EXTRACTION OF Al & Be FROM QUARTZ FOR ISOTOPIC ANALYSIS

Summary

This method is used to separate Al and Be for AMS analysis from pure quartz samples. After adding Be carrier, quartz is dissolved in HF. The solution is sub-sampled for determination of total Al content, 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. This method covers the first two: (i) Anion exchange in HCl (removes Fe^{III}), (ii) Cation exchange in dilute H_2SO_4 and HCl (removes Ti and alkalis, separates Be from Al). The third stage, hydroxide precipitation (eliminates residual alkalis, Mg, Ca), 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 version checked and revised February 2001 by John Stone.

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 have encountered for separating Ti from Be. Please cite:

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

if you use this method.

Al test for quartz purity

Check the Al content of the quartz separate before dissolving it for ^{26}Al analysis. It is important to obtain the lowest possible Al concentration. High Al levels decrease the ^{26}Al/^{27}Al ratio and limit the number of ^{26}Al ions that can be counted, compromising the counting statistics of the measurement. Careful quartz clean-up usually results in Al concentrations of 10–100 ppm. Higher levels commonly (though not always) indicate the presence of impurities such as feldspar, muscovite or insoluble fluorides from the HF treatment. Note - a 99.5% pure quartz separate containing ~0.5% feldspar still has an Al concentration of ~1000 ppm.

Sample weighing

Estimate the amount of sample required for the measurement. 1 mg of Al (which will make ~2 mg of Al_2O_3) is required for the AMS measurement, though larger amounts, up to a few 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: (i) For "hot" samples with high levels of ^{26}Al, the necessary amount of Al can be obtained by substituting carrier for quartz. Adding Al carrier lowers the ^{26}Al/^{27}Al ratio, and should

be avoided for young, low-altitude, or heavily shielded samples. (ii) Conversely, the $^{10}Be/^{9}Be$ ratio increases with sample size, so using larger amounts of quartz will improve ^{10}Be results from low-level samples. (iii) Note, however, that processing samples larger than 30 - 35 g is tedious, expensive, and best avoided. (iv) If you know the approximate age of your samples, you can use the spreadsheet calculator on the lab computers to predict $^{26}Al/^{27}Al$ and $^{10}Be/^{9}Be$ ratios for different quartz and carrier weights. Aim for $^{10}Be/^{9}Be$ ratios > 10^{-13}, and $^{26}Al/^{27}Al$ ratios > 10^{-12}.

For a batch of standard samples (weights ~10-20 g):

Create a log file from the template on the balance PC. Enter the sample IDs. Print a batch worksheet and stick it into the lab log-book.

For each sample:

Tare a clean 100 mL or 250 mL FEP teflon (bottle + solid lid) to at least 3 decimal places. Record the bottle number and its tare weight. Use 100 mL bottles for samples less than 20 g.

Transfer the sample to the bottle with a clean, non-reagent spatula. If possible, move the sample grains all the way into the bottle and tip them directly onto the base. Try to minimise static build-up on the bottle rim and prevent 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 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. Take care not to touch the spout on the sample container.

Carrier addition

Take the current Be carrier bottle and record the concentration. Invert it a few times to homogenise the solution. Be sure drops of condensation around the lid are taken up and mixed in. Weigh it. Record the initial weight (and confirm that it equals the final weight from the previous use).

Load the 0 - 1 mL Gilson pipette with a clean tip. Adjust it to deliver carrier containing ~250 mg Be. 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 Be added. 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-book.

Dissolution

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. 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 beaker of cold water. Don't swirl the bottle at first - the initial reaction doesn't need any encouragement. Never shake the bottle.

Once the reaction has subsided (usually a few hours), the bottles can be placed around the edges of 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 H_2SiF_6 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.

Splitting for Al determination

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 lid on each bottle for its corresponding solid lid and tighten firmly. Check that the bottle is safely sealed (squeeze it gently). Keep a plastic beaker of MQ water on hand, and submerge each lid as you remove it. Set the lids aside to be cleaned.

Homogenise 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 4-figure balance (up to 200 g) or the top-loading balance (weights > 200 g). Record the weights. Subtract the bottle tare weights to calculate solution weights.

For each sample, take a pair of round-bottomed, 15 mL, screw-top vials (marked with "AB" numbers). Record the sample ID, the bottle it was dissolved in and the corresponding two vial numbers. Tare each vial with its lid and record the weights.

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

Open the vials. Open the sample bottle. Use a disposable pipette to transfer an amount equal to ~2% of the solution into each vial (usually 2-3 mL). Re-cap the vials, tightening the lids gently. Re-cap the sample bottle. Rinse out the pipette in a plastic beaker of water. Leave it in the beaker and get a clean pipette for the next sample. Take care with this step - the solutions you are handling are strong HF/H_2SiF_6. 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.

Weigh the vials and record the weights. Calculate the weight of each split. Take care not to splash droplets of the split solutions onto the lids of their vials when moving them in and out of the balance.

After splitting each sample, the aliquots can be dried down to remove HF in preparation for ICP analysis. Return them to the Al-Be lab, taking care not to splash liquid up onto the lids of the vials. Add 5 - 10 drops of 1:1 H_2SO_4 to each and dry at setting ~3 on the hotplate. A small dot of liquid, or a precipitate of Al-Be-Fe-Ti salts should appear in the base of each vial after evaporation.

Cool the vials. Then add 6 mL 1% HNO_3 to each using the repeat pipettor. Re-cap them and let them stand (preferrably overnight) to dissolve.

Weigh the vials immediately prior to ICP analysis. Calculate the weights of the solutions by subtracting the vial tare weights. Record the vial and solution weights.

Analyse for Al and Be by ICP. Multiply the results by the weight of 1% HNO_3, divide by the aliquot weight and multiply by the total weight of the sample solution to determine the total amount of Al in each sample (dividing by the weight of quartz dissolved gives the Al concentration of of the quartz. You should expect to get a value within 10% of your initial test result).

Dry-down and chloride conversion

Uncap each sample bottle and carefully transfer its solution to a large (250 mL) vessel for drying. 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. Record each sample number and the corresponding vessel number.

Using separate disposable pipettes, add 2-3 mL of 6M HCl and 1 mL of 8M HNO_3 to each vessel.

Place the vessels on the hotplates and evaporate at setting 3. Vessels that contain < 100 mL will dry down overnight. Larger volumes may take up to 48 hr. When dry, there will be a thin covering of fluoride and chloride salts on the floor of the vessel, ranging in color from white to orange-brown or grey-green .

To convert the residue to chloride form ...

Take the vessels off the hotplate and cool them. Using a disposable pipette, add ~2 mL of 6M HCl (the amount is not critical; samples with a very large fluoride cake may require a little more). The cake should re-dissolve almost entirely; any residual solid will usually go back into solution after a little warming on the hotplate.

Return the vessels to the hotplate and dry again.

Cool and repeat the HCl addition.

Heat the samples again, taking them down to a few drops. Try to avoid complete dry-down, making it easier to get the samples back into solution for anion exchange. Don't worry if the samples dry completely, however.

The succession of evaporations and re-dissolutions should have eliminated fluoride (as HF) almost entirely. Fe, Ti, Al, Be, alkalis and other metals present should now be in the form of chloride salts, ready for clean-up by anion exchange. The remaining solution is ususally deep yellow-green, due to $FeCl_3$. By the end of this procedure, however, some samples may have thrown a fine, powdery white precipitate that will not re-dissolve. This is TiO_2. Little or no Al or Be co-precipitates with the Ti, which should be removed by centrifuging before anion exchange.

Fe (+Ti) clean-up (anion exchange columns)

Load a column rack with a set of large ion exchange columns. Place a glass beaker under each.

Squirt a few ml of isopropanol (or equivalent alcohol) into each to wet the frit. Let the columns drain.

For each column ...

Squirt a few mL of MQ water 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 prevents trapping of air bubbles in the resin bed. Now continue slurrying resin into the columns to build beds of 2 mL for samples containing < 3-4 mg Fe, or 3 mL for Fe-rich samples. If too much resin has been added, a long glass pasteur pipette can be used to adjust the volume. If too thick a slurry is added and bubbles get trapped in the bed, the column must be emptied and re-packed - bubbles will channel flow through the column and ruin the separation. Once the resin has compacted to the correct height, allow the supernatant to drain through.

Wash the resin bed with 5 times its volume of dilute HCl (1.2 M / "10%" HCl is convenient, though more dilute HCl does a better job). Allow the wash solution to drain through the resin bed.

Condition the resin with 3 bed volumes of 6M HCl. This should be dispensed carefully, maintaining a flat surface at the top of the resin bed. Don't squirt it forcefully from the wash bottle. The resin will darken and shrink as it adjusts to the higher acid strength.

While the conditioning solution is draining, add 2 mL of 6M HCl to each sample container. The precise volume is not critical and can be measured from the marks on a disposable pipette. Swirl the liquid to pick up and dissolve the entire sample from the floor of the container. Do not warm to promote dissolution unless absolutely necessary - evaporation may lower the HCl strength.

Check the samples for any signs of smoky white insoluble material (this will be TiO_2). If any is present, the solutions will have to be centrifuged before running them through the columns. To do this, transfer solutions to disposable 12 mL centrifuge tubes using a clean disposable pipette for each sample. Add a further 1 mL of 6M HCl to the sample containers as a rinse. Pick the rinse solutions

up and add them to their appropriate centrifuge tubes. Cap the tubes and spin at 3000 RPM for 5 minutes. The pipette used for each sample should be reserved (in the original sample container) for loading.

Take a batch of 28 mL teflon vials and record their numbers against sample ID and parent container numbers.

After the 6 M HCl conditioning solutions have drained, carefully remove the glass beakers from beneath the columns. Reserve the acid for use in the mineral separation lab. Replace the glass beakers with 28 mL vials.

Using a separate disposable pipette for each sample (those centrifuged will already have one), 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 not to disrupt the top surface of the resin. Transfer the entire sample. Return each pipette to its sample container.

Add 1 mL of 6 M HCl to each sample container and swirl to pick up any remaining droplets of the original sample solution. (This step is not necessary for samples that were centrifuged, and have already been washed out of their containers).

Allow the loading solutions to drain fully into the resin. Now add the 1 mL wash solutions, taking care to load each into the correct column. Allow to drain into the resin.

Elute Al + Be from the columns by adding 3 times the bed volume of 6M HCl. The first mL should be added carefully from a disposable pipette so as not to disrupt the top of the resin bed. The remainder can be added with the Eppendorf repeat pipettor. 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 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. Titanium is more problematic; some Ti in the form of Ti forms $Ti^{(IV)}Cl_6^{2-}$ which will bind, but a sizable fraction always drains through in the form of cationic or neutral species, ending up 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, scour and wash the sample transfer containers.

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. The dried residue from this step may turn an alarming dark-brown to black color. This is due to charry reaction products formed from organics which bled from the anion resin. Don't worry, it will disappear gradually over the next couple of steps.

Cool the vials and moisten the dry cakes with 5-6 drops of ~2% H_2O_2. Then add 2 mL of MQ water containing a trace of 0.5 M H_2SO_4. The cakes will begin to dissolve, taking on an amber/gold color

($TiO[H_2O_2]^{2+}$) if Ti is present. Reheat the vials. The black charry material will disperse and disappear after a while. Dry the samples down again.

Cool, repeat the hydrogen peroxide/MQ water addition, 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 mL of MQ water, containing a trace of ~2% H_2O_2 and 0.5 M H_2SO_4. 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.

Al-Be separation (cation exchange columns)

Load a column rack with small (~11 mL total volume) Bio-Rad columns. Place a glass beaker under each. Add a few drops of isopropanol (or equivalent alcohol) to each to wet the frit. Allow it to drain through.

Using a disposable pipette, add 2 mL of DOWEX-50 X8 200-400# cation exchange resin to each column. Start by filling each column with a little MQ water. Then, before it drains, slurry in a thin suspension of resin in a few mL of acid, plugging the column and allowing the resin to settle rather than run down the column walls (potentially trapping air bubbles). Allow the head of dilute acid to drain.

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

Condition the columns first by filling the headspace with 1.2 M HCl (allow it to drain through), then 0.2 M H_2SO_4 containing a trace of 2% H_2O_2 (allow it to drain through).

Check the volume in each of the glass beakers and, if necessary, discard.

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 either medium (22 mL) or tall (28 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. Dry them on the hotplate at setting 3. Dry-down will take ~8 hours.

Place a medium (22 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 4M 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.

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. Use the original sample ID, not a beaker or bottle number. (It is useful to note the date to key the sample back to your workbook). Be sure to identify the "Be" and "Al" fractions separately.

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 H_2SO_4. Occasionally they will form a small white cake. This usually indicates an impurity or Al cross-over. The Al fractions will vary in size from sample to sample, but they should dry to a fairly dense white cake in the hollow of each vial.

Pipette 2 mL of 1% HNO_3 into each vial. If pure, both Al and Be fractions will dissolve freely. If necessary, warm the vials for a few minutes on the edge of the hotplate to ensure complete dissolution.

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% HNO_3 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.