# ICP Preparation

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# Introduction

Inductively Coupled Plasma Atomic Emission Spectroscopy, ICP-AES, is a method to perform elemental analysis on a sample in solution (ODP Technical Note 29). This manual covers hard rock sample preparation for ICP-AES analysis. Hard rock samples are prepared via the 'flux fusion' approach. This technique ensures complete dissolution of sample allowing a full elemental analysis. Solutions are stable which allows further analysis, and involves no HF making it a safe and ideal method (ODP Technical Note 29).
Rock samples are crushed to a fine, talc-like powder using multiple cleaning, crushing and grinding procedures. After grinding, loss on ignition (LOI) is determined. Ignited material is fused with flux powder forming a glass sample bead. Fused beads are then dissolved in 10% $HNO_3$. This is further diluted and the resulting solution is processed by the ICP-AES machine.
The complete process (from sample table to ICP-AES machine) takes 3-4 days. Day 1 involves: polishing on the Diamond Wheel, cleaning, and drying samples overnight. Day 2: Crushing in the X-Press, grinding in the Shatterbox, a pre-ignition (for LOI) weight, and placing samples in the furnace overnight. Day 3-4: Taking a post-ignition (for LOI) weight, and fusing the sample bead. The beads are handed off to the chemistry technicians to continue ICP analysis.

# Apparatus, Reagents, & Materials

## Laboratory Apparatus

### General Laboratory Equipment

- Compensated Dual Analytical Balance System
- Drying ovens at 110°C and 60°C

### Rock Grinding

- Splitting room saw
- Buehler grinder/polisher with 70 µm grit diamond grinding wheel
- Sonicator (with small water bath)
- X-Press crusher
- Spex Shatterbox with tungsten carbide (WC) grinding vessel
- Spex Mixer Mill

### LOI/Bead-Making

- Fisher Ashing Furnace
- Sample Bead Maker

### Dissolution/Dilution

- Wrist-action shaker
- Acid baths

## Reagents

- 0.0172 mM LiBr wetting agent (0.15 mg ultrapure LiBr in 10 mL DI water)
- 10% nitric acid (143 mL concentrated nitric acid/L of solution). **Caution!** always add acid to water.
- Isopropyl alcohol, laboratory grade
- Methanol, laboratory grade
- Acetone, laboratory grade
- DI water (18.2 M¿ laboratory water)

## Materials

### Grinding Samples

- Beakers
- Glass cleaner
- Tweezers
- Teflon spatula
- X-Press aluminum die
- Core liner pieces and clear endcaps
- Delrin plugs
- Acid-washed 1-oz glass bottles
- Weighing paper, 6 x 6
- Kimwipes

### LOI/Sample Bead

- Quartz crucibles
- Tongs
- Vials containing 400 mg lithium metaborate flux (preweighed on shore)
- Milligram calibration weighing set
- Weighing paper, 2 x 2
- Acid-washed vials for excess ignited powder
- Agate mortar and pestle
- Pt-Ag crucibles

# Preparing Rock Samples

Rock samples are prepared for ICP analysis using the following procedures on each sample:

1. Cut to size (see ***Cutting Samples to Size***).
2. Polish (see ***Polishing Samples on Diamond Wheel***).
3. Clean (see ***Cleaning Samples***).
4. Dry (see ***Drying Samples***).
5. Crush (see ***Crushing Samples in the X-Press***).
6. Grind (see ***Grinding Samples in the Shatterbox***).

## Cutting Samples to Size

To cut samples for the X-Press, use the splitting room saw following these guidelines:

- Cut samples to ~1–2 cm in length and width. Avoid cutting irregular pieces; ideal samples are cubes. Cut the first samples small to get a feel for rock hardness.
- Avoid veins, infilled vugs, etc.
- Remove as much contaminated material as possible.
- Contact the petrologist(s) if cutting reveals unexpected features.

### Notes about altered samples:

- It may be desirable to hand-pick and separate vesicles and/or veins from whole-rock basalt.
- Speak to the petrologist about this method if alteration is visible.

# Polishing Samples on Diamond Wheel

To remove contamination (drill bit, saw blade, or other unwanted material) and clean the samples, grind each surface on a high-speed, diamond disc.

## Apparatus and Materials

- Buehler Grinder/Polisher
- Sample Beaker

Each sample will correspond to one beaker; collect as many as needed. Beakers need to be cleaned (DI water and isopropyl alcohol) and labeled ( ex. 1, A, or sample label).
Next start the grinding process using the Buehler grinder located in the Xray prep area of the thing section lab (*Figure 1*).
*Note: Make sure that the correct diamond disc is attached to the wheel.* The diamond disc is attached to a magnetic disc which is then placed on the wheel plate. Attach the diamond disc using either the adhesive on the back or an aluminum ring.

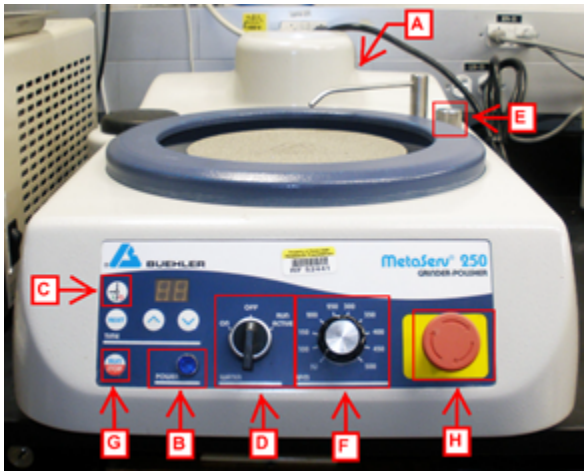


*Figure 1: Buehler Grinder Polisher. A. On/Off switch B. Power Indicator light C. Timer On/Off button D. Water On/Off switch E. Water flow control knob F. Disc speed control. G. Stop/Start. H. Emergency Stop*

To start the polisher flip the 'On' switch in the back. The power indicator light (*Figure 1A*) should illuminate. Press the timer button (*Figure 1B*) to get continuous disc rotation. Turn the water on by flipping the 'Water' switch to the 'On' position (Figure 1C). The water flow can be adjusted by turning the knob shown in *Figure 1D*.
The rotation speed is controlled by the dial shown in *Figure 1E*. The range is 0 rpm to 500 rpm. 150 rpm is a good starting position. Adjust the speed if needed: faster for hard rocks and slower for softer rocks.
With the water on and the RPM adjusted press the 'Run' button (*Figure 1F*). Move the sample back and forth across the disc to prevent making a groove. If there is an emergency press the 'Emergency Stop' button (*Figure 1H*) to stop rotation and cut off the water. To enable the wheel again twist the knob until it pops back out.
Polish the rocks until they're completely smooth and round on all edges. There should no pits or jagged corners. Put the rock into a labeled beaker and polish the next sample. Do this for all samples and then move on to 'Cleaning Samples'.


*Figure 2. Labeled beaker with polished rock inside*

# Cleaning Samples

To remove contamination (oil, skin, and residue from the diamond wheel) wash the polished samples in 70% isopropyl alcohol and DI water. From this point onward, wear gloves when handling samples to avoid reintroduction of contaminants.

## Apparatus and Materials

- Sonicator
- Beakers
- 70% Isopropyl Alcohol
- Tray(s)

Pour either DI water or isopropyl alcohol (70%) into the beaker to cover the sample. Check with the scientists for their preference in solution. There should be enough liquid to keep the sample from floating in the sonic bath (*Figure 3*).


*Figure 3. Sonic Bath*

Fill the sonic bath with a little bit of water and place beakers inside. Sonicate for 15 minutes. You should notice the water becoming cloudy from residue being shaken off the samples. Then follow the wash sequence below:

1. Decant as much of the liquid as possible
2. Sonicate again with DI water for 10 min.
3. Decant liquid into the sink

Repeat the rinse cycle until the water is clear. If the samples are soft and/or clay rich, they won't reach the "clear water" state. Continuing to sonicate will only dissolve the sample. If after 3–4 washings, the water still isn't clear, go to the next step. After the final rinse, decant as much water from the beaker as possible.

## Drying Samples

This step involves an overnight portion and should be done towards the end of the shift.

### Apparatus and Materials

- ICP Prep Oven
- Samples

Place the beakers into the ICP Oven at 110°C for 12 hours (*Figure 4*). Turn on the power button and adjust the knob to 110°C, which is marked on the oven. A thermostat is located inside to double check temperature.


*Figure 4. The ICP Prep Oven located in the X-Ray lab. A. 'On/Off' Switch B. Temperature Setting C. Heating Indicator*

After 12 hours remove the beakers from the oven and place them inside the desiccator (*Figure 5*) while you prepare the X-press station.
*Note: The ICP oven should be kept clean at all times, as samples are left open and are susceptible to contamination. The ICP oven should only be used for ICP samples.*

*Figure 5. Desiccators located in the X-ray lab*

## Crushing Samples in the X-Press

The X-Press is a motorized hydraulic press that crushes samples into smaller pieces.
First clean the X-press with simple green and isopropyl alcohol. Clean the work area and materials with isopropyl alcohol for each sample.
Place a large KimWipe on your working surfaces for your clean materials. Next collect the following supplies that make up the 'crushing unit' of the X-press (*Figure 6*). Materials are located in the drawer labeled 'X-PRESS SUPPLIES' in the X-Ray Prep Area.

- Weigh Paper 6" x 6"
- Core liner
- Two derlin discs
- Stainless steel base
- *Figure 6*: Materials needed for assembly of 'crushing unit'. A. Weigh Paper 6"x6". B. Core Liner C. Two Derlin Discs D. Stainless Steel Base E. Aluminum DieAluminum die.

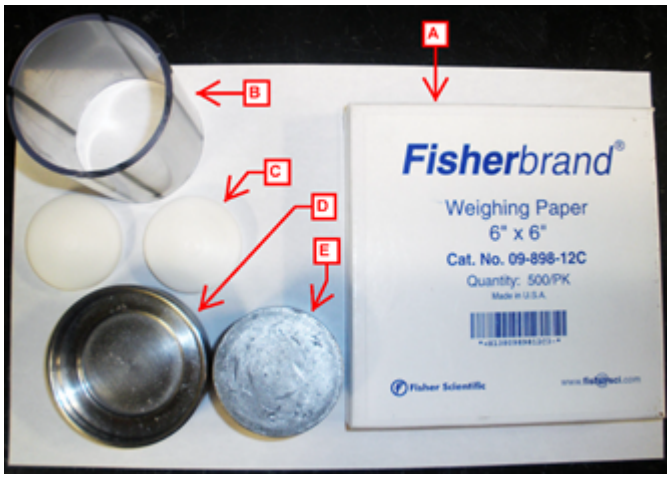


*Figure 6: Materials needed for assembly of 'crushing unit'. A. Weigh Paper 6"x6". B. Core Liner C. Two Derlin Discs D. Stainless Steel Base E. Aluminum Die*

Put on gloves and 'wash' them with isopropyl alcohol. Clean the crushing supplies with isopropyl alcohol and set them down on the clean surface.
Collect sample beakers from the dessicator. Put a piece of parafilm over each beaker and bring them over to the X-press.
Now that the X-press area is clean and the samples are in the lab, assemble the crushing unit as follows:

- Grab the stainless steel dish. This is the base for the crushing unit (*Figure 7*).

*Figure 7. Stainless stell dish*

- Place a piece of Weigh Paper on the Base (*Figure 8*).

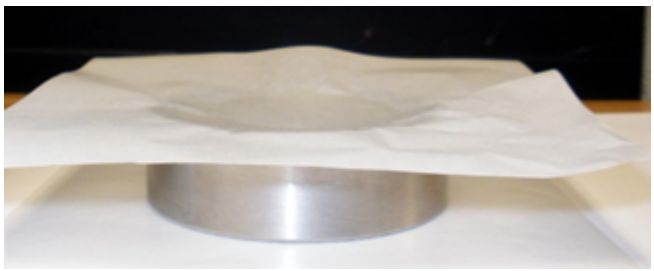

*Figure 8. Dish with Weigh paper*

- Put one Derlin disc on top of the weigh paper (*Figure 9*).

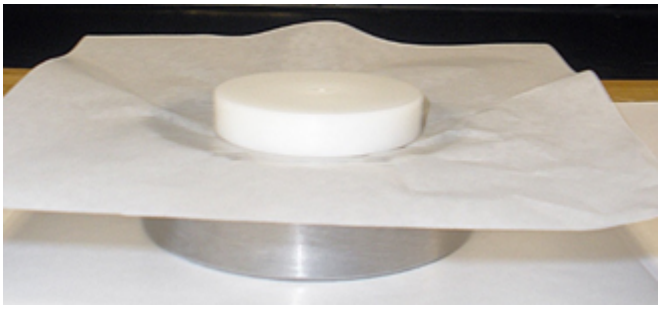

*Figure 9. Derlin Disk Added*

- Place the sample on top of the Derlin Disc (*Figure 10*). These discs can fracture leaving Teflon flakes in the sample so arrange the sample such that the two flattest surfaces are the top and bottom.

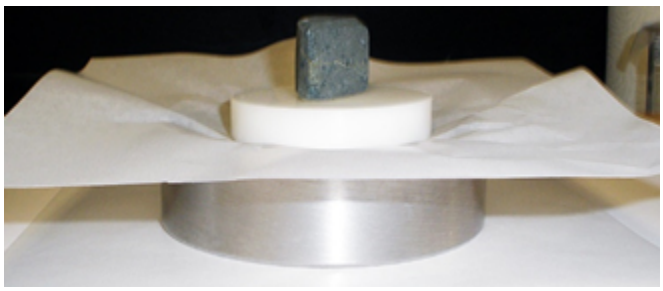

*Figure 10. Sample Added*

- Now place the second derlin disc on top of the sample (*Figure 11*). Again make sure the disc rests flat against sample.

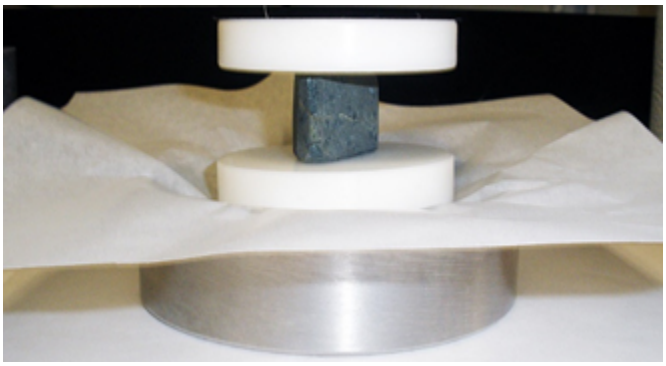

*Figure 11. Second Derlin Disk added*

- Put the aluminum die on top of the derlin disk, holding it until you slip the core liner over the unit (*Figure 12*).

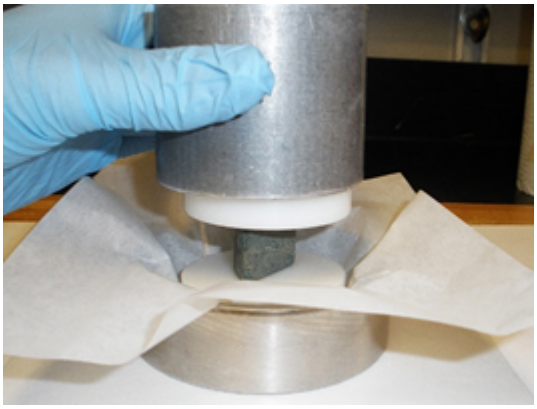

*Figure 12. Aluminum Die added*

- Now slip the piece of core liner over all the pieces and resting inside the stainless steel base (*Figure 13*). This contains the sample pieces inside the unit.

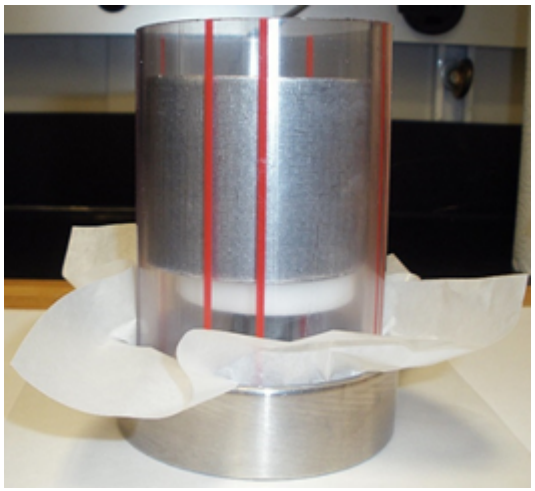

*Figure 13. Core Liner added*

- The crushing unit is now assembled and we can start crushing samples (*Figure 14*).

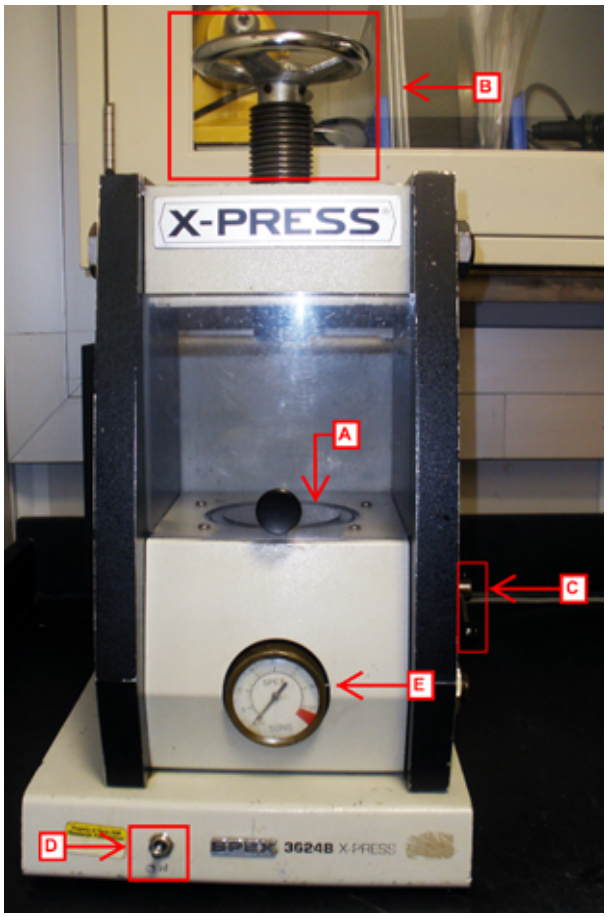


*Figure 14: Overview of the X-Press. A. Metal platform sample rests on B. Jacksrew C. Pressure Relief Handle. D. 'On' toggle E. Pressure Gauge.*

Place the crushing unit inside the X-Press in the middle of the metal platform (*Figure 14 A*). Put in the sliding polycarbonate door. Tighten the jackscrew (*Figure 14 B*) until it rests firmly against the aluminum die. Tighten the 'pressure relief handle' with a clockwise turn *(Figure 14 C*).

*Note: The polycarbonate door sits on two interlock switches that enable operation. If the door is not fully closed or pressing down on these switches the machine will not work.*
Crush the sample by continuously holding down the toggle switch (*Figure 14 D*). The motor and pump can be heard and the pressure will rise (*Figure 14 E*). Once the desired pressure is reached the toggle can be released and the sample will sit under that pressure. For most samples ~5 tons of pressure is enough force to crack it. If you find the need to go past 10 tons, try rotating the sample onto another side and apply pressure again.

*Note: Always wear safety glasses. Do not stand directly in front of the X-Press while it is operating.*

After the sample has cracked remove the crushing unit. To remove the unit, loosen the 'pressure relief handle' and press down on the toggle switch. The pressure gauge should read zero and the metal platform will lower down. When the platform is level with the surface let go of the toggle of start unscrewing the jackscrew. Then open the door and remove the unit. The pieces can be poured into a labeled bottle that will eventually hold the finely ground powder. From here the pieces will then be put into the Shaterbox vessels.
If pieces are still too large then repeat the same setup and crush it again. Look out for and remove any pieces of the Derlin Discs that may have chipped off and gotten into the sample.

## Grinding Samples in the Shatterbox

The shatterbox takes the crushed pieces from the X-Press and grinds them into a very fine powder. The Spex shatterbox is capable of grinding three standard size samples or one large sample. Our grinding vessels used are tungsten carbide.

### Apparatus and Materials

- Shatterbox
- Tungsten Carbide Vessels: Vessel, Puck, and Lid
- Samples
- 1oz Sample Vials
- Sample Labels

Turn on the Shatterbox by flipping the 'On' switch located on the back panel (Figure 15A). The control panel is located on the front of the lid next to the handle (*Figure 15C*).


*Figure 15. Shatterbox. A. Power switch. B. Cover. C. Control panel*

There are two sizes of grinding vessels: small and large. Each size has different components and requires a different setup inside the Shatterbox. The small vessel holds between 5-20 mLs of material and has three components: a container, puck, and lid (*Figure 16*).

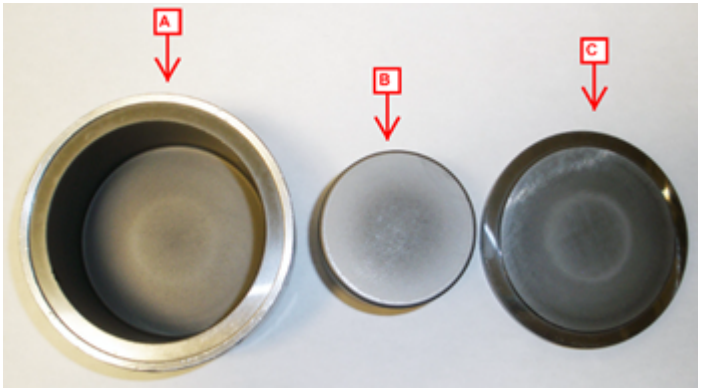


*Figure 16. Small vessel components. A. Container B. Puck. C. LidFigure 16. Shatterbox. A. Power switch. B. Cover. C. Control panel*

The large grinding vessel holds between 20 – 60mLs of material and has five components: a container, puck, inner ring, O-Ring, and lid (*Figure 17*).


*Figure 17. Large Vessel components. A. Container B. Inner Ring C. Puck D. O-Ring E. Lid*

The small vessels have a small indent in the bottom of the container and they will sit in the shatterbox resting on either a three pinned plate (*Figure 18*) or a one pinned plate (*Figure 19*).

*Figure 18. Three pinned rack plate to hold three small vessels in Shatterbox*

*Figure 19. Single pinned rack plate to hold one small vessel in Shatterbox*

The three pinned plate will hold three vessels while the one pinned plate will only hold one. If two samples need to be crushed select the three pinned plate. The large vessel will sit directly in shatterbox without an additional plate below it.

## Loading the Shatterbox

Transfer the sample pieces into the grinding vessel. Pour sample pieces between the puck and the wall of the vessel (*Figure 20*). There can't be any material on top of the puck or inside the sealing ring; otherwise the vessel will not seal properly and the sample can spill inside the Shatterbox. If any pieces are on top of the puck or ring, use gloves, tongs, or a KimWipe to move the sample into the vessel. Put on the lid and start assembling the shatterbox.

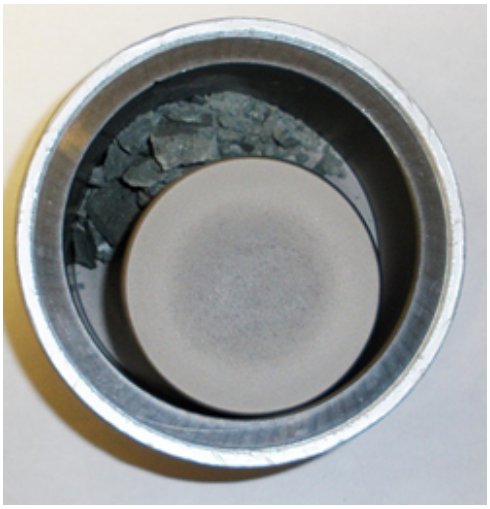

*Figure 20. Small vessel filled with sample pieces. No sample material is on the top the puck or in the lid ring.*

Open the lid, pull out the lever arm (*Figure 21A*), and pull up the clamp arm (*Figure 21B*). This will reveal full access to the inner capsule (*Figure 21C*).

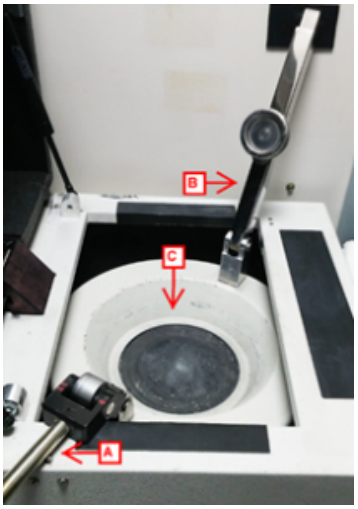


*Figure 21. The inside of the Shatterbox. A. The lever arm B. The clamp arm C. The inner capsule*

Depending on vessel size, you will either put in the pinned plate (small vessels) or the large vessel directly. The shatterbox setup will also vary depending on sample number. If you are crushing one sample use the one pinned plate, whereas for two or three samples use the three pinned plate (*Figure 22*). For crushing two samples, two vessels will be full, whereas the third will be empty without a puck. It is important to maintain balance within the machine to prevent damage.

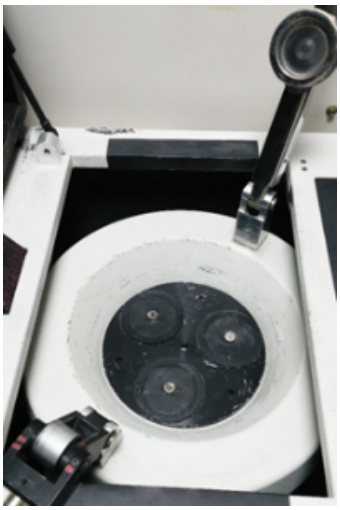

*Figure 22. Inside the Shatterbox with the bottom three pinned rack plate resting inside the inner capsule.*

Now load vessels onto the plate (*Figure 23*). The divet in the bottom of the vessels will settle onto the pins and fit firmly in place.

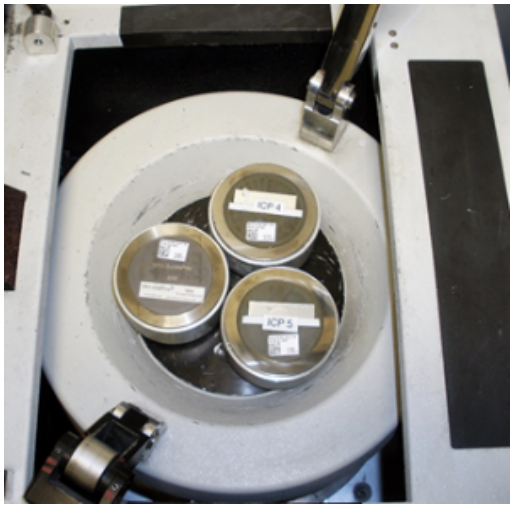

*Figure 23. Three samples loaded into the Shatterbox.*

Put the top rack plate over the vessels. Bring down the clamp arm (*Figure 24A*). The guide on the clamp arm will settle into the boss (*Figure 24B*) when centered properly.

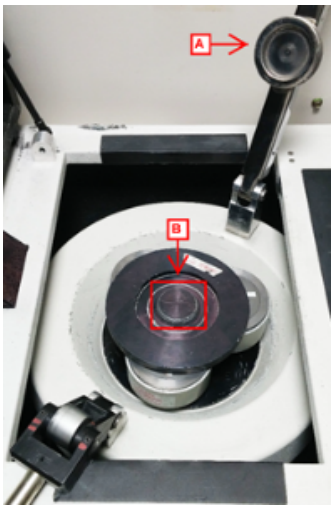


*Figure 24. The top rack plate sitting on top of the three samples. A. Clamp arm. B. the "boss" of the rack plate, where the clamp arm will attach.*

Bring the lever arm down and push it into the end of the clamp arm (*Figure 25B*). Then push the lever arm down over the clamp arm (*Figure 25A*).

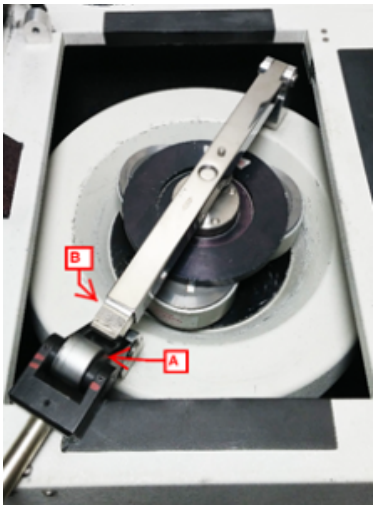


*Figure 25. A. The lever arm inserted into the end of the clamp arm. B. The clamp arm pushed over the lever arm.*

The resistance in the lever arm is very important and must be adjusted before use. There should be moderate resistance in the arm while pushing it down. If the resistance is too low the containers can shake free; whereas, if it's too strong the clamp can break. Ideal tightness is just past the point where the vessels can be rotated while the clamp is down. Adjust the resistance by raising the clamp arm and pushing on the 'locking pin.' Hold the locking pin and turn the guide (*Figure 26A*). Rotating the guide clockwise decreases resistance; whereas counterclockwise increases resistance.

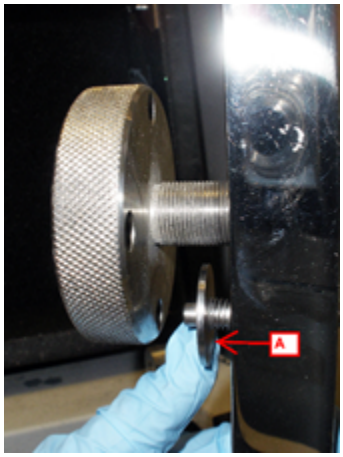


*Figure 26. The lever arm and the guide. A. Retractable locking pin being pushed to allow adjustment of the 'guide' length.*

Now close the lid and turn the emergency stop switch to 'On'. This does not start the Shatterbox but does enable operation. If an emergency shutdown is needed, flip this switch to 'Off' and all shaking will stop even though the timer will continue to count down.
Set the grinding time. The LCD screen displays the current operating time (*Figure 27A*). Adjust the time by pressing on the 'Minute' (*Figure 27B*) and 'Second' (*Figure 27C*) buttons. The timer maximum is 9:59.

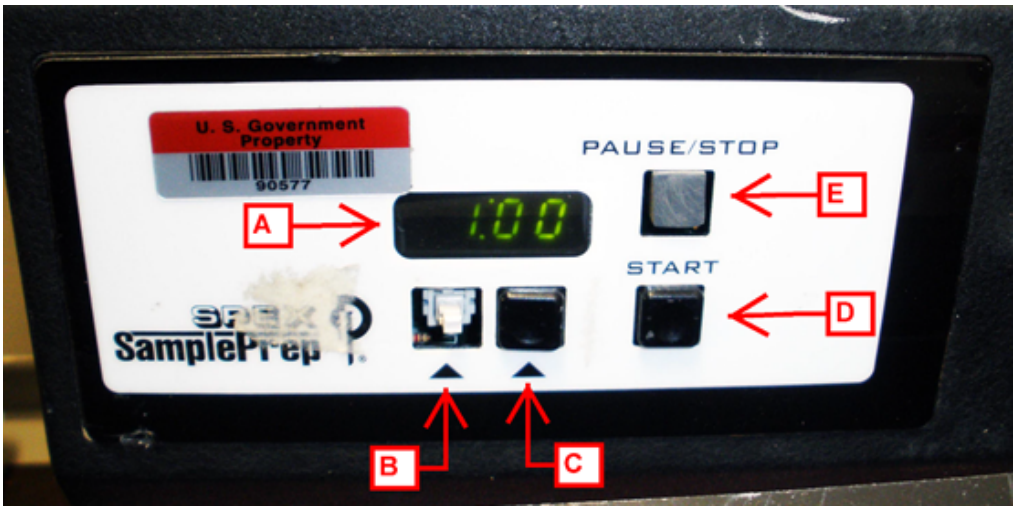


*Figure 27. A. Current operating time. B. Minute button. C. Second button. D. Start button. E. Pause/Stop button.*

When the time is set press the 'Start' button (*Figure 27D*). To temporarily pause the operation press the 'Pause/Stop' button once (*Figure 27E*).To stop the machine press 'Pause/Stop' twice.

**Normal Sounds**: The shatterbox is extremely loud. The foam and strap surrounding the shatterbox helps keep it in place and minimize some of the noise.
**Abnormal Sounds**. If there are any metal on metal sounds shut off the shatterbox immediately. Something inside the shatterbox has probably come loose and will damage the inside of the container.
When the shatterbox cycle is done open the lid and remove the vessels, placing them on the counter. Open the grinding vessel and with clean tweezers take a bit of the powder and feel it against the inside of your wrist. The sample should feel like baby powder, if it does not, repeat the shatterbox cycle.

### Transfer powder into Vial

Disassemble the vessel carefully wearing 'Powderless Nitrile' gloves. Clean off any powder on the lid or puck with clean gloves or a kim wipe. Carefully remove the puck from the vessel. Pour the sample onto a clean weighing paper. If any powder remains, use a clean plastic spatula, brush, or your finger to dislodge it.
*Note: Never use metal to dislodge sample material, as any grooves or scratches in the vessels will increase the risk of contamination.*

## Cleaning the Grinding Vessels

Vessels must be cleaned in between samples and after all samples have been run for the day. Vessels should never be put away wet. This alters and tarnishes the vessel.
*In Between Sample Runs*

1. Wearing nitrile gloves, wash the individual pieces of the grinding vessels with DI water and a small piece of a scouring pad (no soap).
2. After each washed piece piece immediately spray it with isopropyl alcohol and wipe it down with a Kim Wipe. Do not use the ships compressed air line to dry pieces as the air is too dirty.
3. Lay the pieces on, and cover vessels with Kim Wipes.

*After the last run for the day*

1. Take a scoop of quartz sand and put it in your vessel and run it as you would a sample for several minutes.
*2.* Remove the vessel and empty out the sand. Scrub the pieces with DI water and a scouring pad. Then spray with isopropyl alcohol and wipe down with Kim Wipe.
If your vessel is particularly dirty run a combination of quartz sand, a little hot water and detergent (Borax). This can be run for several minutes. A thick paste will form and you clean it with DI water and isopropyl as in the other cases.

# Determining LOI

Loss on Igntion, or 'LOI', compares a mass measurement taken before and after a sample is subjected to extreme heat. Petrologists use LOI as an indication of degree of alteration. Low LOI values suggest relatively fresh, unaltered basalt; whereas high LOI numbers suggest alteration (clay, alteration minerals, etc.).
LOI is determined by weighing a small amount of the sample (~5 g) before and after ignition. Samples typically lose weight as water is driven off, though an iron-rich, water-poor sample may gain weight.

LOI is not required for all types of ICP Preparation. Check with the science party to determine if LOI is a desired measurement. If the science party does not want an LOI measurement move on to the section Making the Sample Bead

## Loss on Ignition

Determining a sample LOI comprises three procedures:

- Pre-ignition weighing
- Igniting samples
- Post-ignition weighing

### Advice on LOI Procedures (from Exp. 366 Methods)

Shipboard sample preparation and LOI determination procedures described in Murray (2000) and updated in recent *IODP Proceedings* volumes (e.g., Reagan et al. [2015] for Expedition 352) are appropriate for a range of sediment and rock compositions, but some care must be taken with unusual sample matrixes. As an example, attempting sample ignitions on carbonate-rich materials can lead to spurious results and issues with contamination if quartz crucibles are used for sample ignitions because carbonates will react with quartz upon heating to both devitrify and decompose the crucible. Alumina ceramic crucibles may be better for carbonates but risk contamination for Al and potentially other elements due to spallation over time. Maximum ignition temperatures of 1000°C and higher are appropriate for ultramafic and some mafic igneous materials but may result in sample sintering and/or sticking to some Si- or Ca-rich materials. Ignition temperatures of <850°C are inadequate to decompose carbonate minerals in sediment samples, even if samples are held at temperature for several hours. In general, igniting samples to at least 900°C as a maximum temperature is advisable to decompose all volatile-bearing phases and obtain reliable measures of LOI.

# Pre-ignition Weighing

## Apparatus and Materials

- Mettler Toledo Dual Balance
- Acid Washed Quartz Crucibles
- 4x4 Weigh Paper
- Reference Weights
- Thermolyne Muffle Furnace

Clean the balance area including the balance plates inside the balance. Any dust or particles on the plate could throw off the weight measurements. Before beginning make sure there are enough acid washed quartz crucibles for your samples. The crucibles are located in the X-Ray lab in a plastic container labeled 'Acid Washed Crucibles'. Wear gloves while handling the crucibles.

Place a large sheet of paper in front of the balances and place supplies here. For each sample you need weigh paper (*Figure 33A*), a scoopula (*Figure 33C*), and a quartz crucible set (*Figure 33B*). Clean the scoopula with isopropyl alcohol in between each sample as it has direct contact with the sample powder.

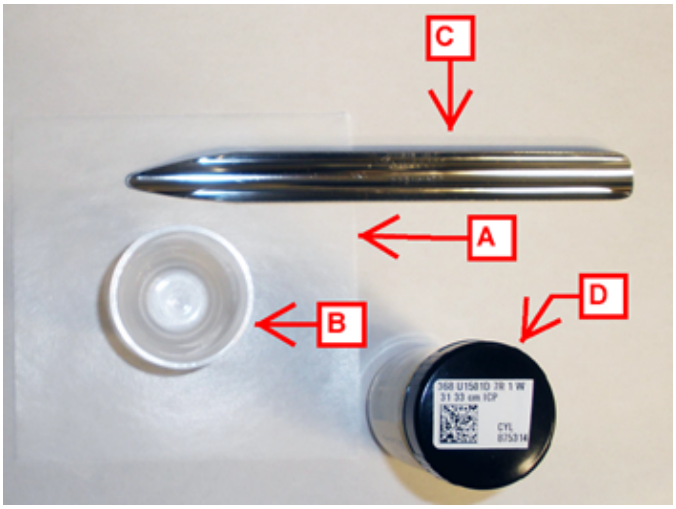


*Figure 33. Materials needed for weighing LOI. A. Clean paper or kim wipe. B. Crucible set. C. Scoopula. D. Samples*

### Setting up the Mettler Toledo Balances

Samples are weighed on the Mettler-Toledo Dual Balance. The Dual balance uses two weighing stations to compensate for shipboard motion: one a 'known' reference weight (*Figure 34A*) and the other an 'unknown' sample weight (*Figure 34B*). The balance takes a series of measurements and uses the average value as the final weight (for a more in-depth guide refer to the Balance User Guide on Cumulus). Each balance has a control panel plate, which constantly record weight. These plates communicate with the "Mettler Balances" program.

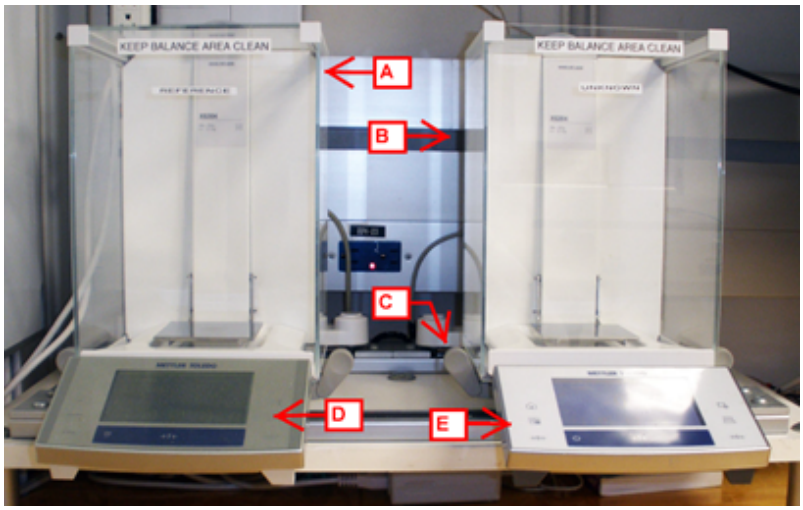


*Figure 34. Mettler Balance Station located in the XRay lab. A. Reference balance. B. Unknown balance. C. Sliding door. D. Reference power module. E. Unknown power module*

Open the Mettler Balances program (*Figure 35*). There are multiple panes and parameters that are set before we start measuring.


*Figure 35. Mettler Balance program window. A. Graphical measurement window. B. Final weight panel. C. Statistics panel. D. Weigh. E. Tare. F. Halt. G. Options panel. H. History panel.*

**Graphical Measurement Window**: Shows a line graph of the live-time measurement weight and the running average weight.
**Final Weight Panel**: Displays the Final Weight after all measurement counts have been made
**Statistics Panel**: Shows the average weight adjusting with time.
*Counter Weight*: Enter in the reference weight *Counts*: The elapsed amount of measurements
*Tare*: Shows and applies the tare or 'zero' value
*Sample ID:* Name the sample being measured
**Commands Panel:** Executable commands
*Weigh*: Starts measurement
*Tare*: Determines the 'zero' weight. This value is applied to the final weight.
*Halt*: Stops a measurement before it has gone through all counts
**History Panel:** Shows statistics on all measurements taken. This file can be exported into an excel file by using the 'Export' button. Note: The 'Export CSV' file does not work.
**Options Panel:** Editable measurement parameters. We measure using the 'Counts' feature. 'Counts' is active when the dot is blue. Change the number of counts or measurements the balance takes here.
At the beginning of a series of measurements, tare the balances. To do this first make sure that the 'Counter Weight' field is set to '0' and then set the 'Count' value. The 'Count' is dependent of the sea state: 600 for calm waters and 1000 counts for rough waters. If seas are too rough than wait until the weather settles before continuing to measure.
**A rule of thumb is that the measurement of a known reference mass shouldn't have a larger deviation than the accuracy desired. For example, our accuracy is +/- 0.05 grams; weigh a reference mass in the unknown balance that is close to the masses you are measuring (e.g., 25 grams) and perform the measurement with the appropriate counterbalance mass in the reference balance pan. You should get a final mass of 24.95—25.05 grams.**
Once parameters are set, select the 'Tare' button. When the tare is complete the 'Final Weight' Section turns orange and the 'History' Section updates (*Figure 36*).

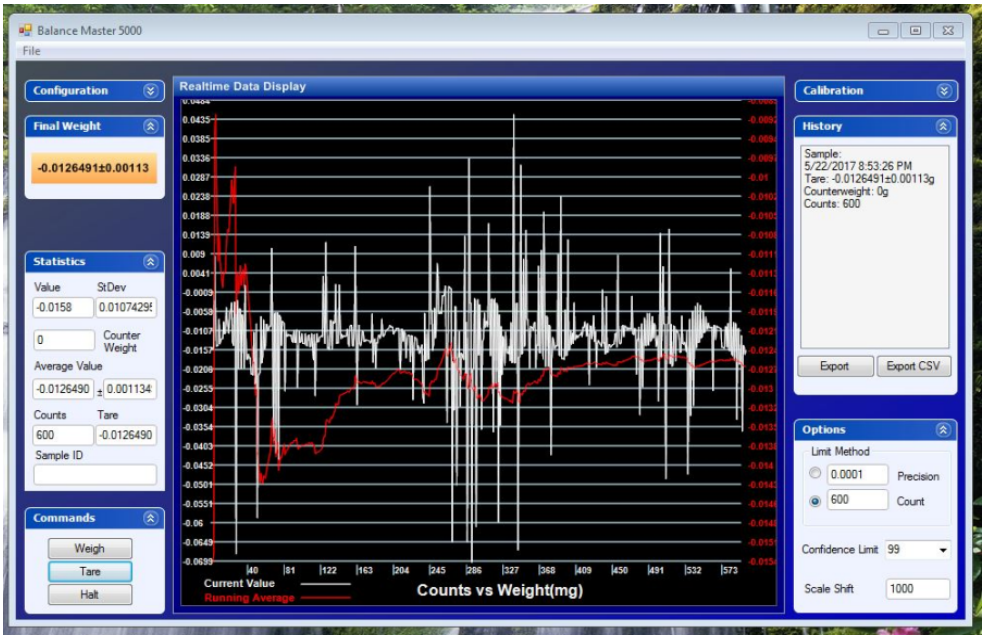


*Figure 36. Mettler Balance program window showing a tare calculation.*

Put in a reference weight into the "Reference' balance. With the tweezers, select the 20g weight and place it in the center of the 'Reference' balance (*Figure 37*). To have a more accurate measurement, the reference weight should be close to the expected 'Unknown' sample weight (roughly ~20g).

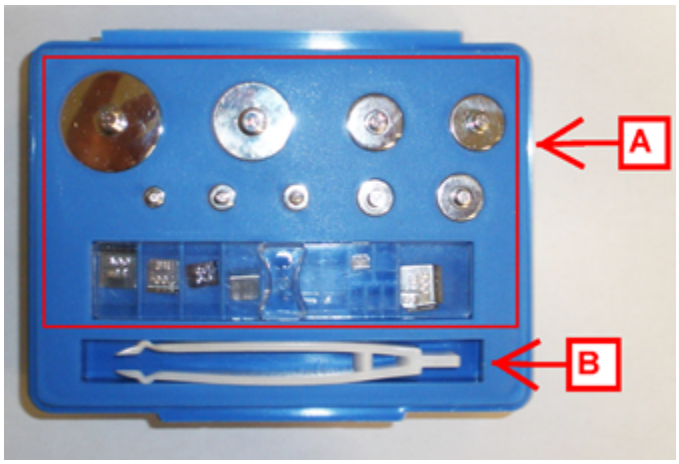


*Figure 37. Reference weights. A. Weights. B. Tweezers.*

## Weighing Crucibles

The quartz crucibles have three sections: an outer (or large) crucible, an inner (or small) crucible, and a lid (*Figure 38*).

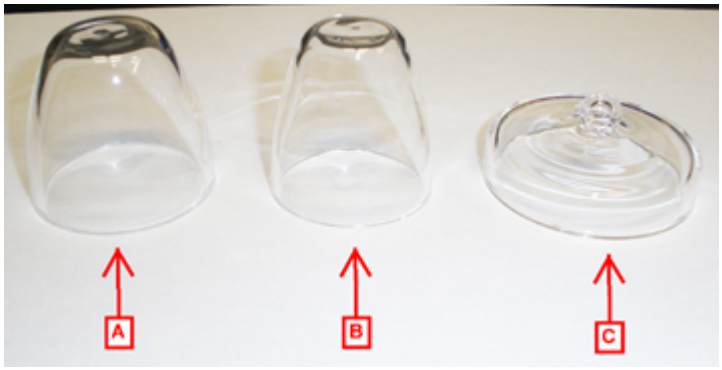


*Figure 38. Crucible components. A. Outer (large) crucible. B. Inner (small) crucible. C. Lid.*

The inner crucible holds the sample material and is the only piece that is weighed. They are assembled as seen below with the inner crucible inside of the outer crucible and the lid sitting over the entire unit (*Figure 39*). Crucible sets (large, small and lid) are engraved and lettered and should be kept as a set. For example, Crucible lid 'A' should always be run with large and small crucible 'A'. If a crucible is unlabeled use a diamond-tipped pen to etch in an unused lid.

*Figure 39. Complete and assembled crucible unit.*

Weight measurements are recorded in an excel spreadsheet which will be uploaded to LIMS at the end of an expedition (*Figure 40*). Open the excel spreadsheet titled 'LOI Template' found in Local Disk > DATA and save the spreadsheet in Local Disk > DATA > IN as 'EXP # LOI'.

| | A | B | C | D | E | F | G | H | I | J | K |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | X368 | | | | | | | | | | |
| 2 | SAMPLE NAME | | | CRUCIBLE ID | CRUCIBLE WT | CRU + FRESH SAMPLE WT | CRUCIBLE + IGN SAMPLE WT | SAMPLE WEIGHT | POST IGNITION LOSS | %LOI | COMMENTS |
| 3 | Hard Rock LOI at 1025 for 4 hours | | | | | | | | | | |
| 4 | SITE | TEXT ID | CORE/SECT/INTERVAL | | | | | | | | |
| 5 | | | | | | | | | 0 | #DIV/0! | |

*Figure 40. LOI spreadsheet.*

The spreadsheet has multiple columns to fill in.'SITE', TEXT ID', 'CORE/SECT/INTERVAL', 'CRUCIBLE ID', 'CRUCIBLE WT', 'CRU+FRESH SAMPLE WT', and 'CRU+IGN SAMPLE WEIGHT'. 'SAMPLE WEIGHT', POST IGNITION LOSS', and '%LOI' are calculated values based on the weights entered in columns E – G.
The first measurement taken will be the initial weight of an empty crucible. To complete this measurement, open the side door and place an empty inner crucible in the center of the '*Unknown'* balance (*Figure 41*). Record the number or letter etched onto the crucible in the excel spreadsheet under 'Crucible ID.'

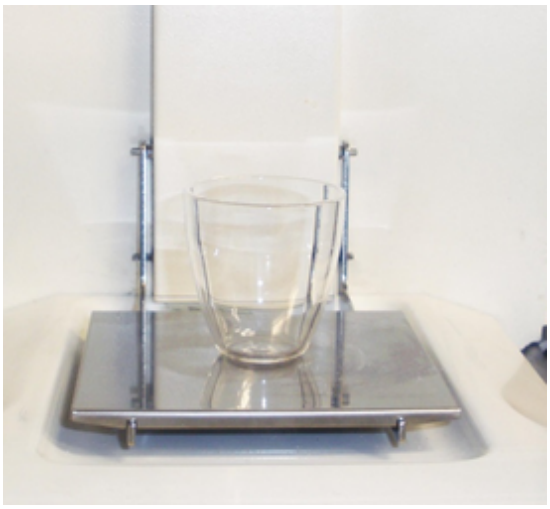

*Figure 41. Weighing an empty inner crucible.*

Close the door and click 'Weigh**'.** Wait for the counts to finish and then record the 'Final Weight' in the spreadsheet under 'Crucible Wt'.

## Weighing Sample

Weigh out 5 grams of sample powder into the quartz crucible within +/- 0.05g (*Figure 42*). The total weight should be the crucible weight + 5 grams within +/- 0.05 grams. For example, a crucible weighs 14.32g, thus the total weight plus the sample will be between 19.27 – 19.37g.

*Note: If there is only a small amount of material, you can use less but the %LOI error will be larger.*

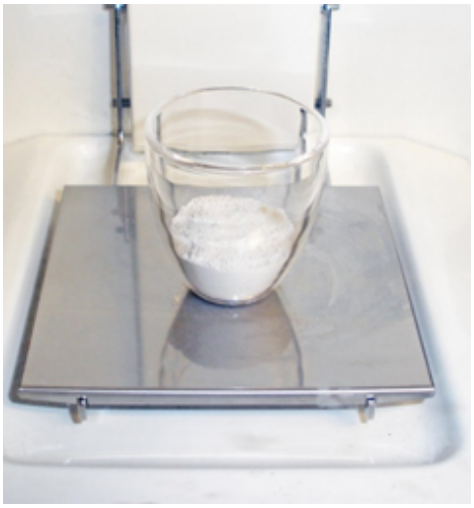

*Figure 42. Crucible with approximately 5g of sample. Pre-ignition measurement*

When the sample is close to this range click 'Weigh.' Press 'Halt' to stop the measurement and either add or remove sample if needed, and then click on 'Weigh' again to take a new measurement.
When a sample's final weight is within the allowable range, record the 'final weight' value into the spreadsheet under 'CRU + FRESH SAMPLE WT'. Carefully remove your sample from the balance. Place your crucible into the larger quartz holder and cover with a lid (*Figure 43*). Repeat this process for all samples. After all samples have been weighed and recorded, take samples from the desiccator and bring over to the muffle furnace in the Chemistry Lab.

*Figure 43. Complete crucible unit with sample, ready for ignition.*

## Igniting Samples

Samples are ignited in the Thermolyne Muffle furnace located in the Chemistry Laboratory. The entire ignition cycle takes approximately 20 hours. After ignition, samples need to be taken out when they come down to ~ 50°C-200°C. If the samples sit for too long they will reabsorb moisture and the 'Post-Ignition Weight' will be inaccurate. Time this accordingly.

### Using the Muffle Furnace

Bring crucibles over to the Muffle Furnace (*Figure 44*). Turn the power switch on and the control panel will illuminate.

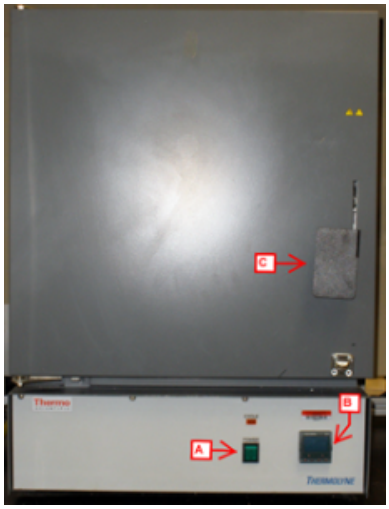


*Figure 44. The Thermolyne Muffle Furnace. A. Power Switch B. Control Panel C. Door handle.*

Confirm with scientists, what temperature and how long samples should be run for. Below is a quick reference guide:

| Material | Ignition Time at °C |
|---|---|
| Basalts | 4 or 5 hr at 1025°C |
| Si-rich sediments | 4 or 6 hr at ~900°C |
| Samples with:<br>• Muscovite<br>• Biotite<br>• Amphibole<br>• Carbonates | 6 hr or more at XXX°C |

A common program is an increase in temperature of 3°C/min to a target temperature of 900°C and a hold of one hour. Then ramp up at a rate of 3°C/min to a target temperature of 1025°C and hold for four hours. This ramp cycle is already programmed into the furnace and corresponds to 'Program 1'. To check or edit a program see additional guides attached to the furnace itself. It is also possible to run the furnace manually without a ramp up cycle. Discuss with scientists their preference

Either enter the desired temperature manually or select your program. If you are running the furnace manually, enter the desired temperature; no other buttons or steps are needed. If selecting a program, press and hold 'Run' (*Figure 45*).

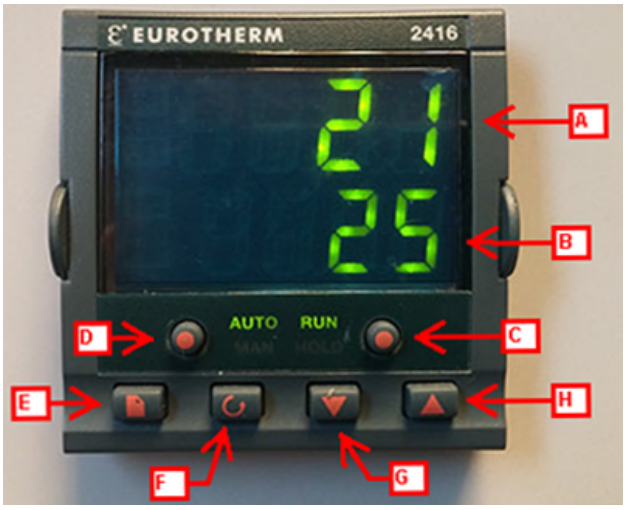


*Figure 45. Control Panel on Thermolyne Muffle Furnace. A. Actual temperature. B. Desired/ Set temperature. C. Run/ stop button. D. Auto run button. E. Page button. F. Scroll button. G. Down button. H. Up button.*

When the furnace finishes it's cycle and cools down to ~50°–200°C, remove the crucibles with tongs. Put samples onto a tray and store tray in the desiccator. Keep samples in the desiccator and remove one at a time while weighing. It is very important for the samples to not reabsorb moisture so begin weighing as soon as possible.

## Post-Ignition Weighing

Post-ignition measurements should be taken immediately after removing crucibles from the furnace. Failure to do so will disrupt the LOI values. Reweigh the crucible plus the ignited sample to determine how much weight was gained or lost. Follow the same weighing procedure as in ***Pre-ignition Weighing***.

1. Record the final weight in the excel spreadsheet under 'CRUCIBLE + IGN SAMPLE WT'. The spreadsheet will populate the columns 'Post Ignition Loss' and '%LOI'.
2. The formula used to calculate LOI is:

%LOI = 100 x (weight change during ignition)/ (fresh sample weight).
***Note**: By convention, weight lost during ignition is recorded as a positive LOI value; whereas weight gained is recorded as a negative LOI value. Report the results to 2 decimal places.*

## Uploading LOI Data To LIMS

Open the Excel File 'LOI Spreadsheet Upload Template' in Local Disk > DATA (*Figure 46*). Put your LOI information into the spreadsheet following the example format. Fill in the Text ID, Analysis, Replicate, Crucible number, and all weights and units including the %LOI.

| Text ID | Analysis | Replicate | Instrument | Display Flag | Component Name | Component Value | Component Unit | Component Name | Component Value | Component Unit |
|---|---|---|---|---|---|---|---|---|---|---|
| | LOI | 1 | | | crucible_number | 18 | NONE | crucible_preignition_mass | 15.574 | GRAMS |
| | LOI | 1 | | | crucible_number | DOG | NONE | crucible_preignition_mass | 15.2065 | GRAMS |
| | LOI | 1 | | | crucible_number | PK | NONE | crucible_preignition_mass | 18.8706 | GRAMS |
| | | | | | | | | | | |
| | | | | | | | | | | |

*Figure 46. LOI Spreadsheet Upload Template.*

Open up the program ‘Spreadsheet Uploader’ Pinned to the Taskbar (*Figure 47*).

*Figure 47. Spreadsheet Uploader Icon.*

Copy and paste your spreadsheet into that uploader. Click the 'Edit' button and 'Validate Sheet'. This checks and highlights any errors that need to be fixed. When the spreadsheet comes up clean, click 'Lims' and 'Upload'. The sheet will turn green when the measurements are successfully uploaded. The data is now in LIMS under Chemistry > ICP-AES Solids >Expanded LOI.

## Cleaning the Quartz Crucibles

1. Wash the crucibles with DI water and a small piece of a scouring pad (no soap).
2. Rinse several times with DI water.
3. Place crucibles in a 10% $HNO_3$ bath for 12 hr.
4. Rinse 3 times with DI water after the acid bath.
5. Dry the crucibles in the oven at a maximum temperature of 60°C.

Some crucibles will develop a thin white cloudy film, become spotted, or start flaking. If any of these things happen throw the crucible away in the sharps container. When the crucible undergoes one of those changes the quartz has started to react at high temperatures, and could start contaminating the sample.

# Making the Sample Bead

Two processes are required to make a sample bead:

- In a vial, mix 400 mg lithium metaborate flux (pre-weighed onshore) either ignited or non-ignited powdered sample, check with the science party to determine which sample type should be used. This step is typically completed by the chemistry technicians.
- *Fuse both sample powder and flux into a glass bead (Figure 28)*. Dissolve the bead in nitric acid. This solution will be further diluted and analyzed by the ICP.

*Figure 28. Fused glass bead.*

## Weighing the Sample

*Note: This process is typically done by the chemistry technicians.*
Weighing the sample is a critical step. The sample weight should be as close to 100 mg as possible. Inaccuracies in the weight will show up in the analytical results. Print small labels for each sample and place on your small, clear capped vial. On the lid label a sticker with the core, section, and interval.

1. Clean the countertop around the balance and the balance pans with isopropyl alcohol. Put sheets of white paper on all the working surfaces.
2. Arrange all supplies on the white paper: tweezers, scoopula, and a sheet of 6x6 weigh paper.
3. Ensure the following items are available and labeled for each sample.
    - 1 bottle of pre-weighed flux
    - 1 new, empty, acid-washed vial for the remaining ignited powder
4. Pre-label the bottles before weighing (one label each on the cap and the bottle).
5. Make two weigh boats. Cut a rectangular strip from your piece of weigh paper and fold up the two long sides. Put one on the 'Tare' Side and the other on the sample side. You will need to make a new boat for each sample. The tare boat will remain there for all of your samples.
6. Close the door of the balance and tare for 100 counts.
7. Remove a crucible of ignited powder from the desiccator. If the powder has hardened from the furnace then transfer the sample from the crucible to a clean agate mortar and grind until it is a loose fine powder. If your sample is fine proceed to the next step.
8. Keep your boat in the weigh pan and with your scoopula measure out 100 milligrams. Be careful not to spill your sample onto the pan. If you do, remove your sample boat and with a small brush wipe away the loose powder.
9. Close the door and weigh the sample, putting more sample on or off until you achieve a reproducible weight that is within ±0.00050 g of 0 (half a milligram).

10. When the sample weight is as close to 100 mg as you can get it (i.e., 0.0995–0.1005 g), open the labeled bottle with the pre-weighed flux and **car efully** pick up the paper with the sample powder on it and transfer all of 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.
11. Homogenize the sample/flux mixture by holding the vial slightly off of vertical and rotating it. Tap it from time to time on the bench top as you rotate it to clear any powder from the sides of the vial. Avoid getting the sample/flux powder stuck around the cap.

## Fusing the Sample into a Bead

The most critical aspect of bead-making is maintaining a constant sample to flux ratio. A ratio of 1:4 suffices in most situations. If samples are small (e.g., volcanic glasses), a sample mass <0.1 g may be used. However, the same ratio must be maintained between the samples and the calibration standards (otherwise the matrix will not match). For example, 0.05 g of sample requires 0.2 g flux.

### Using the Beadmaker

Collect platinum crucibles, platinum tipped tongs, 0.172 LiBr, and pipette tips from the safe above the Bead Maker (*Figure 29*). Get the 10-100ul pipette and teflon spatula from the drawer and clean with isopropyl alcohol. Have a tray of samples that need to be fused and an empty tray for finished beads.

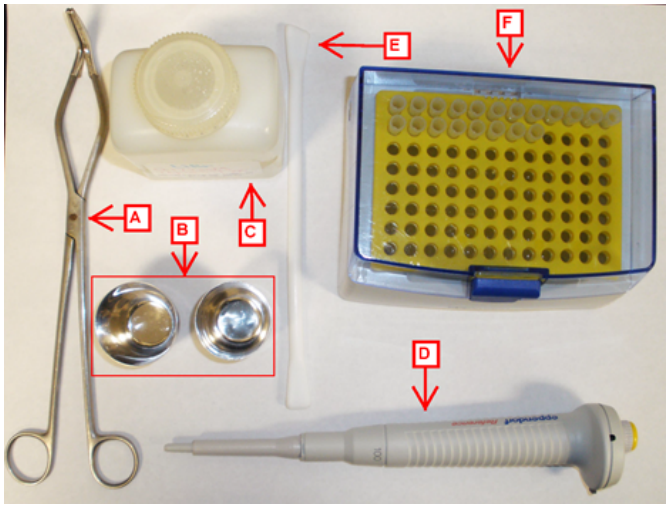


*Figure 29. Bead making supplies. A. Platinum tipped tongs. B. Platinum crucibles. C. 0.172 Libr wetting agent. D. Pipette. E. Teflon spatula. F. Pipette tips.*

Turn 'On' the Bead Maker (*Figure 30*; switch on the right side of the instrument).

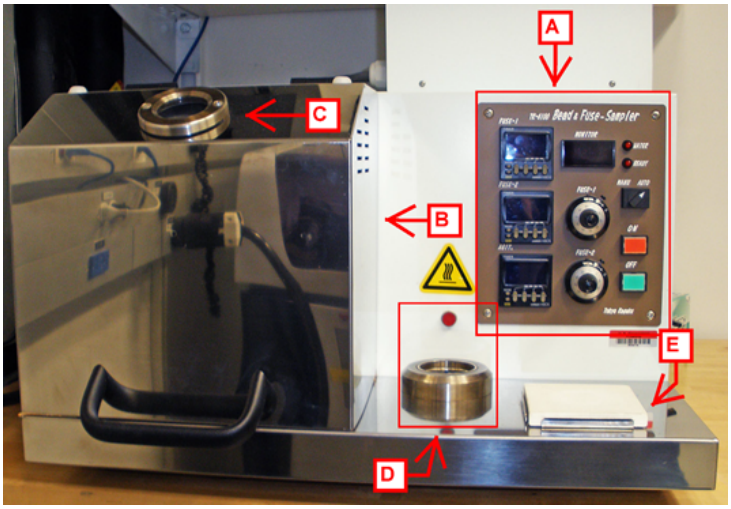


*Figure 30. Beadmaker. A. control panel. B. Site of platinum crucible. C. View port window. D. Fan to cool platinum crucible. E. Ceramic plate used for dislodging the fused bead.*

Next, turn on the water (*Figure 31; 32*). The handle is to the left of the machine on the wall. Raise the handle slightly to turn it on. You will hear a small click once it is in the 'on' position. Now the 'Water' and 'Ready' indicator lights should be on. Do not run any samples unless these lights are on.

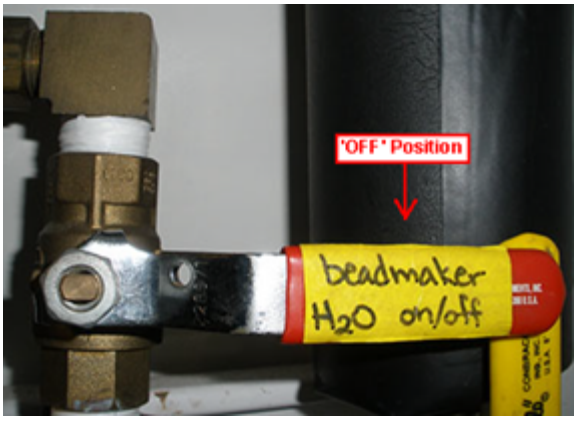


*Figure 31. Water in off position.*

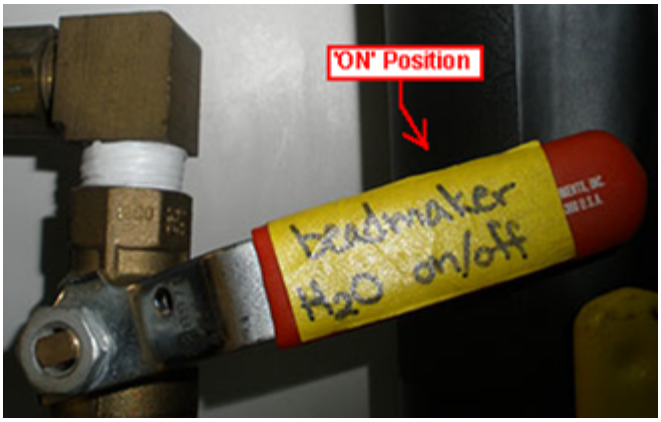


*Figure 32. Water in on position.*

1. Lay a large Kim wipe and a piece of weigh paper down next to the Bead Maker. Unwrap a platinum crucible and place it on the weigh paper. Pour the powder mix into the crucible. The sample should evenly cover the bottom.
2. Pipette 10 µL of 0.172 mM LiBr wetting agent into the center of the sample powder.
3. Open the Bead Maker lid and place sample inside the sample holder. The short wide crucible will fit directly; whereas, the tall narrow crucible will need an additional ceramic ring.
4. Close the lid. Double check both indicator lights are on. Press 'On' to start the program. The process will take 12 minutes and the sample is heated in three stages:
    - Stage 1:700°C for 2 min
    - Stage 2:1050°C for 5 min,
    - Stage 3: 1050°C in agitation for 5 min.
5. Be prepared to remove the crucible as soon as the timer is done. The material hardens very quickly so be ready with safety glasses, gloves, and the platinum tipped tongs before the final stage has finished.
6. With the Pt-tipped tongs, lift out the crucible and swirl the contents around to get the entire sample into one bead. **Wear eye protection!** The bead is very hot and rapid cooling can cause it to shatter and fly out.
7. Place the crucible on its cooling rack. When seated properly the red light behind it will start flashing. When the flashing stops the bead and crucible have finished cooling down.
8. Place a sheet of 6x6 weigh paper on the ceramic plate. Take crucible from the cooling rack and prepare to flip it upside down on the paper to extract the bead.
9. With crucible in hand flip over and give it a firm whack on the weigh paper. The bead should pop off without much resistance. Put the bead back into the vial that contained the flux.
10. If there are small pieces of bead left behind you can use your Teflon spatula to try pry it off. Do not use too much force. The platinum is malleable and will get scratched and damaged if put under too much force. If it still remains, make a note of the sample number and inform the chemistry technician. The residue (if any) should come off during the cleaning process.
11. Repeat process for all samples.
12. Hand off all beads to the chemistry technicians to continue on with the ICP analysis.

**Using the Bead Maker during transit is <u>not advised</u>, due to power fluctuation which could cause damage to the Bead Maker electronics.**

# Cleaning Platinum Crucibles

1. Rinse crucibles with DI water.
2. If beads are stuck to the bottom, sonicate with DI water for 30 min or more.
3. Place crucibles in HNO3 10% bath for 12 hr. If you notice any signs of residue, leave in the acid bath for longer.
4. Clean a Tupperware container with isopropyl alcohol. Lay down sheets of paper towel and a large kimwipes.
5. Take crucibles out of the acid bath and rinse with DI water 3 times. Place crucible in the container. If the crucibles require polishing, see ***Polishing the Platinum Crucibles.***

6. Cover all crucibles with a large Kimwipe and place in the drying oven in the Chemistry Laboratory. Leave overnight.
7. When dry remove crucibles and bring into the XRD laboratory. Wrap each crucible in a small Kimwipe and and place back in the safe. Lock the safe after all crucibles have been put back.

# Polishing the Platinum Crucibles

It may be necessary to polish the crucibles to remove scratches. Do this no more than once per expedition because polishing thins the platinum and in time the crucible will crack. A polishing machine is located in the ICP prep area.

1. Wrap a silk cloth (like the cloth used to clean eyeglasses) around the polishing nozzle.
2. Apply a diamond paste (Grade 30, found in Thin Section Lab) to the front of the silk-covered nozzle and place the crucible over the nozzle.
3. Turn polisher on and polish the crucible bottom for ~30 s (the bottom will be shiny). Be careful because the crucible will get hot. Do not try to remove any deep scratches – the crucibles are not that thick. The least amount of polishing the better.
4. Clean the crucibles with isopropyl alcohol and put in 10% HNO3 bath for 12 hr.

# Using the LOI Furnace to Make Sample Beads

If the bead maker breaks, use the LOI furnace to make beads.
**Caution!** Safety is a major issue with this procedure; use proper personal protection equipment and note where the nearest fire extinguisher is located.

1. Obtain the following safety equipment:
    - Welder's jacket (orange leather) and welder's gloves
    - Face shield
    - Long pants
    - Steel toed boots
2. Have a designated spotter in the room with you when placing samples in and taking samples out of the oven.
3. Heat furnace to 1020°C.
4. Pour the sample powder mix into a Pt-Au crucible.
5. Pipette 10 µL of 0.172 mM LiBr wetting agent into the sample powder.
6. Place each crucible into the oven slowly, one by one. Close the door in between samples. Six crucibles is an appropriate number. If you are not comfortable using the furnace, create beads in smaller batches.

***Note: It is possible to put Pt-crucibles directly onto the furnace shelf; however, it is advised to use a sample holder swing custom made by the ET's. The swing goes into the furnace by the upper vent, and can be rocked back and forth (with the door closed) from the outside. This is advised,as it allows for complete mixing and fusing of the sample.***

1. Wait until the temperature returns to 1020°C., then leave the samples in for 6 min.
2. Remove each sample crucible with the long tongs. When the sample is removed, turn the crucible 45° to one side.

***Note: The furnace drops temperature extremely quickly each time the door is open. If you swirl the sample or tip the crucible from side to side; the bead will not flow together and will be smeared across the bottom of the crucible. If not using a sample holder swing, it is advised to simply tip the crucible to one side.***

1. Place the sample crucible on a ceramic plate to cool. These crucibles are very hot and may burn anything near or under them. Take appropriate precautions.
2. Repeat this procedure until all samples are completed.

# Credits

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