## Reagent molarity calibration

The ultra-clean reagents in the Pb lab are mixed approximately and iteratively directly from their clean teflon bottles in order to avoid contamination from pipets or graduate cylinders. Their molarities are then calibrated gravimetrically using a pycnometer of known volume and weight, and appropriate mass-molarity curves.

## Reagent blanks

Reagent blank amounts are determined via isotope dilution by spiking a 7 mL Savillex beaker designated for reagent blanks with approximately 0.005 g spike (1 microdrop), adding 1 µL of 0.035M H3PO4, filling the beaker with the desired reagent, and drying it down overnight in the laminar flow hood. In the mass spec lab, 3 µL of silica gel-H3PO4 mixture (Gerstenberger and Haase, 1997) is added to the sample spot, and the solution loaded onto a degassed single Re filament for mass spectrometry.

Reagent blank isotopic compositions are determined via isotope dilution by sequentially filling a 7 mL Savillex beaker with the desired amount of reagent and drying it down in the laminar flow hood. In the mass spec lab, 3 µL of silica gel-H3PO4 mixture (Gerstenberger and Haase, 1997) is added to the sample spot, and the solution loaded onto a degassed single Re filament for mass spectrometry.

## Savillex microcapsule cleaning

1. With blue tweezers, uncap each capsule from the first puck, setting the caps on a piece of parafilm. Empty the capsules of liquid by wrapping thumb and forefinger around the capsules, inverting and shaking out into a plastic tub. Fill each capsule with MQH2O and empty, then add six drops of double-distilled 6M HCl to each capsule, replace caps and set aside. Repeat emptying, rinsing and filling with HCl for the capsules in the two other pucks.
2. Add 7 ml of 6M HCl “moat” acid to the inside of the large teflon liner cup. Place all of the pucks on the stem, and slide the assembly into the large teflon liner cup. Cover the liner cup and wrap a piece of parafilm around the edge.
3. Remove the cup to the outer mineral separations lab, remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the jacket cap, then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the 180°C oven overnight.
4. After 12-24 hours, remove the jackets from the oven onto a metal grill under the fume hood and allow to cool. When hand cool, loosen the cap screws, uncap the jackets, and remove the teflon liner, wiping it clean with a damp paper towel. Return the liner to the clean lab. Under the laminar flow hood, unseal the teflon liner, rinse off the cap, extract the puck and stem assembly, rinse with MQ, and remove each puck. Empty the liner of the moat acid, rinse and set aside.
5. With blue tweezers, uncap each capsule from the first puck, setting the caps on a piece of parafilm. Empty the capsules of liquid by wrapping thumb and forefinger around the capsules, inverting and shaking out into a plastic tub. Fill each capsule with MQH2O and empty, then add six drops of double-distilled distilled 29M HF to each capsule, recap and set aside. Repeat emptying, rinsing and filling with HF for the capsules in the two other pucks.
6. Add 7 ml of 29M HF “moat” acid to the inside of the large teflon liner cup. Place all of the pucks on the stem, and slide the assembly into the large teflon liner cup. Cover the liner cup and wrap a piece of parafilm around the edge.
7. Remove the cup to the outer mineral separations lab, remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the jacket cap, then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the 220°C oven overnight.
8. After 12-24 hours, remove the jackets from the oven onto a metal plate under the fume hood and allow to cool. When hand cool, loosen the cap screws, uncap the jackets, and remove the teflon liner, wiping it clean with a damp paper towel. Return the liner to the clean lab. Under the laminar flow hood, unseal the teflon liner, rinse off the cap, extract the puck and stem assembly, rinse with MQ, and remove each puck. Empty the liner of the moat acid, rinse and set aside.
9. Repeat steps 1-5.
10. Repeat steps 6-9.
11. Finally, with blue tweezers, uncap each capsule from the first puck, setting the caps to the side on a piece of parafilm. Empty the capsules of HF by wrapping your thumb and forefinger around the capsules, inverting and shaking out into a plastic tub. Fill each capsule with MQH2O and empty twice, then recap and set aside dry and ready for sample loading. Repeat emptying and rinsing for other pucks.

## Savillex 7ml beaker cleaning

1. Wearing eye protection and gloves, wipe off the outside of capped 7 mL Savillex beakers with a wiper and MQH2O.
2. In the laminar flow hood, uncap each beaker and add a few mL of MQH2O. With a cotton swab, rub the bottom and sides of each beaker gently, discard the MQ and rinse twice more with MQH2O. Add enough double-distilled 15M HF to the beaker to cover the bottom and cap tightly.
3. Place the beakers on the hotplate at 120°C and let flux at least a few hours to dissolve residual silica gel-H3PO4 in the bottom of the beaker. Remove the beakers from the hot plate, and then roll each closed beaker around to collect all the acid condensed on the sides into the bottom, then uncap and dump the acid into the “Waste HF” bottle, tap the beaker and lid on the wiper, then add enough double-distilled 6M HCl to cover the bottom of the beaker.
4. Place the beakers on a hotplate at 120°C overnight.
5. After fluxing, the beakers can be removed from the hotplate and the HCl carefully discarded after swirling, checking to make sure there are no “sticky” spots in the beaker. Any beakers from which the liquid does not cleanly empty should be recycled for another round of cleaning.
6. Fill the beakers again with enough double-distilled 6M HCl to cover the bottom and return to the hot plate for another few hours of fluxing.
7. Remove the beakers from the hot plate, swirl and empty the acid from the beaker, again making sure no acid clings to the beaker.
8. Finally, fill the beaker with MQH2O and empty it, tap the beaker and lid on the wiper and cap for use.

## Accessory mineral loading

Accessory mineral grains are loaded from your petri dish or plucked mount into 3 ml round-bottomed Savillex PFA “hex” beakers for treatment in the clean lab. The hex beakers associated with each dissolution set are stored in the U-Pb clean lab in the upper right cabinet, and may be dry or have a ml of 3.5M HNO3 in them from the last user—empty and add 1 ml MQH2O to each beaker in preparation for loading before bringing them out to the picking lab.

Add some ethanol to the petri dish containing your annealed zircons and transfer each grain into its respective (labeled with a white rectangular sticker) hex beaker using the VWR pipettor that lives near the microscopes. Once transferred, screw the caps onto the beakers and bring them into the clean lab.

**Zircons** are given a series of rinses in 3.5M HNO3 in the hex beakers in the clean lab under a microscope prior to loading for chemical abrasion. **Rutile and titanite** are initially sonicated in 3.5M HNO3 for 15 minutes, since these minerals are not subjected to chemical abrasion), and then subjected to the same rinsing procedure. **Phosphates** are treated the same way except MQH2O is used in place of 3.5M HNO3 for all rinsing.

Samples are chemically abraded and/o dissolved in cleaned 300 µL Savillex PFA capsules. Five capsules are held in a white teflon puck and three pucks fit into a Parr vessel for a total of 15 capsules per assembly. Keep the capsules under laminar flow at all times. Rinse and transfer the grains under a microscope with a pipet (set to around 10 µL) and gel-loading tips.

To load:

1. Depress the plunger, line up the tip with the grain of interest under the microscope, then quickly suck up the grain into the tip, in the smallest amount of liquid, then discard the excess MQH2O from the hex beaker.
2. Add 12 drops of clean 3.5M HNO3 to the hex beaker, and again pick up the grain with the pipet in the smallest amount of liquid, then discard the excess acid.
3. Repeat step 2.
4. Add 12 drops of clean 3.5M HNO3 to the hex beaker, and again pick up the grain with the pipet in the smallest amount of liquid, carry over to the flow hood, invert over the capsule and eject the drop of acid containing the grain into the clean 300 µL Savillex PFA capsule.
5. To make sure the transfer was successful, return the pipet to the hex beaker and suck up and expel some acid several times. If the grain is not in the hex beaker then it must be in the capsule!
6. Once you’re confident the grain is in the capsule, then add a total of 4 drops of double-distilled 29M HF for zircon, titanite and rutile and cap. Do NOT add any dissolution acid to phosphates at this stage.
7. Repeat for each capsule. Rinse each hex beaker, add a ml of 3.5M HNO3, and either set aside for acid washing following chemical abrasion (zircon) or flux on the hotplate overnight before emptying (other minerals).

## Chemical abrasion of zircons

Following Mattinson (2005), all zircons should be treated by the high temperature annealing and chemical abrasion method, to mitigate the effects of Pb loss through selective removal of high-U, radiation-damaged, open system zircon domains. The annealing procedure was described in the mineral separations guidebook.

To chemically abrade zircons:

* 1. After loading your acid washed grains into capsules and adding 4 drops of conc. HF, place all of the pucks on the stem, and insert into the large teflon Parr liner with 7ml of “moat” 29M HF.
  2. Cap the vessel, wrap with parafilm, and remove to the oven lab. Remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the rest of the jacket cap, and then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the 190°C oven for approximately 12 hours; this period has been shown to yield good results for most zircons – occasionally you will find grains requiring a lower temperature due to complete dissolution, or a higher temperature because of persistent Pb loss.
  3. After 12 hours, remove the jackets from the oven onto a metal plate under the fume hood and allow to cool. When hand cool, loosen the cap screws, uncap the jackets, and remove the teflon liner, wiping it clean with a damp paper towel. Return the liner to the clean lab.
  4. Under the laminar flow hood, unseal the teflon liner, rinse off the cap, extract the puck and stem assembly, rinse with MQH2O, and remove each puck. Empty the liner of the moat acid, rinse and set aside.
  5. With blue tweezers, uncap each capsule, and dump the contents into the appropriate hex beaker from your earlier acid-washing step, which should already contain a ml of 3.5M HNO3.
  6. Using a gel loading pipet under the microscope, pipet the grain out of the acid, discard the acid, replace the grain in the hex beaker, and add 10 drops of 3.5M HNO3. Repeat this step with another aliquot of 3.5M HNO3.
  7. Repeat step 6 for all 15 microcapsules.
  8. Rinse each empty microcapsule, and fill with 6 drops of 6M HCl, and place the pucks on the hot plate to clean.
  9. Cap each hex beaker and place in the ultrasonic bath and sonicate for 30 minutes, then transfer the hex beaker to a hot plate at 120°C for 30 minutes. At the end of this hour, empty the 6M HCl from the Savillex microcapsules in preparation for reloading each grain.
  10. Using a gel loading pipet under the microscope, pipet the grain out of the acid discard the acid, replace the grain in the hex beaker, and add 10 drops of MQH2O. Swirl, then repeat pipeting the grain, discarding the water, replacing the grain and adding another 10 drops of MQH2O. Repeat a third time.
  11. Pick up the grain with the pipet in the smallest amount of liquid, carry over to the flow hood, invert over the capsule and eject the drop of water containing the grain into the clean 300 µL Savillex PFA capsule.
  12. To make sure the transfer was successful, return the pipet to the hex beaker and suck up and expel some acid several times. If the grain is not in the hex beaker then it must be in the capsule!
  13. Once you’re confident the grain is in the capsule, then add a total of 4 drops distilled conc. HF and cap, ready for spiking.
  14. Repeat for each capsule.
  15. Rinse each hex beaker, add a ml of 3.5M HNO3, and flux on the hot plate for at least an hour, ready for the next user.

## Sample spiking

The mixed U-Pb spike is stored in a 30 mL dropper bottle with a spaghetti tip and dome cap wrapped in parafilm under the laminar flow hood. This bottle is only ever uncapped under the laminar flow hood! Be extremely careful never to touch the spaghetti tip to any surface and ***of course if you ever drop the spike bottle the world as you know it will end.***

With a damp wiper, wipe down the surface of the hood, and then place a clean small wiper over a clean large wiper under the hood and wet with MQH2O— this minimizes static. Line up the sample pucks on the edge of the wiper, and move the first into position on the center of the small wiper. Remove the cap of the first capsule and set aside. Remove the parafilm wrap from around the cap of the spike bottle, but do not remove the cap; examine for any small loose drops of spike in the dome or on the edge of the spaghetti tip- uncap and carefully shake these free if present. Cap and then weigh the spike bottle on the digital balance and record the starting weight in your notebook and on the spike log sheet.

Back in the hood, carefully uncap the bottle, place the tip over your capsule (but don’t touch it!), and dispense the appropriate amount of spike, usually about 0.01 g, which is around 2-3 “microdrops”. Recap the bottle, and return it to the balance to reweigh; calculate the weight of spike dispensed by difference. Return the spike bottle to the hood, replace the cap on the capsule, and move on to the next capsule. Repeat all of these steps for each capsule. Once finished, record the final weight of the spike bottle on the log sheet, and rewrap with parafilm.

Zircon, titanite and rutile are now ready for dissolution. For dissolution of phosphates, you must now dry down the nitric-based spike solution (and grain) down on a hot plate prior to the addition of 4 drops of distilled 6M HCl to each capsule for dissolution.

## Sample dissolution

Place all of the pucks on the stem, and insert into the large teflon Parr liner with 7ml of “moat” acid, either 29M HF or 6M HCl, matching to the dissolution acid in the capsules. Cap the vessel, wrap with parafilm, and remove to the ovens in the outer mineral separation lab. Remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the rest of the jacket cap, and then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the appropriate oven: zircons and titanates are dissolved in 29M HF for 48 hours at 220°C; phosphates are dissolved in 6M HCl for 48 hours at 180°C.

After 48 hours, remove the jackets from the oven onto a metal plate under the fume hood and allow to cool. When hand cool, loosen the cap screws, uncap the jackets, and remove the teflon liner, wiping it clean with a damp paper towel. Return the liner to the clean lab. Under the laminar flow hood, unseal the teflon liner, rinse off the cap, extract the puck and stem assembly, rinse with MQ, and remove each puck. Empty the liner of the moat acid, rinse and set aside. With blue tweezers, uncap each capsule, setting the caps to the side on a piece of parafilm. Place the pucks on a 120°C hot plate and allow to capsules to dry completely.

When dry, remove the pucks from the hot plate, add 4 drops of double-distilled 6M HCl to each capsule and recap. Replace all of the pucks on the stem, and insert into the large teflon liner with 7 mL of 6M HCl “moat” acid. Cap the vessel, wrap with parafilm, and remove to the ovens in the outer mineral separation lab. Remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the rest of the jacket cap, and then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the 180°C oven overnight.

After 12 to 24 hours, remove the jackets from the oven onto a metal plate under the fume hood and allow to cool. When hand cool, loosen the cap screws, uncap the jackets, and remove the teflon liner wiping it clean with a damp paper towel. Return the liner to the clean lab. Under the laminar flow hood, unseal the teflon liner, rinse off the cap, extract the puck and stem assembly, rinse with MQ, and remove each puck. Empty the liner of the moat acid, rinse and set aside. With blue tweezers, uncap each capsule, setting the caps to the side on a piece of parafilm. Place the pucks on a 120°C hot plate and allow to capsules to dry completely. Once dry, remove from the hot plate and allow to cool for a few minutes. Then add the appropriate loading acid: 2 drops of 3M HCl for zircons, or 3 drops of 1M HBr for titanates and phosphates. Allow to redissolve for at least 30 minutes before chemistry.

## U-Pb separation for zircons

column: 50 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom)

chemistry calibrated in drops from 30ml Teflon dropper bottles, each drop approx. 30 µl

### Beaker prep:

Wipe insides of dirty beakers with clean gloved finger, rinse 2x with MQ-H2O in tub.

Add enough 50% HF from squirt bottle to cover bottom of beaker, place on hotplate to flux for at least 2 hours.

CAREFULLY empty HF from beakers, add enough 6M HCl from squirt bottle to cover bottom of beaker, place on hotplate to flux for at least 2 hours.

CAREFULLY empty HCl from beakers, add enough 6M HCl from squirt bottle to cover bottom of beaker, place on hotplate to flux for at least 2 hours.

Empty HCl from beakers, rinse with MQ-H2O from Teflon squirt bottle, tap dry and cap ready for use.

### Sample prep:

Dry dissolved zircons in 6M HCl to salts on 140°C hotplate.

Redissolve in 60 µl 3M HCl (e.g. 2 drops) to convert to PbCl3-, UO2Cl3-, and UCl62- ions.

### Column prep:

Remove columns from 4N HNO3 bath, rinse outside with MQH2O

Fill and empty column 3x with MQH2O

Fill with MQH2O and slurry in resin

Adjust resin volume to fill column with a convex-up surface projecting into reservoir

Clean columns full reservoir 6M HCl

Clean columns full reservoir MQ-H2O

Clean columns 20 drops 6M HCl

Clean columns 20 drops MQ-H2O

Clean columns 10 drops 6M HCl

Equilibrate columns 8 drops 3M HCl

### Column chemistry:

load sample 60 µl 3M HCl 2 drops (save for Th,Hf)

elute Zr,Hf,REE dropwise: 100 µl 3M HCl 5 drops (save for Th,Hf)

elute Pb 200µl 6M HCl 8 drops

elute U ~250µl MQ-H2O 10 drops

dry the Pb/U cut with 1 microdrop of 0.05N H3PO4 on hotplate under laminar flow

## U-Pb separation for phosphates and titanates (HBr + HCl)

column (Pb\*): tall 100 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom)

column (U): 50 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom)

chemistry calibrated in drops from 30ml Teflon dropper bottles, each drop approx. 30 µl

### Sample prep:

Dry dissolved samples in 6M HCl to salts on 140°C hotplate.

Redissolve in 100 µl 1M HBr (e.g. 3 drops) to equilibrate to PbBr42- ions

### Column prep:

Remove columns from 4N HNO3 bath, rinse outside with MQH2O

Fill and empty column 3x with MQH2O

Fill with MQH2O and slurry in resin

Adjust resin volume to fill column with a convex-up surface projecting into reservoir

Clean columns full reservoir 6M HCl

Clean columns full reservoir MQH2O

Clean columns 20 drops 6M HCl

Clean columns 20 drops MQH2O

Clean columns 10 drops 6M HCl

Equilibrate Pb columns 8 drops 1M HBr

Equilibrate U columns 8 drops 6M HCl

### Pb Column chemistry (100l column):

**Load sample 100 µl 1M HBr 3 drops - collect for U**

**Elute dropwise 100 µl 1M HBr 3 drops - collect for U**

**Elute in bulk 250 µl 1M HBr 8 drops - collect for U**

Rinse matrix in bulk 250 µl 1M HBr 8 drops - discard

Rinse matrix in bulk 400 µl 2M HCl 14 drops - discard

**Elute Pb 400 µl 6M HCl 14 drops - collect!**

Dry the Pb cut with 1 ”micro”drop of 0.035M H3PO4 on hotplate under laminar flow

### U Column chemistry (50l column): repeat this separation twice

Dry wash from Pb column, add 1 drop 6M HCl and redry twice, then add 3 drops 6M HCl to equilibrate to UO2Cl3- and UCl62- ions

Wash columns with 300 µl (10 drops) of MQH2O, and then re-equilibrate with 250 µl (8 drops) of 6M HCl

Load sample 100 µl 6M HCl 3 drops - discard

Rinse matrix dropwise 150 µl 6M HCl 3 drops - discard

Rinse matrix in bulk 300 µl 6M HCl 10 drops - discard

Rinse matrix in bulk 300 µl 6M HCl 10 drops - discard

**Elute U 400 µl MQ-H2O 14 drops - collect!**

Dry the U cut with 1 ”microdrop” of 0.05N H3PO4 on hotplate under laminar flow

## U-Pb separation for phosphates and titanates (HBr + HCl + HNO3)

column (Pb\*): tall 100 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom)

column (U): 50 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom)

chemistry calibrated in drops from 30ml Teflon dropper bottles, each drop approx. 30 µl

### Sample prep:

Dissolve spiked sample in microcapsule with 6 drops 29M HF + 2 drops 8M HNO3 in Parr vessel at 220°C for 48 hours. Dry sample to solids on 140°C hot plate, distilling off HF by adding 1 drop 8M HNO3 three times during evaporation, then redissolve in 4 drops 6M HCl in Parr vessel at 180°C for 12 hours. Dry sample to solids on 140°C hot plate, then redissolve in 100 µl 1M HBr (e.g. 3 drops) to equilibrate to PbBr42-

### Column prep:

Remove columns from 4N HNO3 bath, rinse outside with MQH2O

Fill and empty column 3x with MQH2O

Fill column with MQH2O and slurry in resin

Adjust resin volume to fill column with a convex-up surface projecting into reservoir

Clean columns full reservoir 6M HCl

Clean columns full reservoir MQH2O

Clean columns 20 drops 6M HCl

Clean columns 20 drops MQH2O

Clean columns 10 drops 6M HCl

Equilibrate Pb columns 8 drops 1M HBr

Equilibrate U columns 8 drops 8M HNO3

### Pb Column chemistry (100l column):

**load sample 100 µl 1M HBr 3 drops - collect for U,Th**

**elute dropwise 100 µl 1M HBr 3 drops - collect for U,Th**

**elute in bulk 250 µl 1M HBr 8 drops - collect for U,Th**

rinse matrix in bulk 250 µl 1M HBr 8 drops - discard

rinse matrix in bulk 400 µl 2M HCl 14 drops - discard

**elute Pb 400 µl 6M HCl 14 drops – collect Pb!**

Dry the Pb cut with 1 ”micro”drop of 0.05N H3PO4 on hotplate under laminar flow

### U Column chemistry (50l column): *may do this separation once or twice*

Dry U wash from Pb column, add 1 drop 8M HNO3 and redry twice, then re-dissolve in 100 µl (3 drops) 8M HNO3 to equilibrate to uranyl nitrate anion complexes. For all of these steps don’t handle the dried sample beakers – add drops of acid directly to sample beaker on the hot plate to make sure the small flake of sample doesn’t fly away due to static. Then swirl acid in beaker to pick up the sample.

Wash columns with 300 µl (10 drops) of MQH2O, and then re-equilibrate with 250 µl (8 drops) of 8M HNO3

load sample 100 µl 8M HNO3 3 drops - discard

rinse matrix dropwise 100 µl 8M HNO3 3 drops - discard

rinse matrix in bulk 150 µl 8M HNO3 5 drops - discard

rinse matrix in bulk 300 µl 6M HCl 10 drops - collect for Th?

rinse matrix in bulk 300 µl 6M HCl 10 drops - collect for Th?

**elute U 400 µl MQ-H2O 14 drops - collect U!**

Dry the U cut with 1 ”microdrop” of 0.05N H3PO4 on hotplate under laminar flow

## U-Pb separation for large (10-50 mg) silicate samples (common Pb)

column (Pbc): short 100 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom)

column (U): 50 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom)

chemistry calibrated in drops from 30ml Teflon dropper bottles, each drop approx. 30 µl

### Sample prep:

Rinse your mineral fraction in dissolution-type (round lid) 3 ml beakers.

Add 1 to 2 ml 29M HF (34 to 68 drops) + 200 to 400 µl 16M HNO3 (7 to 14 drops); place in Parr vessel at 220°C for 48 hours.

Add 200 µl 16M HNO3 (7 drops) and dry sample to solids; repeat a total of 3x.

Add 500 µl to 1 ml 6M HCl (17 to 34 drops); place in Parr vessel at 180°C for 12 hours.

Dry samples to solids, then add 250 µl 1M HBr (e.g. 8 drops); this should result in clear solution (if not, place on warm hotplate for 30-60 minutes). This will convert Pb to an PbBr42- anion complex for chromatography.

### Column prep:

Remove columns from 4N HNO3 baths, rinse outside with MQH2O

Fill and empty column 3x with MQH2O, and fill column with MQH2O and slurry in resin

Adjust resin volume to fill column with a convex-up surface projecting into reservoir

Clean columns full reservoir 6M HCl

Clean columns full reservoir MQH2O

Clean columns 20 drops 6M HCl

Clean columns 20 drops MQH2O

Clean columns 10 drops 6M HCl

Equilibrate Pb columns 8 drops 3M HCl

Equilibrate U columns 8 drops 8M HNO3

### Pb Column chemistry (100l column):

*First pass*

**load sample 250 µl 1M HBr 8 drops - collect for U!**

**rinse dropwise 100 µl 1M HBr 3 drops - collect for U!**

**rinse matrix in bulk 400 µl 1M HBr 14 drops - collect for U!**

rinse matrix in bulk 400 µl 1M HBr 14 drops - discard

rinse matrix in bulk 400 µl 2M HCl 14 drops - discard

**elute Pb 800 µl 6M HCl 28 drops - collect Pb!**

dry Pb cut, add 100µl (3 drops) 1M HBr and re-dry, then re-dissolve in 100µl (3 drops) 1M HBr to convert to PbBr42-

wash columns with 300 µl of MQH2O (10 drops) and then re-equilibrate with 250 µl of 1M HBr (8 drops)

*Second pass*

load sample 100 µl 1M HBr 3 drops

elute matrix dropwise 100 µl 1M HBr 3 drops

elute matrix in bulk 400 µl 1M HBr 14 drops

elute matrix in bulk 400 µl 1M HBr 14 drops

**elute Pb 800 µl 6M HCl 28 drops**

Dry the Pb cut with 1 ”micro”drop of 0.05N H3PO4 on hotplate under laminar flow

## U-Pb separation for large silicate samples (HCl/HBr + HNO3/HCl)

*Continued…*

### U Column chemistry (50l column):

Dry U wash from Pb column, add 1 drop 8M HNO3 and redry twice, then re-dissolve in 100 µl (3 drops) 8M HNO3 to equilibrate to uranyl nitrate anion complexes. For all of these steps don’t handle the dried sample beakers – add drops of acid directly to sample beaker on the hot plate to make sure the small flake of sample doesn’t fly away due to static. Then swirl acid in beaker to pick up the sample.

*First pass*

load sample 100 µl 8M HNO3 3 drops - discard

rinse matrix dropwise 100 µl 8M HNO3 3 drops - discard

rinse matrix in bulk 150 µl 8M HNO3 5 drops - discard

rinse matrix in bulk 300 µl 6M HCl 10 drops - collect for Th?

rinse matrix in bulk 300 µl 6M HCl 10 drops - collect for Th?

**elute U 400 µl MQ-H2O 14 drops – collect U!**

Dry U cut, then add 3 drops 8M HNO3 to equilibrate to uranyl nitrate anion complexes; again, add the acid via dropper bottle directly to sample beaker on the hot plate to make sure the small flake of sample doesn’t fly away due to static. Then rigorously swirl acid in the bottom of the sample beaker to make sure you’ve picked up sample in the solution.

Wash columns with 300 µl (10 drops) of MQH2O, and then re-equilibrate with 250 µl (8 drops) of 8M HNO3

*Second pass*

load sample 100 µl 8M HNO3 3 drops

rinse matrix dropwise 100 µl 8M HNO3 3 drops

rinse matrix in bulk 150 µl 8M HNO3 5 drops

rinse matrix in bulk 300 µl 6M HCl 10 drops

rinse matrix in bulk 300 µl 6M HCl 10 drops

**elute U 400 µl MQ-H2O 14 drops – collect U!**

Dry the U cut with 1 ”microdrop” of 0.05N H3PO4 on hotplate under laminar flow

## Th separation for all minerals

Column (Th): 50 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom)

Dry wash from Pb column, add 1 drop 8M HNO3 and redry

Add 3 drops 8M HNO3 to equilibrate to Th(NO3)62- ions

Clean columns 2 x full reservoir MQ H2O

Equilibrate columns 250 µl 8M HNO3 8 drops

Load sample 100 µl 8M HNO3 3 drops - save for Hf

Rinse matrix dropwise 100 µl 8M HNO3 3 drops - save for Hf

Rinse matrix in bulk 300 µl 8M HNO3 10 drops

Rinse matrix in bulk 300 µl 8M HNO3 10 drops

**Elute Th 400 µl 6M HCl 14 drops**

## dry the Th cut with 1 ”micro”drop of 0.035M H3PO4 on hotplate under laminar flowLu-Hf separation for zircons (milli-columns)

column: ~1 ml resin volume, e.g. 0.5 cm i.d. x 5 cm, >5 ml reservoir

resin: AG50W-X8, 200-400 mesh, H+ form (Eichrom or Biorad)

### sample prep:

If spiking, weigh into savillex beaker (preferable round bottomed)

Add zircon wash from U-Pb anion column + 0.5 ml of 6M HCl + a few drops of conc HF

Flux for several hours or overnight on warm hotplate

Dry down sample, and redissolve in 300 µl of 1M HCl-0.1M HF

### column chemistry: (takes about 3-4 hours)

Equilibrate 3 ml 1M HCl-0.1M HF

Load sample & collect Hf 300 µl 1M HCl-0.1M HF

Collect Hf 5 ml 1M HCl-0.1M HF

Wash column 2 ml 2.5M HCl

Collect Lu 5 ml 6M HCl

### column cleanup:

5 ml2M HF

5 ml 6M HCl

5 ml MQH2O

store in bottle of ~0.3M HCl

Hf cut is dried down, a drop of conc HNO3 + a drop of 30% H2O2 are added and sample redried to a small (near-invisible) spot. This can be redissolved in 1M HNO3-0.05M HF for analysis by MC-ICPMS (I like to add about 0.5 ml 1M HNO3-0.05M HF the night before to let the sample completely dissolve – with a 50 µl/min nebulizer a 50-ratio, 5-sec integration cycle analysis uses about 1.2 ml of solution).

If sample is spiked, the Lu cut can be dried down, a drop of conc HNO3 + a drop of 30% H2O2 added and sample redried, then either diluted for mass spectrometry or redissolved in 2.5M HCl for loading onto HDEHP columns for removal of Yb.

## Lu-Hf separation for zircons (micro-columns)

column: ~100 µl resin volume, e.g. 0.2 cm i.d. x 1 cm, ~3 ml reservoir

resin: AG50W-X8, 200-400 mesh, H+ form (Eichrom or Biorad)

### sample prep:

if spiking, weigh into savillex beaker (preferable round bottomed)

add zircon wash from U-Pb anion column + 0.5 ml of 6M HCl + a few drops of conc HF

flux for several hours or overnight on warm hotplate

dry down sample, and redissolve in 100 µl of 1M HCl-0.1M HF

### column chemistry:

Equilibrate 1 ml 1M HCl-0.1M HF

Load sample 100 µl 1M HCl-0.1M HF (immediately collect for Hf)

Elute Hf 1 ml 1M HCl-0.1M HF (also collect for Hf)

Wash column 500 µl 2.5M HCl

Elute Lu 1 ml 6M HCl

### column cleanup:

2 ml2M HF

2 ml 6M HCl

2 ml MQH2O,

store in bottle of ~0.3M HCl

Hf cut is dried down, a drop of conc HNO3 + a drop of 30% H2O2 are added and sample redried to a small (usually near invisible) spot. This can be redissolved in 1M HNO3-0.05M HF for analysis by MC-ICPMS (I like to add about 0.5 ml 1M HNO3-0.05M HF the night before to let the sample completely dissolve – with a 50 µl/min nebulizer a 50-ratio, 5-sec integration cycle analysis uses about 1.2 ml of solution).

If sample is spiked, the Lu cut can be dried down, a drop of conc HNO3 + a drop of 30% H2O2 added and sample redried, then either diluted for mass spectrometry or redissolved in 2.5M HCl for loading onto HDEHP columns for removal of Yb.

## U separation from terrestrial waters

column: 50 µl resin volume, AG1-X8, 200-400 mesh, Cl- form (Eichrom or Biorad)

chemistry calibrated in drops from 30ml Teflon dropper bottles, each drop approx. 30 µl

**Sample prep:**

Dry down ~100 ml of water in a 120 ml Savillex jar on a 120°C hotplate.

Redissolve residue in 0.5 ml conc. HNO3 + 0.5 ml 30% H2O2 and redry.

Redissolve in 150 µl 6M HCl (e.g. 5 drops) to convert to UO2Cl3- and UCl62- ions; if necessary centrifuge sample to load only supernatant onto columns

**Column prep:**

Remove columns from 4N HNO3 bath, rinse outside with MQH2O

Fill and empty column 3x with MQH2O

Fill column with MQH2O and slurry in resin

Adjust resin volume to fill column with a convex-up surface projecting into reservoir

Clean columns full reservoir 8M HNO3

Clean columns full reservoir MQ H2O

Clean columns full reservoir 6M HCl

Clean columns full reservoir MQ H2O

Equilibrate columns 250 µl 6M HCl8 drops

**U Column chemistry: may need two passes**

Load sample 100 µl 6M HCl 3 drops - save for Sr

Elute matrix dropwise 150 µl 6M HCl 5 drops - save for Sr

Elute matrix in bulk 400 µl 6M HCl 14 drops

\*Elute Fe3+ 150 µl 8M HNO3 5 drops

Elute U 250µl MQ H2O 8 drops

†Dry the U cut with 1 ”micro”drop of 0.035M H3PO4 on hotplate under laminar flow

*\* For oxidized surface waters this analyte may be present, co-adsorb as FeCl4-, and elute with U in HCl media, interfering with subsequent mass spectrometry. Fe3+ does not form nitrate anion complexes and so can be eluted in 8M HNO3, however U is only weakly adsorbed in this media [as UO2(NO3)42-, KD~16], hence care should be taken in the amount of 8M HNO3 elution to avoid U breakthrough.*

*† If upon drying down the sample is NOT a clear, colorless to yellow bead of phosphoric acid, redissolve and repeat the column procedure.*

**Mass Spectrometry:**

Redissolve sample spot with 2 µl 1M HCl.

Load 3 µl dilute colloidal graphite solution (1 part Ted Pella graphite to 6 parts MQ H2O) onto the center of a single zone-refined Re filament.

Load sample in 2 µl 1M HCl onto top of graphite, air dry.

Slowly warm filament up to about 2.7A, or until residual H3PO4 fumes off and a very and dull glow appears.