Sm-Nd Sample and Isotope Lab Techniques

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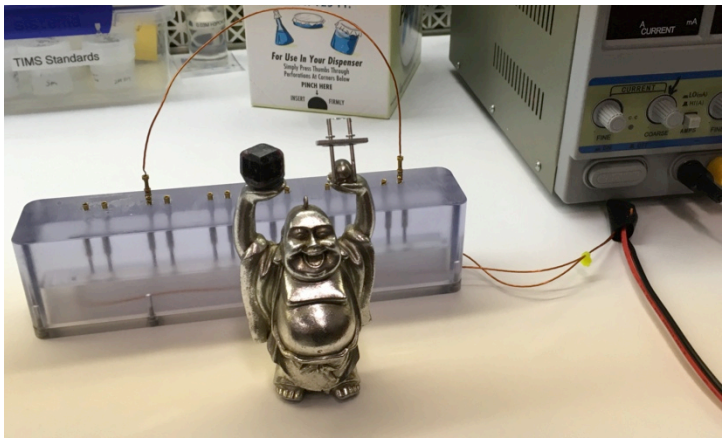
Metamorphic Studies

UA RadIs Lab

Radiogenic **Is**otope



Acknowledgments

The methods described here build on methods pioneered and refined by many people around the world. Some of these are published and many are not. My experience and development of these techniques rely particularly heavily on what I have learned from Steve Goldberg (formerly at UNC Chapel Hill), Drew Coleman (UNC Chapel Hill), and Ethan Baxter (Boston College). The initial setup and subsequent refinement of sample preparation and mass spectrometry at the University of Alabama would not have been possible without help from Elizabeth Bollen, Karen Parker, Matt Gatewood, Matt McKay, Gerrit Bulman, and Doug Tinkham.

Select References for Methodology

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Sm & Nd Isotope Procedure Outline

Solid sample preparation for Sm & Nd Isotopic Analysis
- This is not magic and there is no unique solution
- Think about your procedure and what you are trying to accomplish

Sample Selection & Mechanical Separation
- Evaluate textural evidence compatible with isotopic equilibrium
- Choose representative garnet and whole rock aliquots
- Chisels, drills, and micromills may be useful

Sample Cleaning
- Acetone
- Nanopure water
- Weigh on paper – Mettler AX Balance [see weights]

Garnet Leaching/Partial Dissolution
- Hydrofluoric and/or Sulfuric Acid

Note: all of the techniques below require very clean liquids and labware. UA uses ultrapure water, double distilled acids, carefully cleaned Savillex PFA labware, and custom blown silica columns for ion chromatography.

Dissolving Silicates
- Pulverize [see Grt diss OR rock diss]
- Garnet -use agate mortar & pestle [sample in water then centrifuge]
  - Sieve and/or Frantz
  - Acid leach [nitirc, sulfuric, hydrofluoric]
  - Weigh on paper - Mettler AX Balance
- Rock –use ring & puck mill/shatterbox
  - Weigh on paper - Mettler AX balance [see weights]
- Spike [mixed Sm&Nd 'B' basalt]
  - Garnet -70 ul/100 mg
  - Rock -200 ul/25 mg
  - Blank: 25 ul
- Weigh by difference in teflon vial - Mettler AT balance
- HF & HNO_3 in 15 ml Teflon - 20:1 by volume
- Evaporate
- Add HCl to convert Fluorides to Chlorides
- Evaporate
- Repeat as needed
- Centrifuge

Concentrating Elements: Ion Chromatography
- Bulk REE separation BioRad columns [see bulk REE elution]
- Sm & Nd separation α-HIBA columns [see Sm-Nd elution]
- Drive off α–HIBA

Add Freshly mixed Aqua Regia ± weak phosphoric
Evaporate
repeat until 'clean'
Dissolve in weak HCl*
Check filament loading procedure prior to choosing acid and molarity

Loading Filaments and TIMS

Nd oxide –in general NdO gives a more intense signal than Nd metal from the filament; therefore, this is preferred for low masses. Oxidation may be induced from the loading material TaO slurry and/or bleeding small volumes of O onto the filament. The RadIs lab uses TaO.

There are numerous oxide interferences and a very clean separation from adjacent REE is needed. α HIBA acid separation of the REE is generally preferred and used in the IsoPet and RadIs labs -UA.

Sm metal –in general Sm gives an intense, but short lived signal. Sm-Nd geochronology requires only modest precision. Therefore, the only significant concern is running quickly after reaching ionization temperatures.

Savillex MLA columns (no longer in use) in the UA Isotope Petrology (IsoPet) lab.

end of outline

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Solid sample preparation for Sm & Nd Isotopic Analysis

Introduction

Many Sm and Nd isotope analyses on minerals are produced for geochronology using the isochron method. Isochrons may be anchored by 2 or more isotopic values; however, less than three values on their own result in questionable ages. The best isochrons typically are anchored by 4 or more aliquots with large variations in $^{147}Sm/^{143}Nd$ values in order to produce the most precise isochrons/ages. These large variations in $^{147}Sm/^{143}Nd$ typically require more than one mineral and/or rock in equilibrium. Garnet has one of the highest Sm/Nd ratios for common minerals (e.g., Baxter and Scherer, 2013); therefore, it is ideal for constructing precise isochrons.

Garnet, other minerals, and the rock/matrix should be chosen from a single homogenous and unweathered layer that is likely to be in isotopic equilibrium. Garnet aliquots should be chosen to match the sample and the question at hand. In general, garnet cores, mantles, and rims from individual grains are desirable because this may provide growth duration (e.g., Stowell et al., 2001) or provide a range in $^{147}Sm/^{143}Nd$ values for a precise isochron. Small garnet grains (< 1 mm) generally cannot be separated into core, mantle, and rim samples due to the mass of sample required; however, >3 mm grains can be separated in ideal samples.

Garnet in pelitic rocks typically have higher Sm/Nd ratios than garnet in other rocks. As a result these rocks generally are somewhat more likely to produce a high precision isochron. Metabasites should be ok although they typically have lower Sm/Nd ratios and this can make precise isochrons more challenging.

It is generally best to identify and separate two or more distinct garnet morphologies! These can be core versus rim separates, inclusion-rich and inclusion-poor separates, euhedral and anhedral separates etc… Matrix aliquots should be obtained from near these grains. In general, it is also useful to try and date some rocks that only have one garnet type because in the other rocks equilibrium between garnet and other minerals could be complex.

All aliquot prep should be done with care to avoid contamination. Garnet typically has <5 ppm Sm and Nd; therefore, REE bearing inclusions and lab contamination can be problems. Phosphate minerals, epidote group, and zircon are particularly problematic and should be removed from garnet aliquots! Lab contamination is generally not a problem due to the relatively low REE contents in common manmade objects. However, Nd magnets should not be used in the lab.

Whole garnet are fine for starting, but core and rims of single grains are even better. If the grain has growth zoning then it may be possible to get growth duration. Even when this is not possible core and rim often have different Sm/Nd yielding a better isochron. We use a diamond core bit, micromill, or laser to obtain sections from wafers/slices of garnet grains.

Clean Garnet Separates

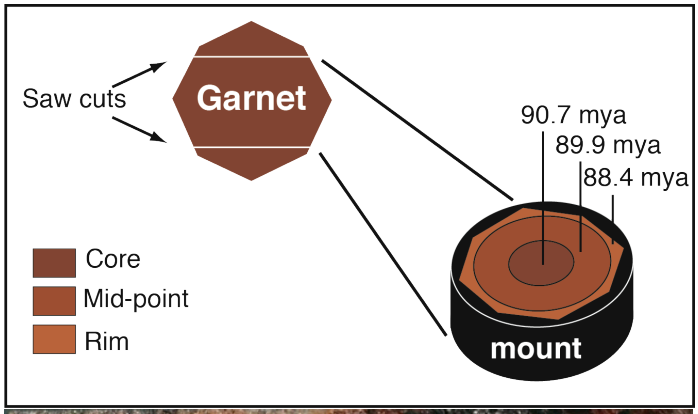
Sm-Nd geochronology requires construction of an isochron between minerals with high (e.g., garnet) and low Sm/Nd (e.g., rock minus garnet or pyroxene) ratios in order to obtain precise ages. Consider the textures and heterogeneity of your sample and then choose aliquots of garnet that are most compatible with isotopic equilibrium between this garnet and the adjacent mineral(s). Garnet often contains less than 1 ppm of Nd; therefore, contamination by matrix material and/or a small mass of inclusions containing REE [e.g., apatite, zircon, epidote, monazite, etc…] can negate obtaining a useful age. Techniques for obtaining clean garnet samples include hand picking grains from the rock, gravity separation [heavy liquids and water table], magnetic separation, hand picking in alcohol [to maximize optics] with a microscope, and leaching in acid to remove those mineral phases more readily dissolved than garnet.

When large garnet grains are targeted for geochronology, multiple aliquots should be obtained from individual grains. These should be separated by radial position from the core and/or by chemical zonation (e.g., Stowell et al., 2001; Dragovic, et al., 2015).

A. Drilling garnet with diamond core drill, water chuck, and drill press. B. Garnet aliquots for a large grain from Garnet Ledge, AK (modified from Stowell et al., 2001). C. Laser milling New Zealand garnet.

A.

B.

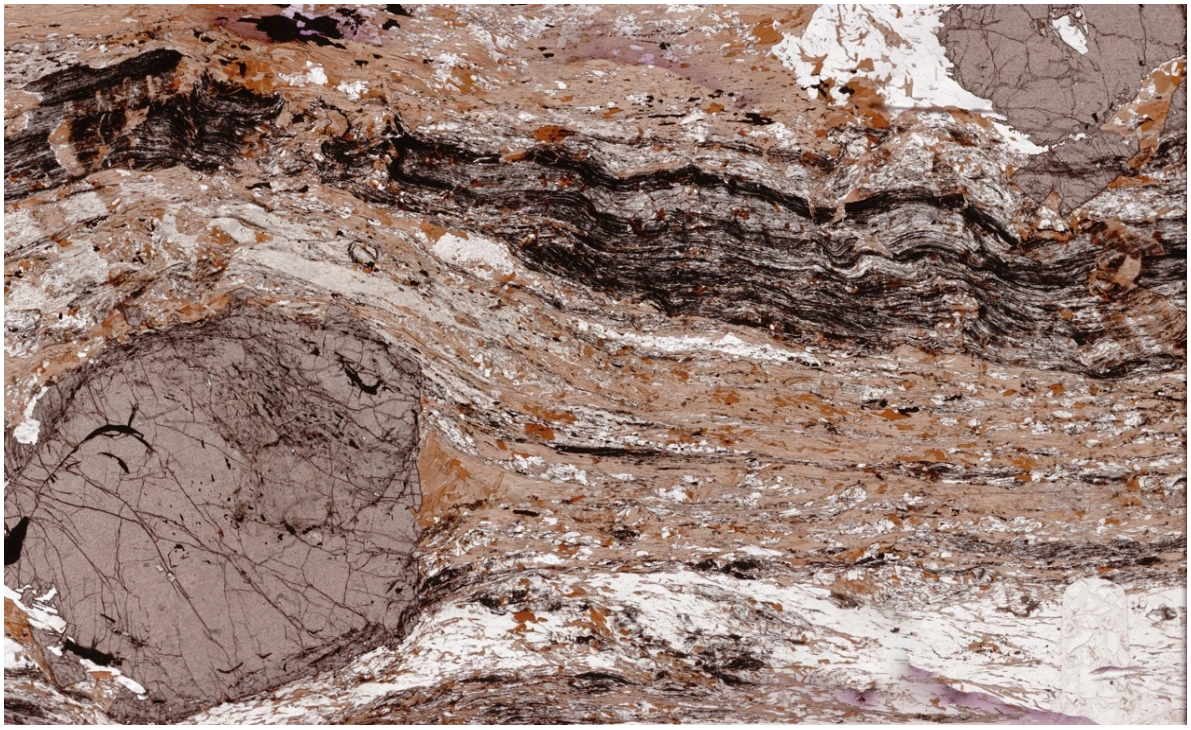


C.

Numerous studies have shown that garnet aliquots, even when appearing glassy and inclusion free, should be crushed, hand-picked, and then leached in acid(s) prior to complete dissolution.

Apatite, monazite, and zircon inclusions are common minerals that will contain appreciable amounts of REE. The phosphates may be easy to remove because they are readily dissolved in sulfuric and hydrofluoric acids. Zircon may be left behind in the dissolution process when using modest temperature Savillex techniques like those described here. This is generally advantageous because the zircon is often out of equilibrium with the garnet and other metamorphic minerals. Perhaps, the most problematic inclusions are epidote group because these silicates are often metamorphic, contain abundant LREE and MREE, and require aggressive acids (e.g., HF) for removal. See discussion of this in Gatewood et al. (2015).

Garnet with numerous inclusions: Townsend Dam VT, TD07-3D



Picking Garnet Aliquots

After separation of the garnet from the rock you are ready to crush and hand pick. Ideally you want 75 – 100 um fragments that are transparent in alcohol with a 2-4x binocular scope. This size fraction will allow you obtain inclusion free garnet for the TIMS. The finest powder is very hard to work with and is generally discarded. So, crush carefully to avoid excessive powder – we use a metal percussion mortar and pestle with garnet wrapped in Al foil packets. We typically crush in the percussion mortar, sieve, and then pick. The sieving removes fine powder which will only make picking more

difficult. Be careful with sieves because they can contaminate your sample if not clean and a couple of zircon or monazite…… We have a small sieve set dedicated to garnet.

Whole Rock and Matrix Aliquots

Isotope equilibrium is the key; therefore, the WR and Mtx should have been in equilibrium with garnet when it grew. We only need ca. 50 mg of WR matrix. But we often pulverize a larger volume (several g) of homogenous and representative material in order to avoid bias. Be sure that the WR includes the approximate ratio of garnet to matrix for the 'sample' as a whole. Migmatite and layered rocks can be tricky and if garnet is from one layer then sample that layer.

Franz Magnetic Separation-Garnet (McKay, 2011)

1. Take pre-picked, crushed garnet (less than No. 60 mesh, greater than No. 200? Mesh) and run a hand magnet (located in the mineral separation lab: 264, in the drawer or on the table) wrapped in a Kim wipe over the separate, removing highly magnetic minerals.
2. Clean and assemble Franz with alcohol and Kim wipes. Following assembly, place small, empty paper cups underneath both chutes at the end of the Franz.
3. Set vibration control to 6-7, and mag to 0.5 to 0.7. It may take some "tweeking" of the control to set the magnet to the right strength to remove the garnet (garnet composition can affect the magnetic susceptibility). Do several tests with small amounts to ensure that most garnet is going into the magnetic fraction.
    a. Magnetic separate will be in the outside (close) cup, non-magnetic separate will be inside (far) cup.
    b. Turn on the magnet and slowly pour the separate (that has had magnetite removed with the hand magnet) into the feeder of the Franz.
    c. Make sure that no grains clog up the slide.
4. Set aside both fractions and label. It is useful to re-run both separates to remove grains that went into the wrong cup due to clogging on the slide. Do not worry about cleaning between runs of the same sample/grain.
5. After both separates have been run, it is useful to run the magnetic separate again with the magnet set at ~0.3-0.4 to remove magnetic inclusions. Place a clean cup under the inside (non-mag chute) and tweek magnet <0.5 until garnet goes into the non-mag cup.
6. The non-mag cup full of garnet can now be picked. If the separation was effective, it may be more efficient to pick inclusions OUT of the garnet separate, instead of picking clean garnet into a new dish.

*Garnet magnetic susceptibility may be controlled by inclusions as well as composition. Be aware that you may be biasing your sample towards inclusion free garnet, depending on the inclusions. If this is a concern, be sure to set the magnet so that all garnet goes into the same cup.

Garnet Leaching Procedures

The type of leaching depends on the number and nature of inclusions. A good general leach scheme that will remove some silicates and most other inclusions uses hydrofluoric and perchloric [see Grt leach EB]. Alternately, sulfuric, perchloric, or hydrochloric acids may be appropriate for phosphates or carbonate.

Each of these leaching techniques entails some danger and difficulties. Consult with experts before proceeding.

After identifying the nature of inclusions and choosing acid, there are still significant choices and experiments to make. This is particularly true with HF leaching. In general, it is very difficult to predict the temperature and duration of leaching that will largely dissolve inclusions without significantly removing garnet.

Sulfuric Acid Leach [courtesy of Gerrit Bulman]

Read entire procedure carefully before starting

1. Pulverize hand-picked and cleaned garnet. Use an agate mortar with the garnet submersed in ultrapure water. Take care not to produce too much fine powder.
2. Centrifuge and remove water with a pipet. Dry.
3. Best results may be obtained from the 100-200 mesh fraction. Therefore, sieving is recommended [Baxter]. Use the 4" diameter plastic sieve with disposable nylon mesh.
4. Leach/clean for 1 hr in ca 1 ml 2M nitric [trace metal grade] @ 25ºC in a clean centrifuge tube.
5. Ultrasonic periodically during leach.
6. Pipet off liquid, dry, and weigh.
7. Separate liquid, dry and weigh.
8. Transfer to Teflon screw cap vial then leach in ca 1 ml 5-6M HCl [trace metal grade] @ 80-100ºC for 6-12 hrs [you may need to experiment with time and T]. For low mass samples reduce T and time.
9. Transfer to tube and centrifuge.
10. Remove liquid.
11. Rinse 3 times with ultrapure water.
12. Dry and weigh [*you may lose ≤30% of garnet with 12 hrs 100ºC*].
13. Load into clean centrifuge tube or 15 ml vial then leach in ca. 1 ml 2x 98% H_2SO_4 @ 180ºC for 24 hrs [this is the phosphate/monazite removal step].
14. Remove leachate. This is aided by dilution with water followed by centrifuging and removal of liquid with a pipet.
15. Repeat dilution and removal as needed.
16. Dry and weigh.

HF Acid Leach [courtesy of E. Baxter, M. Gatewood and B. Dragovic]

Read entire procedure carefully before starting. The specifics are guidelines only and preliminary experiments are advised.

Rough Preparation

1. Cleanly separate garnet from rock.
2. Ultrasonic in ultrapure water.
3. Ultrasonic in alcohol.
4. Dry and weigh.

Fine Preparation

5. Pulverize hand-picked and cleaned garnet. Use an agate mortar with the garnet submersed in ultrapure water. Minimize the production of fine powder.
6. Obtain a 100-200 [**140-250**] mesh fraction - seive through 100 mesh & above 200 mesh
7. keep 100-200 mesh fraction; label and set aside <200 mesh fraction (label it "<200")
8. ultrasonicate 100-200 fraction in alcohol 5 minutes and decant
9. run 100-200 fraction through the Frantz, as needed
10. examine and hand pick out any obvious non-garnet grains; this may take many hours
11. *weigh ALL clean, picked, 100-200 mesh garnet*
12. *you should weigh and set aside ~5-10 mg of clean 100-200 garnet if you need prelim data – mixed spike [BU]*

Leaching/Partial Dissolution

Nitric

13. weigh Savillex beaker and cap *(dry, empty, no label)*
14. add ~2.0mL of concentrated Nitric (pipet and note exact amount)
15. *add, weighed garnet to beaker (~120mg)*
16. heat on hotplate, ~120 C, covered for total of ~180 minutes (note start time)
17. remove and ultrasonic for 5 minutes, after every ~60 minutes (check for each)
18. remove from heat, uncap and decant nitric (note time)
19. add 1.5N HCl, ultrasonic, decant REPEAT
20. add ultrapure water, ultrasonic, decant REPEAT

HF

21. add ~2mL of 1.5N HCl (note exact amount)
22. add ~1.0mL of HF (pipet and note exact amount)
23. heat on hotplate, ~120 C, covered for total of 30-60 minutes (note start time)
24. remove and ultrasonic for 5 minutes, after every 10 minutes (check for each)
25. remove from heat, uncap and decant HF (note time)
26. add 1.5N HCl, ultrasonic, decant REPEAT
27. add ultrapure water, ultrasonic, decant REPEAT
28. add ~1mL of 1.5N HCl (note exact amount)

Perchloric

29. take to perchloric acid hood
30. add ~2mL of perchloric acid (note exact amount)
31. heat on hotplate, ~150 C, covered, for ~1 hour (note temp and time)
32. ultrasonic for 10 minutes (note temp and time)

33. heat on hotplate, ~150 C, uncovered, overnight until dry (note temp and time)
34. remove from hotplate (note temp and time)
35. add 1.5N HCl
36. heat, open for a few minutes, ultrasonic, and decant
37. add 1.5N HCl *AGAIN*, ultrasonic and decant
38. add ultrapure water, ultrasonic, decant REPEAT
39. evaporate sample in box
40. weigh new beaker and cap
41. add sample and weigh total to obtain final Leached Grt Mass

Proceed to full dissolution

An Example of a Partial Dissolution Schedule for 09TD14
[see above for details]

Use the 140-250 mesh size fraction
Frantz to remove magnetite
Nitric leach
Handpick

(1) 60 minutes in HF @ 120°C;
(2) 60 minutes in Perchloric acid @ 150°C then decant and evaporate;
(3) 3 hours in 7N HNO_3 @ 120°C;
(4) 3 hours in H_2SO_4 @ 120°C.
Each step has several washes with HCL and nanopure afterwards.

Spiking Procedures: UNC 'Basaltic' Mixed Spike

Introduction: Isotope dilution procedures require that a spike/tracer be added to the solution prior to loading the filament for TIMS analysis. For Sm and Nd isotopes, we generally use a mixed spike with several Nd and Sm isotopes [known concentrations and ratios]. Spiking can be done at several different times during sample preparation. In general, we spike prior to dissolution. It is critical to obtain optimum ratios of spike to unknown; therefore, mass of the spike and sample must be well determined and the appropriate mass of spike is generally given as a ratio to the unknown mass.

We generally use the UNC mixed spike for basalts UNC 'B19'. This works well for rock and garnet.

Spike [UNC 'B19'] Volume:

- Garnet – use 70 ul/100 mg of garnet
- Rock – use 200 ul /[25 mg] of rock
- Blank – use 25 ul

UNC mixed Sm-Nd 'B' Spike Data

Isotope	atomic fractions	Mass contrib. To mixture at.wt.	Average Nd Spike Atomic Wt.
142Nd	0.004185	0.594	**149.884**
143Nd	0.002466	0.353	
144Nd	0.004982	0.717	
145Nd	0.002175	0.315	
146Nd	0.004402	0.643	
148Nd	0.003665	0.542	
150Nd	0.978125	146.719	
144Sm	0.000590	0.085	**147.036**
147Sm	0.982993	144.500	
148Sm	0.008444	1.250	
149Sm	0.003580	0.533	
150Sm	0.001103	0.165	
152Sm	0.002047	0.311	
154Sm	0.001243	0.191	

Approx. Spike Concentrations (courtesy of Brian Carl, UNC)

Nd=	7.4E-10	mol/g
Sm=	1.4E-09	mol/g

ppm 150Nd=	0.19380	These are for UNC B19
ppm 147Sm=	0.18050	

Rock and Mineral Dissolution

Introduction: Silicate minerals, particularly, difficult to dissolve. In general, strong and/or corrosive acid is required. We generally use **HF which is very dangerous**. HF will produce **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
All procedures require use of Nitrile gloves, lab coats, and safety glasses.
All HF procedures are carried out in the Teflon lined HF hood in BE 2067.
Open HF containers MUST BE inside the closed evaporation boxes.
All perchloric procedures are carried out in the Stainless Steel hood in BE 2067.
FEP bottles and vials are required for these procedures.

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.

Garnet Dissolution

Pulverizing
Pulverize garnet in clean agate mortar and pestle. Note that very fine material <100 microns [<200 mesh] is extremely hard to work with -- DO NOT powder too finely.

Leaching
The type of leaching depends on the number and nature of inclusions. A good general leach scheme that will remove some silicates and most other inclusions uses hydrofluoric and perchloric [see Grt leach]. Alternately, sulfuric, perchloric, or hydrochloric acids may be appropriate.

Each of these leaching techniques entails some danger and difficulties. Consult with experts before proceeding.

Weighing (see Weigh Sheet)

Spiking
Use ca. 70 ul/100 mg of UNC Spike 'B19'. Note that Nd mass in sample [not total mass] should be used to determine spike volume for LOW mass samples

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 [generally 20:1], and
- 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 [~120ºC] overnight (or longer) in this solution with cap on.
3. Carefully remove cap and evaporate to dryness.
4. Use squirt bottle to add 1 to 2 ml of 2x 6 M HCl and heat overnight with cap on.
5. Remove cap and dry in evaporation box
6. Add 1 to 2 ml of 2x 12 M HCl and heat overnight with cap on.
7. Remove cap and dry in evaporation box
8. Add 0.5 ml 2x 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 low mass samples with a clean agate mortar and pestle or for larger samples the *ceramic* ring and puck mill in the SPEX shatterbox. The rock may be powdered finely; however, this may make weigh procedures tricky.

Weighing (see Weigh Sheet)
Carefully weigh 25 to 50 mg. that is representative of the rock sample required.

Spiking
Use ca. 200 uL of UNC Spike 'B19'/25 mg of rock.

Sample Dissolution (see Excel Sheet)

HF Treatment

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

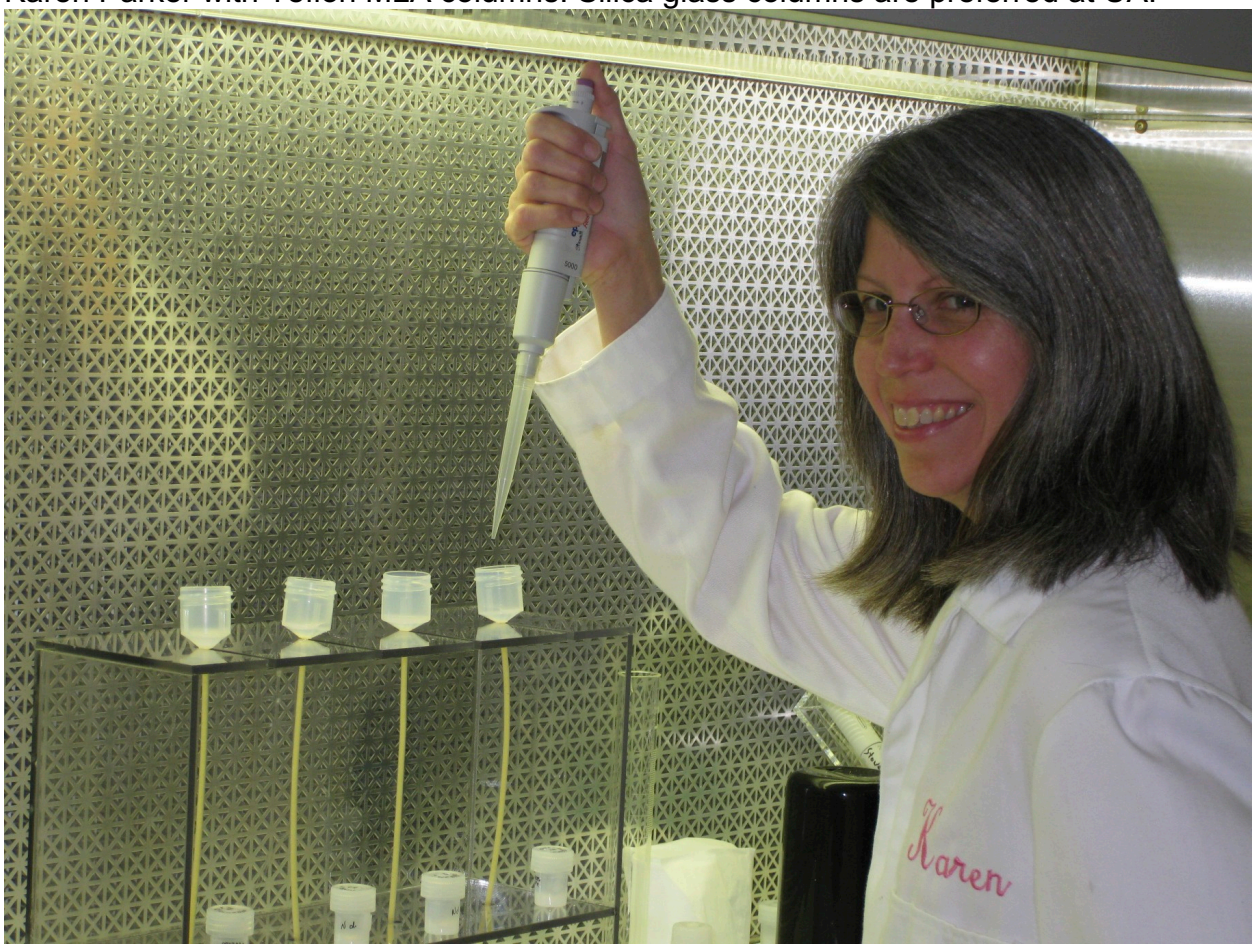
Locate Ca-gluconate prior to working with HF.

REE Separation & Concentration for TIMS

Introduction

Clean separation of adjacent REE for TIMS generally requires two or three ion chromatographic column steps. The initial column or columns are used to remove major elements in order to concentrate a 'clean' REE fraction. A second column may be used to insure removal of all Fe which can interfere with the REE separation. This is very important for Tru-Spec microcolumns where small amount of Fe can interfere with the separation of bulk REE. The final column step separates adjacent REE and allows concentration of Nd and Sm for mass spectrometry. There are numerous final column steps in use including many versions of: LN-spec, HCl, and 2-hydroxy isobutyric acid [methylactic, α-HIBA, or MLA] columns. α-HIBA is efficient for the clean separation needed for running NdO on the TIMS and is used at UA, UNC, and BU.

Karen Parker with Teflon MLA columns. Silica glass columns are preferred at UA.



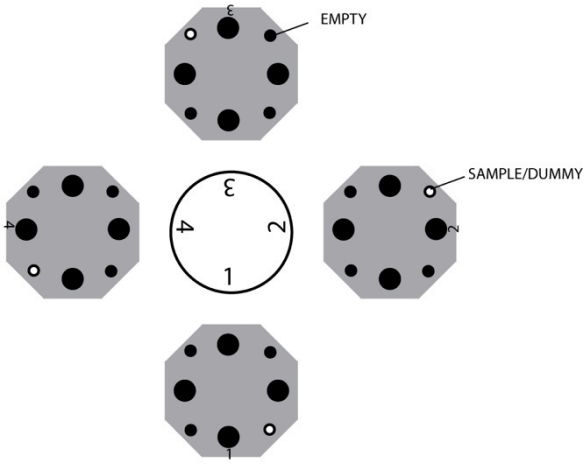
Centrifuge

Rationale: It is important not to load solids on the ion exchange columns. This can disturb the ion exchange directly [chemically] and/or indirectly [clogging].

Centrifuges spin at high speed and require balancing; therefore, it is critical to place sample holders in their calibrated position and orientation. Also, the samples must be balanced by even distribution around the 'circle'.

Beckman TJ-6 Centrifuge

There are four sample holders. These are numbered and the holders must be returned to the correct arm and orientation [matching numbers to the outside]. Samples and dummies must be evenly distributed to all four holders.



The power light on the on/off switch does not work. But, the red rpm light should come on during the start procedure then go off after spinning begins. RPM gauge is inaccurate.

Use the following settings:

Speed = 4.5
Brake = low
Time = 10 minutes
Lock = on

OK, get to work push – Start [you may need to hold for 1-2 seconds]

Check vibration/noise to see if it is spinning

Bulk REE Column Procedures

Use BIO-RAD prefilled Poly-Prep columns – AG 50W-X8 Resin 200-400, H form, 0.8 x 4 cm [BioRad catalog #7316214]

Techniques described here are meant to complement Excel file [see SmNdMethodsXX.xls] that provides forms.

Choose the appropriate Savillex vials (15 ml WR or Grt) and label with Staedtler Lumocolor permanent special F #319 pen.

1. *Vigorously* shake resin columns before use – leave sealed. Be certain to agitate all resin –right down to the tip/frit.
2. Allow resin to settle.
3. Remove/snap off bottom of column, place in rack, and allow fluid to drain into waste cup.
4. Remove cap from the top.
5. Do not allow resin to dry, but wait until fluid is at top of resin.
6. Rinse column with 2 full column reservoirs [ca. 20 ml] of ultrapure water.
7. Rinse column with 2 full column reservoirs [ca. 20 ml] of 6 M HCl.
8. Condition column with 1 full column reservoir [ca. 10 ml] of 2 M HCl.
9. Load sample [after converting to chlorides] in 2 M HCl. Typically, dissolve in 0.5 ml, centrifuge [as needed] and load/pipet 0.2 ml onto the column. This leaves solids and/or 'spare' sample in the centrifuge tube.
10. Set sample with 0.2 ml of 2 M HCl.
11. Set sample with 0.8 ml of 2 M HCl.
12. Wash with 10 ml of 2 M HCl [two steps with 5 ml pipet].
13. Wash with 5 ml of 2 M HCl.
14. Wash with 2 ml of 2 M HCl.
15. Elute REE with 10 ml 6 M HCl into a **clean 15 ml Teflon** vial.

Evaporate samples to dryness – without burning.

Juras, S.J., Hickson, C.J., Horsky, S.J., Godwin, C.I., Mathews, W.H., 1987, A practical method for the analysis of rare-earth elements in geological samples by graphite furnace atomic absorption and X-ray fluorescence, *Chemical Geology*, v. 64, 1–2, p. 143-148.

MLA [α-HIBA] REE Column Procedures ['UA' silica glass columns]

Caution!!

Silica columns are expensive & fragile, all procedures require careful handling & thought!!
MLA or α-HIBA acid is light sensitive – keep all containers of acid and resin in opaque/covered bottles and in a dark cabinet!!

Refill 60 mL Savillex vials as needed. Shake large bottles to mix well before pouring.
Lightly shake resin vial before use – this creates a well mixed slurry
Lightly shake MLA acid vial

Techniques described here are meant to complement Excel sheets [SmNdMethods16.xls] that provide detailed procedures and forms.

Cleaning

1. Carefully expel the resin with a squirt of ultrapure water. If you wish to reuse the frit then you should do this into a clean plastic tray with the reservoir mouth under water so that you don't lose the frit.

   If needed carefully attach Tygon tubing to the bottom of the column, attach the other end of the Tygon to ultrapure water [using a 5 mL pipet tip over the water dispenser] in order to *carefully* push the resin and frit out through the reservoir and into a container of ultrapure water.

2. Rinse 3 times in ultrapure [nanopure] water – holding column over sink and getting water directly from wall mounted filter.
3. Install frits. Put frit in reservoir and then move into place with nanopure water. Frits are #2.5 size [German leather punch] from 50-90 micron pore sheets
4. Carefully rinse columns with Trace Metal 2 M HNO_3. Then soak for no more than 30 minutes. Use a black plastic cap on the base of the column.
5. Place columns on rack and rinse with Trace Metal 6 M HCl.
6. Rinse with nanopure water: 3 times – inside and out.
7. Soak in 2x 2 M HCl at least 3 hours. Use a black plastic cap on the base of the column.
8. With columns on rack, rinse columns 3 times in ultrapure [nanopure] water.
9. For storage on rack, cap and fill with nanopure water.
10. Rinse through 3 times with nanopure water before loading resin.

Preparing samples for columns – read through entire procedure before starting.

1. Completely dry down or evaporate bulk REE vials in evaporation box.
2. Add 0.2 ml of 0.75 M HCl to each vial.
3. Cap tightly and place on hot plate @ ca. 50°C. Allow equilibration overnight.
4. Turn to Excel procedures and calibration sheet. Check to be sure that the column calibration is up-to-date.

Choose the appropriate Savillex vials (7 ml WR or Grt) and label with Staedtler Lumocolor permanent special F #319 pen.

Loading columns – ca. 20 mL MLA /column; read entire procedure before starting

1. Clean columns – as above.
2. Place columns on rack in the laminar flow hood [HHS REE hood].
3. Carefully fill/top off the two 60 ml vials with 0.2 M α-HIBA acid and resin. The supply bottles are in the cabinet below the hood.
4. Replace large acid and resin containers in cabinet.
5. Place clean frit in reservoir and wash into place with ultrapure water.
6. Make sure that frit is NOT crooked and push into place with nylon rod *if needed.*
7. Make certain that frit is seated – squirt ultrapure water thru column to seat the frit.
8. Fill column with ultrapure water be sure to avoid/remove all air bubbles.
9. **QUICKLY** fill with water resin slurry before column drains!
10. Allow resin to gravity settle into dense packing – this should take ca. 2.1 ml of resin. ***If you have air bubbles, reload.*** Dense packing will take some time – ***packed resin should fill to 23 cm above column tip – top should be just below base of reservoir***. Dense resin should extend to 23 cm from tip base to the area where the column widens. Excess resin may be removed carefully with a low volume pipet. Avoid leaving resin on the sides of the reservoir.
11. Check for even resin packing and air bubbles. Significant bubbles will greatly decrease flow and will 'smear' the elution peaks.
12. Check drops of water at tip and waste cup for resin – significant resin loss requires reloading and possibly a new frit.

Eluting Sm and Nd on α-HIBA columns

1. Follow cleaning procedure.
2. Follow resin loading procedure.
3. Check resin for date and find matching calibration.
4. Follow excel procedure sheet. Elute Sm & Nd into **clean 7 ml Teflon vials.**
5. Add 4 ml of **freshly mixed** [a few days old is OK] *aqua regia* [4 pts. 6 M HCl + 1 pt. conc. HNO_3] and one drop of dilute H_3PO_4.
6. Evaporate at 120 to 140°C in evaporation box within HF hood. Evaporate to small "pinhead" drop – do not burn.
7. Repeat [lower amounts of *aqua regia*?] until α-HIBA free. α-HIBA crystals on sides of vials indicate incomplete removal … again…

Typical bead of sample after dry down. Smaller is better.

Cutting Frits

1. Use DBGM (German) leather hole punch set on 2.5 mm and Small Parts porous poly 0.125”, 50-90 µm.
2. Trim excess frit material with an Xacto knife prior to pushing out of punch with plastic rod.
3. Roll carefully in fingers after removal to obtain even cylinder.

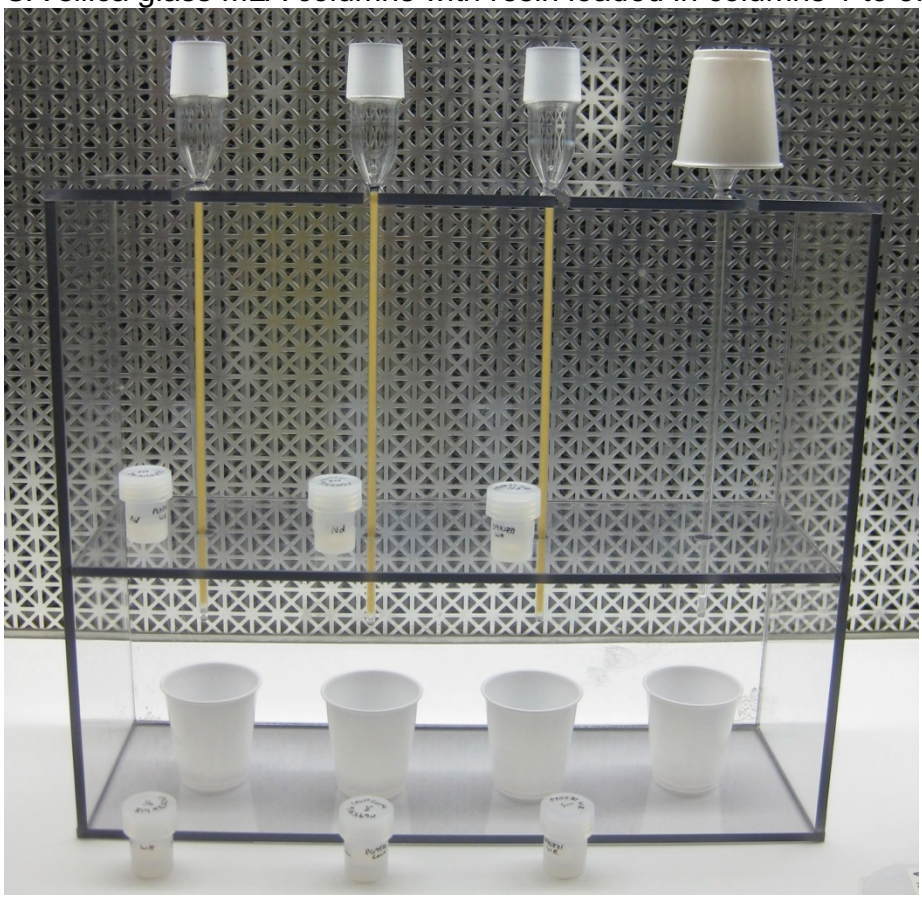
Preparing Blanks

General
Your blank should be 'total' - include all dissolution acid steps & all columns. Therefore, a clean vial should be started at the time of rock/mineral dissolution. It must be spiked and then the same acid volumes should go into this vial as those used for garnet.

Weights (see Weigh Sheet in Excel)

Spiking
Use 25 ul of UNC Spike 'B19'.

UA silica glass MLA columns with resin loaded in columns 1 to 3.



REE Sample Transport

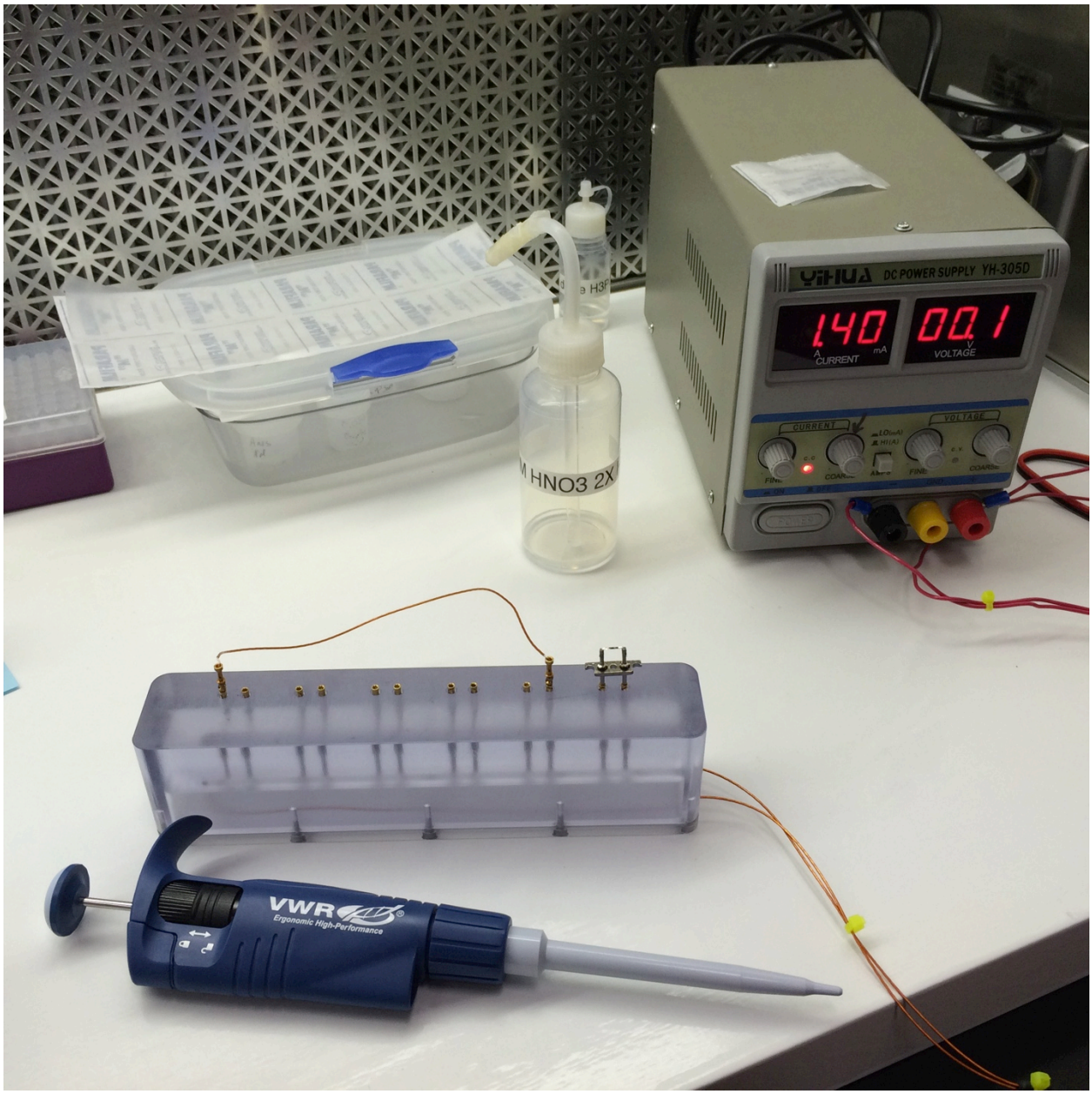
- Transport samples in **200 ul of 2M HCl** (prevents sample spot from spattering)
- Parafilm beakers, place in trays, and put trays in gallon-size Ziploc bags
- Keep sample vials vertical/trays in horizontal orientation.

Loading and Running Sm and Nd on a TIMS [VG Sector 54]

Preparing Samples for Loading

Make certain that all α-HIBA has been driven off before proceeding.
Add two drops of 0.1 M H_3PO_4 to each sample, and dry down to spot on hotplate.

Take the samples to the RadIs lab, Bevill 2062.



Filament loading bench in the **R**ad**I**s lab. I advise only one at a time. The power supply is touchy – be careful.

Loading Procedures

In general, it is best to load all of sample from each vial.

Loading Sm Standard (Ames)

Locate clean degassed Ta centre filaments
Wear gloves

Use needle nose pliers – on filament post - to lift Ta centre filament and insert into the right end receptacle in the loading block [check that the block wire is positioned for the number of filaments that you plan to load]

Turn on the power supply

Turn up current to 1.4 A

Use thin strips of parafilm to make dams on either side of filament center

Turn current down to 0.0 A

Load 1.0 µL of H_3PO_4 onto filament

Dry down slowly at 1.4 A

Load onto filament slowly using micro pipette allowing to dry down between steps

Load 2.0 µL of Sm standard (UNC 1000 ng/ µL)

Turn up current to 1.8 A to completely dry down

Slowly increase the current [ca. 2.4 A] to until you obtain an orange/red underglow –
hold for **5 seconds then *Rapidly* turn down [COUNTERCLOCKWISE]**

Parafilm should have burned off by now. If not hold current ca. 1.9 A til gone – should smoke briefly– turn off quickly

Place sample on block and assemble turret

Loading Sm Sample (Sm 147 Spike)

Add 4.0 µL of 2 M HCl to samples
Locate clean degassed Ta centre filaments
Wear gloves and work in the Laminar flow hood

Use needle nose pliers – on filament post - to lift Ta centre filament and insert into the right end

receptacle in the loading block [check that the block wire is positioned for the number of filaments that you plan to load]

Turn on the power supply

Turn up current [CLOCKWISE] to 1.4 A

Use thin strips of parafilm to make dams on either side of filament center

Turn current down [COUNTERCLOCKWISE] to 0.0 A

> In general, load all of sample onto filament in very small steps using micro pipette and allowing to dry down between each step

Add 4.0 µL of 2 M HCl to sample*
Load first drop then…
Turn up current [CLOCKWISE] to 1.0 A
Continue loading with constant current

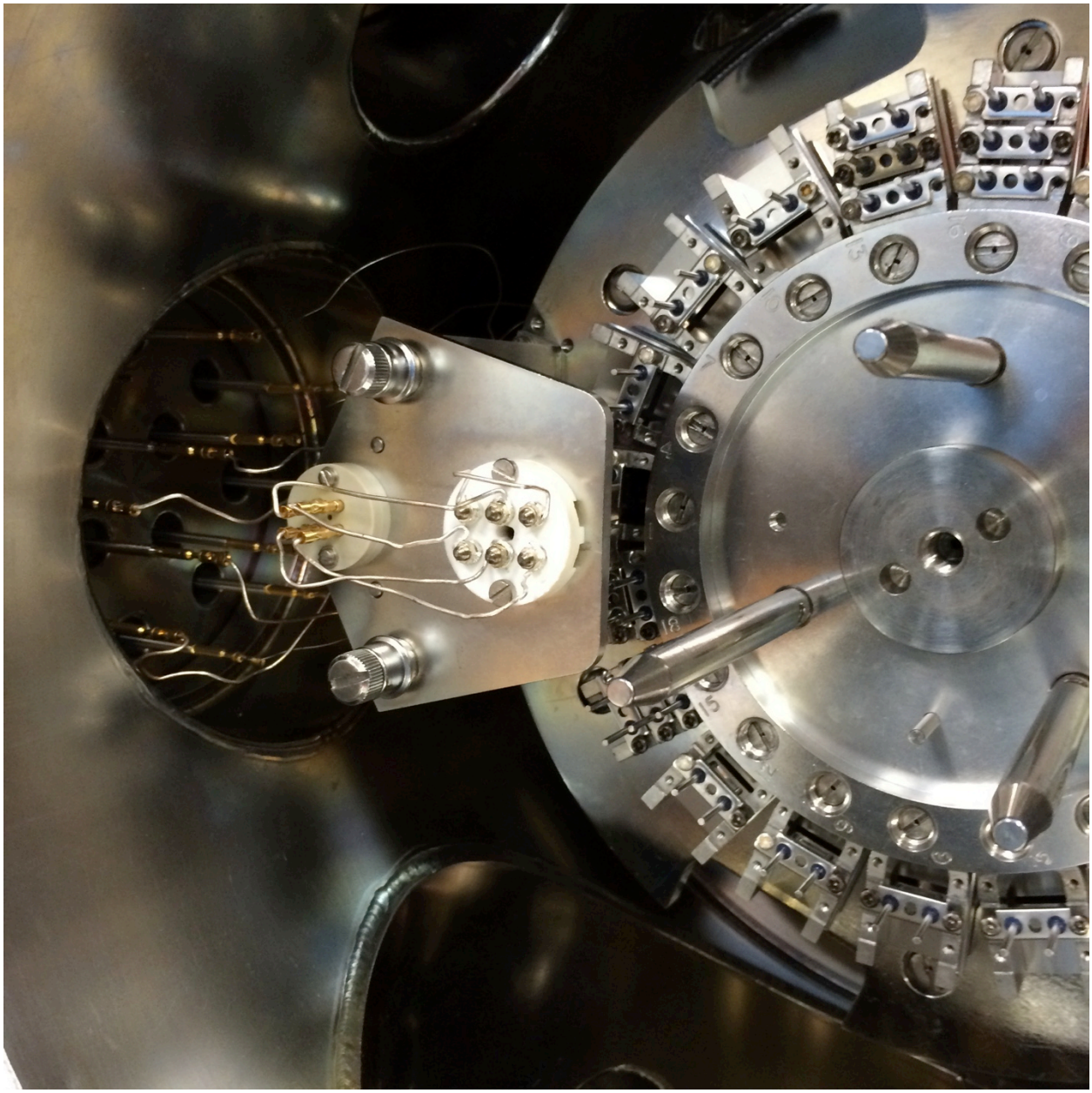
Turn up current [CLOCKWISE] to 1.6 A to completely dry down

Slowly increase the current to until you obtain an orange/red underglow –
hold for **5 seconds then *Rapidly* turn down [COUNTERCLOCKWISE]**

Parafilm should have burned off by now. If not hold current ca. 1.9 A til gone – should smoke briefly– turn off quickly

Place sample on block and assemble turret

* Adding acid to all samples first allows for equilibration and homogenization



VG Sector 54 TIMS turret, RadIs

Loading NdO Standards with Ta_2O_5

Locate clean degassed Re centre filaments
Wear gloves

Use needle nose pliers – on filament post - to lift Re centre filament and insert into the right end receptacle in the loading block [check that the block wire is positioned for the number of filaments that you plan to load]

Turn on the power supply
Turn up current to ca. 1.4 A

Use thin strips of parafilm to make dams centered ca. 2 mm apart on filament center

Turn down current [COUNTERCLOCKWISE] to 0.0 A

Load 1.0 µL of dilute – ca. 0.1 M H_3PO_4 onto filament

Turn up current [CLOCKWISE] to 1.4 A

Load 1.0 µL of JNdi (ca. 20 ppm in 2 M nitric) standard onto filament

Vigorously shake the Ta_2O_5 to homogenize the slurry
Turn up current [CLOCKWISE] to ca. 1.5 A
Using new pipette tip, load 2.0 µL of Ta_2O_5 on to the filament

Turn up current to 2.0 A – allow to dry

Increase the current [CLOCKWISE] until you obtain an orange/red underglow [ca. 2.3 A] – hold for 5 seconds then turn down

Parafilm should have burned off by now. If not hold current ca. 1.9 A til gone – should smoke briefly– turn off quickly

Place sample on block and assemble turret

Loading NdO Samples -Ta_2O_5 (Harvey & Baxter, Chemical Geology, '08)

Add 2.5 µL of 2 M HNO_3 to samples – *this can be done directly in load procedure**
Locate clean degassed Re centre filaments
Wear gloves

Use needle nose pliers – on filament post - to lift Re centre filament and insert into the right end receptacle in the loading block [check that the block wire is positioned for the number of filaments that you plan to load]

Turn on the power supply
Turn up current [CLOCKWISE] to ca. 1.4 A

Use thin strips of parafilm to make dams centered ca. 2 mm apart on filament center

Turn down current [COUNTERCLOCKWISE] to 0.0 A

> Load half to all of sample onto filament in very small steps using micro pipette and allowing to dry down between each step

Add 2.5 µL of 2 M HNO_3 to the sample -- If NOT done earlier!
Load first drop then…
Turn up current [CLOCKWISE] to ca. 1.5 A
Continue loading with constant current
Dispose of the pipette tip

Turn up current [CLOCKWISE] to 1.7 A to load Ta_2O_5

Vigorously shake the Ta_2O_5 to homogenize the slurry
Using a new pipette tip, slowly load 2.0 µL of Ta_2O_5 on to the filament

***Slowly* increase the current to 2.0 A to completely dry down**

Increase the current [CLOCKWISE] until you obtain an orange/red underglow [ca. 2.3 A] – hold for 5 seconds then turn down

Parafilm should have burned off by now. If not hold current ca. 1.9 A til gone – should smoke briefly– turn off quickly

Place sample on block and assemble turret

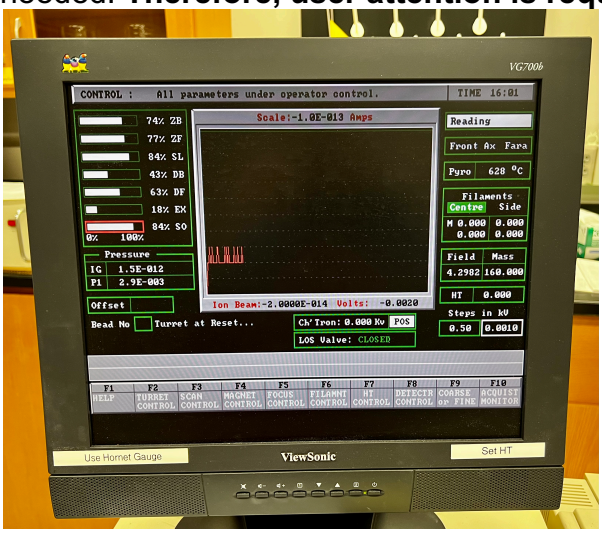
* Adding acid to all samples first, allows for equilibration and homogenization

The UA RadIs Lab

The RadIs lab (BE2062) houses a 1990 vintage VG Sector 54 thermal ionization mass spectrometer (TIMS). The TIMS has one Daly collector, and one fixed and six movable Faraday collectors.

Source MS Electronics Electronics Cabinet 2 Electronics Cabinet 2 PC Control

The DOS-based Micromass software controls the TIMS magnet, sample turret, filament current, ion focus, and analytical software. Manual observations/control of the vacuum and beam intensity are needed. **Therefore, user attention is required!**



TIMS: VG Sector 54 short notes

Notes below pertain to the VG Sector 54 in the UA **R**ad**I**s lab. **These notes are by no means comprehensive - check with an experienced TIMS operator**.

General Operation – Be sure that Faraday Cups are in position/aligned

1. Check vacuum [Hornet Ion Gauge - ***Source***] – should be ca.10^{-8}
2. If vacuum is >2 10^{-7}, Fill Cold Trap on Source with liquid N. Not needed for many 'normal' operations
3. Check vacuum [Hornet Ion Gauge on ***Source***] – should be <10^{-8}
4. Go to Control Screen –**F3**
5. Adjust HT to ca. 8010 V for NdO, 8004 for Sm, and 7993 for Sr **(e.g., F7, S, 8010, enter)**
6. Set mass: For Nd, **mass 160** (^{144}Nd + ^{16}O) in axial cup, OR
   for Sm **mass 149** in Axial Cup **(F4, "M")**
7. Initialize focus: **F5** -focus, **I, Y**
8. Pick bead that you want to run (**F2** Turret control, **S**, Type bead **#**, enter)
   Use flashlight to look into Source – number should read desired bead plus/minus 10 [e.g., bead #3 reads 13]
9. **LOS** (line of sight valve) closed ("**L**") Note the manual LOS valve switch on the MS electronics panel – This *emergency manual switch* should be used in case of excessive signal voltage on Daly or Faraday cups
10. Warm up filament
    From control screen (ESC, **F5** –Main Editor, Tasks, Warm up Filament)
    Choose '*NdO 2.5A 25 min*' for NdO
    Choose '*Sm 2.4A 15 min*' for Sm
    Choose '*Sr 2.5A 30 min*' for Sr

After warmup, when looking for signal. Be sure to pause at Amp and T you expect signal. If nothing, use **Scan Control** from Control Screen: **F3 – scan -0.5 to +0.5 around peak [e.g., 159.5 to 160.5]**

A signal of >200 mV is needed. **Never exceed a 3 V signal!**

When running task with no aiming intensity window, watch signal and close LOS Valve when over 3 V on Faraday cups

[Note: Cannot close LOS during Auto Focus, Baseline measurements and Peak Centering]

NdO Note*: The NdO 1V dynamic analysis routine default setting is aiming intensity of 1 V and +/- 40% window. This is an intense signal appropriate for* ***whole rocks and standards****. It may be too high for low Nd masses. One can use a lower or no aiming intensity [e.g., NdO 0.5V; NdO 400mV no AIM] or manually set the aiming intensity while running the program: ESC, "****I****" (AI), "****T****" for window (e.g. 2.00E-12 is 200 mV, 1.00E-11 is 1V)*

Running NdO [Basalt B spike dynamic mode = NDO ads file]

1. Vacuum on ***Hornet*** Ion Gauge should be ca. x 10^{-8}
2. Set HT to 8010 V
3. Axial mass should be 160 (^{144}Nd + ^{16}O)
4. Run program for warm-up filament- '*NdO 2.5A 25 min*'
   From control screen (ESC, **F5** –Main Editor, Tasks, Warm up Filament)
   use arrow keys to select procedure, then
   select Run button at bottom of screen –press enter
5. Open Line of Site (LOS) "L" press Y 'yes'
6. Find signal by slowly raising filament current to ca. 2.7 A (**F6**, arrow keys)
   check pyrometer – should be 1500-1800°C
7. Should see signal – signal line on graphic display will be white
   If yes, then raise amps to get 10 mV then Auto Focus [**F5** then **A**]
   Go to "step 9"
8. No signal, focus manually (**F5**, arrows for up and down & "**C**", "**V**" to change slit)
   Order of focus: DF, DB, ZF, ZB, SL, EX, SO
9. **No signal**!,
   a. use Scan Control **(F3)** to look for peak. Set start and end masses at -0.5 **(F9)** & +0.5 **(F10)** for axial mass (e.g., 159.5 and 160.5). If you find signal then adjust HT to move peak to correct axial mass
   b. Still no signal then use *Daly* [plug in the axial drive motor] – **F8, D, Y**, enter
   Switch to Faraday when the signal reaches ca. 250,000 cps
   DO NOT ALLOW SIGNAL ABOVE ca. 100 mV OR 500,000 cps
   Focus Manually (**F5** focus control, "**C**" to go up, "**V**" to go down)
   Order of focus: DF, DB, ZF, ZB, SL, EX, SO
   Then with a signal >250,000 cps, switch to Faraday **F8, F, Y, F** [Front] and Enter [unplug Axial Drive]
   Auto focus - **F5, A**, Peak Center - **F7, P**
10. With a weak signal (<3 mV), manually focus (**F5**, arrows & "**C**", "**V**" to change slit)-peak center **(F7, "P")** -increase filament current Repeat…
    With a >3 mV signal, auto Focus **(F5, "A"),** focuses all plates-peak center **(F7, "P")** centers mass on 160
    With a ca. 50 mV signal adjust HT so that Axial Peak is = 160.00 +/- 0.01
11. Watch beam current to see if it grows. Increase Amps to increase signal. Begin run at 200-500 mV – do not push the Amps up rapidly! Ideally, you should run with 500 mV- 1V of signal in axial detector, but you may not get this. Check pyrometer reading, usually Nd starts ionizing 'coming off' around 3.0 A - 1700 °C.

    WR/Mtx samples can usually obtain 1V
    Grt will have lower beam intensity (maybe even as low as 100-200 mV)

12. *Start collecting data*: ESC, **F5** Control Screen, Tasks, General Editor, choose Task [e.g., *NdO 500 mV*], select 'Run' on lower buttons and Enter
    This will collect 30 blocks of 10 measurements -- usually you will need about 10 blocks with a strong signal -- you may need 20+ blocks with low intensity signal

    Use '*NdO 400 mV Grt'* for garnet [90% aiming intensity window] – BE CAREFUL
    or
    '*NdO 500 mV*' for higher mass Nd **[**±75% aiming intensity window]
    Use '*NdO 1V*' for high mass **WR and Mtx** [1V±40% aiming intensity window]

    Can set aiming window when in program, ESC, "**I**" (for aiming intensity), "**T**" for window (e.g. 2.00E-12 is 200 mV, 1.00E-11 is 1V)
13. STATS: anything below 0.0012 % standard error [SE] on $^{143/144}$Nd is OK, but YOU SHOULD RUN UNTIL % standard error is 0.0008.
14. When desired SE is obtained or all hope is lost –press Escape then **Q** for quit
15. Close Line-of-site [**LOS**]-press **L**, then change bead.
16. Initialize the focus: **F5, I, Y**
17. Set mass to 160: **F4, M, 160**.
18. If finished for day then, Reset the HT: **F7, R, Y** – otherwise **F7: S, 8010**
19. If finished for day then, Reset the Turret: **F2, R, Y** – otherwise **F2, S,** select Bead
20. If finished for day then, Esc from Control Screen – otherwise Warm the next bead.

Note the 0.0008 SE on ^{143}Nd/^{144}Nd.

Running NdO Blanks [Daly Single Collector Mode]: (see above for details)

1. Vacuum on ***Hornet*** Ion Gauge should be ca. x 10^{-8}
2. Set axial mass to 166 (^{150}Nd + ^{16}O)
3. Switch to Daly
   Plug in the axial drive motor] – **F8, D, Y,** enter
4. Open the LOS and warm-up blank using the '*NdO Blank 2.0A 20 min*' routine. Watch the cps and DO NOT ALLOW SIGNAL ABOVE ca. 100 mV OR 500,000 cps. If the signal exceeds 500,000 cps then close the LOS and switch to Faraday
5. If you have a signal Auto Focus
   If no signal, try to Focus Manually (**F5** focus control, "**C**" to go up, "**V**" to go down)
   Order of focus: DF, DB, ZF, ZB, SL, EX, SO
6. Should have signal ca. ≤2.5A
7. Increase current until you have 100,000-200,000 cps
8. Start collecting data
9. Use program Single Collector '*NdO Blank Daly*' (with the Daly Cup only)
10. If using the Faraday cups, then use Static Analysis '*UA NdO Blank F*'
11. Try to get 1-2 blocks of data
12. After closing LOS, switch to Faraday and unplug the axial drive motor

Running Sm [Basalt B mixed spike static mode]

1. Vacuum on ***Hornet*** Ion Gauge should be ca. x 10^{-8}
2. Set HT to 8004 V
3. Axial mass should be 149
4. Run program to warm-up filament- '*Sm 2.4A 15 min*'
   From control screen (ESC, F5 –Main Editor, Tasks, Warm up Filament)
   use arrow keys to select procedure, then select **Run** button at bottom of screen – press enter
5. Open Line of Site (**LOS**) "**L**" press **Y** 'yes'
6. Find signal by slowly raising filament current to 2.5-2.7 A (F6, arrow keys)
   check pyrometer [computer] – should be 1500-1650°C
   usually Sm starts ionizing 'coming off' around 2.6 A - 1550 °C.
7. Should see signal – signal line on graphic display will be white
   If yes, then raise filament current to get 10 mV signal and auto focus
8. **No signal**!, Check mass 152 first, then
   a. use Scan Control **(F3)** to look for peak. Set start and end masses at -0.5 **(F9)** & +0.5 **(F10)** for axial mass (e.g., 148.5 and 149.5). If you find signal then adjust HT to move peak to correct axial mass
   b. use *Daly* [plug in the axial drive motor] – **F8, D, Y**, enter
   Switch to Faraday when the signal reaches ca. 250,000 cps
   DO NOT ALLOW SIGNAL ABOVE ca. 100 mV OR 500,000 cps
   Focus Manually (**F5** focus control, "**C**" to go up, "**V**" to go down)
   Order of focus: DF, DB, ZF, ZB, SL, EX, SO
   Then with a signal >250,000 cps, switch to Faraday **F8, F, Y, F** [Front] and Enter [unplug Axial Drive]
   Auto focus - **F5, A**, Peak Center - **F7, P**
9. When you have a 10 mV signal use autofocus [**F5** then **A**]
10. With a weak signal (<3 mV), manually focus (**F5**, arrows & "**C**", "**V**" to change slit)-peak center **(F7, "P")** -increase filament current
11. Obtain >100 mV signal, make sure that 152 –H4 <1.5 V
    Start collecting data: ESC, **F5** control Screen, Tasks, General Editor, choose Task, Static Analysis, then select '*Sm 147 Spike*'

    This will collect 15 blocks of 7 measurements
    147/149 – you should obtain %SE of <0.0030 and ≥50 ratios
    -- usually you will need 6-7 blocks with a good signal

Running Sm Blank [Static Analysis]: (see above for details)

Notes: Blanks are very low mass. So, they will burn up fast. Do not hesitate, move fast! Blanks are mostly spike, so 147 will be largest peak – watch the signal strength and do not exceed ca. 3 V on L1
HT may be 8.004-8.008 [small load often centers at higher HT]

1. Vacuum on ***Hornet*** Ion Gauge should be ca. x 10^{-8}
2. Axial mass should be 149
3. Warm-up using the Sm Blank '*2.4A 10 min*' routine
4. If have a signal on Faraday, manually increase Amps and then focus. Switch to Daly if No signal on Faraday. Once signal is 100,000-200,000 cps, switch back to Faraday.
   For Daly, plug in the axial drive motor] – **F8, D, Y,** enter
   DO NOT ALLOW SIGNAL ABOVE ca. 100 mV OR 500,000 cps
   If you have signal Auto Focus
   If no signal, Focus Manually (**F5** focus control, "**C**" to go up, "**V**" to go down)
   Order of focus: DF, DB, ZF, ZB, SL, EX, SO
5. Should have signal ca. 2.8 A
6. Obtain ca. 10 mV on mass 149 before running – watch L1 [mass 147] – do not exceed 3.5 V. Filament T may be up to 1750 C.
7. Focus **once**, peak center and collect. Use program '*Sm Blank 147 Spik*e'
8. Try to get 2-3 blocks of data
9. Close the **LOS (L)**

Interpreting Nd & Sm Isotope Ratios –a few notes:

Nd

1. 142/144 – ^{142}Nd - product of extinct ^{146}Sm -should be constant ca. 1.141: used for fractionation correction
2. 143/144 – critical sample value, obtain SE <0.0008%
3. 145/144 – should be 0.34840-0.34841
4. 146/144 – used for normalization of Nd isotope ratios, measure of fractionation, > 0.729 = highly fractionated
5. 150/144 – measure of spike to sample – 0.4-0.6 is good

Sm

1. 152/154 - measure of Gd contamination, <1.174 = Gd contamination
2. 147/153 – measure of Eu contamination, high numbers are desirable, infinite = 0 Eu; 100-1000 is good
3. 149/152 – used for normalization of Sm isotope ratios, measure of fractionation, < *ca. 0.5180?* = fractionated
4. 147/152 – measure of spike to sample, you should obtain %SE of <0.0030; 'normal' = ca. 0.56085
5. 147/149 – you should obtain %SE of <0.0030 with ≥50 ratios

Signal Strength: 1 V = $1x10^{-11}$ A

Weighing Tips

1) Remember that we are after **relative weights** (e.g., the difference between the weight of the vial+sample and the vial+sample+spike)
2) The apparent weights WILL drift substantially (milligrams) over hours and days as a function of humidity, static, vibration and evaporation. **THUS, obtain relative weights within a short timeframe** (e.g., 1 hour to weigh the weigh-paper alone followed by the weighpaper+sample). If the balance will not stabilize (i.e., reach a metastable state) in minutes or tens of minutes, do not continue. Instead, allow atmospheric conditions to change (temperature and humidity) and allow your gloves, vials and samples to reach equilibrium with the ambient conditions.
3) Remember, **SPIKE weight is most important**. So take most care with the weights of the vial+sample and vial+sample+spike. Precise relative weights will yield a more accurate assessment of spike mass.
4) Higher humidity (72% and up) reduces static and is associated with shorter stabilization times.
5) **Turn on balance and calibrate at least one hour prior to use.**
6) **Allow all items in the weighing process to equilibrate for several hours with ambient atmospheric conditions**: gloves (nitrile and vinyl), vials (with tops ajar to allow air inside), samples, balance plate, weighing tongs, weigh paper… Otherwise moisture and air with varying densities will add error to even relative weights on the order of minutes.
7) **Do not touch anything with your bare hand**; the oils you will leave behind will evaporate for days, constantly changing the weight of the object you touched. Touching the balance control pad with a bare finger and subsequently touching the balance with a gloved finger, which then touches a vial, may also transfer detrimental oil/moisture.
8) **USE the anti-static 'gun', wrist band, anti-static mat, and the weighing tongs**.
9) **Only touch the vial when necessary with double gloves (Vinyl touching the vial)**. Try opening the vial and returning it to the scale before adding the spike; if the weight changes, your handing has imparted or removed moisture/static or, worse, material. In this case, wipe the vial's exterior with a KimWipe, allow it to equilibrate again, change gloves, and start again in a few hours.
10) Auto-calibrate the balance often.
11) Always use delta range and set the vibration adapter to "unquiet"—the lowest of three wave figures in the display.

Weighing Samples for Sm & Nd Isotopic Analysis

Precise weighing is crucial for isotope dilution analysis
In general mass should be determined to 5 decimal places on the gram
Spike mass is the most crucial - take the time to obtain precision

Teflon is one of the more difficult weighing containers due to static charge and adherence of particles

Allow sample, containers, tongs etc… to thermally equilibrate

Balances

Mettler PM1200 -- 0.001 precision – BE 275
Mettler AX105 -- 0.00001 precision 31 g max – BE 274
Mettler AT261 -- 0.00001 precision 62 g max – BE 275

Balance Settings

Max vibration
Five decimal places -delta range

Calibration & Taring

Calibrate often
Menu
Calibrate
Press Set and wait for internal calibration

Tare
Push Re-Zero and wait for zero

Static

Check weigh containers for dirt - blow off with canned air as needed
Ground wrist with static strap
Use one click of static gun on vials

Sample Handling

Do Not Touch Teflon OR if needed use double glove [nitrile plus heavy vinyl]
Use Mettler weighing tongs for Teflon

Manual Weighing [auto door off] - Mettler AT261

Push On [pull up to turn off]
Place sample on center of weigh table
Press select to close door
Press print to begin weighing [AT261]

Wait for triangle [upper right] & circle [upper left] to disappear
Balance beeps when ready
Small circle next to fifth digit indicates instability in last decimal place

Remove sample

Re-Zero/Tare

Repeat

Cleaning Procedures

Cleaning Savillex Teflon Vials

1. Never use abrasive or sharp objects (including fingernails) on the inside of the Teflon vials.
2. The vials are numbered (etched) with matching vials and lids. These are to be kept together.
3. The WR vials are for higher Sm and Nd concentration (> ~10 ppm) samples and the Grt vials are for any low Sm and Nd concentration (< ~10 ppm) samples. Keep these separate at all times.
4. All 7 and 15 ml vials should be round interior bottoms for focusing the sample into a dot.

'Dirty' or used vials:

1. Remove ink and interior residue with rubbing alcohol and gloved finger.
2. Soak in warm water and Liquinox or Sparkleen 24 hrs.
3. Heat for 24 hr. in 1:1 mixture of reagent grade nitric-water (use Teflon pancake griddle at setting of ca. 60˚C –in perchloric hood)
4. Soak for 24 hr. in ca. 60˚C mixture of 1:1 reagent grade hydrochloric-water (in perchloric hood).
5. Soak for 24 hr. in ca. 60˚C of 1:1 reagent grade nitric-water water (place in perchloric hood).
6. Follow new vial procedure below.

Refluxing of vials prior to use (**Use for new or cleaned v ials**). Squirt ca. 1 ml of acid (use squirt bottle to cover bottom of vial) in each vial:

1. Vial caps should be screwed on tight during refluxing.
2. Hot plate T during reflux ~ 100˚C.
3. Reflux with ultraclean 2x concentrated HF — overnight.
4. Reflux with ultraclean 2x HCl (2 or 3 M).
5. Repeat HCl reflux
6. Rinse in ultrapure water if water is cleaner than acid.

Cleaning Agate Mortar and Pestle [normal procedure]

1. Grind pure quartz sand to powder.
2. Fill Mortar with concentrated **reagent** HCl and soak (with pestle) for ca. 1 hour.
3. Fill Mortar with concentrated **reagent** HNO_3 and soak (with pestle) for ca. 1 hour.
4. Rinse with trace metal grade ca. 7 M HNO_3.
5. Rinse with trace metal grade ca. 7 M HCl.
6. Rinse in ultrapure water. Repeat.

Leaching Agate Mortar and Pestle [Occasional procedure – see Stowell]

1. Clean – as below.
2. Carefully rinse all surfaces with HF. Let sit for 1 minute.
3. Carefully rinse all surfaces with ultrapure water.
4. Fill Mortar with 6 M HCl and soak (with pestle) for several hours. Repeat.
5. Rinse repeatedly in ultrapure water.

Cleaning Pipette Tips

Load and dispense [rinse] 2 M HCl 3 times making sure to get liquid high in the tip. Rinse three times in ultrapure water.

Carboy Cleaning Procedure

1. Remove spigot and thoroughly rinse.
2. Rinse carboy with ultrapure water (5 times).
3. On first and last rinse, fill to brim — otherwise — ~ halfway is sufficient.
4. Drain from spigot.
5. Fill and let stand for up to 2 weeks (if possible).
6. Repeat rinse procedure above and fill for use.

FEP - Fluorinated ethylene propylene - TYPICAL PROPERTIES

Property	Value	Units
Melting Point	**487 - 540** 253 - 282	deg F deg C
Thermal Conductivity	1.45 0.209	Btu·in/h·ft2·°F W/m·K
Heat Distortion Temperature, 66 lb/sq.in (0.455 MPa)	158 to 171 70 - 77	deg F deg C
Service Temperature	-418 to 403 -250 to 206	deg F deg C