X-Ray Lab Cookbook

ICP sample Preparation

Basic Principles of Geochemical Sample Preparation

- Once the sample has been washed in methanol and distilled water, it is not to be touched with bare hands. This will help minimize sodium contamination. Once they are cleaned, every effort should be made to eliminate any and all sources of contamination. Always wear gloves and change them or clean them routinely with propanol during all processes. Clean all surfaces where you will be working with the samples and work on a clean paper at all times. If the floor is dusty, damp mop it before you start work. Close the door to the lab as much as possible when the samples are open. You are attempting to measure trace elements in single-digit parts per, so cleanliness is not just an optional thing. Keep it clean!

- Also keep in mind that the scientists will be able to see many aspects of your sample preparation technique. Many of them may well be more experienced than you are with ICP sample preparation. If your techniques are not clean enough, chances are they will know it and, although they may not say anything, your results will are more likely to be called into question. If you look like you know what you are doing, keep your sample prep area clean, wear your gloves, and so on, you will have less trouble getting the scientists to believe your results. If your lab or your work looks disorganized or sloppy, the scientists will probably assume your results are as well. And they will probably be right.

- On a "hardrock" cruise, it is generally convenient to share the paleo prep lab with the paleontologists. I usually move the shatterbox in there near the starboard side fume hood. I discuss my requirements with the paleontologists before the first site and have had no problems arranging for the space that I need. All I usually ask is that they let me have the port side fume hood for the acid baths, and that they keep the area around the sink near the DI maker clear. I use this area for washing samples and glassware and for cleaning and drying the grinding vessels. There is usually no problem with this, because there are few paleontologists on a hardrock cruise. It is advantageous to keep the shatterbox near the sink with the DI water because that is where the grinding vessels are cleaned. The big one in particular is quite heavy. The shatterbox could be stored in 2nd look between hardrock cruises now, if the biologists can't stand having it in their area. There really isn't room for it in the new (smaller) ICP sample prep lab.

Step 1 - Cut the sample into crushable pieces

Basic principle of this step: It is important that the sample pieces are cut to a size that you will be able to crush in the X-Press, generally less than 1 cm thick. Harder material must be cut in relatively small pieces. Softer (weathered) basalt or sediment can be cut in larger pieces. This is a zen thing to some extent.

- Check the sample size. If the large tungsten carbide (WC) grinding vessel is used, the minimum amount of sample has to exceed roughly 30 g or you run the risk of cracking the vessel (≈$5,000 ea.). The smaller vessels require a minimum of about 10-15 g (≈$2,000 ea.). Smaller samples must be ground in either the WC Spex Mixer Mill, or by hand in an agate mortar, but this is to be avoided if possible. The original sample size should be adequate to provide at least 10-15 g of sample after the cleaning and crushing process. If the sample is not large enough, talk to the curator and the scientists and try to get them to cut a larger sample. If the sample is too small for the shatterbox, it may not be large enough to adequately represent whole rock geochemistry anyway. Resolve this problem early. Don't wait until you get to the shatterbox and realize that the sample is too small.

- Take the samples up to the saw near the sampling table. Clean the saw with the hose before you start and between samples. Wear eye and ear protection when using the saw.

- If the piece is larger than you will be able to crush in the X-Press, or the shape is too irregular to crush, cut the sample as necessary. If you cut the pieces too small, it will take longer to clean and sample material will be lost unnecessarily. If you cut the pieces too bit, you may not be able to crush it and you will have to come back to this step. You can also have an explosion in the X-Press and ruin the sample. I tend to cut the first samples on the small side until I get a feel for the relative hardness from having crushed a few. Drilling times and difficulty cutting the rocks with the Super Saw will also give you and idea if the material is very hard.

- Look at the sample. If there are veins or other obvious impurities in the rock, you may need to discuss this with the petrologist(s) responsible for selecting the samples. They may want you to try to remove this material when you clean the sample, or they may want to select a better sample. They may also want to leave it in there. It is up to them, but make them aware of anything that might skew the geochemistry of the results. The objective (usually) is the get at whole rock geochemistry of the basalt. Veins, infilled vugs and the like are usually not desirable in the sample. Cutting the sample may reveal features that the scientists were not aware of and may want to avoid. Look at the sample carefully and make sure it is as good a sample as you can get, both at this step and at the next one.

- Put the samples back in the bags they came out of. Do not mix them up. Work on one sample at a time so you cannot make a mistake. Take the samples back to X-Ray or up to Thin-Section for cleaning. Do not leave them lying around. Ever.

Step 2. Clean the sample on the diamond wheel

Basic principle of this step: Sample surfaces are ground on a high-speed, diamond-impregnated disk (≈70 μm grit) to remove saw marks, coring bit marks, or any other unwanted material such as surface alteration. We do not want to analyze the super saw blade or the bit.

- Leave the cut samples in the bag and take them to the lapping wheel in the Thin Section Lab (currently on the labstack 8th level, starboard side aft). Do not put them in the beakers for cleaning and try to carry the beakers up the stairwell. The 8" grinding wheel and the spare discs for this step are stored in X-Ray. During a hardrock cruise, you should be able to leave the grinding wheel and the sandpaper in a drawer in Thin Section for convenience. This should be arranged with the thin section technician.

- Remove the thin section grinding wheel and put it somewhere secure where it cannot fall over and be damaged or damage anything else (best to flip it over so it sits on the flat side). Put the 8" wheel in place on the grinder. For most samples, it is best to start with the sandpaper and finish with the diamond-impregnated disk. This saves time and unnecessary use of the diamond disks (which cost about $100). You will probably have to use the aluminum ring with the sandpaper to hold it in place. You can put the diamond disk on with the sandpaper on top of it and then put the ring on.

- Turn the water on with enough flow to clean the wheel, but not full force or you will make a big mess.

- Turn the wheel on. It has two speeds and you can use either one. You may want to start with the low speed until you get the hang of it.

- I like to take off all the corners and edges of the sample first. This will save wear and tear on your fingers in the long run. (Gloves are not necessary for this and I found them to be hard to use, but you can try the nitrile gloves if you want.) Hold the sample against the wheel and take off any and all surfaces that could have come in contact with a saw blade, the bit or the core barrel, or any altered surface. Basically, you want all new, diamond-ground surfaces on each piece of the sample. Irregularly-shaped samples can take a long time to grind down. Make sure the curator or whoever is cutting your samples understands this so they can attempt to cut pieces that will not be tedious to clean. Irregular pieces are also wasteful of material because you have to grind so much off, so they are to be avoided when possible for that reason as well.

- Clean all the pieces with the sandpaper, then take the sandpaper and the aluminum ring off fir the final cleaning, which should not take long. When you have the aluminum ring on, try not to touch the sample to the ring. Move the sample back and forth across the wheel. Do not just hold it in one place and wear out a single groove on the sandpaper or the diamond disk.

- When the pieces are clean, put them back in the bag. Do not mix them up. Work on one sample at a time so you cannot make a mistake.

- When you are finished, put everything back the way you found it. Put the 8" wheel and the sandpaper away and put the thin-section grinding wheel back in place. Clean up any water

you splashed around the grinding wheel, etc. Do not leave a mess. You are a guest in someone else's lab.

- Take the samples back down to X-Ray for the next step. Do not leave them in thin-section.

Step 3. Wash and Dry

Basic Principle of this step: Rock chips are washed in alcohol (methanol) or acetone to remove contaminants such as oils from your skin and residue from the cleaning step. After this step, you never again touch the sample with your hands.

- If you haven't already, check the DI filter for the DI-maker in Paleo. Turn the gauge on if it isn't already and if the filter needs changing, change it. Filters are kept in the HRS cage. Check with the chemists if you are unsure about this stop. If you do change the filter, label it with a sticker of the date/Leg number it was changed.

- Set up a small sonic bath in paleo near sink by the DI water maker. Try to find a nice clean one at the beginning of the cruise and label it and one of the large sonnicators with a sign that says "ICP sample prep only - Please do not use." Put about three inches or so of DI water in the small bath. (Note: You cannot use the large soniccator for this step because that soniccator has to be operated with the water only about 1 inch from the top of the bath or the transducers will be damaged. The large sonic bath is usually only used for cleaning glassware and the Pt/Au crucibles.)

- Get one of the 200 ml beakers from the X-Ray lab for each sample. Make sure it is a clean beaker. Write the name or number of the beaker on the sample bag label and put the rocks in the beaker. (One sample per beaker of course.)

- Pour enough methanol into each beaker to cover each sample and deep enough to keep the beakers from floating around in the sonibath. Sonnicate for 15 minutes.

- Decant the methanol into the fume hood sink (in Paleo) water and rinse the sample about three times in deionized water, agitating the sample and then decanting the water each time.

- Cover the sample with DI water and Sonnicate again for 10 minutes. Repeat this DI rinse several more times, until the water is clear after sonnicating. Note: The water may never go clear for some clay-rich samples or sediments. If three or four times doesn't do it, give up and go to the next step. If it is a sediment sample and appears to be dissolving, you may only do this once or twice. Three times usually does it for basalts.

- After the final rinse, decant as much water as possible (without pouring the sample in the sink). You can use a propanol-cleaned teflon scraper to hold the rocks while you pour the fluid off, but this isn't necessary and actually provides an unnecessary source of contamination. I recommend just pouring the water off carefully.

- Put the beakers on a SS tray and put them in one of the sample prep ovens at 110°C for 8-12 hours (ICP Sample prep ovens are located in the X-Ray Lab and the Paleo Lab). Clean the

ovens well at the beginning of the cruise, before you turn them on. The top of the oven in particular must be clean because the samples are open in the oven. The oven used for ICP sample prep should be used ONLY for ICP samples. We do not share. I put a sign on the oven I am using that says something like "ICP Sample Prep Oven - Do not open, do not use, do not turn off, do not change temperature." This usually works.

- Use a magnetic Bulldog clip to hold the sample bags together and stick them on the door of the oven with a Post-it note indicating the time that set of samples went in to dry. They will be dry in 8-12 hours (I usually wait 12 hours).

Step 4. Crush into 1-cm or less pieces in the X-Press

Basic principle of this step: The sample must be crushed into pieces 3 mm or less on a side for the small grinding vessels or 1/4 to 3/8" for the large grinding vessel. Pieces larger than this can damage the grinding vessels used in the Spex Shatterbox. The large tungsten carbide (WC) grinding vessel is used for samples from 20 to 50 ml. If the sample is too small, you run the risk of cracking the vessel (≈$5,000 ea.). The smaller vessels require a minimum of about 5 ml or material. Samples should be large enough to grind in the small shatterbox. The alternative grinding vessel for very small samples is the alumina ceramic mixer mill vial, which takes much longer, is difficult to clean properly, and is subject to breakage. (I have never used these vessels at all.) Small sediment samples may perhaps be ground by hand with the agate mortar and pestle if they are not too hard.

- Clean the countertop around the X-Press and clean the X-Press inside and out. Start with Windex or something on the counter and finish with propanol and Kimwipes on everything.

- DO NOT have any food or drinks on the counter while you are working. You cannot eat with the gloves on anyway and it looks bad. A coffee cup is maybe OK, but no snacks.

- Put on a pair of the blue powderless nitrile gloves. "Wash" your hands with propanol with the gloves on to make sure they are clean. Repeat this "washing" periodically throughout your work, certainly between samples and after anything that could have gotten the gloves dirty. If you have any doubts, change your gloves. Take no chances.

- Put pieces of white paper down on any surfaces you will be working on. I usually use the large (11.5 x 17) paper and keep a supply of it in the lab.

- Get a supply of clear endcaps and delrin plugs. Clean them thoroughly with propanol and kimwipes and let them dry on the white paper. Be sure to check out the delrin plugs on the Siman checkout sheet. End caps you can get from the core lab. Use new ones from the box, not the ones from the catwalk.

- You will also need tweezers. Clean them well with propanol as well. You will also need some of the large 6x6 weighing papers. I always use the "down" side of weighing paper, theorizing that it is cleaner than the sheet that sat on top and could have had stuff fall on it.

- Get the SS tray of samples out of the oven and the corresponding labels. Use a hot mitt to carry the tray. Put a big kimwipe over the beakers to keep the samples clean while the rocks and beakers cool off and while you work.

- Put a sample label for each sample on an acid-washed1-oz glass bottle. Make labels for the lid of the bottles and put them on as well.

- Put a couple of pieces of 6x6 weighing paper on the 11x17 white paper and get one clean end cap and two clean delrin plugs (precleaned with propanol). Put one delron plug in the end cap and arrange one or more pieces of the sample on the plug. Balance the other plug on the sample pieces. Carefully slip the piece of core liner into the end cap. It need not go all the way in. Leave it as loose as possible so you won't have trouble removing it. Then put the aluminum plug (also cleaned with propanol) carefully into the core liner on top of the delron plugs.

- Pick up the whole thing, being careful to support the end cap from the bottom so the sample cannot fall out. Open the X-Press door and put the sample in the center of the round plate in the center of the X-Press. Keeping the aluminum shaft as vertical as possible, tighten the knob on top until the aluminum shaft is secure. This doesn't have to be tight, just snug.

- Close the plastic door. (The X-Press has a safety interlock and it will not operate unless the door is closed.) Close the valve on the right side of the X-Press. This does not have to be tight either. A very light pressure closes it plenty.

- Stand off to the side of the X-Press, so your body is not in line with the hydraulic gauge on the front. If the thing blows, the most likely place for it to give is at the gauge. DO NOT crouch in front of the gauge with your face 3" from it. Safety glasses are not a bad idea, and always stand off to the side of the thing. Push the switch down to raise the piston. You will hear a "growling" sound. Watch the gauge and try not to go above 5 or 6 tons. Anywhere above 6 tons or so you can break the delron plugs, sometimes in an explosive way. Around 10+ tons, you will break the plugs almost for sure and an explosion in the X-Press is likely. It can blow the sample out the side of the core liner and spread the whole thing around inside the press. You can ruin the whole sample at this step. Take your time and go slowly. If it isn't working, take the thing apart and rearrange the pieces. Sometimes it may take a few minutes for a sample to crack. Leave it on 5 or 6 or maybe 8 tons for a while, maybe even 5 minutes. If it doesn't crack, try letting off the pressure suddenly and then running it back up. The crack sometimes comes on the decompression.

- Several times, maybe many times, you will have to take the assembly apart and remove the pieces that are small enough. Dump the small pieces and powder onto one of the 6x6 sheets of weighing paper and pour the material into the correct bottle you have labeled. Do this right away and close the bottle afterwards. Then rearrange the pieces on the delron plug and reassemble the whole business to crush everything again. You may have to do this half a dozen times or so for an "average" sample. If the material is relatively soft, you may get it in one or two crushes. A large, very hard sample may take many more tries. You may also damage the delron plugs or even the endcaps. If the delron plug cracks at the edge, throw it away and get another one. It will break under very little pressure the next time. If you get pieces or chips of the delron plug in the sample, be careful to pick all of them out. This

shouldn't happen very often. If it does, you were probably too impatient or the piece was too big in the first place.

- When you are finished with all the samples, take the beakers to the DI sink and wash them out well with a test tube brush and rinse them thoroughly with DI water. Put them back on the SS tray and put them in the oven to dry. They are stored in boxes in the cabinet under the bead sampler at present.

Step 5. Grind (in the Shatterbox)

Basic principle of this step: The sample must be ground into a very fine powder and homogenized. If possible, the entire sample should be ground together, in a single grinding vessel to achieve complete homogenization. If the resulting powder feels like talcum powder on your skin, it is fine enough. If you feel grit, it isn't fine enough.

Caution! This step should not be done in very rough seas, particularly in rough seas if you are underway. The small grinding vessels in particular are subject to chipping or cracking if the ship movement is excessive. That is the reason we have never been able to use grinding vessels made of more desirable materials such as agate or alumina-ceramic. We can only use tungsten carbide grinding vessels and we have no spares. (The other ones we have are steel.) If you have to "hang on" from time to time while standing or moving around the ship, it is probably too rough to grind. If it is a rough cruise, you may have to take a larger sample than you might otherwise want to so you can use the large grinding vessel. You can use it in rougher seas, but still, not too rough. Try to plan your work to grind on site rather than while you are underway. If you are in doubt, it is probably too rough. Don't chance it. The small grinding vessels cost about $1500 each and the big one costs about $5000. And there are no spares onboard. Do not be fooled by the other grinding vessels you may find. They are steel and will provide numerous contaminating elements that the scientists will not like.

- If the large tungsten carbide (WC) grinding vessel is used, the minimum amount of sample has to should be 20 to 50 ml or you run the risk of cracking the vessel (≈$5,000 ea.). The smaller vessels require a minimum of about 5 ml of sample. Make sure the sample is precrushed to a size appropriate for the grinding vessel to be used (3 mm on a side for the small vessels and 1/4 to 3/8" on a side for the large vessel.) Note: If the sample is very, very hard, it may not be possible to grind it fine enough using the small vessel, but this would be unusual. Also, in very rough seas, the smaller vessels are more likely to chip, so on a rough cruise or if you have very hard material, you may have to take larger samples so you can use the large grinding vessel. The small vessels are easier to handle, so use them if you can.

- Transfer the sample (<1 cm pieces) to the grinding vessel by pouring in enough sample to make a small talus slope ≈1/2 to 2/3 of the way up the side of the vessel (do this on both sides of the ring in the large vessel). Don't spread the sample around. If any pieces are on top of the puck or ring, use plastic gloves, tongs, or clean paper to move the sample into the cavity.

- Replace the lid to the vessel and carefully place the whole assembly in the Spex Shatterbox. The large vessel sits directly in the shatterbox. The small vessels sit on a plate with pins in it. If you are using the small vessels and have just one sample to grind, place it on the center

pin of the mounting plate. If you have two samples to grind (and you have three undamaged grinding vessels), you can run the third vessel with no puck in it. You cannot run either one or two vessels on the outer pins or the thing will be out of balance and cause much damage.

- Put the rubber pad and the top plate on top of the grinding vessel(s). Bring the safety arm over the top of the vessel, centering the plate beneath the arm's centering bracket. Fasten the arm securely, tightening the knob almost as hard as you can by hand. Use the special Mary Ann tool to finish tightening the nut. It should be pretty darn tight, but not ridiculously tight.

- Assuming the shatterbox is plugged in, turn the timer up to 5 minutes (this timer is approximate) and turn the switch on. Slowly adjust the speed knob (on the left) up until the thing is running smoothly. If it makes any bad noises, shut it off and find out what is wrong. It makes noise, but you shouldn't hear any metal-to-metal sounds. If in doubt, check it out. DO NOT risk damaging the grinding vessels.

- When the thing is up to speed, set a timer. 60-90 seconds is usually enough for the large grinding vessel. The smaller vessel takes about 3 minutes. Try not to exceed three minutes to minimize contamination from the grinding vessel. Don't grind any sample longer than necessary.

- When the time is up, flip the switch off and dial the speed back down to zero. Wait for the thing to quit rocking to open the lid. It takes a few seconds. Use the tool to loosen the knob on the safety arm while holding the spring catch down. Flip the arm back and remove the grinding vessel(s). Put them on a kimtowell or a piece of paper.

- Open the grinding vessel and use a tweezers to remove a small bit of powder and test it on the inside of your forearm. It should feel like talcum powder if you rub it in. If it feels "gritty" you need to grind the sample a little longer. After a while, you may discontinue this test, but do at first to see how long you need to grind the samples

- Use a clean piece of weighing paper of the teflon spatula to clean-off the powder from the top surface of the puck and ring. Using plastic gloves or clean paper towels, carefully disassemble the vessel, putting the puck, ring, and O-ring on the inverted lid.

- Carefully pour the powder from the vessel onto clean paper. Try to minimize airborne dust particles. If any powder remains behind (in the bottom corner), use a clean plastic spatula to dislodge it. It is not necessary to get every grain out of the vessel, but you should get most of it.

- If you are grinding multiple batches of the same sample (i.e., coarse-grained rocks or inter-laboratory standards) transfer the powder to a labeled Ziploc bag, and homogenize as needed.

- Transfer powder to the correct pre-labeled sample bottle. Do not leave the sample open or the sample bottle open any more than necessary.

- Cleaning the grinding vessels. Wearing acetone-resistant gloves (nitrile gloves don't work so well for this), wash the individual pieces of the grinding vessel(s) with DI water and a small piece of a greenie meany' pad (**No Soap!**). You may also use a brush to remove sample

particles from the bottom corner of the vessel. I work on a greenie meannie pad in the sink to minimize the potential to drop the pieces on the hard sink and chip them. When the part is clean, rinse it with DI water and then flush it well with acetone to get rid of the water and speed drying., Do not blow dry with compressed air as the rig air is very dirty. The lid is particularly vulnerable to surface rust if it is not dried quickly and thoroughly. Thorough flushing with plenty of acetone is critical, so the process is pretty aromatic. I recommend using the organic vapor masks for this procedure. The O-ring on the large grinding vessel is washed with water and dried with a paper towel (no acetone).

- Lay the pieces on kimtowells to dry and cover with kimwipes while drying. Parts of the small grinding vessels are a set. Do not mix up the lids or the pucks. When they are dry, put them away as soon as possible. Make sure the vessels are completely dry before you use them for another sample or put them away. If you did it right however, the metal parts don't take very long to dry. The rubber O-Ring is a little slower. (The grinding vessels are presently kept in a drawer under the mixer mill.)

Step 6. Pre-ignition weigh for LOI (Loss on Ignition)

Basic principle of this step: At this step you weigh a crucible, add some sample (about 1 gram or so) and then weigh the sample and the crucible together. After ignition (usually at 1025 for 4 hours), you weigh the sample and the crucible together again and calculate the change in weight. Usually the samples lose weight as water is driven off.. An iron-rich, water-poor sample may gain weight, but most samples will lose. The scientists use the LOI as an indication of how fresh a basalt is. Lower LOI values suggest relatively fresh, unaltered basalt. High LOI numbers suggest a lot of clay in the sample which is an alteration product. For geochemical analyses, you want as fresh (unaltered) a sample as possible. Because the samples were dried at 110°C prior to grinding, the following method assumes that the amount of adsorbed water (H_2O^-) for each sample is negligible.

The following is an excerpt from the Joel Spark's XRF cookbook (Joel actually understood LOI)

> LOI measurements by themselves are generally of limited use due to questions over what species are actually driven-off (H_2O^+, CO_3, S, Cl, F, ?), to what extent they are lost, and how much weight is gained through the oxidation of iron (and possibly manganese and sulfur). Not all samples will lose weight during ignition. It is common to measure overall weight gains for fairly fresh basalts containing little water and over 8% FeO. If one is trying to determine the amount of H_2O^+ in a suite of samples, it is much more specific (and accurate) to use the Carlo Erba CHNS chromatograph in the Chemistry Lab. This analyzer has been very successful at measuring H_2O^+ and CO_2 in altered basalts. A brief account of the CHNS analytical procedure is given in the Leg 140 Explanatory Notes and elsewhere.

- Find the LOI form on the hard drive and customize it as necessary for your cruise. Print out as many as you need. Stick them on a clipboard or in a notebook. I like to work with them on a clipboard and then store them in a notebook until the end of the cruise. Then I throw them away.

- Turn on the balance if it isn't already on and start the Scientech program if it isn't already running. If you have a separate calibration for LOI and another one for making beads, load the appropriate calibration file for LOI weighing.

- Clean the counter, the balance and the balance pans as necessary and put the white paper down where you will be working. Get both sets of weights. Put 15 mg from the blue set on the known and 15 mg from the black set on the unknown. (The black set are the newest, best ones so use them only when necessary and for calibration.)

- Note: When working with the balance weights, always use the tongs to pick them up. When they are not on the pan, put them back in the box. It is OK to keep one weight out that you are quite often, but keep it on a paper or kimwipe in the balance box. Do not put it down where sample powder an spill on it or it could get messed up in any way. Set the weights on the pans gently, being careful not to scratch them. When you are not using the set, keep the box in a drawer. If the weights get dusty, you may clean them gently with a kimwipe and propanol. Never, never, ever touch them with ungloved fingers.

- Close the door and secure it with the velcro and hit the tare function. Wait for 50-75 counts for the filter to do it's thing and then hit the trim function. With the filter, the weighing starts at zero so you get a big "tail" on the curve. You have to get rid of this data (which is bogus) to get a good weight. When the curve "smoothes out" hit the trim to start the weighing (usually in 50 to 75 counts).

- When the curve flattens out enough, you can halt the tare process. Then I usually try weighing one more time to make sure I got a good tare. Hit weigh, wait 50-75 counts and hit the trim. If the weight comes out at pretty close to zero, you have a good tare. (Note: Weighing "by stats" is not a reliable feature if you use the filter. I go "by counts" and set it at 1000 or so, just so it doesn't cut off before I want it to. You just have to zen it in when the weight is believable.)

- Fused quartz crucibles for sample ignition and LOI measurements are stored in the desiccator next to the Scientech balance. Extras are kept in the drawers beneath the X-Press. Get a clean crucible out of the desiccator and record the number of the crucible on the sheet. (Handle the crucibles with gloved fingers or tongs only.) Use the small crucibles only for this. The large ones are nice to work with, but they are too heavy for the balance. It takes too long to weigh them and the results are not accurate or precise. The large crucibles are used now only as "holders" for the small ones, so they don't fall over in the rack. Record the number of the small crucible that the sample will go in on the LOI sheet.

- Put the crucible (without the lid) on the unknown pan and 10 grams (from the blue weight set) on the known and hit weigh. Wait 50-75 counts and hit trim. This will allow you to calculate the correct counterweight for the crucible. If you have 10 mg on the known and a crucible on the other side and get a weight of say 4.765, the crucible weigh something like 14.765 grams. You would use a counterweight of 14.500 grams in this case. You would put another 4.500 grams on the known (for a total of 14.500), hit the trim button and close the door. You may want to weigh the crucible a couple of times just to be sure you get a reproducible weight. Again, it is a zen thing. In rough seas or if the balance is acting

screwy, you will have to weigh longer and do more double-checks. In calm seas, you can back off a bit. Zen.

- Record the weight of the crucible (in four places) on the LOI sheet. If possible, use a target weight of 1.000 grams. This makes the math easier. If you used a counterweight of 14.500 grams, weighed the crucible and got a weight of .256 grams, the delta weight you record is .256 grams. This will also be your target delta weight. Just add 1.0 grams to the known pan (your new counterweight is now 15.500 grams). Leave the crucible on the unknown pan and carefully, tidily transfer about a gram of powder into the crucible (I use the spatula to do this). Reweigh the sample until the delta weight is again about .265 grams. When it is, you will have 1.0 grams of powder in the crucible (the weight shown will be about .265 grams).

- Note: I only believe about three decimal places from the balance and that is all that I ever record on the sheet. The accuracy and precision of the balance is not such that it makes sense to record a weight of 13.64789. If I got that, I would weigh it again, hopefully getting something like 13.74813. The weight I would then record would be 13.748. Even the third decimal place is not always totally reproducible, but in calm seas it usually is pretty believable. The last two decimal places I use for rounding up or down, but that's about it.

- When you have the weight very close, make sure there is no powder on the pan or on top of the crucible where it will spill. Take the crucible off of the pan and tidy up if you have to. For the final weight, make sure the balance door is closed and weigh the thing maybe a couple of times. Record the final weight of the crucible with the sample and calculate the weight of the sample. It is not critical that it be exactly 1.0 grams or whatever your target weight is. It is only important to know with some precision what it does weigh. 1.050 grams is fine. I would take some out if I got 1.500 grams.

- Put the small crucible in one of the big ones and put a lid on it. (Up to this point you have been weighing with the lid off of course.) Put it in a rack in the desiccator until you are ready to ignite the set.

- Keep an eye on the color of the desiccant. If it isn't nice and blue, put it in the oven at 110 for a while to revive it. It is good to do this while the samples are in the furnace. Then you can put fresh desiccant in when you return the samples to the desiccator from the furnace.

Step 7. Ignite the sample in the furnace

Basic principle of this step: The idea of igniting the sample is twofold. First, you need the minerals in the sample reorganized with the elements of interest present as oxides. Geochemical analyses report percentages of SiO2, TiO2, etc. SiO2 may have come from quartz and clays and amphiboles in the original sample, but in the ignited sample the minerals should be gone. Also, the ignition step provides a way to calculate the loss on ignition, giving the scientists a way to evaluate the "freshness" of the sample and do other theoretical calculations. The LOI calculation is usually supplemented by CNS analysis. I don't know exactly what they do with the data, but they invariably request LOI and CNS on basalts.

- Ignite sample(s) in the ashing furnace for 4 or 5 hrs at 1025°C for basalts, ≈900°C for sediments (or Si-rich material). If your samples contain muscovite, biotite, amphibole, or carbonates, ignite the samples for 6 hours or more. Various programs have been used over the years for different material and different cruises. Copies of these programs may be round on a bulldog clip somewhere around the furnace (in the Chem Lab) or the Ashing Furnace folder in the file drawer next to the XRD in MBio. Many of the old programs were used with the original furnace and have a ramp rate of 25 degrees C per minute. This furnace cannot begin to keep up with that rate. I have been using 3 degrees per hour, going to 1000 degrees C and holding for an hour before ramping up to 1025 to hold again for four hours. This whole program takes about 12 hours, which is convenient if you put the samples in before you go off shift and then take them out when you come back on. You could experiment with higher ramp rates, but at the higher temperatures, it just doesn't seem to keep up. When the program calculates that it is at the desired soak temperature, it does not check to see if it made it, and begins the countdown regardless of whether or not the temperature is as it should be. The program I have been using avoids problems with this.

- Put the samples in the furnace before you start it. If you have to open the door later you will lose heat and cause unnecessary problems with the already-fragile ramp rate of the furnace. You can open it up sometime when it is at 1025 if you want to see what it is like to look into hell, but don't make a habit of it. Once for informational/curiosity purposes should be enough.

- Check the program every time you ignite a set of samples. The chemists use this furnace as well and may have changed the program. Hopefully they will do the same before they use it or they may get their stuff a lot hotter than they anticipated if they wind up running your program. If you have a new chemist, make sure he/she knows that you are using the furnace too so they don't get "burned." Their programs seldom exceed 500 degrees C.

- Remove the crucibles when they are cool enough, ideally between about 200 to 50 degrees C. Use the special handle to pick up the rack. Store the rack in the desiccator until you are ready to weigh for LOI and make the beads. This should be done as soon as practical so the sample does not rehydrate. The desiccator reduces the humidity a wee bit, but basically there is plenty of opportunity for the samples to hydrate in there. Try to plan your work so that you can process the samples very soon after they come out of the furnace. If you can't deal with them, don't ignite them. If you really want to leave them around for a while ignited, you might consider storing the rack in the oven at 110 degrees C. The problem with this is that the rack is dirty, so put it on the bottom of the oven the oven after you take the rack out.
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- Note: Be very careful when carrying the crucible rack, particularly if it is still hot. Peer carefully around corners before proceeding. Do not come flying around a corner with a red hot rack of samples and brand somebody who may be coming the other way. If someone is coming toward you, (politely) let them know that the rack is hot and delicate.

Step 8. Post-ignition Weighing for LOI

Basic principle of this step: This is a quick, simple step that should be done as soon as possible after the samples come out of the furnace. The idea is to re-weigh the crucible with the sample in it to determine how much weight the sample has gained or lost. The procedure is the same as the last step of the pre-ignition LOI weighing step. Tare the balance with 15g on each pan, put the appropriate counterweight on the unknown and the crucible with the sample in it on the other pan (no lid). Weight it and finish filling out the LOI sheet.

- Clean up the balance and the counter, put down the paper, etc. Start up the balance program as usual and get the clipboard containing the pre-ignition LOI sheets.

- Put the 15 g on each pan as you did for the pre-ignition LOI and get a good tare. Check the weight to make sure that it comes out close to zero. On a good day, you may be able to use this tare for two or three samples. Lately however, the tare has been drifting so much that I have had to retare after every sample. This may be a temperature thing. I really don't know why it would vary. The balance seems to have moods, which you will eventually attune yourself too if you spend enough time with it.

- Remove the 15 grams from the unknown pan and put those weights in the box. As always, use the tongs to handle the weights. Put them back in the box when they are not in use and be very, very careful not to get them dirty or scratched.

- Use tongs or gloved fingers to get a crucible out of the desiccator and place (gently) on the unknown pan. Leave the lid off for this as it was when you weighed it the first time.

- Get the appropriate LOI sheet for whichever crucible you picked up to get the appropriate counterweight to use. Use the second counterweight (the higher of the two) that you used when the sample was in the crucible. Put the right amount of counterweight on the known pan, close the door, and start the weigh function. Trim the data as usual. Again, the weight should come out to be less than 500 mg if you have the correct counterweight. Occasionally the sample may lose so much weight that you have to reduce the counterweight by 500 mg to avoid coming up with a negative number, but it doesn't happen that often with basalts.

- Weigh the sample a couple of times to make sure you have a reproducible weight. Record the weight on the LOI sheet and calculate the post-ignition sample weight and the LOI. Record this on the sheet as well.

- The formula used to calculate the LOI is shown on the sheet.
  %LOI = 100*(weight change during ignition) / (fresh sample weight)
  Note: By convention, weight lost during ignition is typically recorded as a positive LOI value, whereas weight gained is recorded as a negative LOI value. And the result should be

given to two decimal places only. (Ex. LOI=0.45 not LOI=0.4586). The LOI spreadsheet will round appropriately.

- LOI calculations can either be made using the LOI forms, or the weights can be entered in the "LOI Short Calc" worksheet and the percent LOI will be automatically calculated. I do it both ways, calculating it at the balance first, then double-checking it using the LOI spreadsheet.

- I recommend using the LOI spreadsheet. Keep a copy on the hard drive and then put it on the server somewhere the scientists can get to it. I would call the spreadsheet LOI and put it on Data1 (read only). At present I don't believe there is an ICP folder, but we need to get one. That is where the LOI data should live.

Step 9. Weighing for beads

Basic principle of this step: The idea is to weigh out, as accurately as possible, 100mg of the ignited sample powder. This is added to a vial containing lithium metaborate flux that is preweighed onshore to 400mg. This is then fused (on the next step) to make a glass bead that is dissolved in nitric acid and the resulting fluid analyzed. This is a fairly critical step. The weight should be as close to 100mg as you can possibly get it within the limits of the balance. Inaccuracies in the weight will show up in the analytical results. The scientists and the chemists will be displeased with you if they have to rerun samples because of weighing inaccuracies.

- Clean up the balance and the counter, put down the paper, etc. Turn on the balance and start up the program as usual. Make sure the correct program is loaded and the regression is done.

- Get the almost-completed LOI sheets for the samples you need to make beads for. (The post-ignition LOI should be already done of course.) For each sample, you will need one bottle of preweighed flux and one new, empty, acid-washed vial to put the extra ignited powder in. You can pre-label the bottles ahead of time or do it as you go. I use the small smear slide labels. One goes on each cap and one on the bottle (since the bottles and caps should not be mixed up once the sample/bead has been put in the vial). So, for each sample you will need four smear slide labels. The preweighed flux is in the glass-doored cabinet in the lab. For the extra vials, you may have to wing it until the procedure is more established. You could probably acid-wash some 16-ml wheaton bottles for this if you don't have new flux vials.

- Put the 100 and the 200 mg weights from the calibration set in the black box on the known pan. Fold a small (2x2) weighing paper into four quadrants and smooth it out again to make a nice little "cup." Put it on the unknown pan in a stable position and put a 100 mg weight from the set in the blue box on the paper. Close the door of the balance and tare it (remembering to trim the date after 50-75 counts).

- While you are tareing and checking the tare, clean the small agate mortar and pestle with propanol and a kimwipe and put the mortar on a piece of 4x4 or 6x6 weighing paper (all on the white paper that should already be on the counter in front of the balance.) Keep the pestle in a box with a clean kimwipe in it so the pestle doesn't roll around.

- Using gloves or tongs, remove a crucible of ignited powder from the desiccator. Find the LOI sheet for that to see which sample you are working . If you prelabeled an empty bottle and a flux bottle, you can get them now. Or you can label two bottles at this point. Figure out a method that works for you and stick to it so you don't get the samples or the bottles mixed up.

- .Transfer the ignited sample from the crucible to the clean agate mortar by dumping the powder out gently. Do not tap the crucible on the mortar as the crucible may have dirt from the furnace or the rack on the outside of it. Whatever sample doesn't come out with a gentle dump can stay in the crucible. It is much better to leave some sample in the crucible than to transfer a chunk of the rack into the sample.

- Since you already know the crucible number and have determined which sample you are working with (you did this, right?), the now empty crucible and its lid can go into a plastic or SS tray in which you are collecting glassware that needs to be cleaned. The large "holder" crucible does not come in contact with the sample anyway so it can go back into the desiccator. If it gets smudged or dirty, you can clean it with propanol. The small crucibles get scrubbed out well and then acid-washed.

- Grind the sample to a fine powder with the mortar. Basalts are usually very easy to grind up. Si-rich material can be tougher lumps to crack. If it is a tough one, you can avoid little explosions that blow sample all over the place by putting a piece of weighing paper over the mortar and "grinding" the sample through that until it breaks into smaller pieces. This keeps pieces of sample from flying around all over the place. The weighing paper under the mortar is also to minimize sample lost from being accidentally discharged from the mortar. If it falls on CLEAN weighing paper, you can use the paper to transfer the sample back into the mortar. If you didn't change the paper between samples however, this doesn't work.

- Your tare should be done by now, so you can stop the weighing and remove the 100 mg weight from the paper on the unknown pan. Clean the very small spatula with the bent up tip with propanol and use it to transfer a bit of the ground ignited powder onto the weighing paper. The idea is to replace the 100 mg weight with 100 mg of sample, so the ideal final weight will be zero. Weigh it a few times putting more sample on or taking it off until you get it close, say within a few mg. At this point, you will need to close the door and wait longer to get a good weight. Having the door open lets air in and seems to reduce the true weight by about 1 or 2 mg. The final weight must always be done with the door closed.

- Keep this up until you have a reproducible weight that is at least within 0.00050 of zero (half a milligram). I actually shoot for a positive value of 0.00025 or less (a quarter of a milligram). If I get a number below zero, I tend to try to put a tiny bit more on, assuming that I am going to lose some sample because it will adhere to the bottle. Ideally, I shoot for a single-digit positive number. On a good day (on site in calm seas), I will get numbers like 0.00005 to 0.00010, or even 0.00001. I record this number on the LOI sheet, but I'm not sure why (maybe because I sometimes I get the opportunity to show the sheets to the scientists, so it is an opportunity to show off my weighing technique). I used to record the counts, but I haven't been doing that this lately because it doesn't mean squat. The number of counts is another zen thing. If I have gotten closer and closer to zero on progressive tries and then got a 0.00025, took a teeny-tiny bit off and was getting 0.00001 in just a few hundred

counts in calm seas, I'm not going to sit there for 500 counts to be sure. In rough seas, of course I would have to count longer. If I dump on some stuff and my first weight is 0.00000 in 200 counts (I have had this happen), I will weigh it several more times and wait longer to be sure it is not a fluke. It is all zen, which comes with experience. In general, rougher seas=more counts.

- Do not go too crazy counting for hundreds or thousands of counts two or three times. While you are counting, the sample is hydrating (changing weight) and the tare is drifting, changing your apparent weight. Do it as fast as you can without unnecessarily compromising accuracy. The longer it takes, the more your precision will be slipping. Do not trace one for the other, but try to strike a balance.

- Note: You may find that there are times when the balance just isn't acting right. I actually haven't had this happen much since I started using the digital filter, but it used to happen a lot. I would be weighing beads and the more I put on, the lighter the sample got. If it is in one of those moods, just give up. I think sometimes the engineers are transferring fluids around and the ship is moving in some unidirectional way that the balance program cannot compensate for. The program assumes regular up and down movement. Tides I believe can screw it up, and I had trouble in the locks in the Panama canal when the ship was going up and down. I thought it would be a good time to weigh, but it turned out not to be. If it isn't working, give up and try again later.

- When the sample weight as close to 100 mg as you can get it, open the prelabeled bottle with the preweighed flux in it (the flux should be weighed to 400 mg on shore and sent to the ship). Open the bottle with the flux in it and, ever-so-carefully, pick up the paper with the sample powder on it and transfer the powder into the bottle containing the flux. Snap the paper a few times with a flick of your index finger to make sure everything goes in. I even scrape the paper across the top of the bottle in a final desperate attempt to make sure it all goes in. Throw the paper away unless you are weighing out another bead of the same sample. (If you are weighing standards for beads, you can reuse the paper and may not have to redo the tare after every sample, so weighing standards beads can go quite fast.)

- Homogenize the sample/flux mixture by holding the vial slightly off of vertical and rotating it. You can also tap it on the bench top as you rotate it to clear any powder from the sides of the vial. Do not shake turn the vial far off of vertical or shake it. Avoid getting the sample/flux powder stuck around the cap. This would make it likely that some will stick on the cap or be lost when the cap is removed. Just roll it gently and make an annoying tapping sound.

- Note: Once the sample has been weighed out, it's not necessary to store it in a desiccator or dry it before you make the bead. The small amount of water or CO_2 adsorbed during storage will be lost in the fusion process.

Step 10. Fusing Samples with the NT-2100

The basic idea here is to add the 100 mg of sample powder to 400 mg of Lithium Metaborate flux and then melt the powdery mix into a glass bead.

Materials

- Kimwipes
- Analytical-grade propanol or acetone
- Vials of pre-weighed, labeled sample + flux (0.100g sample / 0.400 lithium metaborate flux)
- LiBr releasing agent (made with 0.150 g ultrapure LiBr powder and / 10 g of DI H_2O)
- Micro-pipettor (set at 10 μL)
- $Pt_{95}Au_5$ crucibles and lids
- Round plastic sample containers
- Sample labels

- **Start-up Procedure**

- Slowly open the water flow valve ball valve located on the port side wall forward of the bead sampler. Open it slowly until you hear a faint click from the bead sampler. I usually turn it just a wee bit past the point where I heard the click to allow for potential pressure decreases in the potable water system that might shut the bead sampler down during operation. This valve handle is usually at about a 45 degree angle if it is set properly. Do not turn it on full. This wastes water and may not be good for the bead sampler.

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- Turn the power switch on. The red ready light and the red water lamp should both come on. Note: If the water lamp is not on, turn-off the power switch and make sure you have proper water flow. Please wait a few minutes for the unit to warm up. After a while, it will beep softly a couple of times, presumably indicating that it is good to go.
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- Open the door on right side of the unit to check the settings:

- TEMP ADJ: Set to 9.0
- ROTA: This is the rotation speed for agitation. Three is the fastest and is probably fine for most samples and sea states.
- MOD: Set on 1 (the center position) all the time.
- TEMP/DC Set this switch on TEMP (up) to display the reaching temperature (rather than voltage) on the MONITOR display on the front panel.
- DCI/DCV Set this to DCV for all normal operations. The DCI setting is for troubleshooting the electronics.

Check the times on the front of the unit. Fuse 1 should be at 120 seconds, Fuse 2 at 90 seconds and AGIT at 120 seconds. Confirm that the switch is set to automatic operation. Manual can be used to remelt a sample, but generally, you should be running on automatic.

- Now the unit is now ready to operate.

Transfer the preweighed sample powder/flux mixture to a clean crucible. (Do not touch the crucibles with ungloved hands.)

Confirm that the pipettor is set to 10ul and pipette 10ul of LiBr releasing agent fluid into the crucible onto the sample/flux powder. Put the lid on the crucible, open the door of the bead sampler and put the crucible into position for fusing. Close the door again. Confirm that the base plate and the quartz ring are in place. These pieces may need to be cleaned from time to time.

Hit the start button on the timer (set for about 5 minutes usually) and the start button on the bead sampler. When the timer goes off, you have about 30 seconds before the process stops.

When fusing is complete and the unit is shutting down, the numbers will suddenly decrease on the temperature indicator. At that time, you can remove the lid of the crucible using the Pt-tipped tongs. Set the lid on the ceramic plate with the side that was facing the sample up and the lid sticking over the edge of the plate (so it is easier to pick up again).

Pick up the crucible with the tongs and hold it down where you can see the sample. Swirl it around across the center and around the edges to pick up every bit of the melt and then tip the crucible sideways so the bead will cool as one piece along the edge. I hold my feet apart while I do this so the crucible and its molten contents are not above my feet. I have never spilled any lava-like molten sample on my feet yet, but my guess is that it would be disagreeable. I always try to wear my boots for this rather than my flip flops and that is probably a good practice, not that it would help much.

Set the crucible on the cooling stand. The fan is turned on by a little optical eye that "sees" when the crucible is set in there. It will run for about three minutes. You can start it running again if you want by picking up the crucible and setting it down again.

The sample will be cool enough to dump out in about four minutes. Have a clean weighing paper on one of the white tiles and try to tip the bead out onto the paper. If it doesn't come out, rap the crucible on the paper, being careful to hit it straight. Do not tap the edges because the crucibles bend very easily.

When you have the bead on the paper, use the paper to tip it into the bottle that the flux/sample mixture was in. Do not mix these bottles up at this point. Make sure the right bead goes into the correct bottle.

The bead is now ready to deliver to the chemists. You can put the lid back on the crucible and set it aside to be acid-washed.

The crucibles are cleaned by soaking them in the 50% HCl bath for a while. Two to four hours. Try not to just leave them in there overnight like we do the quartz crucibles. Theoretically gold reacts with HCl, so we may be losing a bit of crucible every time we clean them. DO NOT try to clean them by wiping them out with Kimwipes or anything else. They have gotten badly scratched by people on the other crew doing this. The crucibles are soft, fragile and expensive. Be careful with them.

- **Shutdown**

- Turn off the power (SOURCE) switch.

- Turn off the cooling water at the valve. The handle should be at 90˚ to the hose when the valve is completely closed.

- **Precautions and Safety**

- Use the correct crucible.
- Do not heat without a crucible in place.
- Always use seconds as units on the timers. The internal, preset program will only work if the timers are all set in seconds.
- When overcurrent is detected, the automatic power cut-off will engage, and an alarm will sound. In this case, the <READY> light will go out. After this, it is necessary to reset the breaker inside the right side panel of the unit.
- When the water pressure drops and/or the water temperature is not in the correct range while operating the equipment, the automatic power cut-off will engage and an alarm will sound. In this case, the <READY> and <WATER> lights will both go out. Correct the water temperature/flow condition and reset the breaker inside the unit.

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