## Primary cation separations

AG 50Wx8 resin (200-400 mesh)

5.65 mL resin volume; 6 mm i.d. x 20 cm height in MQH2O

#### Sample prep:

Dry down dissolved sample in 6M HCl

Re-dissolve in 5 mL 0.1M HF-1M HCl overnight

Transfer to clean 15mL centrifuge tube, centrifuge for 10 minutes

#### Column prep:

Back-wash column with syringe and MQH2O

Condition column with 10 mL 0.1M HF-1M HCl

#### Column chemistry:

Load sample in 5mL 0.1M HF-1M HCl and collect this fraction (Hf)

Collect additional 5 mL 0.1M HF-1M HCl (Hf)

Wash 12 mL 2.5M HCl

**Collect 8 mL 2.5M HCl (Rb ... plus some Ca and K)**

Wash 12 mL 2.5M HCl

**Collect 12 mL 2.5M HCl (Sr)**

Collect 12 mL 2.5M HCl (Lu-Yb)

Wash 12 mL 2.5M HNO3 (selectively elutes Ba)

**Collect 14 mL 6M HCl (Sm-Nd)**

#### Column clean-up:

Clean this column with 2 x 55 ml of 6M HCl

#### Now what?

Rb fraction: Dry using heat lamp and 100°C hotplate. When dry, add a drop of conc HNO3 + a drop of H2O2 and dry again. Then either prepare for Rb clean-up column, or add ~100 µl conc HF, and dry again completely (to precipitate any residual alkaline earths) to ready for mass spectrometry.

Sr fraction: Dry using heat lamp and 100°C hotplate. When dry, add a drop of conc HNO3 + a drop of H2O2 and dry again. Sr is ready for mass spectrometry or for further clean-up with Sr-spec resin.

Lu fraction: Dry using heat lamp and 100°C hotplate. When dry, add a drop of conc HNO3 + a drop of H2O2 and dry again. Lu is ready for clean-up column.

Sm-Nd fraction: Dry using heat lamp and 100°C hotplate. When dry, add a drop of concentrated HNO3 + a drop of H2O2 and dry again. Sm and Nd are ready for further separation.

Hf fraction: Add 1 drop HClO4 to Hf fraction before drying. Dry using heat lamp and 100°C hotplate to a yellowish gel. Add several drops of conc HCl and redry, then repeat to yield a whitish-yellow granular solid which dissolves readily in 5mL 2.5M HCl, which is the loading acid for the Hf clean-up columns.

## Rb clean-up by cation exchange

AG 50Wx8 resin (200-400 mesh)

3 mL resin volume; 6 mm i.d. x 10.5 cm height in 0.6M HCl

#### Theory:

Na (D=13) will wash through column; Ti/Fe/Mg/Ca (D=71-362) will stick to column; K,Cs,Rb (D=26-35) are eluted together

#### Sample prep:

Re-dissolve Rb aliquot from primary cation separation in 0.5 mL 0.6M HCl overnight, ***off of hot plate***

If necessary, transfer to clean 1.5 mL centrifuge tube, centrifuge for 10 minutes

#### Column prep:

Back-wash column with syringe and MQH2O

Condition column with 10 mL 0.6M HCl

#### Column chemistry:

Load sample

Wash 0.5 mL 0.6M HCl

Wash 0.5 mL 0.6M HCl

Wash 50 mL 0.6M HCl

Collect Rb in 20 mL 0.6M HCl

Dry down sample with 1 microdrop 0.1N H3PO4

Add 1 drop 16M HNO3 + 1 drop Ultrex H2O2 to sample “dot” and redry

Ready for mass spectrometry

#### Column clean-up:

Clean this column with 2 x 55 ml of 6M HCl

## Sr clean-up by Sr-spec crown ether resin

Sr spec 50-100 µm resin

50 or 100 µL column volume (same recipe for either)

#### Column prep:

Remove columns from storage bath to rinse tub, rinse 2x with MQH2O

Fill each column from bottom with MQH2O squirt bottle and flick out liquid 3x

Slurry resin into columns and level resin to the top of the column with pipette

Clean column: 3 x reservoir, MQH2O

Equilibrate column: 500 µL (17 drops), 3.5N HNO3

#### Sample prep:

Re-dissolve sample in 0.5 mL (17 drops) 3.5M HNO3

Pipet sample into clean 2mL centrifuge tube and spin for 5 minutes

#### Column chemistry: (reagents dispensed from 30 ml dropper bottles)

load (liquid) sample: 500 µL (17 drops), 3.5N HNO3

dropwise rinse: 3 drops, 3.5N HNO3

wash column: 300 µL (10 drops), 3.5N HNO3 collect all loading, rinse,

wash column: 300 µL (10 drops), 3.5N HNO3 and wash steps for U

wash column: 300 µL (10 drops), 3.5N HNO3 chemistry if needed

wash column: 300 µL (10 drops), 3.5N HNO3 (e.g. water samples)

elute Sr: 500 µL (17 drops), MQH2O

elute Sr: 300 µL (10 drops), MQH2O

Dry down sample with 1 microdrop 0.1N H3PO4

Add 1 drop 16M HNO3 + 1 drop Ultrex H2O2 to sample “dot” and redry

Ready for mass spectrometry

#### Column clean-up:

Rinse resin from columns (3x) and store

## Sm-Nd separation by HDEHP reverse phase chromatography

#### Theory:

Nd, Sm and other REE can be selectively eluted in dilute HCl medium on HDEHP-coated resin (Eichrom Ln-spec, Pin and Zalduegui, 1997)

#### Columns:

Eichrom Ln-Spec resin (50-100 µm)

Savillex PFA columns 4 mm i.d. x 10 cm height in 0.18M HCl (1.25 mL resin volume)

#### Sample prep:

Redissolve REE fraction from primary cation column in 1 drop (30 µl) of 6M HCl.

Carefully redry and then immediately dilute this with 200 µl 0.18M HCl and let sit at room temperature for at least an hour to equilibrate. There may be some solid residue after redissolving in 0.18M HCl—most likely this is resin, and should be left behind on loading. Many poor separations result from loading solids onto the column, causing tailing of Ce and Pr into the Nd cut, and worse Nd into the Sm cut…

Make sure to load the sample directly onto the top of the resin, not onto the side of the column. Don’t disturb the resin bed.

After loading, the sample beaker can be fluxed (closed) with 2-3 mL 6M HCl on a hotplate, emptied, and used to collect Sm. Use a clean beaker to collect Nd.

#### Column prep:

Wipe down the work area and column supports thoroughly with wet Durx wipes. Remove the SmNd columns from their 0.18M HCl bath, and place into the column supports. Clean the columns with 1 ml 6M HCl, followed by 1 ml MQH2O, then equilibrate the columns with 5 ml 0.18M HCl.

#### Column chemistry:

load sample: 200 µL, 0.18M HCl

wash column: 3 x 100 µL, 0.18M HCl

wash column: 10.5 mL, 0.18M HCl

**elute and collect Nd: 4 mL, 0.3M HCl**

wash column: 2 mL, 0.3M HCl

**elute and collect Sm: 5 mL, 0.4M HCl**

Dry down sample with 1 microdrop 0.1N H3PO4. Then add 1 drop conc HNO3 + 1 drop Ultrex H2O2 to sample “dot” and redry. Now ready for mass spectrometry.

#### Column clean-up:

Clean column: reservoir, 6M HCl (can drip overnight with caps on loosely)

Equilibrate column: 5 ml, 0.18M HCl

Rinse outsides of columns with MQH2O

Store column in holder in large 4L beaker of 0.18M HCl

## Hf clean-up by HDEHP (Ln-spec)

column: 1 ml resin volume, ~3.8 cm (length) x 0.6 cm (i.d.), >50 ml reservoir

resin**\***: LN-spec, 100-150 µm, H+ form (Eichrom) **(\*discard after ~12 uses)**

**sample prep for chemistry:** add 1 drop HClO4 to primary columnHf elution and dry down to thick gel

 add 6 drops conc HCl to sample, dry down; repeat a second time

 redissolve sample (now usually white, granular) in 5 ml 3M HCl, ideally

 overnight

#### Column chemistry: (takes about 4-5 hours)

Equilibrate 5 ml 3M HCl

Load sample 5 ml 3M HCl **(Hf cut from primary column)**

Rinse matrix 10 ml 3M HCl

Rinse matrix 10 ml 6M HCl **(residual HREEs eluted)**

Wash out HCl 2 + 2 ml MQ H2O

Stepwise rinse Ti 5 + 5 ml 0.09M HCit–0.45M HNO3-1wt.% H2O2

Stepwise rinse Ti 5 + 5 ml 0.09M HCit–0.45M HNO3-1wt.% H2O2

Bulk rinse Ti 40 ml 0.09M HCit–0.45M HNO3-1wt.% H2O2

Wash out H2O2 5 ml 0.09M HCit–0.45M HNO3

Rinse residual Ti/HCit 20 ml 6M HCl-0.06M HF **(~1/3 of Zr eluted)**

Elute Hf 8 ml 6M HCl-0.4M HF

*(Note: there is no quantitative breakthru of Hf in either 6M HCl or HCit-HNO3-H2O2 mixtures, so for high-HREE (phosphates) or Ti matrices (rutile, sphene) can increase those washes respectively)*

#### Column cleanup:

10 ml1M HF

10 ml 6M HCl

10 ml MQH2O,

backwash with MQH2O and store in bottle of ~0.3M HCl

**sample prep for mass spec:** dry down Hf elution on hot plate under heat lamp

 add 1 drop conc HNO3 + 1 drop H2O2, dry down to destroy organics

 redissolve in 1-2 ml 1M HNO3-0.05M HF, ideally night before analysis

**reagent recipes:**

 0.09M HCit – 0.45M HNO3 6M HCl – 0.4M HF 6M HCl – 0.06M HF

 12 ml 1.8M HCit 225 ml 12M HCl 225 ml 12M HCl

 12 ml 9M HNO3 6 ml 29M HF 1 ml 29M HF

 216 ml MQH2O 227 ml MQH2O 233 ml MQH2O

 0.09M HCit – 0.45M HNO3 – 1wt% H2O2 1.8M HCit

 18.75 ml 1.8M HCit 172.85 g anhydrous HCit

 18.75 ml 9M HNO3 dissolved to 500 ml soln

 12.5 ml 30% H2O2 with MQH2O

 325 ml MQH2O

## Lu clean-up by HDEHP (Ln-spec)

#### Theory:

Lu and Yb can be selectively eluted in dilute HCl medium on HDEHP-coated resin (Eichrom Ln-spec, Pin and Zalduegui, 1997)

#### Columns:

Ln spec (50-100 µm)

Savillex PFA columns 4 mm i.d. x 10 cm height resin bed (1.25 ml resin volume)

#### Sample prep:

Dry the HREE fraction from primary columns using heat lamp and 80°C hotplate.

When dry, add a drop of conc HNO3 + a drop of H2O2 and dry again.

Redissolve sample in 100 µL 2.5M HCl.

#### Column prep:

Rinse outside of columns with MQ, and place in stand.

Equilibrate columns with 3 mL 2.5M HCl

#### Column chemistry:

Load sample in 100 µL 2.5M HCl

Wash column 3 x 100 µL 2.5M HCl

Wash column 30 mL 2.5M HCl (washes away most of the Yb)

Elute Lu in 6 mL 6M HCl

Dry down sample

Add 1 drop 16M HNO3 + 1 drop Ultrex H2O2 to sample “dot” and redry

Ready for mass spectrometry

#### Column clean-up:

Clean columns with 5 mL 6M HCl

Equilibrate with 3 mL 0.18M HCl, leaving a little liquid in the reservoir

Store in 0.18M HCL.

#### Notes:

This procedure removes a large portion of the Yb that elutes off the primary column concurrently with Lu. The goal is to reduce the 173Yb/175Lu ratio to between 0.05 and 0.1, which gives you enough Yb to run accurately for a good fractionation correction, but not so much that the 176Yb interference is too great a correction.

Because of the slow drip nature of these columns, the procedure requires >12 hours. Consider preparing columns and loading samples in the afternoon. For example, the 30 mL of 2.5 N HCl can drip overnight. Next morning, you can elute the Lu fraction, and clean the columns. Drip rate approximately 1 mL in 20 minutes.

## Lu-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: (takes about 3-4 hours)

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:

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, and air dry.

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

## Pb separation by anion exchange in dilute HBr medium

column: 100 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 dissolved samples in 6M HCl to salts on 120°C hotplate
Redissolve in 1 ml 0.5M HBr and redry carefully (HBr likes to spatter)

Redissolve in 1 ml 0.5M HBr to convert to PbBr42-; if necessary, centrifuge in clean 2ml centrifuge tube prior to loading supernatant.

#### Column prep:

Remove columns from acid 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 MQH2O

Clean columns 3 x full reservoir 6M HCl

Wash columns 300 µl MQH2O 10 drops

Equilibrate columns 300 µl 0.5M HBr 10 drops

#### Primary separation:

Load sample 1 ml 0.5M HBr

Elute matrix dropwise 100 µl 0.5M HBr 3 drops

Elute matrix in bulk 1 ml 0.5M HBr 34 drops

Elute matrix in bulk 1 ml 0.5M HBr 34 drops

Elute matrix in bulk 500 µl 1M HCl 17 drops

Elute Pb 1 ml 6M HCl 34 drops

Clean columns full reservoir 6M HCl

Wash columns 300 µl MQH2O 10 drops

re-equilibrate columns 300 µl 0.5M HBr 10 drops

dry Pb cut, add 100µl (3 drops) 0.5M HBr and redry

redissolve in 100µl (3 drops) 0.5M HBr to convert to PbBr42-

#### Secondary purification (if necessary, e.g. whole rocks, ores):

load sample 100 µl 0.5M HBr 3 drops

elute matrix dropwise 100 µl 0.5M HBr 3 drops

elute matrix in bulk 500 µl 0.5M HBr 17 drops

elute matrix in bulk 500 µl 0.5M HBr 17 drops

elute Pb 1 ml 6M HCl 34 drops

Dry down sample with 1 microdrop 0.1N H3PO4; turn down hotplate to just warm, add 1 drop 16M HNO3 + 1 drop Seastar H2O2 to sample “dot” and redry gently (peroxide tends to bubble vigorous if overheated); add 1 drop of 6M HCl to the sample “dot” and redry; now ready for mass spectrometry.

## Ce separation from REE by selective oxidation and solvent extraction

(Rehkamper et al., 1996, Chem. Geol., 129:201-208)

#### Preparation of reagents:

1 10 M HNO3: make this up by diluting concentrated HNO3. The actual molarity is not critical, as long as it is approximately 10 M. Assume that concentrated, singly distilled HNO3 is 15 M.

2. Both the sodium bromate and the HDEHP solution have a finite shelf life (approximately 1 week). Make up small quantities as needed. The actual concentrations of these solutions does not have to be precise, as long as the bromate solution is 5 mM or greater, and the HDEHP is 0.3M or greater.

3. To make up 10 mL of sodium bromate solution: weigh out 7.55 mg of NaBrO3, and add it to 10 mL of 10M HNO3.

4. To make up 10 mL of 0.3M HDEHP solution: weigh out 0.9673 g of HDEHP, and add it to 10 mL of n-heptane

#### Procedure:

1 Convert Nd sample (or REE concentrate) to nitrate salt by drying down TWICE with 5-6 drops conc. HNO3

2 Re-dissolve sample in 100 µL 10M HNO3, transfer to acid-cleaned 1.5 mL centrifuge tube; reflux empty savillex beakers on hot plate with 6M HCl

3 Add 500 µL freshly prepared 5mM NaBrO3 - 10M HNO3 to sample; let stand for 5 minutes

4 Add 500 µL freshly prepared 0.3M HDEHP - n-heptane to sample and cap centrifuge tube

5 Shake sample for 2 minutes; allow to separate

6 Pipette off the less dense organic phase; if Ce isotopic analysis is desired, save; otherwise discard

7 Repeat steps 4 through 6

8 Add 500 µL n-heptane to sample (to remove residual HDEHP)

9 Shake sample for 2 minutes; allow to separate

10 Pipette off the n-heptane; discard

11 Repeat steps 8 through 10

12 Pipette the aqueous phase to a savillex beaker (leave approx. 20 µL in centrifuge tube - this should contain the residual organic film at the top of the aqueous phase)

13 Dry down the aqueous solution; add 3 drops conc. HNO3 + 3 drops H2O2 and dry down to destroy organics

14 Convert to chloride and destroy residual bromate by drying down 2 X with 3 drops 6M HCl

15 Re-dissolve sample in 250 µL 2M HCl, prepare for cleaning on 1 cm3 cation columns (if previously purified Nd, to remove Na); or take up sample in 1 drop 0.1M HCl for loading onto Nd a-HIBA columns (?)

##