

Rock Crushing and Sieving

This process takes place in the basement of the Natural Sciences Complex. This procedure produces a lot of dust so a dust mask is required. Also required are safety glasses and ear protection.

- 1) Select two rock samples. Each sample is assigned 3 Ziploc bags. Label the bags with your samples ID and then **>850 um**, **250-850 um** and **<250 um**. These are the three size fractions that you will sieve out later.
- 2) Take one of your samples and put it into the jaw crusher. **Make sure the collection tray is properly inserted below the jaws.** If the rock chunks are relatively large, add them one at a time to the jaw crusher. Never try to force a large rock chunk into the jaws. Doing this will cause the crusher to jam and it is a huge pain to remove the chunk that got stuck.
- 3) After you have crushed your sample, put your sample into the bag labeled >850 um. It is easier to feed your sample into the plate grinder from the back rather than from the collection tray.
- 4) Go over to the plate grinder and make sure that the two plates are ~2 mm apart. Error in the direction of more space between the plates. If the plates are too close together, you will end up with too much sample that is <250 um in diameter.
- 5) Turn on the dust collector and then the plate grinder.
- 6) Make sure the collection tray is properly inserted and then **slowly** add your sample to the plate grinder. If you add too much sample at once, the grinder will seize. If this happens, **turn off the grinder** and then open up the plates manually.
- 7) After all of your sample has gone through the plate grinder take out the collection tray and dump your samples into a sieve stack. Make sure the sieves are in the proper order with the 850 um sieve on top, followed by the 250 um sieve, and then the pan should be on the bottom.
- 8) Place this sieve on the roto-tap and let it run for ~ 10 minutes.
- 9) While the roto-tap is running, use a brush and vacuum to clean the jaw crusher, plate grinder, and both collection trays.
- 10) Take your second sample and run it through the above steps while the roto-tap is working on your first sample

- 11) After your second sample is through the plate grinder, dump it into the second stack of sieves in the same way you did with your first sample. Place your second sample on the roto-tap.
- 12) Place your first sample's sieved fractions into their appropriate pre-labeled Ziploc bags.
- 13) **Thoroughly** clean the sieves; every grain must be removed. After you have cleaned these sieves, take the second sample off the roto-tap and place the fractions into the appropriate Ziploc bags. Clean sieves
- 14) Repeat process

Magnetic Separation

This procedure starts to remove unwanted magnetic minerals from your sample. If your sample lacks mafics then you can probably skip this step. Take the **250-850 um** fraction and spread a thin film of mineral grains on top of a piece of paper. Next, using the heavy magnets (cover with a chem-wipe) pass over your sample to attract magnetic grains. Do this several times. After removing the magnetic minerals, set your "clean" fraction aside and repeat the aforementioned procedure for the rest of your sample. Note that you will not be able to remove all magnetic grains.

Etching Before Mineral Separation

This etching procedure makes the subsequent mineral separation procedure far more effective. In addition, HCl is highly effective at removing organic material and elements such as Fe. Plan on completing the step below for **at least 6** samples. This procedure is done in 2L bottles.

- 1) Do this step using the top loading balance in the sediment lab"
- 2) Take the **250-850 um** fraction of one sample and add it to a labeled 2 L bottle. If the sample is pure quartz, add between 80-100 grams, anything less, add up to 160 g of sample. If you are aiming for high amounts clean quartz, you can run A and B splits of each sample. The mass of sample used also depends on how much total sample is available. If this will be the first measurement on this particular sample, try to make sure that there is enough material left to prepare at least one more sample. **Record the sample mass in the lab book.**
- 3) Add DI water to the bottle and shake and swirl so that only the finest material, micas, and organics float in the water. Pour out the water with the floating micas and fine material into a bucket. Repeat 3-5 times to get all of the fine material out, as well as some of the micas, until the water is clear. **Note:** Muscovite is extremely difficult to remove, so if your sample is high in muscovite, do this step 10 times to get as much

out as possible. Hopefully, any remaining muscovite will be removed in the later steps.

- 4) Place samples in the hood. Add **6 N HCl** to cover the sample by 2-3 cm (eyeball it). Place cap on bottle and shake lightly so as to help HCl penetrate sample. Place samples in the ultrasonic bath. Ultrasonic cleaner should be filled to the rim with tap water. Etch **(without heat)** for at least 8 hours (longer will not hurt).
- 5) After 8 hours of sonification, decant beakers into acid neutralization bucket. To further wash the samples, add DI water to samples, swirl around, and decant into bucket. Rinse sample 3 times with DI water. When finished rinsing sample, add baking soda to the acid - slowly, otherwise acid will fizz violently and flow out of bucket. Add baking soda (Sodium Bicarbonate: NaHCO_3) until litmus paper test indicates $\text{pH} > 5$. Rinse the sample with DI water three times. **It is safe to pour down the drain liquids between pH 5.5 and 10.5. EPA classifies hazardous waste as $\text{pH} < 2$ and > 12.5 .**
- 6) To each bottle, add DI water to cover sample by 1-2 cm (eyeball it). Add **30 ml of 48% HF and 30 ml of 70% HNO₃**. Only pour HF into bottles that are in a tray that will prevent spilling outside of the hood in case of an accident. If you haven't poured HF before, consult with somebody who has FIRST. Place cover on bottle and swirl lightly. Place samples into ultrasonic cleaner and etch **(with heat) for at least 12 or more hours (e.g., overnight)**.
- 7) After 12 hours, decant into acid neutralization bucket and wash samples three times with DI water.

Mineral separation using LST (lithium heteropolytungstate¹) heavy liquid

This step is a carryover from the old procedures. Use of the magnets (see above) should eliminate the need for LST. However, in rare cases where you might need to use LST (e.g. remove garnets), follow this procedure. Otherwise (most cases), skip to the "Ultrasonic Cleaning" section below.

This step is highly effective at removing non-quartz material. The liquid is non-toxic and thus a fume hood is not needed. Only samples that are high in mafics and/or feldspars need this step. Quartz and most quartz-rich samples can skip this procedure. This procedure is most efficient when running two samples back to back.

¹ Purchased from the Central Chemical Consulting, PO Box Karrinyup Western Australia 6921. (tel) 011 61 8 9447 8982.

- 1) Wash the glass thoroughly with DI water. Make sure the stopcock is closed. Pour ~300-350 ml (eyeball it) of LST into a glass separatory funnel. Fit the Buchner funnel with rubber stop into vacuum flask and place one filter, designed for 12 cup coffee maker, into the Büchner Funnel. Wet the filter with DI water.
- 2) Pour the sample into the separatory funnel using a polypropylene funnel. Stir sample and allow sufficient time (5-10 minutes) for the mafics to sink to the bottom. Drain the mafics from the separatory funnel into the filter paper by temporarily opening the stopcock for short periods of time. Add incrementally small amounts DI water to dilute the LST further to get more mafics to sink. Once the quartz sinks, turn on the vacuum pump to drain the LST from the mafics in the filter paper. Rinse the sample with **sufficient amount of DI water to recover as much LST as possible**. Once the dripping of the filter into the vacuum flask has ceased or slowed considerably, turn off the pump and remove the filter paper.
- 3) Place a new piece of filter paper in the funnel and wet with DI water. Drain the quartz onto the filter. Try to keep the feldspar, and micas, which often float at the top, from pouring onto the filter paper. **However, take some feldspars to maximize the collected quartz.**
- 4) Turn on the vacuum pump and let the heavy liquid drain. Rinse the quartz with a conservative but sufficient amount of DI water to recover as much LST as possible. Place the filter paper back into the 2L bottle that the sample was in originally, folding the lip of the wet filter paper over the edge of the bottle's mouth. Place bottle in oven and let dry (with cap in the oven adjacent to its bottle).
- 5) Drain remaining LST liquid and any particles (e.g., micas) onto new filter paper and discard along with mafics. Be sure to rinse the leftover grains to recover LST.
- 6) To bring the LST back up to the appropriate (quartz floating) density, warm on the hotplate. After enough water has evaporated the LST liquid will achieve a density at which a quartz crystal floats. If the LST liquid evaporates for too long, it will begin to crystallize; simply add DI water to dissolve crystals. Do not leave LST liquid uncovered for a long time otherwise it will get dirty and become reduced (turns blue, black, or purple color). To oxidize the liquid, add 3 to 4 drops of hydrogen peroxide 30% and cover for a day or more.

Ultrasonic cleaning

The two goals of the ultrasonic cleaning are to remove remaining contaminant meteoric ^{10}Be , which is produced in the atmosphere and may be residing in microfractures within the quartz crystals, and to reduce total ^{27}Al (i.e., non-quartz material) so that the AMS can measure the $^{26}\text{Al}/^{27}\text{Al}$ ratio. HF and HNO_3 provide a strong combination to remove non-quartz (total ^{27}Al) and meteoric ^{10}Be . The F^- ion is a very powerful complexing anion, and

forms stable fluorides and fluorocomplexes with many elements, including Si. HNO_3 is a strong oxidizing agent and helps break down compounds by bringing metal cations out of their matrix. In general, Al is a refractory metal (i.e., forms stable and insoluble oxides) and thus it can be difficult to get into solution. At one point this step was completed in 4L bottles, but we have now since switched to 2L bottles. **Acid amounts listed below are for 2L bottles (if you are using 4L bottles, simply double the acid amounts).**

- 1) Your samples should already be in a 2L bottle from the previous step.
- 2) Fill all bottles to the 3/4 to 4/5 level (eyeball it) with DI water. Place bottles in the working hood. In hood, add 25 ml HNO_3 first, and then 30-40 ml 48% HF. If the sample is pure quartz (quartz vein sample), add 30ml HF. If the sample is not pure quartz, add 40 ml. Only pour HF into bottles that are in a tray that will prevent spilling outside of the hood in case of an accident. Cap and place bottle in ultrasonic cleaner. Fill ultrasonic cleaner to within one half inch or so of the top. The bath should have "evaporation balls." Turn on the **ultrasound with heat. Let run for 8 hours.**
- 3) Drain acid into acid neutralizing bucket. For simplicity, add baking soda to a few inches of water into the bottom of the bucket, and add this acid waste to it. Rinse bottle and quartz three times with DI water. It is safe to pour down the drain liquids between pH 5.5 and 10.5. EPA classifies hazardous waste as pH <2 and >12.5.
- 4) Repeat Step #2, leaving the sample in the heated **bath overnight or at least 12 hours.** Repeat step #3.
- 5) Repeat Step #2, leaving the sample in the heated **bath 24 hours.**
- 6) Repeat step #3, but rinse the **bottle 6 times.** And, rinse the lid, and the area around the bottle rim. At this point the samples **might** be clean, however, some samples may have remaining feldspars. If this is the case, run the samples through additional 24-hour runs as needed.
- 7) Put bottle in oven to dry with lid ajar. Keep oven 40-50 C.
- 8) As soon as quartz is dry, take out of oven. Pour sample onto a creased sheet of paper, and then pour sample (using the paper as a funnel) into a clean 50 ml centrifuge tube. Be sure to record the weight of the clean quartz by taring the balance first.

***If not enough quartz is produced, re-do this procedure for a sample labeled "B," or if the Al content is too high upon the ICP test (see below), re-run the entire sample for just a 24 hour run.

Testing quartz purity

A small aliquot of sample is taken in order to measure total cation concentrations using inductively coupled plasma mass spectroscopy (ICP-AES) to look at cation content with three goals in mind: 1) high Al content (>200 ppm) in most cases indicates non-pure quartz, 2) the [Al] provides a target value to use when adding Al standard to sample during final quartz dissolution, and 3) the total cation load must be known before samples can run through the cation columns in the dissolution process. **This step is essential to ensure that future column work runs smoothly**

1. Empty ~0.25 – 0.4 grams of quartz into a tared empty 90 ml savillex jar and record its mass. Place all savillex jars in the hood. Add a few ml of 48% HF to each savillex jar using a disposable pipette. Be careful and keep track of this pipette. Once finished with it, rinse thoroughly before placing into trash. Put on savillex lids until snug and place beakers on the hot plate. Turn hotplate on setting 4 (with the current hotplates that range b/n 1 – 10), for 5-6 hours or until samples are dissolved.
2. After the quartz has dissolved completely, remove lids from savillex jars. Leave until all HF evaporates.
3. Once the HF has dried off, turn off the hotplates and add a squirt of dilute HCL from a squirt bottle. Wash down the beaker sides and cover the bottom to ensure that acid touches all dried crud. Leave for a few minutes while the sample, still warm and still on a warm hotplate, dissolves. After 5 or so minutes, add ~10 ml of DI water to each beaker.
4. Tare an empty 15 ml vial or measure the mass of all vials and record. In the hood, transfer the sample to a 15 ml vial and measure mass of vial and sample.
5. Samples are ready for measurement. Provide estimated ranges for total cations so that the machine can be calibrated against a shorter range of standards (allows better precision).

If total Al is > 150-200 ppm, carry out an additional 24 hour ultrasonic HF/ HNO₃ for that sample.

Using the ICP spreadsheet, calculate the total cation load values (ug) for each sample. Our cation columns can only handle ~8,500 – 9,000 ug before they become overloaded. If your sample is greater than this value, you will either have to: 1) reduce the amount of quartz to use in the dissolution, or 2) split your sample over two cation columns. Alternatively, you could run the sample through more 24 hour ultrasonic bath steps and see if the total load is reduced.