Appendix 5: Quartz preparation and separation of cosmogenic Be

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Initial quartz separation

Sample crushed and wet sieved to approximate size fractions (125 – 250 µm).

Dry sample in oven at 40°C.

Run sample through Frantz magnetic separator to separate non-magnetic grains.

Take sample weight.

Wash sample with ca 300 g with deionised water

Add 10% HCl (36% HCl : H_2O = 1:3) to the sample (in an open container)

Notes: remember to add acid to water (~330:660 ml); <150g of sample per container

Repeat if the carbonate content is high (e.g. foaming)

Add sample and ~250 ml 10% HCl to 1 l bottles

Place on hotdog rollers for ~1 day @ 60°C (~50°C on machine)

Wash with deionised/distilled water 4-5 times, 50 ml at a time. Each time, add water, swirl around, decant off.

Note: tip liquid of sample bottles into bucket, wash sample 3 times until water is clear

Repeat step if solution is very dirty (yellow)

Quartz cleaning and etching using Hydrofluoric acid

No more than 80g of a dirty sample or 120 g of a clean (quartz-rich) sample should go in each 1 litre HDPE bottle. All shaking, rolling or ultrasonic should be done heated:

Make ~5% HF solution:

Per 1 litre: 100 ml conc. (~48%) HF (analytical grade), 10 ml conc. (~68%) HNO_3, 890 ml deionized H_2O

Or per sample bottle (max. 300 ml): ~37 ml conc. HF, ~5 ml HNO_3, ~250 ml H_2O

Note: add water, then HNO_3, then HF to sample

Add 500 ml 5% HF to sample and spin on heated rollers for ~1 day

Note: Turn off rollers overnight

Wash with deionized/distilled water

Note: wash at least 4x, dumping into waste bucket; calcium carbonate should then be added to bucket (binding with fluoride) and soda ash (neutralising acid)

Add 500 ml 5% HF to sample and shake for 2 days

Wash with deionised/distilled water

Add 500 ml 5% HF to sample and shake for 2 days

Wash with deionised/distilled water

Repeat until sample is pure quartz (either visual inspection or < 5% weight change)

Wash with Millipore H_2O until pH ~neutral, then dry and weigh sample

Note: dry in oven in bowls with filter paper

If the samples are still impure, use heavy liquid separation or hand picking to remove impurities.

Sample Decomposition

IMPORTANT: From this point on, use only p.a. grade or cleaner acids only, and use distilled or Millipore water

Note: clean beakers prior to use (enough large (240ml or 90ml) Savillex beakers for dissolution and small (22ml) Savillex beakers for outputs); 1) wipe and rinse, 2) clean with HCl (~1:3 with H_2O), 3) with HNO_3 (~2:5), and 4) with 7M HF (~1:4), just covering the base each time and rinsing with Millipore water in between.

Final Quartz Leach

Take the precise weight of a 90ml or 240ml Savillex screwtop jar and lid

(maximum ~50g quartz in 90ml jar and maximum ~150g in 240ml jar)

(if using the quick dissolution, only use the largest Savillex jars)

Add 7M HF (48% conc. HF (28M): Millipore H_2O=1:3) till the sample is covered by ~5mm excess liquid

Heat ~1 hour (maximum) @ 120°C with lid

Allow to cool and wash with Millipore H_2O

Note: 4x rinses per sample

Add Aqua Regia (conc. (14M) HNO_3: conc. (12M) HCl =1:3) till the sample is covered by ~5mm excess liquid

Note: to make batch for ~13 samples (~500ml of Aqua Regia), add 450ml HCl and 150ml HNO_3

Leave uncovered until all brown gas has gone, ~30 minutes

Heat with lid ~1 hour minimum @ 120°C

Note: if leaving for a long period (i.e. overnight), tighten lid and leave off hotplate

Allow to cool and wash thoroughly with Millipore H_2O

Repeat 4-5 times

Dry sample on hotplate (over ½ day or overnight)

Allow to cool and take the precise weight (including Savillex jar and lid)

Carrier addition and sample dissolution

Add carrier 0.4 mg Be

(i.e. if the carrier conc. = 405 ppm then 0.37 g of carrier solution = 0.15 mg Be, or if carrier conc. = 375 ppm then 0.45 g = 0.15 mg Be)

Take the precise weight of carrier added (to 0.000 g or better)

Notes: pour approx. carrier to be used into a cleaned bottle, add carrier to sample using 100-1000µL pipette, measure mass loss from the carrier (take precise weight and then tare after each).

Dissolution

The stochiometric reaction for quartz dissolution is: $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$

(e.g. you will need 116 ml 28M HF to dissolve 50 g quartz, however, in practice you will need a bit more)

Add 28M HF (remember p.a. quality or better) in increments till the sample is covered with ~5 mm excess liquid

The first couple HF additions may generate a strong exothermic reaction, so be careful

Allow to react unheated for ~15 minutes

Heat without lid @ ~120°C, eventually evaporating to dryness (down to 100°C overnight)

Repeat until all quartz is dissolved

Note: after the 2nd or 3rd HF addition, the reaction should be less volatile, and you can add HF up to twice the quartz volume.

Carefully remove from hotplate and allow to cool

Note: static electricity that can cause sample flakes to jump out of the beaker – wetting your gloves a bit and/or placing wet paper towels beneath the beakers can help reduce this effect.

BeF_2 – Water Leach

BeF_2 is water soluble while many other cations (including Al) are less so.

Add 15ml Millipore H_2O to fluoride cake (to cover bottom of beaker)

Shake and heat gently for ~20 minutes on hotplate

Pipette off 15ml supernate (containing water-soluble BeF_2, TiF_4, $Fe(II)F_2$ but no AlF_3) into clean 22ml Savillex beakers (or 180ml beakers for dirty samples).

Repeat these three steps 1 more time with 5ml Millipore H_2O (a total of 20ml liquid for clean samples of 45ml for dirty samples)

Heat the samples at ~120°C to evaporate the solution (22ml Savillex beakers for clean or 180ml for dirty samples)

Add 10ml 6M HCl

Transfer solution into cleaned 15ml centrifuge tubes

Centrifuge for 5 minutes @ 3500 rpm

Pipette into 22ml beakers, leave on hotplate at 120°C

Load only the supernate to the columns in the following step.

If available, check the purity of your samples at this point using ICP-OES

Column Fe

2ml Biorad AG1-X8 100-200 mesh (anion) resin in 15ml Eichrom columns stored in H_2O.

Note: to prepare new columns 1) place empty columns in stand with shot glasses below, 2) add tip to one column, add 2ml of H_2O and mark line (then mark line on other columns), 3) add water and resin to a small beaker and agitate, 4) wet filter for each column and check they are dripping, 5) pipette resin into each column, letting it settle, and continue until resin reaches the marked line, 6) to store, fill with H_2O, cap tops and add tips to ends.

Open column and let the water drip out (drain to waste container)

Add 5ml + 5ml 0.3M HCl to clean the resin (drain to waste container)

Add 2ml + 2ml + 2ml 6M HCl to condition the resin (drain to waste container)

Add sample Collect Be (+Al) in 22ml Savillex beakers

Add 2ml + 2ml + 2ml 6M HCl to elute Be Collect Be (+Al) in 22ml Savillex beakers

Add 5ml + 5ml 0.3M HCl to clean the resin (drain to waste container)

Add Millipore H_2O and seal the columns for storage.

Heat the samples at ~120°C to evaporation

Add 4ml (20ml for dirty quartz) 0.4M oxalic acid (binds Al and Ti for faster passing through resin) to each column

Note: to make up 0.4M oxalic acid, add 2x ~50.6g oxalic powder (measured on tared filter paper) to cleaned 2L bottle, then add ~2L Millipore H_2O, shake and leave to dissolve for ~2 hours.

Warm the samples at 60°C with lid for ~2 hours

Note: the acid breaks if too warm

Remove from hotplate and allow to cool down for at least 30 minutes

Transfer the samples to new 15ml centrifuge tubes

Centrifuge for 5 minutes @ 3000 rpm

Load only the supernate to the columns in the following step

5ml Column Be

5ml Biorad AG50-X8 200-400 mesh (cation) resin in 15 ml Eichrom columns stored in H_2O.

Open column and let the water drip out (drain to waste container)

Add 5ml + 10ml ~5M HNO_3 to clean the resin (drain to waste container)

Add 5ml + 5ml Millipore H_2O to remove HNO_3 from the resin (drain to waste container)

Add 5ml + 10ml 0.4M oxalic acid to condition resin (drain to waste container)

Add sample (20ml 0.4M oxalic acid) (drain to clean container)

Add 5ml 0.4M oxalic acid to wash the sample down (drain to clean container)

Add 5ml 0.4M oxalic acid to wash the sample down (drain to clean container)

Add 50ml 0.4M oxalic acid: to elute Fe, Al, Ti etc. (drain to clean container)

Add 5ml + 10ml Millipore H_2O to remove oxalic acid (drain to clean container)

Note: sample in H_2O and oxalic acid will need to be collected in 2x clean 50ml centrifuge tubes per column

Add 15ml + 25ml 0.5M HNO_3 to elute Na (drain to clean container)

Note: Na will need to be collected in 1x clean 50ml centrifuge tube per column

Add 20ml 1M HNO_3 wash (drain to clean container)

Note: post-Na wash will need to be collected in 1x 50ml (or 2x 11ml) clean centrifuge tubes per column

Add 20ml + 20ml 1M HNO_3 to elute Be Collect Be in new clean 90ml Savillex beakers

Add 40ml 5M HNO_3 to clean resin (drain to waste container)

Note: post-Be wash will need to be collected in 1x clean 50ml centrifuge tubes per column

Add 5ml + 15ml H_2O remove 5M HNO_3 (drain to waste container)

Add Millipore H_2O and seal the columns for storage

Heat the samples at ~120°C to evaporate the solution

Add 11ml 1M HNO_3 to dissolve the sample and transfer to a new 15ml centrifuge tube

Be precipitation

Redissolve the precipitate in 5ml 1M HNO_3

Transfer to new 11ml or 15ml centrifuge tubes

Add ~0.5ml concentrated NH_4OH to each sample

Centrifuge for 5 minutes @ 3000 rpm

Decant the supernate

Add 3ml H_2O and shake well to dissociate the precipitate

Centrifuge for 5 minutes @ 3000 rpm

Decant the supernate

Repeat the above three steps

Measurement of $^{10}Be/^{9}Be$ ratios

Send to GNS to be measured by the 0.5 MeV XCAMS Accelerator Mass Spectrometer.