Strontium Separation Procedures

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Radiogenic Isotope

UA Sr Chromatography

Sr Sample prep/Dissolution* for Non-silicates e.g. carbonates (adapted from UNC)

Supplies: Scale, weigh paper, gloves, dropper bottle of 3.5M 2X HNO_3, Savillex vial, and a microscope.

Fold the weigh paper before putting it on the scale. Place weigh paper onto the scale, after the scale has settled hit the tare button. Tare the scale, then weigh out between 2 to 5 mg of sample. If you do not have a lot of sample, weigh between 2-3 mg in case you need to run the sample again. If your samples are powder, static electricity can make it difficult. Reduce static by filling a few beakers with water and placing them near the scale. Gently pour the sample into the Savillex vial and add 550 uL of 3.5M HNO_3, ca. 15 drops from the dropper bottle. Cap and let stand overnight. Use a microscope to determine how much sample has dissolved.

Sr Columns

Supplies: gloves, waste cup, dropper bottle of 3.5N 2X HNO_3, dropper bottle of Nanopure H_2O, dropper bottle of 0.1 M H_3PO_4, Sr spec resin bottle, Nanopure H_2O squirt bottle, small **glass** column (**very fragile-handle with care**), column stand, elution form.

Sr Chromatography is used to separate the Sr cations from other ions in the sample. This is an on-off column, which means that unlike Nd columns the timing of the collection stage is not critical because there are no similar cation (other REE) peaks before or after the Sr elution. The sample is dissolved in 3.5M HNO_3 because at this molarity, Sr strongly partitions to the resin and other ions do not. Figure 1 shows the distribution coefficient plotted against HNO_3 molarity (Chiarizia et al 1992). Note that at 3.5 M, the D value for Sr is considerably higher, and that the D value for other cations is decreasing.

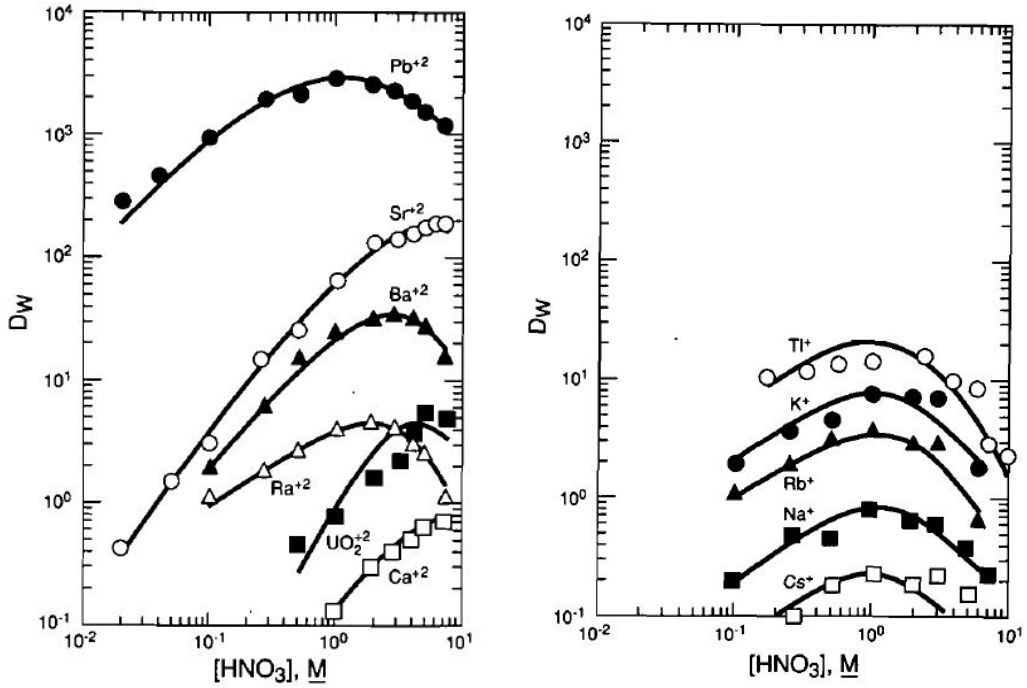

Figure 1. Weight Distribution coefficients for selected cations plotted against HNO_3 molarity. At 3.5 M the D values for other cations are decreasing whereas the D value for Sr is increasing.

Column Set-up:

The columns are stored in Nanopure H_2O in a Teflon beaker covered with plastic wrap to keep clean shown in Figure 2. These are **glass** columns and **very fragile-handle with care!!!** Use the Nanopure H_2O from the squirt bottle to rinse the inside and outside of the column over a plastic tub in the sink or over a large beaker. Rinse each column out with Nanopure H_2O three times. Start by squirting water in through the bottom of the column until the skinny neck of the column is filled with water. Then flip the column over and fill the reservoir with water and let it run out. After rinsing the column 3 times, use a plastic rod to push a frit** from the reservoir down to the end of the column. Make sure the bottom of the frit is even with the bottom of the column. Fill the column with water and check that it is draining correctly with no air bubbles as this will cause the column to stop. If there is an air bubble, expel the bubble by squirting water in through the bottom of the column until the skinny column is filled with water (Figure 3). Then flip the column over and fill the reservoir (Figure 4). Place the column over a waste cup on the stand. Before the water drains from the reservoir, put resin into the column by dropper bottle or pipetting. It is important that you get the resin to the desired level before the water drains out of the reservoir, as this will result with an air bubble in the neck of the column and will prevent the column from functioning. The desired height of the resin bed is at the top of the neck. This is important because if it is lower than the top surface tension, air bubbles will be trapped on top of the resin each time that liquid is added. If you have this problem, the best method is to use the 20-200 uL pipettor and suction out the air bubble each time that you put anything on the column as needed.

Sr Elution:

1. Rinse the column with Nanopure H_2O twice. Using the Nanopure H_2O squirt bottle fill the reservoir with water. This rinse removes any residual Sr that may be in the resin. While Sr partitions to the resin when in a 3.5 M HNO_3 solution, Sr strongly partitions to water over the resin. Prepare your samples by centrifuging to remove any solids leftover from dissolution.

2. After the water has completely drained, precondition the columns with 3.5 M HNO_3.

3. Load the samples on to the columns using a 100-1000 uL pipettor. When pipetting the sample out of the centrifuge tube, avoid solid material at the bottom.

4. After loading, you will do several rounds of bulk rinses with 3.5 M HNO_3. These rinses remove other Ions leaving Sr in the resin. After the final bulk rinse, ensure that all of the columns have completely drained.

5. Uncap the clean Savillex vials and place them under the columns to elute Sr with Nanopure H_2O. After elution, add one drop of 0.1 M H_3PO_4 directly into the sample vial. After adding the H_3PO_4, place the samples uncapped on hotplate at ~120-140°C to dry down. The sample will dry down into a small clear, brown, or black bead at the bottom of the vial. After dry down, remove from hotplate and cap. The samples are now ready for loading on Re filaments.

Clean up

1. After finishing, wash the columns out using Nanopure H_2O. Start by squirting the water in through the bottom of the column and dump the resin/water into an empty waste cup. Remove frit with plastic rod and discard. For each column, rinse three times and then place in a Teflon beaker filled with Nanopure H_2O. ***Dispose of the waste in the resin waste container. Clean the plastic rod by rinsing several times with Nanopure H_2O, wiping with 2 M 2X HCl on Kimwipe, rinse with Nanopure H_2O twice, and return to drawer.
2. After this, wipe down the work-station with Nanopure H_2O and Kimwipes and make sure all supplies are put away in the appropriate spot.
3. Carefully rinse columns with Trace Metal 2 M HNO_3. Then soak in Trace Metal 2 M HNO_3 for no more than 30 minutes in the Teflon beaker loosely covered with plastic wrap.
4. Rinse columns with Nanopure H_2O and place over a waste beaker on rack. Optional-Rinse with Trace Metal 6 M HCl.
5. Rinse with Nanopure H_2O: 3 times – inside and out.
6. Soak in 2x 2 M HCl at least 3 hours in the Teflon beaker loosely covered with plastic wrap.
7. With columns on rack, rinse 3 times in Nanopure H_2O.
8. Store columns in Teflon beaker filled with Nanopure H_2O and cover with plastic wrap.
9. Rinse 3 times with Nanopure H_2O before loading resin.

***For silicate rocks** follow the instructions for "Rock and Mineral dissolution" pages 11-12 in Sm-Nd Sample and Isotope Lab Techniques . See in Appendix at end of this procedure

****Cutting Frits**

1. Use DBGM (German) leather hole punch set on 2.0 mm and porous poly 0.125^{mm}T, 10^{mm} x10^{mm}, and 90-130 µm.
2. Trim frit with Xacto knife prior to pushing out of punch with plastic rod.
3. Roll carefully in fingers after removal to obtain even cylinder.

***Before adding more resin waste to the waste container, decant as much liquid off the top as possible and discard in sink.

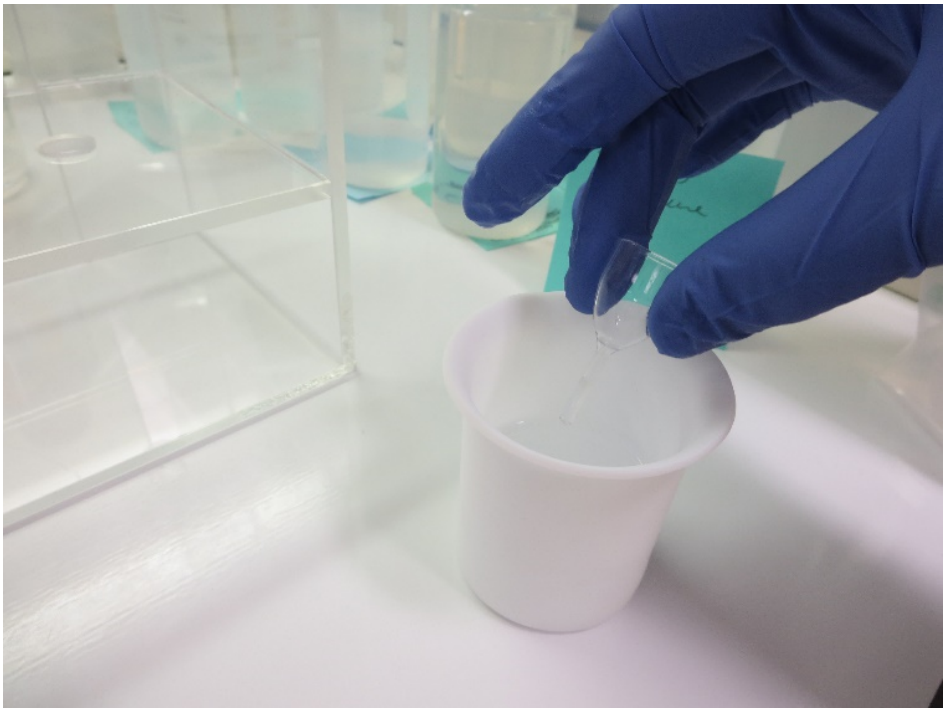

Figure 2. Glass columns are stored in Nanopure water in a Teflon beaker.

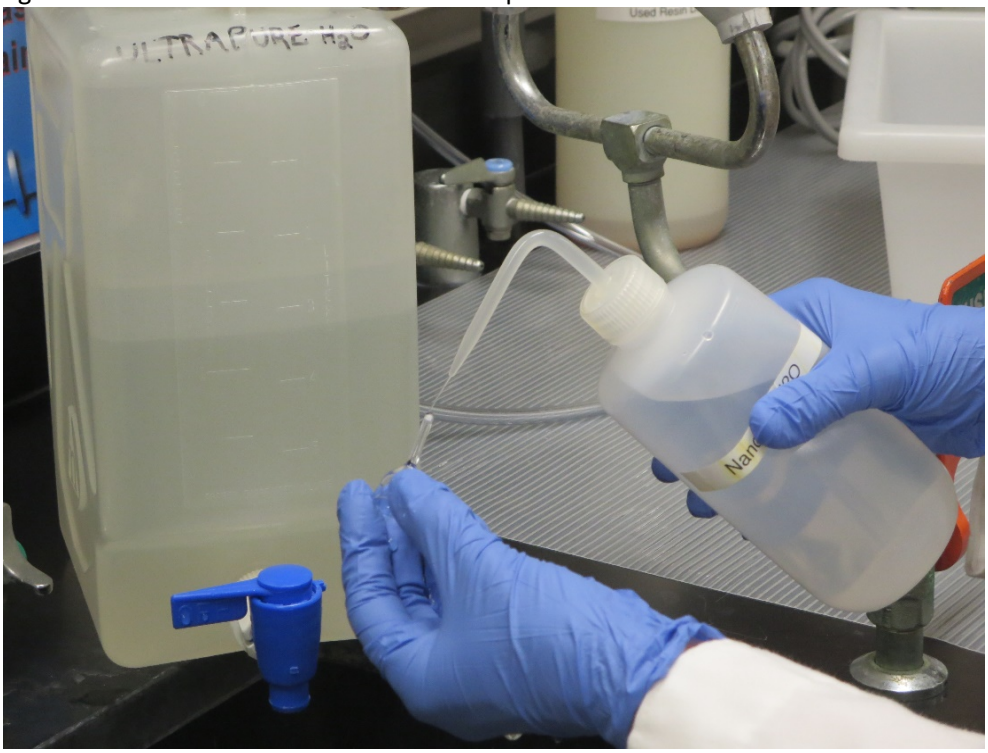

Figure 3. If there is an air bubble, expel the bubble by squirting water in through the bottom of the column until the skinny column is filled with water.

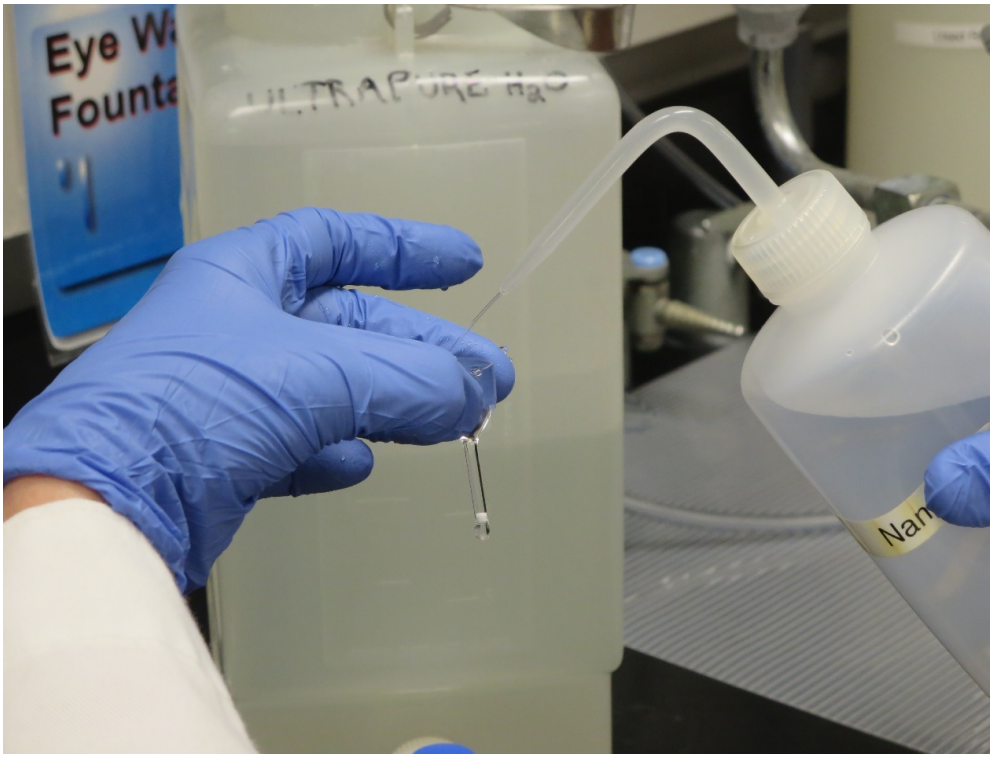

Figure 4. After expelling the air bubble and filling the skinny column with water, flip the column over and fill the reservoir.

Appendix

Rock and Mineral Dissolution **(**adapted from "Rock and Mineral dissolution" pages 11-12 in Sm-Nd Sample and Isotope Lab Techniques)

Introduction: Silicate minerals, particularly, difficult to dissolve. In general, strong and/or corrosive acid is required. We generally use **HF which is very dangerous acid**. HF will produce **very dangerous burns** [on skin, lung, or digestive system] that will continue until the acid is stopped by reaction with Ca [do not let this happen on your bones]. Perchloric acid may also be used for leaching and dissolution. This acid is **extremely volatile and reacts violently with organics**. Both HF and Perchloric acid have specific requirements for safe use; therefore, they must be used in hoods and with containers designed specifically for them. BE 2067 has 1 HF and 1 Perchloric hood.

USE OF HF and Perchloric Acids REQUIRE TRAINING -- SEE STOWELL

Standard dissolution: HF and small amounts of nitric acid readily dissolve silicate minerals with or without a 'bomb' – a bomb will work much more quickly and is likely to do a better job on 'tough' accessory phases.
Sample Dissolution: (see Excel Sheets)
Dissolve 'finely' powdered samples in Teflon vials (SAVILLEX) placed on a teflon or ceramic top hot plate (T not critical ~80-120˚C). Periodically use ultrasonic cleaner to increase dissolution rate.

Dissolution comprises two steps:

- HF and HNO_3 mixture, and then HCl.

1. HF and HNO_3 solution is prepared from 7M HNO_3 and conc. HF.
Conc. (Optima) HNO_3 is between 12 & 14.5 M. A 7M solution is obtained from a 1:1 dilution with ultrapure water. HF & HNO_3 solutions are mixed to a 20:1 solution (volume) which, if the samples are small, can be made from 1 ml concentrated HF and ~10 drops of 7M HNO_3.
2. Heat sample [80-120ºC] overnight (or longer) in this solution with cap on.
3. Carefully remove cap and evaporate to dryness.
4. Add a few ml of 6 M HCl and heat overnight with cap on.
5. Remove cap and dry in evaporation box
6. Add a few ml of 12 M HCl and heat overnight with cap on.
7. Remove cap and dry in evaporation box
8. Add 2 M HCl

The later steps convert fluorides to chlorides and drive off silica. The evaporated chloride is dissolved in 2M HCl for the first [cation] column.

Use appropriate [garnet or rock] procedures sheet [Excel file]

Rock Dissolution

Cleaning
The sample material should be ground or cut to remove weathered material and ink/paint from sample numbers. The resulting sample should be cleansed with acetone prior to pulverization.

Pulverizing
Pulverize rock samples in the *ceramic* ring and puck mill [SPEX shatterbox] or for small samples use a clean agate mortar and pestle. The rock may be powdered finely; however, this may make weigh procedures tricky.

Weighing (see Weigh Sheet)
Carefully weigh ca. 150-200 mg.

Spiking
For Sr isotope dilution: Use ca. 40 ul of Sr 84 spike/100mg of rock
Sample Dissolution (see Excel Sheet)

HF Treatment
HF is extremely damaging to skin and flesh. Ca-gluconate is the best material for neutralizing HF and should be kept available next to workstations. This is generally in a light blue box/tube near the hood.

Locate Ca-gluconate prior to working with HF. Alternately, you can make your own…
Thoroughly mix 625 mg Calcium Gluconate with 25.36 g KY-Jelly.

Cleaning Eichrom SrSpec Resin (from UNC)

(Note: This must be done for new resin – resin is not reused as it retains too much Sr "memory.)

1. Put resin in Teflon bottle with MQ H2O – no more than about 1/10 of bottle volume should be resin. Fill bottle ~full with MQ H2O, shake well, and then put on hot plate at temperature of 50-60 degrees C. It helps a LOT if a squirt of 13M HNO3 is added to the bottle, although I don't do this to every wash -- perhaps 1/3 to 1/2 of them.

2. After the slurry has been on the hot plate for several hours you will note that there is quite a bit of resin that appears to be floating at the top of the bottle. This is because some of the resin is temporarily bound to air bubbles. Gently swirl the slurry to get rid of bubbles -- this will allow all of the resin to sink. You might have to do this twice, letting the slurry sit for at least 15 minutes between swirls.

3. After all resin sinks, I usually let it "cook" on hot plate overnight or for at least a few hours.

4. Next, carefully pour out almost all of the water. By pouring slowly, it is possible to dump out all but several mls of the water. The first few times this is done, you probably will lose a small amount of really fine resin -- this is okay, and is actually desirable. But, if it looks like you are about to pour out a lot of resin, stop pouring.

5. Add MQ water and (HNO3) and repeat steps 1 - 4, probably 15 - 20 times. (Thus, cleaning will take several weeks.)

6. Make a mark on Teflon storage bottle each time a wash is done.

7. Before resin is used, Sr blanks must be run to check level. (Put some of the resin in columns and pass solutions through them as though you are processing samples.) We routinely are well under 100 pg, usually 20 – 50 pg.

How to mix 0.1M H_3PO_4

Phosphoric acid properties:
MW = 97.995g/mol
Density = 1.69kg/L or 1690g/L
Molarity = 17.245778 mol/L
85% phosphoric acid in concentrated H_3PO_4 solution
M = mol/L

How much phosphoric acid do you need?
For 30 ml drop bottle:

1690g/L * 0.85 =1437g/L
1437g/L /97.995g/mol = 14.66mol/L

M1 * V1 = M2 * V2 Where M = Molarity and V = volume

V1 = M2V2/M1 = (0.1M)(30ml)/14.66M

V1 = 0.2046 ml of acid

How much nanopure water do you need?
Total volume will be 30 ml, so 30 ml - 0.205 ml of acid = 29.795 ml of nanopure water

1. Measure 29.795 ml of nanopure water into the clean 30 ml dropper bottle using a graduated cylinder and pipetter.

2. Then add the acid by pipetting 0.205 ml of Ultrex concentrated H_3PO_4 into the dropper bottle with the water.

Secure the cap and move the bottle upside down and back and forth to thoroughly mix the solution.