Be and Al Extraction
University of Vermont
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ALWAYS WORK IN THE ORDER OF THE BATCH SHEET

NOTE: Our methods evolve as we learn more. Most recent methods can be found at http://geology.uvm.edu/morphwww/cosmo/lab/whatwedo.html

OVERRIDING GOALS

No sample cross-talk.
100% yield to ICP step
Careful and accurate mass determination
Certain sample ID
Safety

HELPFUL HINTS

Keep pipette tips clean by injecting from outside the beaker
Gloves only on the outside of beakers, never on lip or inside
Hot plate always sub-boiling to prevent splash
Make sure drips from pipettes are never transferred between samples
Hands off the counter when calibrating and weighing in
Use two people for sample weighing in
Always keep pipettes vertical. If you have tipped a pipette or see liquid on the body of the pipette, rinse well with DI water.
Release pipettes slowly to prevent splash.
Stay alert; don't work when you are tired

SAFETY

Stay alert; don't work when you are tired
Always wear splash goggles in the lab. Always.
No street shoes or stocking feet allowed in lab. You must have and wear lab shoes every time you enter the lab. Lab shoes must remain in the lab
Always wear heavy smock and heavy gloves when using warm Nitric.
Always use face shield and lower hood sash when adding Perchloric.
Clean up even the smallest spill promptly.
Never use liquids without a spill tray.
Be waste must go in Be waste containers.
If you spill acid on yourself, use the drench shower immediately.
Before leaving lab for any reason, remove all lab gear including shoes.
WASH YOUR HANDS AS YOU LEAVE THE LAB.

Before Going in the Lab

Select seven samples with similar suspected isotopic compositions that have been "mineral tested" and final ultrasound etched. These samples are stored on shelves above the balance.

Use the "Ratio Estimation" spread sheet to determine the amount of Be and Al carrier which you need to add to each sample. Strive for ratios >1.5 E-13. Make sure you will have at least 2.5 mg Al and 0.25 mg Be. Samples with over 2500 ug of Al require no Al carrier. Most samples require no Al carrier. Most samples use 250 μg of Be or 0.25 ml of SPEX carrier solution.

Input sample ID's into the data reduction spread sheet and print out a copy of the LAB DATA sheet. Note on this data sheet the amount of carrier you need for each sample and the amount of quartz to dissolve. The first sample should be a blank. If low ratios for Be are expected (<10 –13) use two blanks and six samples. Take this data sheet into the lab with you.

Loading Samples

Enter the lab, change shoes, put on clean gloves, smock, and splash goggles.

Use orange mylar labels to label eight 240 ml Teflon beakers with sample IDs and a Blank ID. The beakers should have drilled out lids. The blank ID should include the batch number (i.e. the blank for batch 78, would be 78-blank). Sample IDs should start with the batch number then a hyphen and the sample name. Duplicate samples should be assigned the suffix "X".

Turn on the balance at least 15 minutes before starting. Level the balance.

After at least 15 min. have passed, check balance calibration with the 200 g weight, the 200 g weight tared before adding the 1 g weight, and the 1 g weight alone. If the balance does not read all combinations correctly, calibrate with the 200 g weight and try again. Note the draft shield must be on for all tareing and weighing.

Line up the quartz tubes in the same order as the labeled beakers reflecting their order on the printed copy of the Batch data sheet which you should have in front of you on the clipboard.

Wipe down the lid to the balance with isopropyl alcohol to eliminate static interference.

Get out and top up (if necessary from the 500 ml bottles) the small bottles labeled Be and Al "clean" 1000 ppm carrier. Place the small bottles in white spill tray.

Take out the pipettes and set them as needed. The Eppendorf Pipette(set to 5) should have a new 2.5 ml tip on it. Fill the Eppendorf with Be carrier and discard the first shot of 250 ul to waste. The 1 ml Wheaton Pipette should have a new tip on it. Place the pipettes on the appropriate racks.

With the static shield in place,TARE the balance. Place the first beaker with its lid on the balance in the Aluminum static shield, record the mass of the beaker and lid.

Remove the beaker lid. TARE THE BALANCE. Weigh in the desired amount of quartz (up to 40 g), pouring directly from the 50 ml tube, replace the balance lid and record the weight. TARE the balance

Use the Eppendorf Be pipette to deliver about 0.250 ml of Be carrier through the hole on the balance cover; record the weight of Be on the data sheet. Add enough Al carrier to ensure a total of > 2500 ug Al in sample. Move the beaker to the hood.

Repeat the above procedure for each sample. Blanks are handled similarly but get 3 ml of Al carrier and of course, no quartz.

Dissolution

DO THIS DURING THE DAY WHEN SAMPLE BEHAVIOR CAN BE CLOSELY WATCHED

Moisten each sample with NANOPURE water. Use a cleaned graduated cylinder or beaker to deliver 4 times as much HF as quartz to each beaker. Do the HF transfer in a spill tray in the hood. Use DI water to rinse the cylinder or beaker into one of the beakers before removing the cylinder from the hood.

ADD 100 ML OF HF TO THE BLANK.

Place the beakers on the hot plate, make sure the beakers are sitting flat. Let the beaker sit for 1 hour unheated. (Samples may need to sit overnight for very fine samples.) Turn the hot plate up to warm. Let sit for an hour. Turn the hot plate incrementally closer to 175; let sit one hour at each increment. At ~90 degrees C on the Spotcheck heavy fuming may occur. Back temperature off slightly from this point until fuming stops, and leave at this temperature overnight once you are sure that everything is stable. Next day- turn up hot plate in 25 F increments sitting one hour at each temp. After samples have been sitting at 275 F add extra HF if it is necessary (due to crystallization on lid, or due to extra large samples). Let sit overnight again, then aliquot. Never turn the hot plate above 275 F. (This temp corresponds to ~120 C on the Spotcheck thermometer- this temp works for dissolution.) If samples start to fume heavily, turn down the hotplate. BEWARE of fine grain (or large) samples. Leave such samples overnight at setting below 225 before turning up or they will boil. Make sure that the surface temp of the hot plate is subboiling. EXTENDED heating will sometimes result in silica reprecipitating on the beaker lid. IF THIS HAPPENS, ADD MORE HF THROUGH THE HOLE IN THE LID.

Leave beakers on the hot plate until all quartz is dissolved, usually requires at least one overnight. Samples are finished when no quartz is visible on the bottom of the beaker or floating in solution.

When all quartz has dissolved, turn off hot plate or remove samples and allow them to cool.

NOTE: Hotplates may differ in actual temperatures which correspond to the hotplate settings. Also, temperature regulation may deteriorate as the hotplate is used. Keep an eye on actual temperature by using a Spotcheck thermometer. 90 C on the Spotcheck (~= 175-225 on hot plates) is where the bubbling or fuming occurs. Be particularly cautious when adjusting the hotplate in this region (check back every few minutes). Back hotplate temp down 25 degrees and leave overnight if heavy fuming occurs.

**FOR CHERTS- sit overnight cold. Next day- 2 hours on warm. Take two hours at each of two intervals between warm and 200. At 200, sit several hours. Then 2 hours at 225, one hour at 250, finally leave at 275 over another night (add extra HF here if needed.)

ICP Aliquot Removal

PLACE ALL BEAKERS IN BATCH ORDER

When samples are cool, place Ohaus balance on far left side of acid hood. Check calibration and calibrate if necessary. Place a spill tray in the hood.

Set up the pipette rack with (8) acid-cleaned 5 ml pipette tips.

Prepare (16) 22 ml Savillex beakers and sit them in their rack. There should be a pair of beakers labeled for each sample and the beakers should be in the order that the samples were entered in the batch sheet. One should have the sample ID and the number (2.5) on a yellow label; the other, next to it in the rack should have the number (5) on a red label with the sample ID.

PLACE THE LARGE HF FILLED BEAKERS IN ORDER. Tare the balance. Weigh the first acid filled-beaker and record the total weight of beaker, lid and acid on the data sheet. Place the beaker on the spill tray.

IF THE AMOUNT OF ACID IN THE BEAKER IS LESS THAN 100 GRAMS ADD 1.2 N HCl UNTIL THE ACID MASS IS GREATER THAN 100 GRAMS (swirl to get mixture homogeneous) AND REWEIGH. RECORD THE FINAL WEIGHT.

Place the first small beaker on the balance and tare with balance lid closed. Tap the top of the FIRST large beaker to dislodge condensate. Use the pipette to withdraw 2.5ml of liquid through the hole in the top of the first large beaker, inject this liquid into the small beaker on the balance and record the mass on the data sheet. Repeat for this sample, using the other labeled small beaker and the same pipette, this time taking and weighing about 5 ml. (KSN note: I aliquot back of hood to front and remove lids before I replace beaker.) **Change tips between samples**. Repeat for all other samples. Place small beakers on hotplate to dry off sub-boiling.

CAREFULLY remove lids from large beakers and place beakers on hotplate to dry off sub-boiling.

Put lids in NANOPURE water bath to dilute HF. Then, use squirt bottle and 1% nitric to rinse lids into acid waste. NANOPURE rinse lids and place in hot 20% nitric bath.

Place tips in rinse container with 1% HNO_3; dispose of liquid in acid waste bottle in hood. Wash tips in water and dispose in Be waste.

ICP Aliquot Dilution

After the small beakers have dried off completely....

Prepare (16) purple capped 15 ml tubes and sit them in a rack.

Place balance back in the hood. Check balance calibration as described above.

Place the first small Savillex beaker containing the dried aliquot on the balance in the hood and TARE. Use repipettor to add 10 ml of 1.2 N HCl to the beaker. Record mass on data sheet. Place clean lid on beaker, cap tightly. WITH HOTPLATE SET TO WARM, PLACE ALIQUOT SAMPLE BACK ON HOTPLATE TO REDISSOLVE. You will begin to see condensation on the inside of the lids as the samples begin to heat. Shake vigorously, vortex, and set aside. Repeat for all samples.

Take the first tube off the rack, pour the contents of the beaker into the tube and TRANSFER the label. Repeat for all other samples.

Place the tubes in the order required for the ICP and place the entire rack under the wash hood. Rinse small beakers well with nanopure, and sit overnight in 1% nitric acid.

Perchloric Treatment

For this step wear heavy gloves, a heavy smock and a face shield. Perchloric acid is a very strong oxidizer and will react violently with organic material.

Remove 240 ml beakers from the hot plate, one at a time. Take care not to melt the hood base with hot beakers by setting them on a spill tray. There should be a small white, yellow or brown cake on the inside bottom of the beaker. Use a small adjustable VWR pipette to add 1 ml of perchloric acid from the labeled Teflon beaker to each of the sample beakers. Shoot the acid on to the cake directly. Carefully swirl the beaker until the cake is saturated. The cake may fizz lightly. For a few samples, the cake does not dissolve completely. Keep swirling until sample has dissolved and solution is milky yellow. For samples that are very large, an additional ml of perchloric acid may be necessary.

Return the beaker to the hot plate. USE MIDDLE HOTPLATE FOR QUICKER DRYDOWN. Repeat until all beakers have been treated. **Turn HOT PLATE UP TO MAX TEMP** and let fume about 2 to 2.5 hours until dry. White fumes will be given off. Hot plate temperature should not exceed 250^{o}C; service limit of Teflon. Maximum temperature on the Presto griddles does this nicely. **Wait until samples no longer give off white fumes.**

Repeat treatment three more times for a total of four fumings. **Let beakers cool. TURN HOT PLATE DOWN TO 300 !!!! AND LET SIT FOR at least 20-30 minutes.** Use squirt bottle to add several ml of 8 N HCl to each sample. Return to hotplate and dry off with the hotplate set to ~275.

Anion Columns

RESIN TYPE: Biorad resin AG1X8

When the 8N HCl has dried off, remove samples from hotplate and add 1 to 2 ml of 8 N HCl. Swirl to dissolve. If beakers are still hot, this assists the dissolution of the sample. Samples should dissolve completely. If they do not, agitate with a disposable pipette. If a sample remains undissolved, add another ml of 8 N acid.

Transfer beakers with dissolved samples to column hood.

Drain any remaining 1.2 N HCl from the columns. Condition the anion columns with 10 ml of 8N HCl rinsing the walls well. Run acid into waste bottles and dispose in acid waste. Make sure that there is at least 250 ml of 8 N on hand before starting process.

Take four beakers to column hood and place each in front of an anion column. **Make sure valve is closed.** Use pipette to transfer liquid to column gently trying not to disturb resin. To rinse beaker and increase yield, add several more ml of 8 N acid to beaker and use pipette to place drops in column. **Place beaker under the column**. Now, open valve just a little and SLOWLY run liquid in until level drops just below top of resin. Proper elution speed is < 1 drop/second. Add several ml of 8 N HCl to the column to wash down sides and run in SLOWLY. LESS THAN ONE DROP EACH SECOND IS THE CORRECT RATE. MORE RAPID ELUTION WILL FAIL TO REMOVE FE. ERR ON THE SIDE OF SLOW DRIPS.

Add 10 ml 8 N HCl and elute all SLOWLY into the beaker. Too rapid elution will cause the Fe bearing solution to bypass the resin. The Be and Al are quickly removed from the column. The Fe is retained. Be and Al are in the liquid in the beaker.

Put beaker back on hotplate and evaporate HCl to dryness. Set hotplate to ~225 . This will take about 8 hours at a sub-boil to dry down.

Clean columns by running 7.5 ml of 1.2 N HCl into a waste bottle. REPEAT with a second rinse of 7.5 ml of 1.2 N HCl. Run through slowly. Use the acid to wash down the insides of the columns well. Use extra acid if needed. Discard this liquid in the acid waste; it may be yellow containing iron and some Ti. **Repeat the above steps for the next four beakers.**

Store columns in 1.2N HCl.

Precipitation for Ti and Ca Removal

Using the Eppendorf, add about 20 ml of 1.2 N HCl to each beaker and if needed, use a disposable pipette to dissolve the sample. Transfer the sample into a LABELED, acid washed (50 ml) centrifuge tube. Pouring works well. Place watch glasses over the beakers and set them aside for reuse after the precipitation is done. Repeat for all 8 samples.

Adjust the pH of each sample to 3.8 to 4.1 using NH_4OH, check pH using narrow range pH paper. **It is better to side toward 3.8 than 4.1.** Use the pipette to stir the solution or cap and vortex. USE THE MICROLITER PIPETTES to deliver a drop of sample to the paper. Do not let the pipette touch the paper. If it does, replace the pipette with a new one before reentering the sample. TREAT pipettes as Be waste. Rinse the used pH papers into the acid waste container, first using DI water , then 1% nitric acid, then a final rinse of DI water.

At about pH 3, a slight cloudiness will indicate initial precipitation of Ti hydroxide. For a 20 ml sample in 1.2 N HCl this requires about 1.25 ml of 30% NH_4OH followed by dropwise addition of dilute NH_4OH. Use the Eppendorf pipette to deliver the NH_4OH.

When the correct pH is reached, centrifuge each sample. The supernatant now contains the Be and Al. Ti and Fe are in the precipitate.

Decant the supernatants into clean, 50 ml centrifuge tubes, TRANSFERRING THE LABEL from the first tube. Adjust the pH of each sample to > 8.1 and <8.9 using narrow range pH paper. This requires about 0.20 ml 15% NH_4OH. + 3 drops 3% NH_4OH. Vortex and centrifuge the samples. Check the pH. The Be and Al are now in the precipitate.

Decant the supernatant to the acid waste container and add approximately 3 ml of 3 N HCl to each of the remaining precipitates so that they redissolve. Vortex the samples and transfer to its original 250 ml Teflon beaker. Be certain that the centrifuge tube label matches the beaker into which you intend to rinse. Rinse each test tube several times (2 additional times)with 3 N hydrochloric acid (HCl) into the corresponding labelled beaker to increase sample yield.

Dry off the HCl at a sub-boiling setting (250-275 on hotplates.) This should take an hour or two.