity for either anions (negatively charged ions, in the case of an *anion exchanger*) or cations (positively charged ions, in a *cation exchanger*). The ion exchange procedure involves filling narrow, pipette-like tubes (*ion exchange columns*) with resin, which is retained by a porous filter. The filter allows liquid to flow through the resin beads. Ions that bind strongly to the resin are retained in the column, whereas those that do not pass through with the acid solution. Typically, the column assemblies are pre-washed with acid to clean them and allow the resin to equilibrate with the acid that will be used in the separation. Then the samples are added to the columns with a pipette. Finally, one or more acids (or other ionic solutions) are added to the columns to "*elute*" the species of interest.

In the initial anion exchange separation, the samples are loaded onto the columns in strong (6M) HCl. Any Fe present in the samples forms the yellow-green anionic species $\text{Fe}^{(\text{III})}\text{Cl}_6^{3-}$, which binds to the resin. Al, Be, most of the Ti, and various other cations present in solution simply pass through. The sample, with Fe removed, is caught in a beaker.

The solution in this beaker is dried on a hotplate with a little sulfuric acid. This converts the cations to sulfate salts as the solution dries (volatile HCl is expelled, less-volatile H_2SO_4 is retained). The sulfates are then re-dissolved with a little hydrogen

peroxide and water redox for Al-Be separation using cation exchange. This is the starting point for the *cation exchange separation* that we will carry out today.

For the second separation, we use a resin that has a strong affinity for cations. After rinsing and conditioning the resin with 0.5M H_2SO_4 , we add the dissolved sample. In this fairly dilute acid, Al, Be and most other metals bind tightly to the resin. Ti, Na and K do not bind as strongly, so by washing the resin with ~10 mL of 0.5 M H_2SO_4 we expel these elements from the column, leaving Al and Be still strongly bound to the resin. Now, however, by changing the washing acid to 1.2 M HCl, we can remove Be selectively. Al is left behind on the resin. Finally, by increasing the acid strength to 3M HCl, we remove Al. The end result is two small beakers of HCl, one containing pure Be, the other Al. Magic!

Procedure

Fe clean-up (anion exchange columns):

(This step was done on Monday by Greg and Courtney)

A column rack has been loaded with a set of ion exchange columns. The anion resin has been washed but requires final conditioning. Place the plastic tray under the columns to catch the conditioning solution.

Condition the resin with ~ 5-6 mL of 6M HCl from a disposable pipette. Add the first mL by running drops down the column walls - try to keep the top surface of the resin bed flat to ensure uniform flow through the column when the sample is added. The resin will darken and shrink as it adjusts to the higher acid strength.

The samples are in the large teflon beakers from which the HF sample solution was evaporated to . The bright yellow-green color signifies quite high Fe concentrations. Check for any signs of smoky white insoluble material (this will be TiO_2). If any is present, solutions will have to be centrifuged briefly before running them through the columns.

Once the conditioning acid has drained, place a 30 mL teflon vial beneath the column.

Record your sample ID, its parent container number and the number on the 30 mL vial.

Using a separate disposable pipette for each sample, load the sample solutions onto the columns. Drip the solution down the column wall, reaching as far as possible into the column with the pipette. Do NOT pour the sample into the column. Try to transfer the sample quantitatively. Try not to disrupt the top surface of the resin. Return each pipette to its sample container.

Add ~1 mL of 6 M HCl to the sample containers and pick up any remaining droplets of the original sample solution.

Allow the loading solutions to drain fully into the resin. Now add the 1 mL wash solutions. Allow to drain into the resin.

Elute Al + Be from the columns by adding ~10 mL of 6M HCl. Add the acid with a clean, disposable pipette (not one that has touched a sample). The first mL should be added carefully so as not to disrupt the top of the resin bed. In strong HCl, Fe(III) forms a range of anionic Cl^- complexes FeCl_4^- , FeCl_5^{2-} and FeCl_6^{3-} , which bind tightly to the anion exchange resin. These can be seen as a brown stain in the top few mm of the resin. Al and Be do not form strong Cl^- complexes and wash through the column as HCl is added. Titanium is a bit more problematic; Ti(IV) can form TiCl_6^{2-} , which binds, but some Ti always remains as a cation or forms a neutral species, neither of which is retained by the resin. Thus, most of the Ti from the sample passes through the column with the Al + Be.

Replace the glass beakers beneath the columns. Wash Fe + Ti off the resin with a few bed volumes of dilute HCl (HCl will drip yellow-green due to Fe after a few mL). Discard the resin and wash up the columns. Rinse out and discard the sample and dispensing pipettes. Rinse out and discard the sample tubes.

Add 1 mL of 0.5 M H_2SO_4 to each vial and dry on the hotplate. The dried residue from this step may turn an alarming dark-brown to black color. This is due to charrpy reaction products formed from organics which bled from the anion resin. Don't worry, it will disappear gradually over the next couple of steps.

Al-Be separation (cation exchange columns):

(Divide the work so that everyone can do some part of the procedure. Take care handling the acids. Take your time and don't crowd the fume hoods).

A rack of small ion exchange columns has been set up in the fume hood. The columns have been conditioned and are ready to go.

The samples are in 20 mL teflon vials. The amber color is due to $\text{Ti}^{(\text{IV})}\text{O}_2 \cdot \text{H}_2\text{O}$.

Load each sample onto its column using a clean disposable pipette. Ti will form a narrow brown band at the top of each resin bed, then begin to move down the columns. While the sample solutions run in, add 1 mL of 0.5 M H_2SO_4 containing a trace of 2% H_2O_2 to each beaker as a rinse. Swirl the beakers to pick up any droplets of the original solution left over from the first load. Add the rinse solutions to the columns.

Once the rinse solutions have drained into the columns, gradually add 8 mL (4 bed volumes) of 0.5 M H_2SO_4 (containing a trace of 2% H_2O_2) to each. Allow it to run to waste into the glass beakers. Watch the Ti move down the resin and elute from the columns. For Ti-rich samples, it may be necessary to add a further 1-2 mL of 0.5 M H_2SO_4 to completely remove Ti. Take care not to exceed this amount, and risk losing Be.

Remove the glass beakers and replace them with medium (20 mL) teflon vials. Record the number of each vial against its corresponding sample.

Elute Be from the columns with a further 10 mL (5 bed volumes) of 1.2 M HCl ("10%" HCl; this will have to be added in 2 lots. No need to allow the first to drain completely before adding the second).

After the Be fraction has drained through, remove the vials and add 5 drops of 8 M HNO_3 to each vial. Dry them on the hotplate at setting 3. Dry-down will take ~8 hours.

Place a tall (30 mL) round base teflon vial under each column. Record the number of each vial against its corresponding sample.

Elute Al from the columns with 6 mL (~3 bed volumes) of 3M HCl.

After the Al fraction has drained through, remove the vials, add 0.5 mL (~10-15 drops) of 8M HNO_3 to each and dry on the hotplate at setting 3. Dry-down will take ~4 - 6 hours.

The end result will be small white cakes of pure Be nitrate (or its oxide - the nitrate seems to break down in the hot beakers) and pure Al nitrate in each of the beakers. The final steps are to: (i) re-dissolve these and precipitate them as Be and Al hydroxides, (ii) bake the hydroxides in quartz tubes to make oxides, (iii) mix the oxides with Nb powder (Be) or Ag powder (Al), and finally, (iv) pack them into target holders for AMS analysis.