

Extraction of Al & Be from Quartz for Isotopic Analysis

Derived from the University of Washington protocol developed by J. Stone

Summary

This method is used to separate Al and Be from pure quartz samples for AMS analysis. After adding Be and Al carrier, quartz is dissolved in HF. The solution is sub-sampled for measurement of total Al content, and then dried to remove Si. Al and Be are separated from the remaining metals (typically Fe, Ti, alkalis, Mg and Ca) and purified in 3 stages: 1) Anion exchange in HCl removes Fe^{III}, 2) Cation exchange in dilute H₂SO₄ and HCl removes Ti and alkalis and separates Be from Al, 3) hydroxide precipitation eliminates residual alkalis, Mg, Ca, and is carried out prior to loading cathodes for AMS. The procedure described below will cope with up to ~10 mg of Fe and 3-5 mg of Ti, assuming the total amount of Al, Be and other metals is less than 3-5 mg. It can be modified to accommodate larger samples by increasing the size of vessels, ion exchange columns, etc. Strength and quantities of reagents specified for the ion exchange procedures may vary, depending on the size of columns used, type and age of resin, etc. The ion exchange procedures should be calibrated independently before using this method on valued samples. Yields close to 100% can be obtained.

Version

This is a modified version of the University of Washington protocol. This was Perry Spector's version as of November 2013 modified by Brenda Hall for the University of Maine lab in September 2014 and modified further in June 2019. This version is based on instructions created by John Stone and Greg Balco.

References:

The cation exchange procedure is based on one developed by Bob Ditchburn of IGNS Inc., New Zealand. It is the most reliable and efficient method I know for separating Ti from Be. Please cite one or both of the following papers if you use this method:

Ditchburn, R. G. and N. E. Whitehead (1994) The separation of ¹⁰Be from silicates. *3d Workshop of the South Pacific Environmental Radioactivity Association*, 4-7.

Ditchburn, R. G., I. J. Graham, and A. Zondervan (2000) Analytical methods for measuring Be and U-Th isotopes in loess. *Institute of Geological and Nuclear Sciences science report 2000/09*. Lower Hutt: Institute of Geological and Nuclear Sciences. 10p.

Aluminum check for quartz purity

Check the trace-element content of the quartz separate before dissolving it for ²⁶Al-¹⁰Be analysis. It is important to obtain low concentrations of Al, Ti, Mg, Ca and alkalis. High Al levels decrease the ²⁶Al/²⁷Al ratio and limit the number of ²⁶Al ions that can be counted. This will reduce the statistical precision of the measurement. High levels of Ti and other trace elements may complicate the chemical separation described below.

Careful quartz clean-up usually (though not always) results in Al and Ti concentrations of <100 ppm. Higher levels of Al may indicate the presence of impurities such as feldspar, muscovite, garnet, or sparingly soluble fluorides from the HF treatment. Note, a 99.5% pure quartz separate containing ~0.5% feldspar still has an Al concentration of ~1000 ppm. See the UW method file "Mineral separation and quartz clean-up" for information about mineral separation procedures.

Al checks are made by ICP optical emission spectroscopy (ICP-OES) analysis. See the accompanying method file "Trace-element analysis of quartz" for a description of quartz sample preparation for ICP analysis.

Al-Check preparation:

Select a set of Al-check beakers (5 mL teflon), one for each sample. Record each beaker's weight. With a clean spatula, transfer 0.05-0.35 g of sample into the beaker. Doing this in front of the anti-static machine helps keep quartz grains from being flung about by static. Weigh and record the weight of the beaker and sample. Add a small amount of 1% HNO₃ to wet the grains and cap the beaker. Thoroughly clean the spatula with alcohol and a chemwipe after transferring each sample.

Uncap Al-check beakers and place on a hotplate in the fume hood. Don the HF safety gear and get a clean 100 mL Teflon reagent beaker. Carefully pour 2-3 mL of full-strength HF into the reagent beaker for each aluminum-check (use up our nearly empty bottles of HF). Add 2-3 mL of this HF to each sample with disposable pipette until all is used. Clean beaker and pipette by filling beaker with MQ water (DO NOT REMOVE FROM HOOD) and running water through the pipette. Add 1 mL of 8% H₂SO₄ to each beaker and set hotplate to ~200 °F. The HF is heated in stages so that it does not all evaporate before the sample can dissolve. After about an hour, set hotplate to ~275 °F. The samples will dry down to a droplet of H₂SO₄ overnight.

Cool the samples.

Tip: Check the samples for solid material. An opaque, white, crystalline material indicates that the quartz is not clean enough for Be/Al chemistry. Fluffy white bits may indicate garnet. Samples may have a dark material which is probably ilmenite or organic material, both of which can be HF-resistant. Ilmenite or organic material can be ignored as they will not interfere with the chemistry and will only slightly contribute to the total error via an overestimation of the quartz weight. More Al and Ti are acceptable in older samples as very little material is needed. For example, for ~1 m.y. Cloudmaker samples, only 2-3 g of sample is needed. So even with high (~300 ppm Al) you can still run the sample. High Ca values (generally >100 ppm, less if the sample is large) will cause problems in the sulfate conversion and should be avoided at all costs.

Add 5 mL of 1% HNO₃ to each beaker, and then cap beakers. The solutions are now ready for ICP analysis, and **should be weighed and recorded immediately before ICP analysis.**

To get ppm of sample, take ppm of solution and multiply by weight of solution (here, ~5.1 g). Divide by g in sample.

i.e., 3.6 ppm Al in ICP solution x 5.1 g of ICP solution = ~18 micrograms of Al in ICP solution, obtained from dissolving 0.1 g of rock. Thus, ~180 ppm Al in rock.

Clean Sample Dissolution and Processing

Sample weighing

Estimate the necessary sample amount:

Note if you want to measure ²⁶Al: 1 mg of Al (which will make ~2 mg of Al₂O₃) is required for the AMS measurement. 2 mg, are easier to handle. For a sample containing 50 ppm Al, you will need to dissolve at least 20 g of quartz to obtain sufficient Al. Note that: 1) For "hot" samples with high levels of ²⁶Al, the necessary amount of Al can be obtained by substituting Al carrier for quartz. Adding Al carrier lowers the ²⁶Al/²⁷Al ratio, and should be avoided for young, low-altitude, or heavily shielded samples. 2) Conversely, the ¹⁰Be/⁹Be ratio increases with sample size, so using larger amounts of quartz will improve ¹⁰Be results from low-level samples. 3) Note, however, that processing samples larger than 30 g is tedious, expensive, and best

avoided. 4) If you know the approximate age of your samples, you can use the spreadsheet calculator on the lab computers to predict $^{26}\text{Al}/^{27}\text{Al}$ and $^{10}\text{Be}/^9\text{Be}$ ratios for different quartz and carrier weights. Aim for $^{10}\text{Be}/^9\text{Be}$ ratios $> 10^{-13}$, and $^{26}\text{Al}/^{27}\text{Al}$ ratios $> 10^{-12}$.

Weighing:

For a batch of standard samples (weights ~10-15 g):

Turn on the anti-static device.

For each sample:

Weigh a clean 125 mL or 250 mL FEP Teflon (bottle + solid lid) to at least 4 decimal places. Record the bottle number and its weight. Use 125 mL bottles for high-level samples of less than 10 g. Use 250 mL bottles for larger samples. Late Holocene samples will require larger bottles.

Transfer the sample to the bottle using either: 1) A clean, non-reagent spatula, 2) **A scoop and cone of weighing paper inserted into the bottle mouth** (*tip: this prevents grains from clinging to the bottle threads*), 3) By snipping a corner of the ziplock bag (only if you plan to use the entire sample). Try to transfer sample grains to the bottom of the bottle; working near the anti-static device helps prevent grains from jumping to the sides, neck, or screw threads of the bottle. Cap the bottle.

Re-weigh the bottle and enter the combined (bottle + sample) weight.

Using 1% HNO_3 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 and to remove any grains higher on the sides. Take care not to touch the spout on the sample container.

Carrier addition

Take the current Be carrier bottle and record the concentration and origin (i.e., Phena 1A, 500 ppm). Invert it a few times to homogenize the solution. Be sure drops of condensation around the lid are taken up and mixed in. Weigh it. Record the initial weight (it should match closely the final weight from the previous use).

Load the carrier pipette with a clean tip. Adjust it to deliver carrier containing ~250 μg Be. Note, carrier concentration is usually 500 – 800 ppm, so this will usually require ~0.35 – 0.5 mL. Don't make the mistake of adding 0.25 mL, which will usually contain a lot less Be than you need. 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.

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.** Record the weight. Move the spiked sample bottle to another counter to remove all possibility of spiking it twice. 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 lab-ware 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 and parafilmed. The bottle should live inside a ziplock and inside the humidifier box.

Repeat with Al carrier for samples that contain less than 1.5 mg Al. Use enough carrier to bring the total Al in each bottle up to 1.5-2 mg. Usually you will need to adjust the pipette for each sample.

All of the necessary data (sample and carrier weights) must end up in the database and a printed copy should be taped into the lab book.

Print the chemistry tracking sheet and place on the bench in the Al-Be lab.

Dissolution

HF is a SERIOUSLY DANGEROUS chemical capable of causing death!!!!. Don gloves (inner purple ones, outer heavy rubber ones), sleeve guards, face shield, and apron. Only work when alert and focused. Never work alone at night or on weekends.

Weighed and spiked samples are taken to the hood. In the fume hood, for each sample:

Uncap the sample bottle and store the solid cap in a clean plastic bag or in the clean hood. Using the bottletop dispenser, add 5 mL of AR grade HF for each gram of quartz. Round up in increments of 10 mL. The tracking sheet lists the amount of HF required for each sample. *Note: John pours amount for all in a graduated cylinder and then pours from that into each sample, rather than pouring multiple times from the bottle. These are all approximate measurements. Roughly 5mL per g sample weight plus 5 mL for good measure. i.e., 3 g sample = 20 mL HF. We generally use the bottle-top dispenser, rather than pouring HF.*

Re-cap each sample bottle tightly with its corresponding vented (drilled) cap, and place bottles on a hotplate. Check that the bottle is not sealed, so that fumes can escape and pressure won't build up (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 tub of cold water. Don't swirl the bottle at first - the initial reaction doesn't need any encouragement. Never shake the bottle.

Normally, there is no visible reaction. Set the hotplate to the "warm" setting, and then gradually increase the temperature to 200 °F over the next 24 hours. Keep an eye on it over the first hour or so to make sure it doesn't start to over react. Samples should dissolve within ~ 24-48 hrs with heat. The bottles should be swirled occasionally to mix up the dense layer of H_2SiF_6 which forms over the quartz grains. Wear full protective gear including face shield 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.

If not in a hurry, samples can be left in the unvented bottles and not put on the hot plate. Dissolution will take about a week. Small samples could be weighed directly into the dry down vessel (doesn't work with large samples, because balance cannot handle the weight of the larger dry down vessels).

Splitting for Al and Be determination (all the red text: can be skipped if not running ^{26}Al , but a good archive)

Once the samples have dissolved completely, turn off the hotplate and allow the bottles to cool to room temperature. This may take a few hours. Tilt the bottles to recover droplets of condensation from the walls and lid. Exchange the drilled cap on each bottle for its corresponding solid lid and tighten firmly. Check that the bottle is safely sealed (squeeze it gently). Keep a tub of DI water on hand, and submerge each lid as you remove it. Set the lids aside to be cleaned.

Homogenize the solutions by swirling and inverting the bottles, mixing dense H_2SiF_6 up off the floor of the bottles and droplets condensed on the walls. Splits of these solutions will be used to measure total Al concentrations, so they must be well mixed.

Weigh the bottles on the 5-figure balance (up to 100 g) or the top-loading balance (weights > 100 g). Record the weights.

For each sample, take a pair of round-bottomed, 5 mL, screw-top beakers. Weigh each beaker with its lid.

Return the samples to the fume hood, along with the beakers for aliquotting.

Set up a large hotplate in the fume hood for the sample dry-down.

For each sample in turn:

Open the vials. Open the sample bottle. Use a disposable pipette to transfer an amount equal to ~2-3% of the solution volume into each vial (usually 2-3 mL - we used 1 mL, less if small sample).

Tip: Split two different volumes for each sample (e.g. 2 mL and 3 mL) so that you use two different points on the ICP calibration curve.

Re-cap the vials, tightening the lids gently. Re-cap the sample bottle. Dispose of the pipette in a plastic tub of water. Use a clean pipette for the next sample. Take care with this step - the solutions you are handling are strong HF/H₂SiF₆. The actual amount transferred doesn't matter too much - there is plenty of leeway in the ICP measurement. If you think you've misjudged the size of your splits, don't worry. Do not return any excess solution to its parent bottle.

Carefully transfer the remaining solution to a large vessel for drying (tall 250 mL vessels for low-level samples, short 100 mL vessels for high-level samples). Rinse out the bottle with a few mL of MQ water and add the rinse to the dry-down vessel. Take care not to let any sample solution splash back onto the MQ wash bottle. Empty bottles and caps should be placed carefully in the teflon bucket of water with a little baking soda. Submerge all surfaces and set aside for cleaning.

Non-carrier beryllium: If it was not possible to rid the quartz of all beryllium, you can measure the total Be concentration in your samples via ICP after dissolution and dry down. To do this, you first need to weigh the dry-down vessels before they are used. After dry down, add ~2 mL 6M HCl, and slowly reduce the solutions on the hotplate to ~0.5 mL. Do not fully dry down; this is to try to fully re-dissolve the samples. Then, add 20 mL H₂O. Weigh samples in dry-down vessels prior to splitting. Be sure samples are well mixed and split ~0.5 mL from each sample (prepare splits as per usual). Dry down the remaining sample solutions.

Preparing the splits for ICP analysis

After all the samples have been split, **weigh the split vials** and record the weights. Take care not to splash the split solutions up onto the lids of their vials when moving them.

Return the splits to the fume hood, taking care not to splash liquid up onto the lids of the vials. The aliquots can now be dried down to remove HF in preparation for ICP analysis:

Uncap each vial and set it on the hotplate. Add 1 mL 8% H₂SO₄ to each and set the hotplate to ~275 °F. HF / SiF₄ will evaporate overnight, leaving a small pool of H₂SO₄ in the base of each vial.

Cool the vials. Do not add H₂O (next step) to hot H₂SO₄.

Using a pipette, add 2 mL H₂O to each vial. Return the hotplate to 275 °F and evaporate again. This removes the last of the HF/ H₂SiF₆ from the beakers. Residual H₂SiF₆ will lead to low Be and Al totals in the ICP analysis and must be thoroughly removed.

Cool the vials again. Add 8 mL 1% HNO₃ to each using the repeat pipettor. Re-cap them and let them stand (preferably overnight) to equilibrate. The final acid strength (1% HNO₃ / 1% H₂SO₄) is matched to the ICP standards to avoid matrix effects.

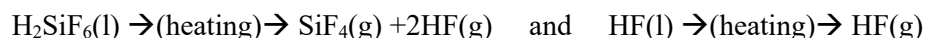
Weigh the vials immediately prior to ICP analysis. Record the weights in the database.

Analyze for Al and Be by ICP (see the method file "ICP analysis").

Upload the results to the database, which will report back the total amount of Al and Be in each sample. You should expect to get duplicate analyses of the two splits (i.e. 4 analyses) for each element which are consistent to within ~ 1-2%. Total Be results should closely match the amount of carrier added (98% - 102%). Total Al results less carrier, divided by sample weight, should match the value of your initial Al check within ~ 10-20%.

Dry-down, cation removal, and chloride conversion of main sample

Drying down the solutions eliminates F⁻ and Si via the reactions:



Place the vessels on the hotplate and evaporate at ~275-300 °F with the hotplate tilted slightly (prop two legs up on eraser slivers); this helps collect the sample in one corner of the vessel. Small vessels that contain < 100 mL will dry down overnight. Larger volumes may take 24 hours or more. You may also notice tiny insoluble grains (ilmenite, zircon, etc.).

Re-dissolve samples in ~2-3 mL 6M HCl - amount not critical. Wet all sample and dry down again. This will remove any leftover fluoride. Don't worry about black flecks.

Repeat HCl addition again and dry down. Use ~2-3 mL HCl.

Take back up in ~3 mL 6M HCl.

The samples are now ready for cleanup by anion exchange, which will remove the iron-chloride molecules.

Insoluble grains: Check whether there are any insoluble grains at the bottom of the beakers (they may be quite fine grained). If you suspect that they may be garnet or, especially, beryl, you will want to remove them, otherwise let them be. To remove them, transfer solution and grains to a 15 mL centrifuge tube. Centrifuge samples to sink the grains. Pipette all solution back to dry-down vessels except for the very last bit containing the grains. Rinse tubes with ~1 mL HCl re-centrifuge, and add this to the dry-down vessels. Note - centrifuging is really only necessary if there are a large number of grains or a cloudy solution - or if the resin is to be reused. Most grains can be removed simply by not pipetting them up in the next step.

Fe, Ti clean-up (anion exchange columns)

Load a column rack with a set of anion exchange columns (John uses 20 mL Biorad Economy Pak, but we use the 11 mL Biorads . Place waste beakers under the columns.

For each column:

Run a few mL of MQ water smoothly down the wall of the column, and before it drains, pipette in a loose slurry of anion exchange resin (AG-1 X8 200-400#) from the stock soaking in dilute HCl (use a disposable pipette). The aim is to block the column and back up a head of dilute acid so that the resin bed can be built up

from suspension. This avoids trapping air bubbles in the resin bed. Now continue slurring resin into the columns to build the resin beds up to 2 mL (more, e.g. 3 mL will only be required for very Fe-rich samples). If too much resin has been added, a long disposable pipette can be used to adjust the volume. *Note: in our lab, we fill the 11 mL Biorad columns to the base of the tapered neck.*

If bubbles get trapped in the bed, the resin must be re-suspended and re-packed (bubbles will channel flow through the column and ruin the separation). Once the resin has settled and compacted to the correct height, allow the supernatant to drain through.

Wash the resin bed with 5 times its volume of 0.3 M HCl (usually 10 mL - 3X bed volume is sufficient but more washes the column). Allow the wash solution to drain through the resin bed.

Condition the resin with 3 bed volumes of 6M HCl (usually ~6-9 mL, depending on how much resin is used). This should be dispensed carefully, without disturbing the top of the resin bed. The resin will darken and shrink as it adjusts to the higher acid strength.

After the columns have been conditioned, remove the waste beakers and load the samples as follows:

Take a batch of labelled 28 mL Teflon vials.. **Place each vial under its appropriate column.**

Using a separate disposable pipette for each sample, load the sample solutions onto the columns. Avoid sucking up the last drop or so if any insoluble material. 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 not to disrupt the top surface of the resin. Return each pipette to its sample container.

Add 1 mL 6M HCl to each beaker as rinse (use a separate, clean pipette), avoiding any insoluble minerals. Swirl to pick up any last droplets of sample solution. Can add this rinse before main sample has drained. You can do it all for one sample, before moving on to next. Yellow/orange Fe band appears at top of resin.

Allow the loading solutions to drain fully into the resin.

Elute Al + Be from the columns by adding 3 times the bed volume of 6M HCl (usually use 7 mL). Keep the pipette tips clear of the column walls to prevent cross-contamination. 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 will form a yellow-brown band at the top of the resin column. Al and Be do not form strong Cl^- complexes and elute from the column with the HCl. Some Ti in the form of $\text{Ti}^{(\text{IV})}\text{Cl}_6^{2-}$ will bind, but most will drain through as cationic or neutral species, ending up with the Al + Be.

Remove the vials containing the Al + Be and set them aside in the hood.

Discard the resin and wash up the columns. Rinse out and discard the sample and dispensing pipettes. Rinse out, scour and wash the sample transfer containers. *Note: if there is a significant amount of insoluble material, you may want to dry and weigh it to adjust the initial quartz weight. Normally, however, this amount is insignificant.*

Conversion to sulfate

Once Al + Be have been eluted, add 1 mL of 0.5 M H_2SO_4 to each vial and dry on the hotplate at ~275 °F. Residues will range from a syrupy drop of H_2SO_4 (small samples, blanks) to a cake of sulfate salts (larger samples). The residue from this step may turn an alarming dark-brown to black color. Don't worry, this will disappear gradually over the next couple of steps. *Note: Do NOT add peroxide with the sulfuric acid in this step as it will form Cl gas!*

Extra info: The dark-brown to black color is due to charry reaction products formed from organics which bleed from the anion resin. H_2SO_4 reacts with organic material to form water and elemental carbon, which is responsible for the charry appearance.

Once dried down, cool the beakers and add 2 drops of ~2% H_2O_2 (if using 30% H_2O_2 , 2 drops is still fine – note that 30% H_2O_2 decreases strength rapidly with time). Then add 2-3 mL of MQ water with disposable pipette. The cakes will begin to dissolve, taking on an amber/gold - red color ($\text{TiO}[\text{H}_2\text{O}_2]^{2+}$) if Ti is present. Reheat the vials. The black charry material will disperse and disappear after a while. Dry the samples down again. Red may creep up walls.

Cool, repeat the H_2O_2 / H_2O addition taking care to wash down beaker walls, and dry the samples a second time. At the end of this procedure, the samples should end up either as compact white cakes or small, syrupy droplets of involatile H_2SO_4 . If they remain charry or discolored, repeat the peroxide/water addition and dry them down a third time.

Take the samples up in 3-4 mL of MQ water, containing a couple drops of 30% H_2O_2 or trace of 2% H_2O_2 . Warm them a little if necessary to get them back in solution. Don't risk evaporating too much water - keeping the acid strength low for column loading gives a sharper elution and cleaner Ti-Be cut. The samples are now in ~0.2 M H_2SO_4 , ready for loading on the cation exchange columns. They can be stored indefinitely in this form. Weaker acid is better - results in sharper Ti split.

Extra info: Ca^{2+} can be problematic during sulfate conversion (before cation columns) because crystalline calcium sulfate (CaSO_4 – same composition as gypsum) may form, which is difficult to re-dissolve. Also, during cation exchange, Ca^{2+} (and other cations) compete for adsorption sites with other cations and causes cations to elute faster (e.g. Ti may elute with only 4-5 mL of acid rather than 10 mL, and Be elutes right after Ti).

Al-Be separation (cation exchange columns)

Load a column rack with small (~11 mL total volume) Bio-Rad columns. Place waste beakers under the columns. Note: samples with relatively high amounts of Al or Ti and which have given hints of problems along the way should be run through the larger columns, using 4 mL resin, instead of 2 mL.

Using a disposable pipette, add 2 mL of DOWEX-50 X8 200-400# cation exchange resin (can use AGI 50Wx8) to each column. Resin should fill to the base of the neck. Allow any MQ water or dilute acid from the loading procedure to drain.

Strip the resin by filling each column headspace with 3 M HCl (i.e. ~9 mL, equal to 4-5 bed volumes). Allow it to drain completely.

Make up a beaker of ~0.2 M H_2SO_4 containing a few drops of 30% peroxide (or trace of 2% H_2O_2 .) This is 4 parts 0.5 M H_2SO_4 to 6 parts MQ water (can use roughly 50-50). Accurate volumes are not important; the aim is to match roughly the acid strength of the sample solution. Mix well. Condition the columns by filling the headspace with this solution. Allow it to drain through.

Discard any leftover conditioning acid in the waste container, and replace it with 0.5 M H_2SO_4 containing a dash of 2% H_2O_2 . (about 0.5 mL peroxide to 50 mL acid). Check the volume of acid in the waste beakers below the columns and, if necessary, discard it in the acid-waste container.

Tip: Before adding sample, add ~1-2 mL MQ water to each sample and mix with the sample pipette. Use this to wash off walls of beaker. Cations adsorb to the resin better in weaker acids. When strong acids are added, the overwhelming number of protons bond to the adsorption sites, eluting the cations.

Load each sample onto its column using a clean disposable pipette. Ti will form a narrow red-brown band at the top of each resin bed. While the sample solutions run in, add 1 mL of 0.5 M H₂SO₄/trace of 2% H₂O₂ 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 their respective columns.

Once the rinse solutions have drained into the columns, gradually add 10 mL (5 bed volumes) of 0.5 M H₂SO₄/trace H₂O₂ to each. Watch the orange-brown Ti bands 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 H₂SO₄ to completely remove Ti and column drips clear. 15 mL of the sulfuric acid eluent can be run through the columns without risk of losing Be and we've not seen problems with as much as 18 mL, although care should be taken (may want to capture the acid draining through as a backup). *Yellow drips start with the first Ti - this shouldn't be immediate upon adding the acid. Drip will go clear when Ti is gone. If Ti comes off too fast at start, do not add any extra mL of acid, because Be is right behind Ti.*

Remove the waste beakers and replace them with labelled 28 mL Teflon vials.

Elute Be from the columns with 10 mL (5 bed volumes) of 1.2 M HCl. Add the first few mL carefully to each column, to avoid disturbing the resin. You will need to add this in two stages. 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 HNO₃ to each vial. Dry them on the hotplate at ~275 °F. Dry-down will take ~8 hours.

Place a second tall 28 mL round base Teflon vial under each column.

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 - 0.5 mL) of 8M HNO₃ to each and dry on the hotplate at ~275 °F. Dry-down will take ~4 - 6 hours.

Tip: Al fractions dry to a cake that has a tendency to jump out of the beakers, so use the large hotplate and organize the beakers so that the spacing between them is maximized.

Tip: make sure there are clean centrifuge tubes for the next step. Tubes should be washed in dilute nitric - sit about a week, rinsed twice with water and dried in oven.

Al & Be recovery and storage

For each sample, label TWO clean 15 mL screw cap centrifuge tubes - one for the Be fraction, one for the Al fraction (if Al is not being run, then you need only 1). Be sure to identify the "Be" and "Al" fractions separately, if applicable.

Once the Be and Al fractions have dried, cool and remove them from the hotplate. The Be fractions should have contracted to a tiny, clear droplet of concentrated H₂SO₄. Occasionally they will form a small white cake. This may indicate residual Ti, an impurity, or, most commonly, Al cross-over. The Al fractions will vary in size from sample to sample, but they should dry to a small, dense white cake in the base of each vial.

Pipette 2 mL of 1% HNO₃ into each vial. If pure, both Al and Be fractions will dissolve freely. Al samples can be slow to dissolve, so, if necessary, warm the vials for a few minutes on the edge of the hotplate to

ensure complete dissolution. Be fractions may precipitate a white-ish disk that is likely the surface of the H₂SO₄ droplet. This can be slow to dissolve.

Carefully tip each solution into its correct centrifuge tube. Al fractions generally come away freely from the round bottom vials. Don't worry if a last drop clings to the floor of the Be beakers.

Pipette a second 2 mL aliquot of 1% HNO₃ into each vial as a rinse. Warm it, run it around the beaker and add it to the correct centrifuge tube.

Cap the centrifuge tubes and store for hydroxide precipitation.

Note: If the Be sample is troublesome to dissolve, even with heat, additional acid can be added as an aid. A lot of precipitate that won't dissolve implies a problem, likely calcium sulfate. Intractable samples usually can be dissolved with the addition of a lot of extra acid or water and heat. Such samples almost certainly will need to go back through cation columns again. Check the Ca ppm in the original ICP check. If the original Ca was low, this problem should never materialize.

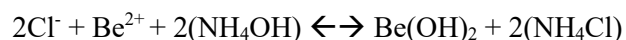
Al, Be recovery and cathode preparation for AMS analysis

Precipitate, ignite, and pack Al and Be samples shortly before the accelerator run in which they will be measured. Superstition holds that Al-and Be-oxides slowly rehydrate if left for weeks or months after baking and will produce lower beam currents. Cathodes packed in advance of a run (or cathodes which have to be stored after a cancelled run) should be stored in the desiccator cabinet in the Al-Be lab. Refresh the desiccant pack (3 hours in the oven at 80 °C) before doing so.

Beryllium Hydroxide Precipitation

Mix a solution of 1-part ammonium hydroxide with 2 parts MQ water and mix well. The exact ratio isn't critical.

Add ~6 drops to a sample, close the centrifuge tube, and use the vortex mixer to homogenize. Continue to add ~5 drops at a time and spin with the vortex mixer until a white, almost translucent precipitate forms. Looks like sugar in poorly stirred jello. Also note that meniscus tends to occur along the tubes. Precipitated Be(OH)₂ is easiest to see against a bright light (e.g. the window) immediately after removing the tube from the mixer or against a dark background. The pH should be ~8 (though it can be a bit higher) for Be(OH)₂ to precipitate. Once the first sample has precipitated you will have an idea of how many drops are required to precipitate the sample (often ~20, but possibly more). All samples should have exactly same amount. If they don't, test pH. If pH is >7, then Be has been lost. The reaction in this step is:



After all samples have precipitated Be(OH)₂, wait 10-20 minutes for the precipitate to flocculate (this helps the solution separate better in the centrifuge), and then centrifuge at 2,600 RPM for 5 minutes. Again, these should be all the same. Pour the supernatant into the sink, retaining the white hydroxide gel. Fill to 5 mL with MQ water, spin again on the vortex mixer, wait for the precipitate to flocculate, centrifuge again, and pour off the liquid.

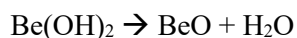
To dry the Be(OH)₂, first label the centrifuge-tube caps so that they don't get mixed up. Next, place the centrifuge tubes in a rack laid on its side (though prop up one side of the rack with the centrifuge caps so that the tubes are at a shallow angle) in the oven set to the normal temperature (70 °C). This allows any residual

liquid to flow down onto the side of the tube, away from the $\text{Be}(\text{OH})_2$, rather than accumulating in the base of the tube. Takes overnight to dry.

Note: Once in a great while a sample - usually a blank - doesn't precipitate. Although this might mean that Be was lost, more commonly the Be is still there. Transfer back to a teflon beaker, add a few mL of 1-2M HCl and 10-20 drops of 8M nitric acid. Dry down to fume off the ammonium chloride. This may need to be done twice (if a bulky cake appears). If no cake, proceed again with the precipitations steps. It should precipitate this time. If not, remove a small split of the sample and process for an ICP check to confirm presence of Be.

Occasionally a sample may have too much precipitate, which indicates poor separation in the cation columns. In this case, the sample should be redissolved with a little 3M or stronger HCl, tipped back into a beaker, and placed on the hotplate. Rinse tube with a little more HCl and add to beaker. 1mL of 0.5M sulfuric acid should be added and the sample dried down. Then, it can proceed back through cation columns again.

Conversion to beryllium oxide



Cut 4x4 in. weighing paper into four (2x2 in.) pieces until there is at least one for each sample. Also get out a cleaned quartz crucible for each sample and a small square of parafilm.

Place a piece of paper down in the clean hood with a chemwipe on top of that.

Fold two adjacent edges the weighing paper towards the center and then grasp the corner between the two folds so that it points outward and the two folded pieces are roughly vertical, making a small scoop. Place it on the chemwipe. This will catch your dried hydroxide precipitate.

Don a mask. Wave the centrifuge tube in front of the ionizer to reduce static before tipping it onto folded weighing paper. From here, transfer it to one of the clean nitric-etched glass vials. Cover it with parafilm. Repeat this process for each sample. Place crucibles in block heater, taking care to put the first sample in spot A. Record the position of each sample as the crucibles are not labelled (labels will come off in the flame).

Tip: hydroxide pellet may stick in tube bottom. Tap tube gently or use scissors to wrench tube bottom to dislodge. To transfer to vial, tap onto weighing paper. With crucible firmly on the table, ease pellet into vial.

Fetch a propane torch, stand and crucible tongs and set them up in the hood well away from the walls.

Light the torch.

After removing the parafilm from the vial, grasp the vial with the tongs about halfway up. Wave the crucible through the flame cautiously at first (if not completely dry, may sputter and jump out if heated too fast). Once tested, hold sample in the flame for a minute. Sometimes the sample begins to glow, in which case I hold it in the flame for 30 to 40 seconds more. Some samples never glow, in which case a minute should be more than sufficient. Remove it from the heat and place it back in the same spot in the heating block in the hood to cool.

Niobium addition

Clean the niobium scoop (#1 curette) with a chemwipe and alcohol.

Set up a large chemwipe in the downflow hood, along with the sample vials and the niobium with scoop.

Make sure samples are COOL.

For each sample...

Add 1 rounded scoop of niobium powder, being careful not to touch the vials with the scoop (best to invert scoop over vial and tap in with scissors). If you do touch it, wash the scoop. Each sample should end up with roughly equal amounts of niobium powder and sample.

Add a clean drill bit to the tube, and then label a cathode and cathode container with the sample name. Record the cathode # in the logbook. Place the vial in the cathode and the cathode in the cathode container. Discard test tube and chemwipe in Be waste bag.

Beryllium cathode packing

First, prepare the glove box. Wipe out the floor of the box with MQ water, which you should leave in the box. Make sure the Be waste container has a bag with enough room for chemwipes and vials. Place chemwipes, ionizer, hammer, and the rack of cathodes inside of the box.

Put on sleeves and close the sample door from the inside. You'll be here for a while, so you might want to grab a stool, too.

Lay down a chemwipe on the bottom of the box and place the cathode holder onto it. Put a cathode onto it. Remove the corresponding vial and begin crushing the BeO pellet with the drill bit and mixing it with the niobium powder. Try to cover the pellet with niobium before crushing too much to avoid static. Use the side of the drill bit like a rolling pit to pulverize sample. Once it is completely crushed and roughly homogeneous, scrape down the inside of the vial with the drill bit to gather all of the powder into the very bottom.

At this point, you can either remove the drill bit and place it on the chemwipe (remember which end is the business end) or hold it between two of your fingers while you do the next step.

Upend the vial into the small cylinder and hole on top of the cathode.

Inspect vial to make sure it is empty. Place the empty vial in the Be waste bag. Tap around the sides of the cathode with the hammer until all the powder has made it into the hole.

Place the business end of the drill bit into the cathode hole and press down until it slides in. Holding the cathode and drill bit like a nail, firmly tap the bit until it you hear a solid, sturdy sound and are certain that it has been sufficiently packed down. Remove the drill bit. Repeat tapping of sides and nailing of drill bit at least three times.

Gently upend cathode on the chemwipe to remove any loose powder. Put the cathode into the cathode container and close the cap. Place the drill bit into the small beaker of alcohol with the business end in the liquid. Put chemwipe into the beryllium waste bag.

Between each sample be sure to wipe down the cathode holder to prevent cross-contamination.

You can check your cathode to see if they have been thoroughly crushed on the microscope in the main lab.

Aluminum hydroxide precipitation (rough draft)

For aluminum samples, silver is used as a conductor in the cathode, and you want aluminum to be in a fine matrix of silver. LLNL doesn't want silver in the cathodes, however we add some, dispersed among the sample, to make the Al_2O_3 easier to grind (corundum is Al_2O_3 and has a hardness of 9) and because it seems to help keep the beam currents stable. Maximum ion currents don't seem to vary much with the amount of Al or the Ag:Al ratio, at least up to 10:1. John used to use just silver, and no niobium.

The AgNO_3 solution is ~8 mg Ag per mL, in very dilute HNO_3 (0.01 M or less, to minimize the amount of base required for neutralization). Add AgNO_3 solution to give a ~2.5:1 (weight) ratio of Ag/Al (be wary of filling the tube too full, making it hard to mix or leaving too little room for the Na_2CO_3 solution). For our

typical 1.3-1.5 mg Al samples, use ~0.5 mL of the 8 mg/mL AgNO_3 solution described above. No need to measure it very accurately, 0.5 mL from a disposable pipette is fine.

Spin the Al and Ag solutions on the vortex mixer before beginning the neutralization/precipitation.

Silver does not precipitate from ammonia solutions, so we use Na_2CO_3 to precipitate Al samples. The Na_2CO_3 solution is fairly strong (1 g Na_2CO_3 to 10 mL H_2O). If the solution is much weaker, too large a volume will be required for neutralization and the tube won't mix well on the vortex mixer. Bring the sample solutions to pH 8-8.5 by cautiously adding drops of the Na_2CO_3 solution. Don't add it all at once. The initially acidic sample solution will bubble off CO_2 as the Na_2CO_3 is added. You want this to happen gradually and not spatter out of the tube. $\text{Al}(\text{OH})_3$ will appear at pH ~5, and its solubility minimum is ~ pH 6-7. Ag_2CO_3 (or whatever it is which actually precipitates) won't appear until pH > 7. pH 8-8.5 seems to be the best compromise (at which point the sample should look cloudy and milky); at higher pH, Al starts to re-dissolve. Also, at pH 8-8.5, the Al and Ag compounds flocculate together and settle quickly without separating from one another. Don't worry if the Ag compound turns slightly grey (i.e. Ag metal forms). However, the precipitate blackening rapidly may indicate that the pH is too high.

Give samples time to flocculate.

Centrifuge at fairly low RPM (1500-2000) for a few minutes. Discard the supernatant.

Add 5 mL DI H_2O . Re-suspend with a vortex mixer (the two compounds won't separate) to rinse thoroughly.

Allow to flocculate for a few minutes. Centrifuge again at 3000 RPM. Discard the supernatant and dry the precipitate overnight in a cool oven (~70°C). It will blacken (Ag_2CO_3 breaks down to Ag_2O ?), shrink substantially and will generally dry into several small, friable lumps. These can be removed from the tube with a gentle tap. At Ag:Al = 6:1 – 8:1, the dry aggregate is much more friable than pure $\text{Be}(\text{OH})_2$ or $\text{Al}(\text{OH})_3$, so don't try to handle it or move it around with tweezers. Samples seem to keep forever in this form.

Conversion to aluminum oxide

Transfer the samples to quartz vials in same way as for Be. The $\text{Al}(\text{OH})_3$ flakes can stick to the tube walls tenaciously, so you may need to vigorously tap the tube to loosen the flakes.

Bake samples (similar as for Be), converting $\text{Al}(\text{OH})_3$ to Al_2O_3 . Once sample is red hot, bake for 1:30. Aluminum has a higher propensity of jumping out of the quartz vial than Be, so use the spatula to try to contain runaway flakes.

- Prevent the sample from getting white hot. At this temperature, the silver could melt and make it very difficult to remove the sample from the quartz tube.
 - o Use a normal propane torch instead of a Map Gas torch, which burns hotter

Niobium addition

Add niobium. Samples already contain silver as a conductor, so not quite as much niobium is needed as for Be samples.

- 1 rounded scoop

Aluminum cathode packing

Crushing sample: Al_2O_3 is what they make sandpaper out of (also what corundum is (hardness 9)), so it is quite difficult to crush and disaggregate. Unlike for BeO, don't get a chunk of sample under the drill bit and press until it disintegrates, for you greatly risk sending bits of sample flying out of the tube. Rather, place the drill bit over the sample and very lightly tap, or hammer the sample until it falls apart.

- Al cathodes don't need to be packed in the glove box, but can be packed on the lab bench instead
- Don't overpack the cathodes. The packed surface should ideally be ~1 drill blank diameter down in the hole.