## Millipore water system

Ultra-clean water is prepared by filtration, reverse osmosis, electro-deionization, and ion exchange through a Millipore Elix 5 UV, and a Millipore Milli-Q Gradient system.

The system is for the most part self-maintaining. Periodic maintenance is done by trained staff only.

When water is drawn from the outlet of the Milli-Q Gradient (or directly from the storage tank), a float in the storage tank falls until it triggers the Elix system to start (tank capacity < 85%). The Elix will start, flush for five minutes, and then start producing water; this water will be directed toward the tank through the three-way valved mounted on the wall. The water quality rapidly reaches >15 MΩ, therefore it is not necessary to direct the initial product water toward the drain.

To draw a preset amount of water from the Milli-Q Gradient (e.g. into a carboy):

1. Rapidly flip the handswitch on the Milli-Q trigger down and then back up. This will put the Milli-Q into operate mode with only a small amount of water produced.
2. Press and hold the right “MENU” until the “Preset Volume” message appears.
3. Set the desired volume of water to be delivered by pressing the two middle arrow keys.
4. Press and hold the left “OPERATE/STANDBY” until the preset volume activates (shows 0.001 L at the bottom right of display).
5. Flip the handswitch on the Milli-Q hand-trigger down to start production; its a good idea to let the first 5L or so go to the drain prior to filling a carboy. For water for chemistry, deliver 15-20 L to a carboy, and then fill your bottle.
6. When delivery is completed, flip the handswitch on the Milli-Q hand-trigger up to return the Milli-Q to pre-operate mode.

## Methylactic acid preparation

Have on hand: Sublimated MLA; MQ H2O; 60 mL Teflon weighing jar; 2L Teflon bottle; Concentrated isothermally diffused or otherwise ultrapure NH4OH

### Prepare MLA solution:

1) Tare weighing jar

2) Add 41.644g MLA (with packing, will all fit into weighing jar)

3) Clean funnel with MQ

4) Pour MLA through funnel into the 2 L Teflon bottle with a magnetic stir bar inside

5) Add MQ

6) Add 30-40 mL concentrated NH4OH

7) fill to 2 L mark (on shoulder of bottle)

8) Allow to stir at least overnight

### Adjust pH

9) Add NH4OH in ≈10mL increments until pH is close to that required, allowing time for meter/probe to equilibrate

## Reagent molarity calibration

The clean reagents in the general chemistry lab are mixed approximately by hand, or by using clean pipets and/or dedicated clean graduate cylinders. If necessary, reagent molarities can be calibrated gravimetrically (± 0.1M) using a pycnometer of known volume and weight, and appropriate mass-molarity curves (e.g. for U-Pb reagents). Alternatively molarity can be calibrated more precisely (± 0.01M) by titration with sodium hydroxide and phenolthalein indicator (e.g. for cation, Sm-Nd reagents).

To titrate:

1. Prepare a titrating stand with two clean, dry burets, several small beakers, and several small ehrlenmeyer flasks.
2. Fill one buret with acid of interest and other buret with appropriate calibrated molarity NaOH.
3. Add one drop of phenolthalein indicator to a small ehrlenmeyer flask.
4. Place a white paper or wiper beneath the burets to better visualize the indicator transition (clear to pinkish-purple).
5. Add an appropriate quantity of acid to the flask and record its volume.
6. Add NaOH to the flask slowly, swirling the flask gently, to near the estimated neutral point.
7. Continue to add NaOH dropwise to the flask, swirling constantly until the color transition occurs,
8. Record the volume of base and calculate the acid normality.
9. Back-react the solution by adding more base and then more acid to reproduce the titration estimate.

## Reagent blanks

Reagent blanks are determined by spiking a 7 ml PFA beaker with the necessary enriched isotopes, adding 1 µl of 0.1N H3PO4, filling the beaker with the desired reagent, and drying it down overnight in the vertical laminar flow hoods in the Radiogenic Pb laboratory.

## PFA beaker cleaning

1. Wearing eye protection and gloves, remove ink from beakers with methanol and a small wiper. Uncap a set of beakers (e.g. 20) and place them into the rectangular water basin marked “Wash” kept beneath the lab sink. Fill the basin has enough MQH2O to cover the beakers plus a small amount of dishwashing soap. Let the beakers soak for at least 15 minutes.
2. Clean the dirty beakers in this bucket with your gloved finger (you can use a small wiper too), making sure you rub the bottom and sides very well. As you finger clean the beakers place them into the second water basin (without soap) marked “Rinse”. *This step physically disrupts and removes any residual sample/phosphoric acid in the beaker.*
3. Take a round plastic tub with cover (kept under the hood) and once more finger clean beakers from the rinse basin and place them into the tub. Rinse the beakers 2X with MQH2O from the water carboy next to the sink. See someone if the water level in the carboy is low and you don’t know how to fill it.
4. Lay out a couple of large DURX wipers under the hood and line up the beakers, tapping out any excess water. Check your gloves for holes (discard if you find any) and then put on a second pair of gloves and check eye protection. Using the squirt bottle of 25% HF labeled “for beaker cleaning” in the column box, fill the beakers with enough acid to cover the bottom. Screw the lids on tightly and place on the hotplate at 120°C overnight. *This step dissolves any residual sample/phosphoric acid, and efficiently leaches HFSE from the beakers.*
5. Remove the beakers from the hotplate. Lay out some large DURX wipers under the hood, and find the “Waste HF” bottle in the column box. Again wearing two pairs of gloves inspected for holes and eye protection, roll the closed beaker around to collect all the acid condensed on the sides into the bottom, then dump the acid into the “Used HF” bottle, tap the beaker and lid on the wiper, and place them into a clean empty tub. When all the beakers have been emptied, close and store the “Used HF” bottle. Rinse the beakers in the tub 2X with MQH2O.
6. Place the rinsed beakers into the “2X 6N HCl” baths, dividing them between the two containers if necessary (20 per bath max). Place baths on the hot plate at 120°C for at least 3 hours. *This step cleans the inner and outer surfaces of the beaker.*
7. Remove the 6N HCl baths from the hotplate. Using tongs, remove the beakers from the bath, placing them into a clean, empty plastic tub. Rinse the beakers 2X with MQH2O. Lay out some large DURX wipers under the hood and line up the beakers, shaking out any excess water. Using the squirt bottle of 6N HCl labeled “for beaker cleaning”, fill the beakers with enough acid to just cover the bottom. Screw the lids on tightly and put the beakers on a hotplate at 120°C overnight. *This final step leaches contaminants from the inner surface of the beaker.*
8. After fluxing, remove the beakers from the hotplate, roll the closed beaker around to collect all the acid condensed on the sides into the bottom, then open the beaker and discard the acid, tap the beaker and lid on the wiper, and check to make sure there are no “sticky” spots in the beaker. Any beakers from which the liquid does not cleanly empty should be recycled for another round of cleaning. Screw the lids on the clean beakers tightly and place in the “Clean Beaker” plastic box under the drying hood.

## 3 ml PFA beaker cleaning

1. After use, rinse the beaker and lid with MQH2O; tap firmly to remove water.
2. Add 2 ml concentrated HCl to beaker and cap tightly. Using the special blue tweezers, insert the six 3 ml beakers into the large teflon Parr liner with 7ml of 6M HCl “moat” acid. Cap the liner, wrap with parafilm, and remove to the ovens in MG-217. Remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the rest of the jacket cap, and then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the 180°C oven for 12 hours.
3. Remove Parr vessels from oven, cool, remove the liner from the jacket and wipe down thoroughly. The liner should still be sealed--bring into clean lab. In the clean lab, loosen Parr vessel cover by tapping around edge with a spare liner, then use a square of Parafilm to twist open, breaking the seal.
4. Remove the six 3 ml beakers from the Parr liner with the special blue tweezers, rinse the outsides with MQ-H2O, and dry with a DurX wiper. Uncap each beaker, discard the acid and rinse with MQ-H2O.
5. To each 3 ml PFA beaker, add 0.2 ml conc HNO3 + 1.8 ml conc. HF and carefully cap the beaker tightly. Using the special blue tweezers, insert the six 3 ml beakers into the large teflon Parr liner with 7ml of 29M HF “moat” acid. Cap the liner, wrap with parafilm, and remove to the ovens in MG-217. Remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the rest of the jacket cap, and then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the 220°C oven for 48 hours.
6. Remove the six 3 ml beakers from the Parr liner with the special blue tweezers, rinse the outsides with MQ-H2O, and dry with a DurX wiper. Uncap each beaker, discard the acid and rinse with MQ-H2O.

## 23 ml Parr vessel cleaning

* 1. After use, finger-clean teflon insert and lid with MQH2O; tap firmly to remove water.
  2. Add 4 ml concentrated HCl to insert and cover with its lid.
  3. IN THE OVEN LAB, seal in appropriate jackets, record in oven log, and place in small (cool- 180°C) oven overnight.
  4. Remove from oven, cool in hood, remove from jackets and wipe clean
  5. IN THE CLEAN LAB in the laminar flow hood, break seal by tapping on the top of the lid with a large Parr insert, carefully remove the lid from the insert, discard the acid into a water-filled basin, tap firmly onto a DurX wiper to remove any droplets from lid and insert.
  6. Add 1 ml concentrated HNO3 + 3 ml concentrated HF to each insert and cover with its lid (nitric first, then HF); place the loaded vessels into a tupperware, and carefully bring them to the OVEN LAB (MG-211).
  7. IN THE OVEN LAB, seal each insert in its lettered jacket and place in 180°C oven overnight.
  8. Remove from oven, cool in hood, remove from jackets and wipe clean
  9. IN THE CLEAN LAB in the laminar flow hood, break seal by tapping on the top of the lid with a large Parr insert, carefully remove the lid from the insert, and discard the acid into a water filled basin, tap firmly onto a DurX wiper to remove any droplets from lid and insert; store in tupperware labelled “clean, dry, ready for use”.

## Spiking

First, thoroughly clean the weighing table area with a wet DurX wiper. Enriched isotopic spikes should generally be weighed into clean PFA beakers prior to introduction of the sample powder. Exceptions are relatively coarse grained mineral separates which are easier to dry down into the beaker prior to spiking. Check the quality of the pipettor prior to use, e.g. make sure there is no liquid or corrosion evident at the opening of the pipettor. Use a clean pipet tip for every transfer of spike to beaker, carefully extracting the spike without touching the pipet tip to the side of the bottle, in order to avoid contamination of the spike bottle. It is often easiest to zero the balance with the beaker on it, transfer the spike and record the weight. When delivering multiple spikes to the same beaker only have one bottle open at a time to avoid cross-contamination.

## Sample weighing (mineral separates)

Following appropriate sample leaching and rinsing, the wet sample is easily transferred to preweighed foil-wrapped PFA beakers. Make sure you weigh the beaker with the foil wrapping! These can then be set on a hot plate to dry. Once dry the sample in the foil wrapped beaker is generally immune to static dispersal, and can be reweighed and the sample weight found by difference. The beaker can then be zeroed and the sample spiked with the appropriate enriched isotope tracers.

## Sample weighing (powders)

1. To avoid messy powder dispersal by static, add approx. 100 µl of water to each (previously spiked) labeled 15 ml PFA beaker. Then wrap the bottom of the beaker in aluminum foil. This foil wrapper can be reused for each sample beaker.
2. Place a 3 x 3” piece of weighing paper onto the balance pan. If you spill powder on the balance pan this makes it easy to clean up!
3. Place your foil wrapped beaker on the balance, tare the balance and then weigh out the appropriate amount of sample into the foil-wrapped beaker using a teflon coated spatula (cleaned between samples with methanol, then MQH2O, and wiped dry), and record the weight.
4. Finally swirl the beaker to incorporate all of the sample powder into a slurry prior to capping the beaker.
5. Repeat the foil wrapping, taring and weighing of powder into each sample beaker, making sure to carefully clean the spatula between samples.
6. When finished, discard the weighing paper and thoroughly clean the weighing table area with a wet DurX wiper.

## Sample dissolution (23 ml Parr vessels in oven)

1. To each 15 ml PFA beaker containing the spiked sample, add 1 ml conc HNO3 + 3 ml conc HF and swirl to take up all sample powder into a slurry. Place the capped beakers on a hot plate at a setting of “**8**” (150°C) with the overhead lamp on to flux for 4 hours, then uncap the beakers and let the sample dry down. *This step with begin the silicate breakdown and evolve some of the silica as volatile SiF4 gas.*
2. To each PFA beaker, add 1 ml conc HNO3 and swirl to take up the sample into a slurry. Dump contents of each beaker into the appropriate Parr vessel, add 3 ml conc. HF to each beaker, swirl and again dump into the appropriate Parr vessel. Reserve the labeled PFA beakers for later use. Place the filled vessels carefully into a flat Tupperware container.
3. Take the Parr vessels to the outer mineral separation lab and place each vessel in its respective jacket --> wrap with teflon film, slide into jacket, 286-AC flimsy, 287-AC thick, flat plate, spring, top. Be sure to wear gloves, coat and eye protection! Hand tighten cap onto jacket, and place in 180°C oven for 4 days.
4. Remove Parr vessels from oven, cool, remove from jackets and wipe down thoroughly. The bombs should still be sealed-- place bombs into flat Tupperware container and bring into clean lab.
5. Loosen Parr vessel cover by tapping on bench; remove cap and empty contents of bomb back into the appropriate labeled PFA beaker from initial weighing.
6. Add 1ml conc HNO3 to each Parr vessel, swirl and dump into the appropriate PFA beaker; if the sample is “sticky” use a pipet tip to rinse and transfer sample from the Parr vessel to the PFA beaker. Place the beaker on a hot plate uncapped @ 120°C under lamp and dry down the solution to a dry sample cake.
7. Add 0.5 ml conc HNO3 to sample, and again dry down the sample solution to a dry sample cake.
8. Add another 0.5 ml conc HNO3 and finally dry down the sample solution to a very dry sample cake.
9. Add 1 ml conc HCl to sample, cap, swirl and sonicate for an hour, then add 4 ml 6N HCl, cap and flux overnight on hot plate (120°C).
10. If your sample is by now not completely in solution, transfer the sample back to the appropriate Parr vessel, seal, remove to oven lab, seal in jackets and place in a 180°C oven overnight.
11. Remove from oven, cool remove from jackets, and wipe down thoroughly. Return them to clean lab, unseal and transfer contents to respective PFA beaker; if the sample is “sticky” use a pipet tip to rinse and transfer sample from the Parr vessel to the PFA beaker. Sample should be completely dissolved.

## Sample dissolution (6 x 3 ml PFA bkrs in 125 ml Parr vessel in oven)

1. To each 15 ml PFA beaker containing the spiked sample, add 1 ml conc HNO3 + 3 ml conc HF and swirl to take up all sample powder into a slurry. Place the capped beakers on a hot plate at a setting of “**8**” (150°C) with the overhead lamp on to flux for at least 4 hours, then uncap the beakers and let the sample dry down. *This step with begin the silicate breakdown and evolve some of the silica as volatile SiF4 gas.*
2. To each 15 ml PFA beaker, add 0.2 ml conc HNO3 + 1.8 ml conc. HF and swirl to take up the sample into a slurry. Carefully pour contents of each 15 ml beaker into the appropriate 3 ml PFA beaker. Using the special blue tweezers, insert the six 3 ml beakers into the large teflon Parr liner with 7ml of 29M HF “moat” acid. Cap the liner, wrap with parafilm, and remove to the ovens in MG-217. Remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the rest of the jacket cap, and then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the 220°C oven for 18 to 36 hours.
3. Remove Parr vessels from oven, cool, remove the liner from the jacket and wipe down thoroughly. The liner should still be sealed--bring into clean lab. In the clean lab, loosen Parr vessel cover by tapping around edge with a spare liner, then use a square of Parafilm to twist open, breaking the seal.
4. Remove the six 3 ml beakers from the Parr liner with the special blue tweezers, keeping them horizontal, then rinse the outsides with MQ-H2O and dry with a DurX wiper. Uncap each beaker and place on the hotplate.
5. Add 0.5 ml conc HNO3 to each beaker, and dry @ 120°C under lamp to a dry sample cake. **Repeat this process two more times.**
6. To each 3 ml PFA beaker, add 2 ml 6M HCl and carefully cap the beaker tightly. Using the special blue tweezers, insert the six 3 ml beakers into the large teflon Parr liner with 7ml of 6M HCl “moat” acid. Cap the liner, wrap with parafilm, and remove to the ovens in MG-217. Remove the parafilm from the teflon liner, and slide into the large steel jacket, making sure the bottom plate of the jacket remains loose. Assemble the rest of the jacket cap, and then use the torque wrench to tighten down the cap screws in an alternating star pattern. Place the assembled jacket into the 180°C oven overnight.
7. Remove Parr vessels from oven, cool, remove the liner from the jacket and wipe down thoroughly. The liner should still be sealed--bring into clean lab. In the clean lab, loosen Parr vessel cover by tapping around edge with a spare liner, then use a square of Parafilm to twist open, breaking the seal.
8. Remove the six 3 ml beakers from the Parr liner with the special blue tweezers, keeping them horizontal, then rinse the outsides with MQ-H2O and dry with a DurX wiper. Uncap each beaker and visually inspect – you should have a clear (though likely colored) solution with no visible solids. Pour the contents into a 15 ml PFA beaker for subsequent column chemistry preparation. Start cleaning the 3 ml beakers immediately (conc HF + HNO3 overnight, 6M HCl overnight).

## Sample dissolution (15 ml PFA beaker on hot plate)

*For Pb isotope samples, see sequential dissolution procedure, or:*

* 1. Add 3 ml 6M HCl to each sample, swirl to take up all sample into a slurry, cap tightly, and place on 150°C hotplate for 2 hours. After 2 hours, pipet away acid (discard), then rinse sample by adding 0.5 ml MQH2O, swirling and pipeting away liquid (discard); repeat 3x.
  2. Continue below.

*For all samples:*

1. To each PFA beaker containing the spiked sample, add 1 ml conc HNO3 and swirl to take up all sample powder into a slurry, then add 3 ml conc. HF to each beaker, swirl and cap tightly, and place on 150°C hotplate.
2. After several days, uncap each beater, add 1ml conc HNO3 to each beaker, place on hot plate uncapped @ 120°C under lamp and dry down the solution to a dry sample cake.
3. Add 0.5 ml conc HNO3 to sample, and again dry down the sample solution to a dry sample cake.
4. Add another 0.5 ml conc HNO3 and finally dry down the sample solution to a very dry sample cake.
5. Add 1 ml conc HCl to sample, cap, swirl and sonicate for an hour, then add 4 ml 6N HCl, cap and flux overnight on hot plate (120°C).
6. Sample should be completely dissolved (translucent, without signs of any solids).

## Sample aliquoting

To aliquot your completely dissolved sample (in case you want to save or spike a smaller aliquot of sample), first label a set of clean beakers and record their empty weights (with caps).

In the fume hood, quantitatively transfer your sample to the new beaker, cap, and then record the full weight on the balance; determine the weight of the sample solution by difference.

Record the empty weight of the original beakers (with caps).

Using an appropriate pipettor, transfer the required aliquot of sample from the new beaker to the original beaker. Do this in the fume hood and make sure to use a new pipette for each sample! Cap the beakers and record their full weights; determine the weight of the aliquot by difference.

## Reagent Characteristics and Preferences

The information below has been extracted from the following references:

1 Bock, Decomposition Methods in Analytical Chemistry. New York: Wiley, 1979.

2 Gorsuch, The Destruction of Organic Matter. Oxford: Pergamon, 1970.

3 Dolezal et al., Decomposition Techniques in Inorganic Analysis. New York: Elsevier, 1966.

### Sulfuric Acid:

Commercial “concentrated” sulfuric acid contains 98% H2SO4, corresponding to the azeotrope in the water-H2SO4 system with a very high boiling point of 339° C. Dilute sulfuric acid has virtually no oxidizing power, however the hot concentrated acid will oxidize almost all organic compounds, itself being reduced to SO2, S, or H2S (ref 1). Note that because of its high boiling point, the sulfate matrix is very difficult to remove from samples by conversion to another acid— as a result, residual sulfate can interfere with ion exchange chemical separations. In addition, the fact that PbSO4 is insoluble in water and weak acid solutions makes sulfuric acid especially undesirable for application of Pb isotopes.

### Perchloric Acid:

Perchloric acid and water form an azeotrope with 72.4% HClO4 by weight, boiling at 203° C, and is commonly labelled as “concentrated perchloric acid”. This azeotropic mixture can be stored without danger and can be purified by distillation. Solutions containing more than 72.4% HClO4 decompose to chlorine oxygen and water— *the anyhydrous acid decomposes violently and thus acid more concentrated than the azeotrope is to be completely avoided*. *Concentrated perchloric reacts energetically with organic material and thus contact between the acid and rubber, textiles, etc. is to be minimized.*  Spills should be diluted before mopping up with lab wipes— these wipes should then be thoroughly rinsed with water prior to discarding. Numerous perchlorate salts are higly volatile thus fume hoods venting large quantities of perchloric acid must be specially construction to avoid condensation points for salts (ref 1).

Dilute aqueous solutions of perchloric acid are *not* oxidizing, either warm or cold. Only hot (>160° C) concentrated acid (60-72% HClO4) is a powerful oxidant. Because of the danger of explosions with organic matter, perchloric acid is rarely used on its own to decompose organics. Mixtures with sulfuric or nitric acid are normally used, which dilute the perchloric acid, and also ensure that easily oxidizable compounds are broken down by the other acid at low temperature, before the perchloric acid begins to exert its oxidizing power above 160° C.

### Hydrochloric Acid:

The system H2O-HCl forms an azeotrope containing 20.4% HCl with a boiling point of 109.7° C, however the commercial “concentrated” acid contains 36-38% HCl. Concentrated aqueous HCl is most commonly used in organic analysis to liberate metal ions from biological fluids like blood, serum or plasma, or from edible oils or mineral oils wihtout actually destroying the organic matter (ref 1). HCl alone in any concentration does not break down organic matter.

### Aqua Regia:

This mixture of HNO3:HCl in the ratio 1:3 is useful for the breakdown of metals and sulfides. The effectiveness of the reagent is probably due not only to the complexing power of the chloride ion, but also to the catalytic effect of molecular Cl2 and NOCl and of the chloride ion present during the reaction. These catalytic effects however do not affect organic matter, thus the mixture is generally not suitable for application to organic decomposition (ref 1).

### Nitric Acid:

Reagent grade “concentrated” nitric acid (14N) contains 65-69% HNO3, corresponding to the composition of the azeotrope which has a boiling point of 121.8° C. A solution containing more than 69% is commonly referred to as “fuming nitric acid”. The acid is completely miscible in water: recall that when a dilute solution of nitric with water is heated to boiling, the water is lost and the boiling point increases until the azeotrope composition is reached at a b.p. of 121.8° C— at this temperature the solution will evaporate to dryness.

The destruction of organic matter with nitric acid alone proceeds in most cases only with difficulty (ref 1). On the other hand, mixtures of nitric with other strongly oxidizing reagents including H2O2 or sulphuric or perchloric acids are very widely used for the destruction of organic matter. As previously discussed, sulfuric acid is to be avoided for Pb isotopic work and more generally for all samples for which ion exchange chemistry is utilized. Mixtures of nitric acid with perchloric acid may have some utility, and a method is transcribed below.

### Hydrogen Peroxide:

Hydrogen peroxide (H2O2) is fully miscible in water and is most commonly commercially available as 30% solution by weight. 50% solutions of H2O2 can also be obtained and react more vigorously (ref 1,2). All solutions should be handled with care as H2O2 causes serious injury to skin: wash affected areas thoroughly with water.

The oxidizing power, or redox potential, of H2O2 increases with the acidity of the solution to which it is added, thus its use in combination with strong mineral acids is quite effective. A method using a mixture of nitric acid and H2O2 is described below. Of great utility is the fact that any surplus of hydrogen peroxide present in solution after a decomposition reaction can be almost entirely destroyed simply by heating to boiling (107° C), or complete drying.

## Decomposition of organic matter

The following method for the decomposition of organic matter is extracted from Bock, Decomposition Methods in Analytical Chemistry. New York: Wiley, 1979)

Organic substances to be decomposed are first treated with concentrated nitric acid alone, in order to eliminate easily oxidized sample material, avoiding over-vigorous reaction when the hydrogen peroxide is added.

The sample is then evaporated to dryness, and concentrated nitric and hydrogen peroxide are added to the sample in the ratio of 10:1. Any reaction at this point is allowed to subside before heating the mixture (open beaker) to just below the boiling point (120° C). Care is taken that any reaction does not proceed too vigorously.

After a significant amount of the solution has evaporated, 30% H2O2 can be added dropwise to the hot solution to finish the oxidation. This may or may not involve the elimination of traces of color from the solution.

The solution may then be evaporated to dryness for conversion to the appropriate ion exchange chemistry matrix.

## Preparing water samples for isotopic analysis

If spiking the sample, weigh the appropriate tracer into a large PFA beaker (e.g. 15-60 ml depending upon sample size).

Add your water sample to a clean centrifuge tube and spin for 10 minutes; weigh (if spiked, if not spiked then just transfer) the supernatant into your large PFA beaker by pipet – leave the last few ml of sample in the bottom of the centrifuge tube with any solids; repeat as necessary to achieve the desired volume (weight) of water, e.g. usually 30-50 ml.

Add 1ml conc HNO3 to each beaker, place on hot plate uncapped @ 120°C under lamp and dry down the water to solids.

Remove from the hotplate, add 1 ml conc HNO3 to sample, swirl and let dissolve, then add 3 drops of Ultrex H2O2 to each beaker, and let react off the hotplate for approx. 15-30 minutes.

Return beaker to the hotplate and again dry down the sample solution to solids.

Redissolve the sample in the appropriate loading acid for column chemistry, e.g. 0.5 ml 3.5M HNO3 for Sr, 0.5 ml 0.5M HBr for Pb, or 0.5 ml 3M HCl for U, and transfer to a 1.5 ml centrifuge tube for centrifugation prior to loading on columns.

## Sequential dissolution for feldspars

The following method for the sequential dissolution of feldspars for initial common Pb analysis is extracted from Housh and Bowring (1991).

1. Transfer mineral separate to a clean, round bottom 15 ml PFA beaker in ethanol.
2. Pipet away ethanol (discard), then rinse mineral separate by adding 1 ml MQH2O, swirling and pipeting away liquid (discard); repeat 3x.
3. Add 2 ml 3.5M HNO3 to mineral separate; cap and place on 120°C hot plate for 30 minutes.
4. Pipet away acid (discard), then rinse mineral separate by adding 0.5 ml MQH2O, swirling and pipeting away liquid (discard); repeat 3x.
5. Add 2 ml 6M HCl to mineral separate; cap and place on 120°C hot plate for 30 minutes.
6. Pipet away acid (discard), then rinse mineral separate by adding 0.5 ml MQH2O, swirling and pipeting away liquid (discard); repeat 3x.
7. Add 1 ml 1M HF to mineral separate; cap and place on 120°C hot plate for 15 to 30 minutes, depending upon sample size. Goal is to dissolve approx. 10-20% of the sample per sequential 1M HF leach step.
8. Pipet the 1M HF solution into a clean 5 ml PFA beaker, then rinse mineral separate by adding 0.5 ml MQH2O, swirling and pipeting liquid into the same 5 ml PFA beaker; repeat 3x.
9. Repeat steps 7-8 as desired (two to three times or until sample is reduced to very small residue.
10. You can aliquot 1 ml of the 2.5 ml total solution into a second beaker for U-Th-Pb ratio measurement by ICPMS if desired. Dry this 1 ml down, redissolve in 1 ml of 8M HNO3 and redry for storage. When ready for ICPMS, redissolve in 2 ml 2% HNO3 overnight on hotplate, then dilute up to 10 ml total volume of 2% HNO3 in a centrifuge tube.
11. Dry the desired HF leach steps to solids, then convert to 0.5M HBr ready for column chemistry – see instructions for “**Pb separation by anion exchange in dilute HBr medium**”

## Conodont preparation for Sr isotopes

The following method for the cleaning and partial dissolution of conodonts for initial Sr isotope analysis is composited from the methods of:

*Bailey, T. R., McArthur, J.M., Prince, H., and Thirlwall, M.F. (2000). "Dissolution methods for strontium isotope stratigraphy: whole rock analysis." Chemical Geology 167: 313-319.*

*Ruppel, S.C., James, E.W., Barrick, J.E., Nowlan, G., Uyeno, T.T. (1996). “High-resolution 87Sr/86Sr chemostratigraphy of the Silurian: implications for event correlation and strontium flux.” Geology 24:831-834.*

* + - 1. Under the picking microscope, transfer conodont element(s) to a clean 5 ml PFA beaker in ethanol.
      2. In the clean lab under the microscope, pipet away ethanol (discard), then add 1 ml of double-distilled acetone and place the capped vials in the ultrasonic back for 15 minutes.
      3. Pipet away acetone (discard), then rinse conodonts by adding 1 ml MQH2O, swirling and pipeting away liquid (discard); repeat 3x.
      4. Add 1 ml 1M ammonium acetate (CH3COONH4) to conodonts; cap and place on 50°C hot plate for 15-30 minutes.
      5. Pipet away ammonium acetate (discard), then rinse mineral separate by adding 1 ml MQH2O, swirling and pipeting away liquid (discard); repeat 3x.
      6. Add 1 ml 1M acetic acid (CH3COOH) to mineral separate; cap and place on 50°C hot plate for anywhere from 6 hours (small conodonts) to 12 hours (large conodonts). The residual conodont elements will take on a whitish frosted appearance but should retain most of their structural integrity.
      7. Pipet away acetic acid (discard), then rinse mineral separate by adding 1 ml MQH2O, swirling and pipeting away liquid (discard); repeat 3x. During this step some heavily leached conodont elements might fragment; carefully pipet away liquid while retaining as much of the solids as possible in the beaker.
      8. Add 6 drops of 16M HNO3 to dissolve residual rinsed conodonts; swirl and let dissolve in about 5 minutes, then add 2 drops of Ultrex H2O2 to each beaker, and let react off the hotplate for approx. 15 minutes.
      9. Return beaker to the hotplate and dry down the sample solution to solids.
      10. Redissolve the sample in the appropriate loading acid for column chemistry, e.g. 0.5 ml 3.5M HNO3 for Sr-spec separation.

## Barite removal (and/or dissolution for isotope analysis)

The principle of the dissolution is an anion replacement reaction, where sulfate is replaced by carbonate in a weakly alkaline solution, forming acid-soluble sodium sulfate and barium carbonate. This is composited from the methods of:

*Breit, G.N., Simmons, E.C., Goldhaber, M.B., 2013. Dissolution of barite for the analysis of strontium isotopes and other chemical and isotopic variations using aqueous sodium carbonate. Chemical geology. Isotope geoscience section 52, 1–5. doi:10.1016/0168-9622(85)90043-0*

1. Thermally anneal your mineral separate prior to treatment, to makes sure zircon retains its closed system behavior during chemical attack.
2. Transfer up to 2 grams of sample into a 30 ml (tall) savillex vial, add 5 ml of 6M HCl, cap and agitate with the vortex mixer, and then flux on hot plate for an hour to dissolve any carbonate or phosphate.
3. Decant acid and rinse with 5X with a full vial of MQ H2O to remove any residual acid.
4. To the decanted sample add solid Na2CO3 in a ratio of approximate 10 parts Na2CO3 to 1 part sample. Fill the vial with MQ H2O, cap and agitate with the vortex mixer.
5. Place the savillex vial into a large Parr PTFE liner with 7 ml of water in the moat, and place in steel jacket in oven at 180°C for > 12 hours.
6. Remove the savillex vial from the Parr vessel, decant the solution, and rinse with 5X with a full vial of MQ H2O to remove any residual carbonate solution.
7. In small aliquots add 6M HCl and allow to react; continue to add 6M HCl until reaction is completed, then cap and flux on hot plate for an hour to dissolve any residual solids.
8. Decant acid and rinse with 5X with a full vial of MQ H2O to remove any residual acid.
9. The solid residue should be only silicates or oxides, including zircon.