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Isotope Geochemistry Lab Handbook

Lamont-Doherty Earth Observatory of Columbia University

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Credits

This Handbook is the product of efforts by many people.

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Notice to Non-Lamonters

This handbook is posted on the Lamont Isotope Geochemistry Lab Website (http://www.ldeo.columbia.edu/isotopelab/) and freely available to the geochemistry community. All comments and suggestions for modifications to our procedures are welcome and encouraged.

Please send them to Steve Goldstein: steveg@ldeo.columbia.edu.

Introduction

This handbook is meant as a guide to procedures in the Chemistry and Mass Spectrometer labs. **It should cover most routine analyses. Many of the analyses we make are non-routine,** and while experienced users are likely to deviate from some of these procedures, it is very important that all new members of the group should follow these guidelines.

This handbook is not a substitute for a mentor. All inexperienced users must go through all procedures with an experienced mentor until comfortable with the procedures.

All members of the lab are responsible to be aware of the important general information in this handbook.

Of utmost importance for all lab users is lab safety. Safety rules are for the benefit of everyone. Many of the procedures we use are potentially dangerous to the user and others. If safety procedures are followed, then we can expect that nobody injuries will be kept at a minimum.

The lab safety guidelines in this handbook must be followed. Anyone found deviating from them may lose their lab privileges.

*This Handbook will be con*stantly updated. Users should make sure they are using the latest version, based on the date *on the title page.*

Emergencies:

If there is an emergency situation anytime:

1) **Dial 555 to report an emergency immediately.** Dialing 555 sets off an alarm on the main LDEO switchboard, which is monitored all the time, and the Safety and Security Office will immediately respond.
2) Immediately notify Steve Goldstein.
3) Notify any other senior members of the lab who are affected.

Reporting Lab Infrastructure Problems

If there is ever a problem with lab infrastructure (non-working fume hoods, roof leaks, etc):

1) Immediately call Dick Greco at LDEO Buildings and Grounds.
2) Notify Steve Goldstein

Phone Numbers:

LDEO Safety and Security Office (Ray Long)	x8860.	
LDEO Buildings and Grounds (Dick Greco)	x8602	
Katie Donnelly	358-4059	
Marty Fleisher	212-864-7167	
Steve Goldstein:	x8787	(LDEO)
	359-5137	(home)
	729-4846	(cell)
Gary and Sidney Hemming	201-768-5828	

Behavior in the Labs

The chemistry labs at LDEO have many users. It is of the utmost importance to respect the rights of others. Behavior should be governed by common sense and the golden rule.

General Behavior Reminders:

- Anyone who does not show sufficient respect for the needs of others is subject to loss of lab privileges.
- Clean up after yourself. Everywhere – in the chemistry or the analytical labs. Once a procedure is finished, there should be no sign that it took place. If something is left running overnight on analytical equipment, it must be cleaned up within 2 hours of the next time the person is at LDEO.
- Be respectful of other people's things. Do not use anyone else's equipment or reagents without their permission.
- Do not take general use materials (e.g. titrating vessels, lab scissors, tools, beakers) out of their proper lab. If there is a good reason to do so, then leave a note and return it to its proper place immediately when finished with it.
- **All solutions and powders must be labeled.**
- We recognize that people make mistakes. If something goes wrong, please tell us so that we can fix it. Honesty helps everyone. Covering up for a mistake often causes a lot of extra work for a few of us and down time for all of us. Anyone caught covering up will be in big trouble.
- If you signed up for analytical time, you must be there. If you have to cancel, you are responsible to let other people know that there is open time.
- Keep a detailed lab notebook.
- Fill in any and all logbooks.
- Be careful with equipment used in common.
- All lab users are expected to contribute to maintenance. Almost everyone in the lab is assigned a maintenance task. These tasks must be performed and marked on the task checklist. If the checklist is not checked, then it will be assumed that the task was not performed.
- Before beginning work anywhere, tidy up the work area. If working in the lab, wipe down the lab bench.

Users who transgress the above general behavior guidelines will lose lab privileges.

- **All lab users must be familiar with Safety Rules, and they must be followed.**
- If you see someone showing poor lab practice, please help them by informing them.
- If a general use item is running low (e.g. pipette tips, kimwipes, filament wire, etc) let the person responsible for re-stocking know well in advance.

- Help with the general cleanup effort. If you see something on the floor or on a table that should be in the trash, please take a moment and put it there.

Chemistry Lab Safety Rules

Safety rules exist for the benefit of everyone. Anyone following poor safety practices not only endangers his or her self, they endanger everyone in the lab. The safety procedures followed in our laboratories must be in compliance with Columbia University safety rules. The full handbook is available on the web at:

http://www-admin.ldeo.columbia.edu/internal/safety/CU%20POLICY%20FOR%20SAFE%20USE%20OF%20CHEMICALS.htm.

Here we only include a summary of some important lab practices:

1) **Safety glasses must be worn** when working with or near chemicals, or other potential face and eye hazards.

The LDEO Safety Office will acquire any type of glasses needed, including prescription safety glasses.

2) In practice this means that you have to wear safety glasses in the cleanlab and Room 8. Safety glasses are required in the Axiom lab and the loading room when handling chemicals!

3) **Chemical suits** must be worn in the clean lab at all times. Lab coats should be worn in all chemistry labs when working with hazardous chemicals.

4) **Wear appropriate gloves** when handling chemicals and other materials that may be harmful to hands. There is no reason to throw away a perfectly good pare of gloves. **Gloves should be re-used**. Store them inside out and reuse them until they are ready to be disposed.

5) Wear closed toed shoes in laboratories.

6) **Do not work with sandals** in room 8, the Axiom lab or the loading room!

7) Eating or drinking is not allowed in wet chemistry laboratories.

8) Long hair, ties, long scarves etc. must be tied up in areas where entangling in machines or hanging into chemicals might occur.

9) Do not put anything on the lab floors as people might fall over it.

10) **Concentrated acids** should be opened only in the hoods

11) **When working with HF wear double gloves** and make sure not to leave any drops of HF anywhere as someone else might get injured later from it. Gloves in contact with HF should be disposed.

12) Use perchloric acid only in the designated hoods and attached drying boxes. Never dry down organics (e.g. alpha-HIBA) in the hoods designated for perchloric.

Anyone who shows poor safety procedures will lose chemistry lab privileges.

Storage of Acids, Bases, and Solvents

All containers (storage or squeeze bottles, squirt bottles, savillex beakers, etc.) in the lab must be labeled. Any unlabelled solutions found will be confiscated.

Original Containers and Distilled Acid Storage Bottles

Separate the following acids and chemicals that are in original containers spatially from each other, which means each category should be stored in a separate cabinet or shelf.

(1) Strongly oxidizing acids	-	concentrated nitric acid (~16N HNO_3).
		Perchloric acid (needs to be dated, when it is received in the lab and when it is opened)
		Never store strongly oxidizing acid bottles directly on wood.
(2) Other non-organic acids	-	hydrofluoric acid (HF)
		hydrochloric acid (HCl)
		dilute nitric acid (HNO_3)
		Hydrobromic acid (HBr)
(3) Organic acids		acetic acid
(4) Bases		Sodium hydroxide (NaOH)
(5) Solvents	-	Alcohol, Acetone
(6) Toxic	-	Carbontetrachlorid (CCl4) is at this point stored in Room 8, back room, in the left hood. Do not move.

In practice this means that all stored chemical in their original containers should be stored in deep trays that could contain the chemical in case a container breaks. Different trays have to be used separating the chemicals as listed above.

Solvents must be stored in the special solvent cabinet.

Working solutions

Working chemicals can be stored together, however, 16N nitric acid has to be contained (put in a plastic beaker that could contain the liquid in case the container breaks/leaks).

Rules for chemical waste

1) Each waste container must be labeled with an orange waste label.
2) Waste label must indicate EACH chemical put in the waste container, where the name of the chemical should be written out (e.g. "nitric acid" instead of "HNO_3", "alpha-hydroxyisobutyric acid" instead of "a-HIBA")
3) All non-organic acids can be discarded in one waste container with the exception of hydrobromic acid HBr and concentrated nitric acid (~16N HNO_3).
4) DO NOT dilute acid before disposal.
5) HBr needs its own container.
6) Organic acids (e.g. a-HIBA = alpha-hydroxyisobutyric acid) need their own container.
7) Solid waste (e.g. resin waste) needs its own container. Please put name of resin on the orange waste label (e.g. Eichrom Sr-Spec).
8) DO NOT date the waste label until it is ready to be moved to the main accumulation area (Traffic Dept.).
9) All waste alcohol, even from squeeze bottles, goes into a solvent waste bottle.
10) Solvent waste can be combined with the exception of halogenated solvents. We do not use these in the Clean Lab or Room 8.
11) Waste water should go down the sink. Most rinse water can go down the sink.
12) If there is any question as to whether a reagent should go into chemical waste, it is better to regard it as chemical waste.
13) Waste containers should be filled no more than 90% of capacity. **If the waste container is a blue 5 gallon one or a white 2 1/2 gallon one, fill them only to 2/3 maximum capacity.** Do not allow accumulation of waste in the labs but call security at x8860 to arrange pickup.

    If an additional waste container, or a different type, is needed, contact the LDEO Safety Office.

Lab Notebooks

Good lab notebooks are an important component of good lab practice. The importance of good records cannot be overemphasized. All lab members are expected to keep detailed lab notebooks. The more information in a lab notebook, the more likely it is that any problems that come to light can be traced. *If a lab member is unable to show that they are keeping good records of their work, they may lose lab privileges.*

Sample Preparation

Rock Crushing

When rock crushing and milling, safety glasses and face mask are mandatory.

1) Rocks are selected based on mineralogy and freshness and cleaned up. Altered, weathered surfaces are sawed off, and saw marks are removed with a grinding wheel.
2) Rocks are initially crushed between 2 steel plates (grade 4340 probably), using a hydraulic pump. Plates are 6.5 and 7 inches in diameter, and about 1.5 inches thick.
3) The resulting rock chips are sieved for size, as only those smaller then 1/4 inch in diameter can be crushed in the mill. Chips are rinsed with MilliQ water and cleaned in an ultrasonic; first with MilliQ water and then with Methanol, for 30 minutes each.
4) Chips are dried and then picked under the microscope. This is to ensure that only the cleanest and freshest rock chips are crushed. For the pre-contamination step (see below), chips do not need to suffer the same scrutiny.
5) All rock samples are crushed in an alumina mill and shatterbox. When only small amounts are available (<50 milliliters), samples are crushed in an alumina mortar and pestle.
6) To crush in the alumina mill, 50-60 milliliters (ml) of clean picked material is necessary; 25-30 ml for the pre-contamination step and 25-30 ml for the actual sample crushing. 25-30 ml are required for each step, in order to provide sufficient cushioning around the puck and along the mill walls.

Comments

- Do not sonicate with methanol as it evaporates unnecessarily

Using the mill

1) Always wear gloves when handling the mill! This is to protect the mill from any source of contamination.

2) First crush 25-30 ml of coarse grain sand in the mill. Quartz is a hard mineral and a very effective cleaning agent. The sand must be relatively pure quartz. Our sand was obtained from a construction company (Unimin) in North Carolina.

3) Sand is crushed for 270 seconds. Powder is dumped (in the trash, might want to wear a face mask, silica powder isn't good for you), and the mill is rinsed with water. Use gloved fingers to wash it out, and then rinse first with MilliQ and then Methanol. Squeeze bottles work best. The Methanol washes out most of the water and allows the mill to dry much quicker. Wash the lid and puck in the same fashion being very careful to not dirty the puck while handling it. Place all items under a heating lamp to dry.

4) Next is the pre-contamination step. This usually requires 180-270 seconds, depending on the hardness of the rock. This aliquot is crushed to reduce the effects of cross contamination, all the microscopic grooves and holes will become filled and lined with that rock's powder, as opposed to the sand or some other contaminant. Wash and dry in the same process as above.

5) Lastly crush your clean, microscope picked, aliquot of rock. 270 seconds works for most rocks, even some very tough basalts. Transfer powder to a clean glass vial. Glass is better than plastic because it reduces static.

6) The recipe for the alumina mortar and pestle is the same as for the mill. Clean the mortar and pestle by crushing sand, rinse with MilliQ and methanol, do a pre-contamination step, and lastly crush sample.

ICP-MS chemistry for Trace Elements

General Information

A standard batch of samples for ICP-MS trace element analysis includes:

- 10-14 unknown samples
- At least 4 standards for which the chemical composition is known. Standards should span a range of concentrations and be well matched to the unknowns.
- A “high” standard-used for controlling instrumental gain and monitoring drift. This standard should be well matched to the unknowns. If many runs are planned it is best to use the same high standard for all runs.
- A blank. As the high and blank are run repeatedly throughout the analysis, you will need to prepare several of these solutions. (Six high standard and two blank preparations are usually sufficient).
- An internal standard solution, which will be added to all samples and standards as a way of controlling instrumental gain and monitoring short term drift during the run.

Internal Standard Solution (ISS)

It is advisable to make the ISS early in the procedure as it needs time to homogenize. Four litres of internal standard solution will be needed for each ICP-MS batch. Use elements in your ISS that you don’t care about in your rocks. We use Germanium (74Ge), Indium (115In), Thulium (169Tm), and Bismuth (209Bi). Elements should span the mass range of elements you will be measuring.

Make a concentrated Internal Standard Stock Solution. This makes it much easier to prepare all subsequent batches of ISS. Be sure to clean the chosen metals (elements) for Pb and other possible contaminants; this is done by running dissolved material through Pb columns (see Pb chemistry below). To make the Internal Standard Stock Solution (ISSS) with ~ 25 ppm Ge, 4 ppm In, 5.6 ppm Tm, and 7.2 ppm Bi., add:

- 4 ml of 1000ppm Ge solution
- 1.01 ml of 792ppm In solution
- 1 ml of 1439 ppm Bi solution
- 1.12 ml of 1000ppm Tm solution

Then:

- dilute with quartz distilled (QD) water to 200 ml
- The ISS should be 0.2N HNO_3** (Double Distilled), as this normality ensures that all elements stay in solution.
- In, Tm and Bi concentrations should be between 5 – 10 ppb. Indium has the lowest concentration because we tune on that mass. The sensitivity will be highest on Indium and decrease on either side of that mass range.

- Ge has a higher concentration (~60 ppb), as the isotope we measure is only 1/3 of the total abundance. Also lower masses have lower sensitivities since we tune on In^{115}.

To make the Internal Standard Solution, mix:

- 50 ml of 16N HNO_3**
- 5 ml of Internal Standard Stock Solution
- about 4 litres of QD water

Add at least 1 litre of water before the acid and Internal Standard Stock Solution. Add the remaining volume of water in 500 ml increments, and shake between each aliquot to hasten the homogenization process. It is advisable to shake the ISS as much as possible, as a poorly homogenized solution will compromise the precision and reproducibility of the run.

Weighing and dissolving ICP-MS samples

This procedure is intended for silicate rocks of volcanic origin (basalt-rhyolite). It does not apply to sediments. For sediment procedures, see below.

15 ml Teflon beakers are used for ICP-MS chemistry.

1) Weigh out 0.05 grams of sample into each beaker. Samples are weighed to within 0.0005 grams (anywhere between 0.04950- 0.05050 grams). Record weight. (ICP-MS samples are weight calibrated so it is important to not lose any sample once it is weighed.)
2) After weighing, add a couple drops of quartz distilled water to wet sample and thereby reduce static. Don't underestimate the power of static! If more than a couple drops of water are added to each sample they will need to be dried down, otherwise they will dilute the acids.
3) • Each of the six high standards is measured out individually (to avoid long dry downs).
4) Add 1 ml HF and 0.5 ml 7N HNO_3, and put on hot plate overnight at 125°C. (The HF is concentrated and Seastar grade. The HNO_3 acid is concentrated (~16N) double distilled (**), and diluted 1:1 with quartz distilled water.)
5) Dry down on hot plate at 125°C.
6) Add 15-20 drops concentrated HNO_3** to each sample, and dry down again.
7) Repeat previous step. This breaks up the fluorides. Samples should look white on dry down.
8) Add 2 ml QD water and 2 ml 7N HNO_3 to each beaker, put on hot plate overnight at 125°C.

The next day samples should be dissolved. Hold closed beakers up to the light and check that samples are clear solutions.

Preparing the 2K solutions

Most convergent margin and MORB volcanic rocks are run at a 2000:1 and 10,000:1 dilution. These provide adequate concentrations within the machine's detection limits to yield high precision data.

1) Transfer contents of each beaker to a labeled 100 ml bottle.
2) Use 1 ml QD water to rinse out beaker and dump in bottle.
3) Repipette 95 ml of internal standard solution into bottle. Shake well.
4) All highs and blanks can be combined, respectively.

The elements typically measured in the 2K are:

Rb, Sr, Y, Zr, Nb, **Mo, Sn, Sb, Cs**, La, Ce, Pr, Nd, Sm, Eu, Tb, Gd, Dy , Ho, Er, Yb, Lu, **Hf**, Ta, **W, Tl**, Pb, **Th, U**. (Bolded elements are only run in 2K)

Preparing the 10K solutions

Make this solution at least 24 hours after the 2K, so that the 2K solutions have time to homogenize.

- Pipette out 6 ml 2K solution into new tared bottle, record weight.
- Repipette 24 ml of internal standard solution. Shake well.

The elements typically measured in the 10K solution are:

Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, **Ba**, La, Ce, Pr, Nd, Sm, Eu, Tb, Gd, Dy, Ho, Er, Yb, Lu, Ta, Pb. (Bolded elements are only run in 10K)

Distillation of Pure Reagents

QD Water Distillation

1) Make sure the chiller is plugged in and running. Lift up the lid to the plastic bin and see that the antifreeze is flowing through the 2 hoses.
2) Plug in the QD still to the wall.
3) Turn the valve on for the distilled water located in the hood where the acids are distilled. There is a black line that shows you how far to turn it. Be sure to see that the level in the QD still is refilling. It will refill very slowly, but sometime the line from the distilled water to the still gets air bubbles in it and prevents the still from refilling. Make sure to check the still periodically to know that it is refilling it before leaving over night. If there are air bubbles in the line you must clear them. Sometimes if you turn on the water strong at first then the bubbles will clear out by themselves. If not then manually force bubbles into the still by manipulating the hose. When the water is running into the still unobstructed then you can see a slight shimmering on the top of the water.

HCl Distillation

1) Refill the top HCl still by turning the knob to the HCl reservoir. When the reservoir is full the top still can fill up quickly so pay attention. Don't walk away. Fill to the line indicated on the top still.
2) Plug in the HCl still to the wall. There is a box that regulates the top and bottom stills. They should always be turned to max. Don't touch this, just plug and unplug in the wall. If the lower still looks low than you can unplug it from the box till it fills up again.
3) If there is acid in the overflow bottles then pour it back into the main reservoir to be distilled again. You can also use these bottles to pour in fresh acid to the reservoir.
4) When there is enough acid that has been doubly distilled then carefully remove the bottle from under the bottom still and wipe down the bottle with a wet kim wipe. You will have to pour the HCl into a smaller bottle. Make sure the bottle you pour into has been rinsed clean with QD. When pouring from the main bottle into the bottle people in the lab will use do not let the bottles touch. This can introduce contamination.
5) Be sure to fully label the bottle with what acid it is, that it is double distilled and the date when poured into the bottle.

HNO_3 Distillation

1) Refill the top HNO_3 still by turning both the valve near the reservoir and the one on the supply tube to the top still. This still doesn't fill as quick as the HCl, but don't walk away. Fill to the line indicated.
2) Plug into the wall. There are 2 plugs, one for the upper still, one for the lower still.
3) If there is acid in the overflow bottles, pour back into the reservoir. Also use these bottles to refill the reservoir

4) When changing the bottle remove the top carefully and have an empty bottle ready to replace the bottle you're taking off the still. Make sure that that bottle has been rinsed well with QD water and wiped down with a wet kim wipe. Switch the bottle off the still with the empty one.

5) Make sure to label the bottle as HNO_3, that it is double distilled, and write the date when it came off the still. Write a bottle number (1,2,3..) on there and make a note of which bottle you used for your chemistry in your notebook, along with the distillation date, so that if there are any problems they can be easily tracked down to a specific bottle at a later date.

If there are blanks on the acids then write that on the bottle as well. If the acid has been titrated recently then put it on the bottle. Be sure to put dates next to each of these things so that everyone knows the last time this was done. Take off these labels when the bottle is empty to avoid confusion.

Sample Processing for Chemistry

Rinsing samples:

All rock powders, mineral separates, and rock chips should be rinsed in QD water in an ultrasonicator, unless analyzing a soluble phase that would be lost is the objective of the procedure.

For isotopic analyses of Sr in carbonates, for example, a small amount of the carbonate will be lost, but there will be plenty of Sr left for analysis.

To leach or not to leach?

Before isotopic analyses of ocean floor basalts, oceanic island samples, and island arc samples, it is essential to subject them to a mild leach. We have had much bad experience with unleached samples showing a component of seawater Sr,

If samples are old enough that radioactive decay may have affected the isotope ratios, it is very important to consider whether the leaching procedure may preferentially dissolve an important phase. If the sample is young enough that all phases are expected to have the same isotope ratios, then it should be leached.

Because leaching may affect the trace element analyses, these should be performed on unleached aliquots of the same sample.

Refractory mineral phases – Bombing, fluxing, and sintering?

If a sample is likely to contain refractory phases (such as zircon, Ti-oxides, etc.) that may affect the results, then attempts must be made to dissolve the refractory minerals. This would hold for all siliceous rocks where REE or Pb isotopes are to be measured, including andesites, dacites, rhyolites, and sediments.

Leaching procedures of minerals and volcanic rocks

Leaching volcanic rock powders

1) Add 6N HNO_3, enough to cover powder
2) Cap samples and leave on hot plate at 150°C for 1 hour
3) Rinse samples with QD 5 times
4) Save leachates

Leaching Basaltic Lava Chips

1) Cover the chips with 8N HNO_3.
2) Sonicate for 10 minutes.
3) Pipette off liquid after sonicating and save leachate.
4) Rinse 4 times with QD water.

5) Dry.

Leaching of basaltic glasses

1) Place glass chips in cleaned (i.e. acid fumed) teflon beaker
2) Add enough 8N HNO_3 to completely cover glass chips
3) Close beaker tightly and sonicate for 10 minutes
4) Pipet off acid and save in an acid cleaned 2 ml centrifuge tube labeled "leachate"
5) Add enough QD water to completely cover glass chips
6) Close beaker tightly and sonicate for 20 minutes
7) Pipet off liquid and discard as waste
8) Leaching completed; You have exorcised the palagonitic demons; Rejoice.
9) Rinse 4 times with QD water.
10) Begin dissolution.

Leaching of mineral separates

H. Brueckner Leaching Procedure (good for mineral phases from fresh rocks):

1) Leach 1 hour in warm (100°C) 2.5 N HCl;
2) then leach 1 hour in warm 6N HNO3;
3) then leach 15 minutes in cold 5% HF. Make sure all serpentine is gone.
4) Decant leachate and save in bullets.
5) Rinse 5 times in QD water before dissolution.

J. Snow Leaching Procedure (very good for cpxs from abyssal peridotite or altered rocks):

This involves three leaches on each sample using a leaching solution of 6.2N HCl + 5% HF (95 ml 6.2N HCl plus 5ml conc. HF). Weight the samples between leaches.

1) First leach: at room temperature for 5 minutes
2) Second leach: in an ultrasonic bath for five minutes
3) Third leach: in an ultrasonic bath for then minutes followed by ten minutes in a drying oven at 125ºC.
4) Rinse three times with QD water, dry down the samples..

Zindler-Jagoutz Leaching Procedure (good for cpxs from fresh peridotite):

1) First leach: samples washed in hot (~100ºC) 2.5 N HCl for 20 minutes
2) Second leach: samples washed in cold 5% HF for 10 minutes, then immediately rinsed with several aliquots of cold 2.5N HCl (to remove possible fluoride complexes).
3) Rinse with 5 aliquots of water

Marine Sediment Leaching Procedure:

Our laboratory routinely measures the Sr and Nd isotopic composition of Fe-Mn oxides and detrital clay fraction of marine sediments. The following is the procedure necessary to extract the Fe-Mn oxide fraction, as well as remove carbonate and authigenic precipitates marine clays. Three steps are outlined; leaching carbonate with buffered acetic acid, washing, and reductive leaching of Fe-Mn oxides with hydroxylamine hydrochloride (HH). This procedure is adapted from Chester and Hughes, Chem Geol. 2, 249-262, 1967.

Preparing leaching solutions:

For 1ml solution of buffered acetic acid:

1) Begin with 500 ml H_2O.
7) Add 82 g of NaAc
8) Add 27 ml of HoAc (glacial)
9) Fill to 1 L with QD water

For 1 molar solution of hydroxylamine hydrochloride (HH):

1) Begin with 500 ml H_2O.
2) Add 1.3893 g HH.
3) Add 250 ml of Acetic acid
4) Fill to 1 liter of QD water.

Carbonate leaching procedure:

1) Bulk sediment samples from either dry or wet cores are placed in capped 15ml centrifuge tubes. For samples larger than 1 cc, or containing abundant carbonate, these samples are best leaching in 50ml centrifuge tubes.
2) Carbonate removal begins after adding buffered acetic acid to the samples. CO2 is liberated during this reaction, so that pressure increases in the capped tubes. In order to prevent leakage and spraying while leaching is in progress, only fill the centrifuge tubes to 2/3 capacity.
3) Use vortex mixer to dissaggregate samples, place on rocking table for 6 hours.
4) Afterwards, take from rocking table and fill with buffered acetic acid to 14ml, allow to sit 6-12 hours, or overnight.
5) Acetic acid with dissolved carbonate is removed after centrifuging, at medium speed for 20 minutes, and poured to waste.
6) Centrifuge tube is refilled with buffered acetic acid, dissaggregate using vortex mixer, and placed on rocking table for 6 hours.
7) Leaches are repeated until all carbonate is removed, signs of which include:
    a) Color of samples are uniform and dark-medium brown.

b) There is no CO2 gas pressure build-up during leaching.

c) No bubbles form when vial is opened (except from shaking).

For sediments from deep cores (low carbonate), 0.5cc samples, decarbonation usually takes 3-4 leaches. One extra leach is performed to assure complete removal of carbonate.

Fe-Mn oxide leaching procedure

1) Samples are washed with QD or millipure water, two or three times, before progressing to Fe-Mn removal. This is done by filling the centrifuge tube with water, dissaggregate using vortex mixer, centrifuging on low speeds for 30 mins, and pouring clear water to sink. High or medium centrifuge speeds create sediment clumping which are nearly impossible to dissagreggate. Take care not remove fine fraction when pouring out water.

The leach takes on a yellowish or light brown coloration when all the acetic acid with dissolved carbonate is removed. This is because all charged species (from the acetic acid and dissolved carbonate, etc.) have been removed and the solution is pure water. The lack of ionic charge allows colloids to become suspended in the solution. When this coloration appears, attempt to remove coloration by centrifuging for long durations (>1 hour), or by adding a few drops of clean buffered acetic acid solution and centrifuging.

2) Discard water to sink.

Fe-Mn oxide removal is done by placing the sample in a reductive solution, hydroxylamine hydrochloride (HH). The first leach, which can be analyzed for authigenic marine Nd and Sr, should be of the shortest duration (2 hours) to prevent attacking the sediment.

3) The centrifuge tube should be filled to 14 ml, dissaggregated using vortex mixer, and placed on rocking table for 2 hours.

4) This first leach, for Nd and Sr isotope analysis, should be poured carefully into a clean labelled centrifuge tube, which should itself be centrifuged down before being poured into a beaker for element separation chemistry. Utmost care should be taken to make sure that no sediment is transferred into the beaker.

To remove the remaining Fe-Mn oxides, two HH leaches are to be performed, the first of 6 hours duration, the second 6-12 hours or overnight. These leaches can be discarded to waste. Chester and Hughes, Chem Geol. 2, 3, 249-262, 1967.

Removal of Opal and Alumina

The procedure to remove amorphous silica and alumina assumes 0.5 gram of $CaCO_3$ free, Fe-Mn oxide free sediment

1) -Transfer iron free sediment to 250 ml Teflon or nickel beaker (i.e. avoid silica glass beakers)

2) -Add ~100ml 2% Na_2CO_3

3) -Agitate strongly with ultrasonic probe-about 2 minutes.

4) -Heat to boil for 5 minutes.

5) -Transfer to centrifuge bottles.
6) -Centrifuge until clear, discard supernate.
7) -Rinse 3x with distilled water

Chemistry Lab Guidelines

Lab Drawers

All people who are using a drawer for storage of materials must have their names on the drawers. If a drawer is shared, all the users must be listed.

Everything in unlabelled drawers is subject to confiscation.

Labware

Do not use anyone else's labware without permission.

Blanks

The importance of measuring blanks cannot be overemphasized. In general, too few blank measurements are made. Blanks can have specific purposes (to determine purity of solutions or portions of procedures such as columns). However, everyone should check the cleanliness of their sample preparation process by *regularly* measuring total procedural blanks.

A total procedural blank means, in general, that every step that is performed with a sample, beginning with dissolution, is also performed on a blank.

Labelling of samples

Pay the utmost attention to make sure that samples are in the correctly labeled beakers. Mislabeling and mixing up of samples is amazingly common in geochemistry labs.

HF addition to samples

HF can be absorbed by the skin and destroy bone material. Be very careful when using it.

Silica is dissolved by HF and volatilized as SiF_4. *In order to avoid the formation of insoluble fluoride precipitates during dissolution*, estimate the number of moles of Si in a sample, make sure the excess amount of HF is not excessive (e.g. a factor of 3 times the amount needed) and add an appropriate amount.

For example, for a 50 mg sample of a rock with 50% SiO_2, using this rule of thumb one would add ~0.25 ml of concentrated (40% or 22.6 M) HF.

However, for a given amount of sample, an appropriate amount of solution should also be added. A quarter ml is too little total solution for 50 mg of sample. Use nitric acid to obtain a reasonable amount of solution.

Sample size and amount of acids

The procedures below are appropriate for ~50-100 mg of silicate sample. *For larger samples, it is important to scale the procedure.*

Drying down samples and use of cleanboxes

Drying box space is limited and it is essential that users pay attention to the rights and needs of others.

- **Drying boxes that are being used are to be opened only by the user.**
- Drying box users must leave a note (a stick-um will do) **with name, date and time the boxes are occupied, and when they are expected to be vacated**. When samples are finished they should be removed immediately. *If the user of a cleanbox is unidentified, the samples may be removed.*
- *Avoid putting samples too close to eachother on the hotplate.* If they splatter they will contaminate eachother and the data will be bad.
- Avoid drying the samples at too hot a temperature.
- Avoid drying samples to an ash – it will not easily dissolve. In general it is worth the trouble to make sure samples are not excessively dry.
- If $HClO_4$ is used, then the sample must be strongly dried in order to drive out all of it. This must be closely monitored. *$HClO_4$ may only be used in specially authorized $HClO_4$ hoods.*

Pipettes!

Most people in the lab use the same pipettes. Misuse of pipettes can damage them and lead to contamination of samples. Be very careful and use good lab practice.

- Avoid letting sample into a pipette tip too rapidly. It will splash into the pipette itself.
- If a pipette tip has solution, keep the pipette nearly vertical.
- **If solution gets into the pipette, inform the person responsible for lab maintenance.**

Sample Dissolution Procedures

Sintering procedure

Sintering is a method used for dissolving refractory phases, i.e. those that do not dissolve easily like zircons. It is important to dissolve zircons for analyses of samples for Hf, REE, and Pb. It may be used if the samples are likely to contain zircons and Hf and/or Nd isotopes are to be analyzed. If Pb is to be analyzed, a careful evaluation of the blanks must be made before proceeding.

1) Weigh samples into the crucibles (100 mg?)
2) Add sodium peroxide in a ratio of 6:1 (sodium peroxide:sample) into the crucibles.
3) Carefully mix them together and finally cover with a thin layer of sodium peroxide.

4) Put crucibles in a muffle furnace at 480+/-10 degree for 0.5 hour.
5) After sample cools to room temperature, add water carefully in small amounts, resulting in a vigorous exothermal reaction.
6) Keep adding water until the reaction fully ceases. The result is a suspension of precipitated cation hydroxides in strong NaOH.
7) Transfer the suspension and centrifuge them, discard the NaOH supernate, which contains silica.
8) Add water to the precipitate and centrifuge again.
9) Transfer the supernate liquid into a second vial. Add HCl is added to the decanted liquid to test whether there is still silica, indicated by blurring of the liquid.
10) Continue to add water, centrifuge, and add HCl to the decanted supernate liquid until no more silica gel forms.
11) Dissolve samples in 12N HCl and transfer into beakers.

Microwave Bombing Procedure

Bombing is an alternative to sintering, and likely to give a lower Pb blank. A careful evaluation of the Pb blank must be made, however, before using this procedure on samples.

1) Weigh samples into Teflon beakers. Total sample number has to be even.
2) Add HF and 0.5 ml DD 7N Nitric acid into the beaker and dry down
3) Add 15 drops of DD 7N Nitric acid and dry down
4) Use 10 ml of DD 7N Nitric acid to dissolve the sample and transfer the bulk into clean centrifuge tubes
5) After centrifugation for minimum 30 minutes, transfer the solution into original beakers. The remaining undissolved part will be transferred into another set of beakers, dry down before putting through bombing.
6) Add 4ml DD concentrated Nitric acid, 100 ul Hf and 100 ul Perchloric acid into the beakers and tighten them.
7) (Use the special bomb Teflon cylinder casings for holding the beakers) Clean the inside of the white inner cylinder and dry them down at 50^{o}C on the hot plate. The outsides of cylinders have to be dry!
8) Put beakers into the inner white cylinders, add 10ml DD Nitric acid into the cylinders, cap them and fit the white cylinders into the brown outer cylinders. Cap the outer cylinders and put the lids on according to the number marked on cylinders. (All the contacting surfaces have to be dry) Number the outside of the cylinders according to the number of beakers since acid will wash away whatever is written on the beakers. Put cylinders in special holding box with stand.
9) Before bombing, cylinders have to be put into vessels and tightened up using torque wrench. (See Jamie before you do it for the first time)

10) Put vessels into the microwave following the right number and fit the vessels correctly into the holders. Outside of the liner and vessels have to be dry.

11) Enter “start” on the control panel and wait for a few seconds to open the microwave and check the spinning.

12) Run program 12 (Geochemistry special program)

13) Upon finishing of the program, wait for at least an hour to open the microwave and open the cylinders.

14) Open cylinders and drain the acid in the cylinder, wash cylinder with QD water for twice in order to dilute the acid outside the beakers before handling. (See Jamie for detailed instruction for first time users)

15) Take out the beakers from the cylinders and number them accordingly. Wash cylinders with water and dry down naturally before storage.

Conventional Bombs

1) Dissolve the samples in the normal manner as if the sample is not to be bombed (see procedure below), but do not dry down.

2) Ultrasonicate the solution in order to disaggregate any surface precipitates on remaining minerals.

3) Centrifuge samples. Remove the solution, being careful to avoid removing solid matierial. Store the solution.

4) Wash twice more with QD water or acid and add to the stored solution.

5) Quantitatively add the remaining material to the into the Teflon vessels. Be very careful as small mineral crystal may not be easy to see.

6) Add an appropriate amount of Hf and HNO3 to the bomb, and place the bomb in the metal jacket.

7) Place the assembled bomb in the oven at 150 degrees and leave for a couple of days.

8) Let the oven cool, or remove the bombs. Be sure they are cool before opening.

9) Carefully open the bombs, remove the Teflon vessels. Open them,

10) Dry them down, being careful to not overdry.

11) Add 7 N HNO_3 or 6N HCl and heat in order to dissolve the material.

12) Centrifuge. Add the solution to the stored solution of the sample. Hopefully there is no solid material left.

13) If there is solid material, repeat from Step 2.

Dissolving silicate rock powders without bombing or sintering.

This procedure is for rocks that do not contain refractory phases, or those that do not require total dissolution.

1) Add HF and 1 ml 7N HNO_3, cap beakers, and put on a hot plate overnight at 125°C

2) Dry down on hot plate at 125°C
3) Add 30-40 drops concentrated HNO_3 to each sample and dry down again
4) Repeat previous step (this should break down the fluorides and samples should look white on dry down)
5) Add 4 mL QD water and 4 mL 7 N HNO_3 to each beaker, or 6N HCl (depending on needs for additional chemistry). Cap the beakers, and put on a hot plate overnight at 125°C. The next day samples should be dissolved. Hold closed beakers up to the light and check that samples are clear solutions
6) Dry down.

Dissolution of basaltic glasses – (after leaching)

1) Add 8N HNO_3 and HF to each sample and one blank (NOTE – add nitric before HF)
2) Leave on hot plate overnight at 150º
3) Check to see if samples have dissolved completely by holding closed beaker up to the light and swirling. You should see a white fluffy solid residue if everything is dissolved (NOTE – you may see some very small, I mean tiny, black specs – these are oxides – if these are the only black things you see don't worry).
4) If sample is not completely dissolved (i.e. there are large black chips remaining in the beaker), add a bit more HF, and put back on hot plate at 150º
5) Once samples are completely dissolved, dry down completely at 125º
6) Add ~1 ml concentrated HNO_3, cap, swirl and place on hotplate at 125º for ~ 1 hr
7) Dry down completely
8) Add 1 ml 8N HNO_3
9) Leave on hotplate at 150º overnight
10) Dry down completely
11) Do a dance

Procedure for CPX, OPX and AMPH digestion

1) Sample size up to 200 mg. Preferentially use the 15 ml beakers.
2) If applicable, add the spike before dissolution.
3) Add a solution of HF + $HClO_4$ (8:1), up to 4 ml depending on sample size (~ 1 ml for 50 mg). Cap and leave overnight on a hot plate at 150˚ C.
4) Next morning open the beaker and evaporate to dryness on a hotplate at 200˚C. Be sure that the sample is well cooked and dry. It helps to put aluminum around the beaker for better heat distribution and to avoid static that could make the sample travel out of the beaker at high T.
5) Usually, $HClO_4$ condensates as a film on the walls of the beaker. If the sample is not loose, tilt the beaker, place a drop of water on the side of the beaker. Rotate the beaker so

that the drop sweeps the side without allowing the drop to touch the sample. Discard drop (careful that sample does not drop out). Rinse the walls of the beaker with drops of QD water and let dry again at 200˚C.

6) Repeat all over again till you get rid of all the perchloric and don't see any more film in the inner part of the beaker.
7) Add (0.5ml for 50 mg) 1 to 2 ml of concentrated HNO_3, swirl and evaporate on a hotplate at 150˚C.
8) Repeat.
9) Add 1 to 2 ml of concentrated HNO_3, swirl and evaporate.
10) Add (0.5ml for 50 mg) 1 to 2 ml of 8N HNO_3, cap and leave overnight on a hotplate at 150˚ C.
11) Next day open the beaker. Before beginning chemistry the minerals MUST be in solution. If so, dry down and proceed to column chemistry.

Dissolving Basalt Chips

1) Add HF and 1 ml 8N HNO_3, Leave overnight on hot plate.
2) Evaporate to dryness
3) Add 1 ml conc HNO_3, Swirl and evaporate
4) Repeat.
5) Add 1 ml 8N HNO3 and leave overnight.
6) If in solution, done. Go to Pb chemistry.
7) If not, completely in solution, add 0.5 ml conc HCl. Swirl, Cap and Let sit for 1hour.
8) Add QD to fill to half beaker volume.
9) Evaporate and go to Pb chemistry.

Coral Processing for U-Th Analysis

Cleaning, weighing and spiking:

1) Start with thoroughly clean coral cut or crushed into pieces a few millimeters in size.
2) Sonicate repeatedly in MQ H_2O until wash is no longer cloudy.
3) Drain and dry in dry down box or in oven (low heat).
4) Accurately weigh about 1 g of sample in cap of 17 ml Savillex beaker.
5) Weigh appropriate amount of $^{229}Th/^{236}U$ spike into beaker itself. Be sure to dilute with MQ H_2O to prevent severe reaction.
6) Add weighed sample to beaker.

7) To dissolve coral add concentrated HNO_3 a few drops at a time until all solid is dissolved (about 1 to 2 ml). To ensure complete equilibration of spike with sample allow to stand overnight before proceeding.

Iron Co-precipitation:

1) Prepare Fe solution by dissolving solid Fe in 7N HNO_3. This reaction will take a few days.
2) To clean Fe solution, pass through anion exchange column (see below for column prep). In 7N HNO_3, any U or Th will stay on the resin while the Fe passes through.
3) Dry down and dissolve in 6 N HCl.
4) Check Fe concentration by drying down a small aliquot and weighing.
5) Adjust concentration to about 9 mg $FeCl_3$ per gram by adding appropriate additional HCl.
6) Add 3 or 4 drops Fe solution to dissolved coral sample.
7) Add NH_4OH to achieve a pH of 7-8 (check w/pH paper) and Fe will precipitate. Do not make solution more basic than pH 8 or $Mg(OH)_3$ will also precipitate.
8) Centrifuge for 30 minutes at full speed and discard supernatant. Rinse solid in with MQ H_2O and centrifuge again and discard supernatant.
9) Dissolve solid in 1 ml 7N HNO_3 and reflux at 110° C until solution is clear.
10) Evaporate to dryness and dissolve in 0.5 ml 7N HNO_3. Sample is now ready for ion-exchange column.

Dissolving Insoluble Residues

Often despite all efforts there is an insoluble fluoride residue. This procedure should be performed for the first time with an experienced individual. Note that there is a high Pb blank.

Large Volume:

1) Add 1-2 ml concentrated HNO_3
2) Add 7ml $HClO_4$ (Perchloric Acid)
3) Heat the samples at 250°C (The Savillex beakers begin to melt ~260°C.)
4) After dense white fumes appear, add 1 ml concentrated HF. Return the samples to the hotplate to fume. (Repeat this step until the samples are completely dissolved.)
5) Dry the samples down.
6) Dissolve in HNO_3.

Small Volume:

1) Add 50 µl concentrated HNO_3
2) Add 100 µl $HClO_4$ (Perchloric Acid)
3) Heat the samples at 250°C (The Savillex beakers begin to melt ~260°C.)

4) After dense white fumes appear, add 50 µl concentrated HF. Return the samples to the hotplate to fume. (Repeat this step until the samples are completely dissolved.)
5) Dry the samples down.
6) Dissolve in 50 µl HNO_3.

Column chemistry procedures

Tru-Spec for REE separation

Tru-Spec chemistry (Eichrom TRU resin - TR-B25-A) is used to separates the REE from Sr, Rb, and other cations.

Tru-Spec columns:

Columns have a volume of 100 ul. Pb columns may be used.

1) Dry Eichrom TRU Spec resin is placed in long beaker or centrifuge tube.
2) Wash with 1N HNO3, allow to *fully* settle.
3) Discard floating resin.
4) Wash with QD water, allowed to settle.
5) Discard floating resin.
6) Repeat water wash 5-6 times, until no resin floats.
7) Fill column with resin to neck, or slightly overfill. If underfilled, bubble/gap may form at resin top preventing flow

Tru-Spec procedure:

1) Wash column with 3 times each with 8 drops reservoirs of 1 N HCl to remove contaminant REE.
2) Dissolve sample in 0.5 ml of 1 N HNO_3.
3) Prime column with 8 drops of 1 N HNO3 to charge the resin.
4) Centrifuge sample for 20 min on high.
5) Load sample on column with 0.5 ml of 1 N HNO3. Pipette avoiding solids
6) Collect Rb, Sr and other cations with 4 drops of 1 N HNO3.
7) Continue to collect Sr and other cations with 8 drops of 1 N HNO3.
8) Continue to collect Sr and other cations with 8 drops of 1 N HNO3.
9) Collect REE with 8 drops of 1 N HCl.
10) Continue to collect REE with 8 drops of 1 N HCl.
11) Dry Rb-Sr cut on hotplate set at 150 C.
12) Dry REE cut on hotplate at 100 C or less.

Sm-Nd Chemistry

Columns for Sm-Nd chemistry

Nd and Sm were separated using an 800 microliter ion-exchange TEFLON column from Savillex

It is extremely important that the volume of the resin is as equal as possible to 800 microliter, as slight changes in the resin volume could compromise the elution curve of REE.

Preparing Sm-Nd columns

The resin is BIO-RAD AG50W-X4, 200-400 mesh (hydrogen form), CATALOG No 142-1351 from BIO-RAD Laboratories

1) Disperse it in water a few times and pour off the fines
2) Bathe it in 6N HCl overnight a couple of times, and agitate it
3) Pour off the acid (and any more fines),
4) Dilute the acid with a few batches of QD H_2O (3 times).
5) Add some water and then put a little ammonia in until the pH is close to 7.
6) Pour off the water. If you have any old batch of alpha-HIBA resin left, add it to the new one. Let that equilibrate, check the pH, and you should be ready to go.

Preparing alpha-HIBA

1) Dissolve alpha-HIBA crystals in clean water aiming for 0.15 molarity. Formula weight or molecular weight of alpha-HIBA crystals is 104.11 grams/mole
2) Amount of alpha-HIBA crystals you want to use: 100 grams; moles of alpha-HIBA in 100 g is 0.96 moles
3) Desired molarity (moles solute/liters of solution) for alpha-HIBA: 0.15. Amount of water you need to add for 100 g of crystals = 6381.56 ml
4) Adjust the pH to 4.8 adding Ammonia to the solution
5) calibrate the elution curve:
    a) take 1 ml of the mixed REE in Inner lab, dry it down and pick it up in 100 microliters of alpha-HIBA acid
    b) proceed with alpha-HIBA column chemistry and collect every 500 microliters of eluent
    c) dry down samples and pick up in whatever acid you need for ICP-MS or AXIOM analyses
    d) analyze at the ICP-MS or AXIOM and
    e) let everybody know what the new elution curve is.

Alpha-HIBA Chemistry

Alfa HIBA column chemistry changes with every new batch of alfa HIBA acid

Please check that you are using the correct resin and acid prepared for your elution curve

Alpha-HIBA Column Chemistry based on acid prepared on February 14, 2003:

1) Nd columns (800 microliter)
2) Load column with Alpha-HIBA resin
3) Charge the resin with 1ml of Alpha-HIBA acid
4) Pick up sample in 100 microliter 0.15 M Alpha-HIBA acid
5) (sometimes it is very tricky to get the REE cut into solution in Alpha-HIBA acid.
6) Be careful and do not dry down too hard the REE cut from TRU spec or Sr spec chemistry,
7) if that happened dissolve the REE cut in 1N Nitric or HCl, look the sample while it dries
8) and do not let it dry completely; when it is a very tiny droplet add the 100 microliter of Alpha-HIBA, it should go directly into solution)
9) Load sample in 100 microliter Alpha-HIBA HREE come out
10) Wash with 200 microliter Alpha-HIBA HREE come out
11) Wash with 200 microliter Alpha-HIBA HREE come out
12) Wash with 2 ml Alpha-HIBA Gd + Eu come out
13) Elute with 2 ml Alpha-HIBA Collect Sm
14) Wash with 2.5 ml Alpha-HIBA
15) Elute with 2.75 ml Alpha-HIBA Collect Nd

Alpha-HIBA Cleanup

1) Dry down at high temperature, 180-200 ˚C
2) Dissolve repeatedly with few drops of aqua regia and dry down at 180-200 ˚C. Repeat till the sample is clean from Alpha-HIBA
3) If you have a spare night just add a few drops of aqua regia to your eluted Sm or Nd, cap and let sit overnight on a hotplate at 150 ˚C
4) The next morning open and dry down, magically Alpha-HIBA should be gone.
5) If any of the previous does not work, add some perchloric and dry down at high temperature.

Pb Chemistry

EXTREMELY IMPORTANT NOTE: Atmospheric Pb is everywhere. It is your most feared enemy when doing Pb chemistry. Take every, I mean every, precaution possible to avoid contamination by clean lab fuzzies or any other unsavory items. Clean all lab surfaces before

beginning chemistry. Do chemistry on a raised plastic stand. Never reach over an open beaker. Never lean over a beaker to look inside it. Wipe all beakers before opening them. I know this seems out of control, but it makes an immense difference. Find out for yourself if you don't believe me.

Pb blanks:

Every batch of Pb chemistry must include a total procedural blank.

1) Perform all of the dissolution procedures on a blank.
2) When the last step is performed, spike your blank with ~100 mg of dilute 208/235 spike or 10 mg of 206/235 spike.
3) Continue with Pb chemistry as outlined below.

Constructing Pb columns

The Pb columns are constructed from PTFE 4:1 H/S Clear Shrink Tubing, 3/8" diameter (from Zeus Industrial Products - www.zeusinc.com). Columns are 100 microliter volume.

1) Find the column making implements. These include a heat resistant teflon stick with a rounded end and a thin metal stick that fits in the end of the teflon stick.
2) Cut a section of tubing ~2" long.
3) Place one end of the tubing around the teflon stick (the tubing should surround the thin metal stick protruding from the teflon stick).
4) Hold the tubing inside a heater at ~600 degrees and rotate it so that the tubing shrinks around the metal stick. Once the tubing has shrunk, take it out of the muffle furnace and let it cool by running water over it.
5) Remove the tubing from the implements and voila, you have a Pb column.
6) Wedge a small piece of frit material in the bottom of the column.
7) Push the frit up into the column high enough that the volume in the stalk of the column is 100 ul.
8) The volume of the reservoir should be ~1.3 ml (the exact reservoir volume will vary depending on who made the column).
9) Cut off excess column length with a pair of ceramic scissors found in the clean lab

Preparing Pb columns for chemistry:

Resin used is AG1 X-8 100-200 mesh anion resin.

1) Turn the column over and fill it from the bottom with water.
2) Then turn the column right side up and fill the reservoir with water. Before proceeding, make sure that there are no bubbles in the stalk of the column.
3) If there are no bubbles, rejoice and fill the column with AG1-8X 100-200 mesh resin by loading the resin into the reservoir with a pipette. At this point, your task is to fill the column stalk with resin just up to the neck of the column trying not to leave excess resin

lying in the reservoir. If you succeed, you may commence with the separation of Pb from your sample.

Pb chemistry procedures

4) Pick up all samples and blank in 1-1.5 ml 0.7 N HBr
5) Leave on hotplate for at least 2 hrs. Overnight is better
6) Pipette off HBr and tranfer to 2 ml acid cleaned centrifuge tube. Be sure to get as much liquid as possible. Don't worry if you pick up some solid in the pipet as well. Just put it all into the centrifuge tube
7) Centrifuge samples to drive all solid to the bottom of the centrifuge tube
8) Rinse Pb columns with 240 µl QD 3X
9) Rinse with one reservoir 6N HCl 3X
10) Rinse with 240 µl QD
11) Charge the resin with 240 µl 0.7 N HBr
12) Load sample onto the column – at this point you should begin collecting into the original beaker ion which you dissolved your sample
13) Add 300 µl HBr 3X
14) Add 240 µl 2N HCl - this is waste don't collect it
15) Elute Pb – Add 0.5 ml 6N HCl 2X – collect in new beaker labeled " sample # - Pb"
16) Dry down Pb
17) Pick up in 0.5 ml 0.7 N HBr
18) Rinse columns with 240 µl QD 3X
19) Rinse with 1 reservoir 6N HCl 2X
20) Rinse with 240 µl QD
21) Charge resin with 0.5 ml HBr
22) Load sample onto the column – this waste don't collect
23) Add 300 µl 0.7 N HBr 3X – this is also waste
24) Add 240 µl 2N HCl – this is waste
25) Elute Pb - Add 0.5 ml 6N HCl 2X – collect in beaker labeled "sample # - Pb"
26) Dry down (add 2-3 drops of phosphoric acid before you dry down so that you can see the spot when it dries down)

Sr Spec Column Chemistry

Sr Spec columns

The Sr column is made of teflon shrink tubing. Sr chemistry is performed using a 30 µl column volume.

The Sr columns are constructed from PTFE 4:1 H/S Clear Shrink Tubing, 3/8" diameter.

Sr chemistry is performed using a 30 µl column volume, with a ~0.5 ml reservoir volume.

To make Sr columns, use the 6 mm diameter mold, and place the 1mm diameter metal needle at the end. Cut 10 cm of tubing for use. Place one end of the teflon tubing on the mold (the side with the metal needle) and slide tubing up 14mm (to the end of the brown part of the mold). Place the end of the mold without the tubing in a copper rod. Preheat the oven to 500 degrees. Stick the tubing into the back of the oven, but hold the door open and hold onto the rod. Rotate the rod around for even heating. Rotate until tubing has shrunk to the mold. Take rod out of the oven, stick tubing and mold in deionized water, but do not bend column (because it is still soft and this will destroy the column). Twist tubing off the mold once it has cooled. Make sure the bottom of the reservoir is smooth.

Make a frit for the column using the frit punch and make 1mm diameter frits from a sheet of the X-4900 1/16" Fine Sheet UHMW frit material. Use the frit screwdriver tool to push the frit into the column bottom. Calibrate the column capacity by pippetting 30uL QD into the column and then adjusting the frit until the water hits the mouth of the column.

Place columns in 6N HNO3 overnight.

The Sr Spec resin should just be enough to slightly protrude from the neck of the column into the reservoir.

Rb-Sr column procedures

The procedure below allows for collection of REE in the case that Nd will be analyzed from the same split. If not, follow the procedure without collecting the REE cuts

1) Take Sr-REE cuts from Pb chemistry or the Sr cut from Tru-Spec chemistry and dry down.
2) Pick sample up in about 0.5 ml 3N HNO_3.
4) Wash 3x reservoir with QD to clean columns to remove any Sr.
5) Add 8 drops of 3N HNO3 to equilibrate the columns.
6) Load sample in 0.5-1.0 ml 3N HNO3.
7) Wash out other elements with 8 drops 3N HNO3. Collect for REE and Rb.
8) Continue to wash out with 8 drops 3N HNO3. Collect for REE and Rb.
9) Continue to wash out with 8 drops 3N HNO3. Collect for REE and Rb
10) Collect Sr by eluting with 3 reservoirs of QD water.

After finishing the chemistry, discard the resin in the resin waste bottle and clean the columns by placing them back in their container (which should contain a mixture of QD water and

concentrated Nitric Acid) and sonicating them for 20. Once the sonicating is done, place the acid-water mixture in the appropriate acid waste container and store the columns in with fresh QD and Nitric acid.

Hf separation column chemistry

Hf columns:

The first column uses Bio-rad 10ml columns and volume of resin is 600ul. The resin is AG1-X8 (anion resin) 100-200 mesh.

The second column uses made using Teflon heat shrink tubing. The upper reservoir needs to be more than 10ml and resin volume is 1ml. To make the columns use TFE 3/4" 4:1 heat shrink tubing, and shrink under 400 degrees. The resin is EICHROM Ln-spec resin 1ml (100-150um H+ form).

Hf Separation Procedures

Sample Prep for Hf column chemistry

1) Dissolve samples in 1.5ml 4N HF.
2) Centrifuge sample for 30min. at high speed.
3) Transfer the residue into beakers with 5ml concentrated HF capped on hotplate at 100 degrees over night.
4) Centrifuge again 30min, high speed.
5) Dilute the leachate to 4N HF. Sample is ready to load on columns.

First Column:

1) Wash the columns with 10ml QD water.
2) Wash the columns with 10ml 6N HCl-1N Hf.
3) Wash the columns with 2 ml 4N HF.
4) Dissolve sample in 6N HCl.
5) Load sample on column the column.
6) Elute REE with 10 ml 4N HF.
7) Elute Hf, Zr and Ti in 10ml 6NHCL-1NHF

Second Column:

1) Clean resin with 10ml QD water
2) Wash resin with 10ml 6NHCl
3) Wash resin with 10ml 2NHF.
4) Precondition resin in 2ml 3NHCL

5) Dry down sample and load in 5 ml 3N HCl
6) Rinse with 10ml of 3N HCl to remove matrix elements, leaving HREE behind.
7) Wash out HREE with 10 ml 6N HCl.
8) Add 2 ml QD to wash out HCl.
9) Add 2 ml QD again to wash out HCl.
10) Add 55ml 6NHCl-0.06N HF to wash out Zr and Ti.
11) Collect Hf with 12ml 6NHCl-0.2N HF.
12) Clean resin for re-use with 10ml 6N HCl.
13) Continue to clean resin with 10ml 2N HF.
14) Repeat last two steps once more.
15) Rinse resin with 10 ml QD water
16) Store columns in QD H2O.

U-Th chemistry for carbonates:

Columns for U/Th separation

Columns are made from 5/8" PTFE (Teflon) heat shrink tubing with a shrink ratio of 4:1, available from Zeus Products, 620 Magnolia Street, Orangeburg, SC 29116. Phone: (800 526-3842).

1) 6 cm lengths of tubing are shrunk in a muffle furnace on a 5/8" mandrel inserted about half way into the tube. This kept half the tubing at the full 5/8" while the remainder shrunk to about .178" ID (manufacturers specification).
2) Afterwards, about 1 cm was trimmed from the wide end of the tube, and a frit was installed (press fit) into the narrow end of the tube. This results in an exchange column with about a 0.5 ml resin capacity and 3 ml reagent reservoir.

U-Th Column Chemistry:

1) Mix Dowex AG1-X8 200-400 mesh resin with enough MQ H_2O to make a thick slurry.
2) Add about 0.5 ml resin to columns, filling resin chamber to top.
3) Wash resin with 2 ml 7N HNO_3, 1 ml 0.1 N HCl, 6 N HCl, and 1 ml MQ H_2O in succession, letting each reagent drain through resin before adding the next.
4) Repeat this two more times.
5) Condition resin twice with 20 drops of 7N HNO_3.
6) Load sample in 0.5 ml 7N HNO_3.
7) Wash resin twice with 30 drops of 7N HNO_3 to remove Fe.
8) Collect Th by washing with 6 N HCl: 15 drops, 30 drops & 30 drops.
9) Collect U by washing with 1 N HBr: 15 drops, 30 drops & 30 drops.

10) Dry down U and Th separates and dissolve in 1 ml 7N HNO_3.

11) Repeat dry down and dissolution. Samples are now ready for dilution and analysis by ICP-MS.

TIMS Procedures

Regular Mass Spec Cover Slip Cleaning

1) Fill beaker of dirty cover slips with MilliQ water enough to submerge the coverslips
2) Put half a capful of ultrasonic soap in beaker
3) Sonicate for 1/2 hour
4) Pour out water
5) Rinse several times with MilliQ water until no more soap is left
6) Put coverslips into the clean jar
7) Fill clean jar with enough methanol to submerge the coverslips
8) Sonicate for 1/2 hour
9) Pour methanol back into the reusable bottle
10) Put jar into oven until dry

Polishing Mass Spec Cover-slips

To be done at least once per month.

Prior to step 1 from the regular cleaning, mix cleansing powder and tap water on watchglass in loading room with toothbrush. Rub each coverslip on all sides using toothbrush with the mixture. Once done with all coverslips, rinse jar and coverslips with tap water until no cleanser left. Then proceed on with step 1 in regular cleaning.

Cleaning Turret Blocks

To be done twice per year if used normally.

1) Ultrasonicate blocks with deionized water and ultrasonic soap
2) Rinse blocks with deionized water until soap removed
3) Rinse blocks 3 times with QD water
4) Rinse blocks with methanol
5) Dry blocks in oven

Cleaning Filament Posts

1) Remove old filament wire by filing it off
2) Put filament posts into small glass beaker
3) Put MilliQ water in beaker (enough to cover posts) and a small amount of sonicating soap
4) Sonicate for 20 minutes

5) Rinse with MilliQ until no more soap left
6) Submerge filament posts with MilliQ
7) Sonicate for 20 minutes
8) Pour our water
9) Submerge posts with methanol in reusable bottle
10) Sonicate for 20 minutes
11) Pour methanol back into bottle
12) Dry down posts in oven

Filaments:

Degas filaments at least two days before loading samples. The oxidized coating that forms helps to keep samples from spreading or popping off.

Preparing Filaments

Filament material is very expensive! Do not waste it!

The method described below uses the smallest possible amount of material.

1) Do not cut filament in pieces but take long piece (e.g. Re) or roll (e.g. W)
2) Spot weld end of filament to one side of the post
3) Pull filament tight over the second post and attach about 2mm
4) Take small scissors and cut filament off as short as possible
5) Attach end of filament to post
6) (filament ends standing off the posts could cause shortages under HV)

Degassing of Filaments

24 filaments in the holder

1) Make sure that ion gauge is OFF ! (sensor 1)
2) Turn turbo pump off to open degasser (bottom control box ON/OFF switch)
3) Put in holder and attach wires
4) Check that connections are good and set up filament control
    a. turn on filament control
    b. Switch to voltage mode
    c. Hold display setting button and crank up to 60 volts (this is setting upper limit)
    d. Let go of button and voltage should drop to zero (if not connection is bad)
    e. Switch to current, DON'T hold display setting button

f. Turn current up to 0.1 amps, if it goes up connections are good.

5) Close degasser, turn turbo pump on
6) Wait until all the green lights of the turbo pump are on (better 10 minutes)
7) Then turn ion gauge on (sensor 1, press emis.)
8) When pressure down to $2*10^{-6}$ start turning up filament current slowly
9) Never let pressure get higher than $8*10^{-6}$
10) Degas tungsten at 3.8 amps, rhenium at 4.8 amps for 20 min
11) When done turn off filament control panel and ion gauge
12) Allow 1 hour for filaments to cool down before opening the degasser
13) Empty degasser should be closed with turbo pump on

Loading Samples on filaments

Sr loading procedures:

You must first figure out how many ng of Sr are in each sample. You ideally would like to load ~100 ng of Sr. Be sure to add enough water or acid to your sample to be able to take 1µl of solution to load ~100 ng of Sr.

Cautionary note: Sr-Spec resin has a very high K_d for HNO3. If there is any resin in with the separated Sr, then if HNO3 is used the Sr is likely to stick to the resin and may not make it to the filament.

In addition, it is important to load solution and not resin.

Separating Resin from Sr:

If there is resin with the separated Sr:

1) Add 0.5 ml QD H2O and sonicate for 15 minutes.
2) Centrifuge at high speed for 15 minutes.
3) Pipette out solution, taking care to avoid resin.
4) Dry down.

Loading Sr samples.

1) Dam a W filament with parafilm on both sides *if you wish* (at ~1.3A)
2) Pick up 1µL of the sample and put on the center of the filament wire
5) Dry down sample very slowly at 1.1 amps
6) When the sample is ALMOST dry, but not completely, add 1µL of Sr Loader without turning off amps and continue to dry down at 1.1 amps.
7) Turn off the light in the laminar flow hood

8) When dry, bring up the current until the filament just begins to glow faintly and hold for 20 seconds

Loading Sr Standards

1) Dam a W filament with parafilm on both sides *if you wish*.
2) Pick up 1µL of the NBS987 (or ~100 ng) and put on the center of the filament wire
3) Dry down NBS987 very slowly at 1.1 amps
4) When the NBS987 is ALMOST dry, but not completely, add 1µL of Sr Loader.
5) Continue to dry down at 1.1 amps
6) Turn off the light on the laminar flow hood.
7) When dry, bring up the current until the filament just begins to glow faintly and hold for 20 seconds

Nd Loading Procedures

Use Rhenium filaments

Parafilm dams are not necessary (though Conny uses parafilm with success for small mineral samples)

Nd STANDARD: La Jolla Nd Standard, generally, 70 to 140 ng of solution is loaded. USE YOUR OWN ALIQUOT.

Nd SAMPLES: Dissolve your samples in 0.5N Nitric or whatever you like.

1) Load 1 ul or fraction thereof, and dry at 1.2-1.4 amps
2) When dries to a thin film, turn heat up steadily and slowly till it gloves (let it glove for 1 second). Then turn it down. It is ready to go into the machine.

Pb Loading Procedures:

1) Load sample/standard on Re filament.
2) Dry at around 1 amp.
3) Add 2 uL of silica gel, immediately add 0.4 uL of 0.5M H_3PO_4 while still wet.
4) Dry at around 1.3 amps. Allow it to dry completely. Standards turn clearish and smooth. Samples may be blackish but they are fine. Again let completely dry.
5) Slowly turn up until it glows. Should turn nice smooth white. Only turn up to dull glow for a few seconds and then turn down.

Procedures for changing the Turret on the TIMS

Loading the Turret:

1) Use gloves

3) Take your box with your samples numbered inside, and the sheet of paper that you filled out when loading and fill the turret according to the order that you loaded.
2) Posts should be loaded so that the opening where the screws go faces the center of the turret.
3) Make sure both the blocks and posts are secure in the turret.
4) Place clean cover slips on each block. Make sure that you can see your sample through the slit in the cover slip.
5) For blocks that are closed on the end use the cover slips that are open ended
6) For blocks that are open on the end you can use either the open or closed ended cover slips.
9) Jiggle the turret a bit so that you're sure that nothing will fall off once the turret is in the machine.

Changing the turret:

1) Be sure the Mass spec is ready:
2) High voltage off.
3) Filament currents off.
4) Ion gauge off.
5) LOS valve closed.
6) Open the source. The source should be under vacuum, so…
7) turn off the roughing pump first, by turning the knob until no red is showing
8) turn off the turbomolecular pump by pressing the on/off switch
9) give it a couple of minutes and then slowly lift off the cold finger. You'll want to be patient and lift slowly to break the seal. Once the cold finger is off place it to the side and open the door to the source.
10) Remove the source plate by unscrewing the 2 screws and place to the side. Do not lie the plate on the wipers as this may bend them.
11) Remove the turret currently inside by attaching the turret tool and unscrewing. Place that turret on a piece of paper and cover with plastic wrap. Put the name of the person who's turret it is on the paper if you know so they can claim it.
12) Use the turret tool to seat your turret in the source. Carefully rotate the turret to check that the posts are correctly aligned to go between the 2 middle wipers. You do not want the wipers to be deflected very much to the inside or outside. If a post needs to be adjusted use the block tool to push them out of pull them in so that they are properly aligned. **Rotate the turret in both directions fully to make sure all the posts go through smoothly.**
13) Be careful when replacing the source plate…try not to jam it in there. You'll want to try and replace it so that it the wipers are in between posts in case the posts are seriously

misaligned. Also make sure the source plate is flush and screwed in tight. Remove the turret tool if you haven't already.

14) Before closing the door to the source wipe the perimeter of the door where it seals with a kimwipe. You'll want there to be no dirt etc. so that you can get a good vacuum.

15) Before replacing the cold finger you'll also want to use a kimwipe to clean the part of it that makes the seal to achieve a good vacuum. Also check that the O-ring is in place and well seated before you place the cold finger.

16) With all this done you are ready to put the source under vacuum again. Turn on the roughing pump, wait for ~20 seconds and then turn on the turbo pump.

17) Wait ~15 minutes, then turn on the ion gauge.

Running the TIMS

Liquid Nitrogen

LN_2 should NOT be used to reduce pumpdown time. Anyone who uses it in this manner is liable to lose laboratory privileges.

If LN_2 is used, the reservoir must be monitored and re-filled. *Do not allowed it to run out over the course of a run.*

TIMS Logbook

It is essential that everyone keep a record of analyses in the Logbook.

At the beginning of each day, each user **must log in:**

1) The date.
2) Name.
3) Types of analyses to be run (e.g. Sr isotopes).
4) Types of samples to be run.
5) Temperature and humidity.
6) High voltage for a good mass calibration.
7) Source pressure.
8) Flight tube pressure.

The record of the results must be logged in within a day of running.

Comments are useful for all users. *Comments on the behavior of the instrument, etc. should be written in the log book every day.*

If anything strange is observed, it should be logged.

Failure to observe these procedures may result in loss of running privileges.

Turning up the high voltage:

1) Turn the high voltage to 4000 v.

2) Watch the HV gauge on the instrument rack for at least 15 seconds. *If the needle is unstable, turn down immediately.*
3) Turn the high voltage to 6000 v.
4) Watch the HV gauge on the instrument rack for at least 15 seconds. *If the needle is unstable, turn down immediately.*
5) Check the last HT reading.
6) Turn the high voltage to the last HT reading.
7) Watch the HV gauge on the instrument rack for at least 15 seconds. *If the needle is unstable, turn down immediately.*

Running Sr

Throughout the heat up period, keep an eye on the pressure for any large increases. If the pressure goes up, stop what you are doing until the pressure goes back down.

1) Turn up side filament current coarsely to ~1.2 amps. This can be done quickly.
2) Continue more slowly, watching the source pressure to make sure the filament does not outgas, to a faint glow (usually ~2 amps). **If the source pressure increases, stop, decrease filament current one step, and wait a few moments for the pressure to stabilize.**
3) Make sure mass is 88
4) Open LOS and check to see if there is a signal on mass 88 at this point.
5) If there is no signal on mass 88, keep turning the filament up in fine steps until you see a signal.
6) Continue with Samples or Standards, depending on what you are running.

Samples: If your sample has Rb, then it should be burned off.

1) Change the mass to 85
2) If there is a signal, close LOS, note starting filament current, and turn side filament up quickly in coarse steps to 3.3 amps, hold for a short moment and quickly turn it down to previous level.
3) Open the LOS valve and make sure there is no longer a signal on mass 85.
4) Repeat if there is still a Rb signal.
5) Change the mass to 88.
6) Continue as with a standard

Standards:

1) Open the LOS and increase filament in fine steps to a few hundred mV of 88.
2) Autofocus
3) Turn side filament up until the 88 signal is ~1 Volt

4) Peak center, and set the high voltage so that the center is between 87.99 and 88.01
5) Turn side filament up until signal is ~2 Volts
6) Autofocus
7) Peak Center, and set high voltage
8) Turn up side filament until signal is ~4 Volts
9) Autofocus
10) Peak center
11) Run srdy88ax experiment

Running Pb.

Throughout the heat up period, keep an eye on the pressure for any large increases. If the pressure goes up, stop what you are doing until the pressure goes back down.

1) Make sure you use the latest Pb program.
2) Run standards first. This way you will get a feel for running and comfortable with signal intensity.
3) Raise filament current with coarse adjustment until filament reaches ~ 1000-1050º. Very important to use a pyrometer.
4) Use fine adjustment to raise filament temperature to ~1100º. If 50 ng was loaded there should be a pretty large signal**. IMPORTANT NOTE** – Watch the pressure in the source with each increase in the filament current. If the pressure goes up past 1 x 10^{-6}, wait until the pressure drops before raising temperature further.
5) At 1100º open the LOS – you should see a beam on Pb
6) Focus the beam several times
7) Do a peak center
8) Increase the intensity until you have at least 3.7 V on ^{208}Pb or 100 mV on ^{204}Pb stopping to peak center, focus, and just generally take it easy on the way up to this intensity. Monitor the temperature of the filament constantly and record this in your notebook
9) When you've reached at least 1200º and you're satisfied that everything is focused and centered, run the sample.
10) Make sure blocks plot on Pb fractionation lines.
11) Ha! You thought you could rejoice and do a dance? No such luck. You must do both double spiked and unspiked analyses to get data.

Running Nd

Throughout the heat up period, keep an eye on the pressure for any large increases. If the pressure goes up, stop what you are doing until the pressure goes back down.

1) If you are the first person to measure Nd after a turret change, with the HT and filament current OFF, allow O_2 to leak into source chamber until the pressure reading is ~4.5 x 10^{-4} mbar. Hold for ~20 seconds, and close the oxygen.
2) Set mass to 160 and turn up the HT.
3) Turn up side filament current coarsely to ~1.2 amps. This can be done quickly.
4) Continue more slowly, watching the source pressure to make sure the filament does not outgas, to a faint glow (usually ~2 amps). **If the source pressure increases, stop, decrease filament current one step, and wait a few moments for the pressure to stabilize.**
5) Allow Nd to stew at the faint glow for 30 minutes.
6) Open the LOS and increase current on filament in fine steps until you see a signal.
7) Autofocus.
8) Increase filament in fine steps to a some tens of mV of 160.
9) Peak center and set HT so that the center is between 159.99 and 160.01.
10) Slowly open O2 leak valve until the source is at 1 x10^{-6} mbar. **Do not exceed this pressure.** The signal intensity should at least double.
11) Autofocus.
12) Turn filament up until signal is ~500 mV.
13) Sample is ready to run.