XRD Sample Preparation Clay Separations

- Health, Safety and Environment
  - Reagents necessary for Clay Separation
  - Chemical Hazards
    - Ethylene Glycol (Ethanediol)
    - Hydrochloric Acid, Concentrated, or 2 M for Carbonate Dissolution
    - Acetic Acid, Glacial, or 10% for Carbonate Dissolution
    - Borax
  - Disposal of acid solution
- Clay Separation Procedure
  - Removing Carbonates before Clay Separation
    - Acetic Acid Treatment
    - Hydrochloric Acid Treatment
  - Separating Clay
    - Suspending Material
    - Standard IODP Clay Separation Method: Not for Semi-quantitative Analysis
    - Alternative method from Exp. 379
  - Preparing the Mount
    - Clay Mount to use with the D4 Bruker
    - Clay Mount to use with the PANalytical Aeris
    - Putting Material on Mounts
- Additional Clay Treatments before Scanning
  - Treating with Ethylene Glycol
    - Vapor Treatment
    - Quick Treatment
  - Heating Samples
  - Clay Separation Method for removal of Chlorite (not recommended onboard the JR)
- Troubleshooting
- References

Clay Separations focus on separating the clay size fraction, <2 µm, from the rest of the material. In order to get only that size fraction we prepare the sample in a different way compared to bulk analyses. **Do not freeze dry samples waiting for clay separations.**

If the samples have already been dried the treatments will still work but using fresh, wet samples is easier. Below are outlined various treatments and methods we do on board the *JOIDES Resolution*.

Health, Safety and Environment

Clay separation requires the use of hazardous chemical reagents. Please read carefully the following before starting.

Reagents necessary for Clay Separation

- Ethylene glycol or ethanediol: used for clay glycolation
- 2 M HCl 16.4% v/v: used for carbonate dissolution
- Glacial acetic acid, 10% v/v solution: used for carbonate dissolution
- Distilled (dionized reagent) water (DI)
- 1% w/v Borax solution

Chemical Hazards

Ethylene Glycol (Ethanediol)

Ethylene glycol is toxic and should not be ingested. It is also harmful if inhaled or absorbed through the skin and eyes. Proper personal protective equipment (PPE) should be used when handling this compound. Ethylene glycol is kept in a safety cabinet in the Thin Section Lab (*Figure 1*).

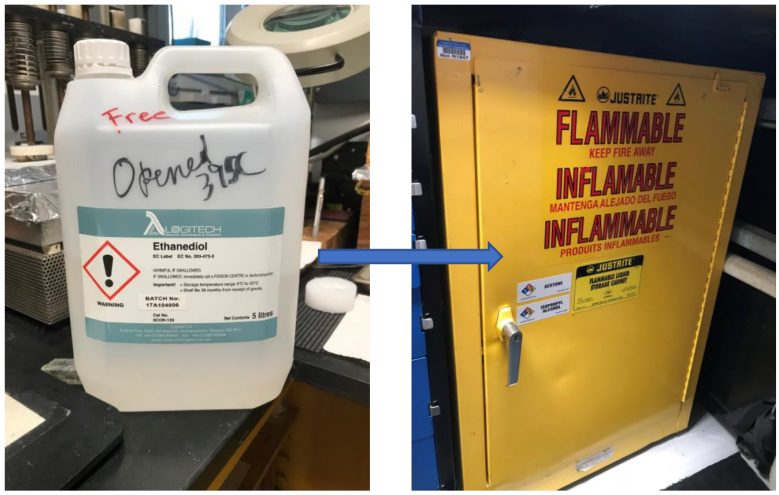


Figure 1. Safety cabinet in the Thin Section Lab

Hydrochloric Acid, Concentrated, or 2 M for Carbonate Dissolution

Concentrated hydrochloric acid HCl (~12M) is highly dangerous. It can cause severe tissue damage on contact, is highly toxic, and the fumes present similar risks of poisoning and chemical burns. When mixed with water, hydrochloric acid liberates large quantities of heat, so appropriate care should be used when diluting this compound. Note that the 2M hydrochloric acid used in the carbonate dissolution procedure is still dangerous and should be treated with the appropriate care.

Acetic Acid, Glacial, or 10% for Carbonate Dissolution

Glacial acetic acid (~100%) is highly dangerous. It can cause severe tissue damage on contact. When mixed with water, glacial acetic acid liberates a lot of heat, so appropriate care should be used when diluting this compound. When diluted to ~10% concentration, it is very similar to white vinegar, so while it is still acidic and could cause tissue damage, it is not as hazardous. Acetic acid (10%) is kept with Borax below the sink in the ICP preparation part of the Thin Section Lab (*Figure 2*).

Figure 2. Acetic acid (10%) stored in the Thin Section Lab

Borax

This chemical largely consists of potassium sulfate and is not expected to be a health hazard. It is used as a laundry booster (*Figure 3*). It is stored in the Thin Section Lab with the Acetic acid (*Figure 2*).

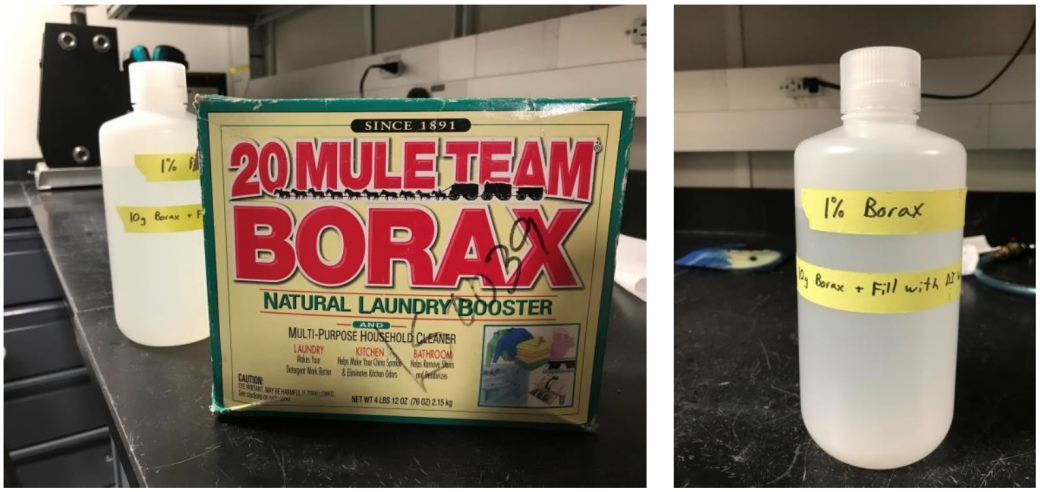


Figure 3. Borax

Disposal of acid solution

Technique for clay separation requires the use of acetic acid. To dispose acid solution properly and environment-friendly, use the **black** sink in the Chemistry Lab or in the Thin Section Lab (*Figure 4*). These sinks are directly connected to a specific container in the ship dedicated to acid treatment. **DO NOT USE OTHER SINKS !!!** Use flowing water to dilute the solution.

*Figure 4. **Black** sink to dispose acid solution*

Clay Separation Procedure

XRD analyses on clay separation requires several preparation steps:

1. Removing carbonates (to better identify the clay minerals)
2. Suspending material particles (to separate the < 2 m clay size fraction from the rest of the particles)
3. Heating samples (to identify the presence of kaolinite and chlorite)

Removing Carbonates before Clay Separation

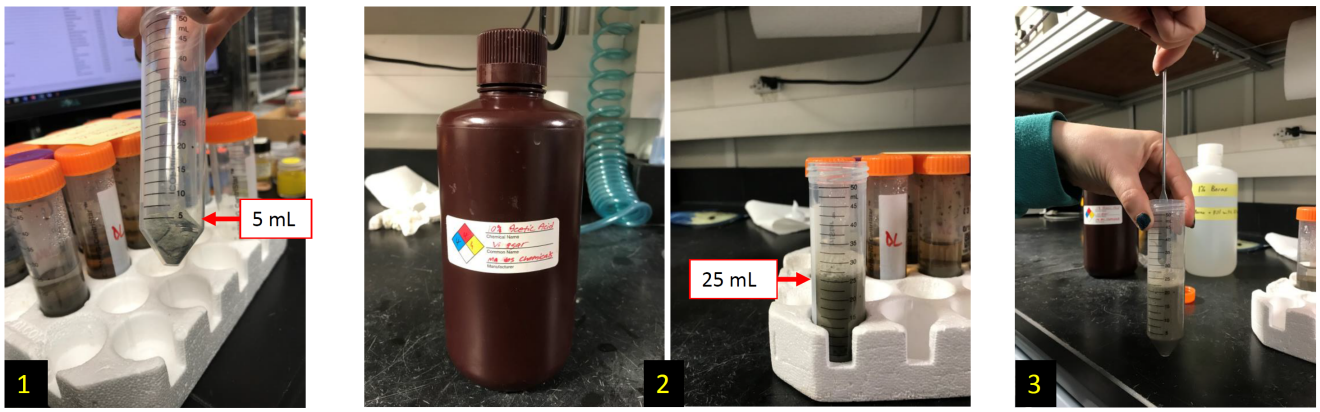
It may be necessary to dissolve the carbonates in the sediment to better identify the clay minerals. The goal is to remove as much carbonate as possible to isolate the material contained within the carbonate for analysis. There are two standard methods for removing carbonate aboard the *JOIDES Resolution*: (i) hydrochloric acid (HCl) and (ii) acetic acid. Ask the Science party which method they prefer. If there is no preference, use acetic acid.

Acetic Acid Treatment

This is the recommended treatment for carbonate removal. The process is slightly more involved than the HCl procedure, but far less damage is done to the mineral structure. The following steps are from Kitty Milliken (UT-Austin) and are shown in *Figures 5* to *8.*

1. Place ~2 cm^3 (or 5 mL) of **undried** (preferred) sample into a centrifuge tube (*Figure 5, Step #1*).
2. Add ~25 mL of 10 % Acetic Acid (*Figure 5, Step #2*).
3. Mix and shake well (*Figure 5, Step #3*). Let sit for at least 1 hour to decarbonate (until the reaction ceases). Close the centrifuge tube with its cap but not too tight to avoid unnecessary overpressure.
4. It helps to place the centrifuge tubes on the shaker in the cold room of the Chemistry Lab (*Figure 6, Step #4*). Do not tight the tube too strong in the arm as it can break while vibrating. Set a shaking time of about 30 seconds (it is a good start) and a power value of 1. After using the shaker, s hake the tube to ensure the reaction has stopped (i.e., no more bubbles).
   Note: Please note that sample with a large amount of carbonate (more than 50%) may require more than 1 treatment of Acetic Acid to reach complete decarbonation.
5. Next step is to spin the sample in the centrifuge (*Figure 7, Step #5*). Make sure to choose the correct tube holders. It is very important to balance the centrifuge, and to evenly distribute weight. Put samples diametrically opposite to each other. If you run a odd number of samples, keep the balance by filing up an additional centrifuge tube with DI to have an even number of tubes in the centrifuge. Turn on the centrifuge in the Chemistry Lab (*Figure 7, arrow A*). Press the "Speed" button (*Figure 7, arrow B*) and select a speed of 1500 rpm (rotation per min) by using the arrows to increase or decrease the value (*Figure 7, arrow D*). Press the "Time" button and select a time of 15 min by using the arrows to increase or decrease the value (*Figure 7, arrow C*). Press the "Start" button to start the centrifuge (*Figure 7, arrow E*).
6. Decant the acetic acid solution and dispose of the acid solution properly in an appropriate sink (*Figure 8, Step #6*).
7. Add 25 mL of DI (nanopure water) to the centrifuge tube (*Figure 8, Step #7*). Shake to get rid of the acetic acid. Centrifuge again for 15 min at 1500 rpm.
8. Decant the clear water. Repeat the "wash cycle" (i.e., centrifugation) with DI. Wash at least 3 times to remove all Acetic Acid (until it does not smell vinegar too strong).

Note: If the centrifuge in the Chemistry Lab is busy/used by Scientists, there is another centrifuge in the Paleo Prep room of the Core Deck.

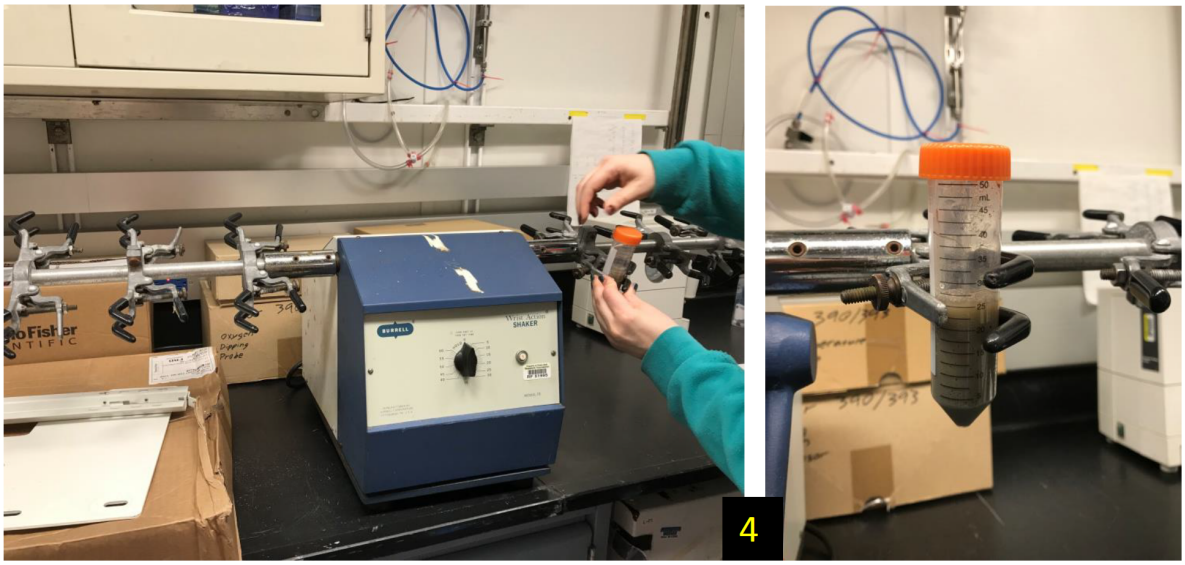


1. ~5 mL of sample in a centrifuge tube

2. Add ~25 mL of acetic acid

3. Mix well

Figure 5. Decarbonation with acetic acid.



4. Shake with the shaker to help decarbonation

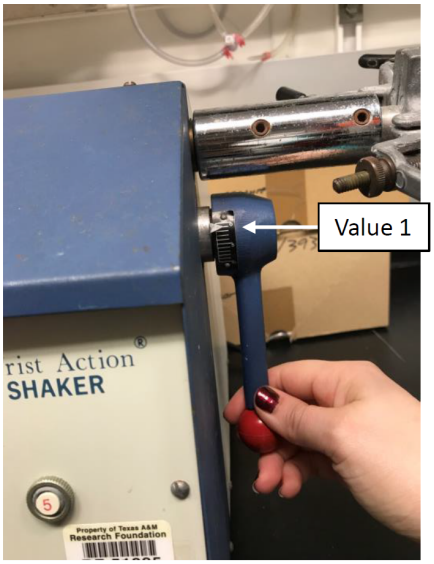
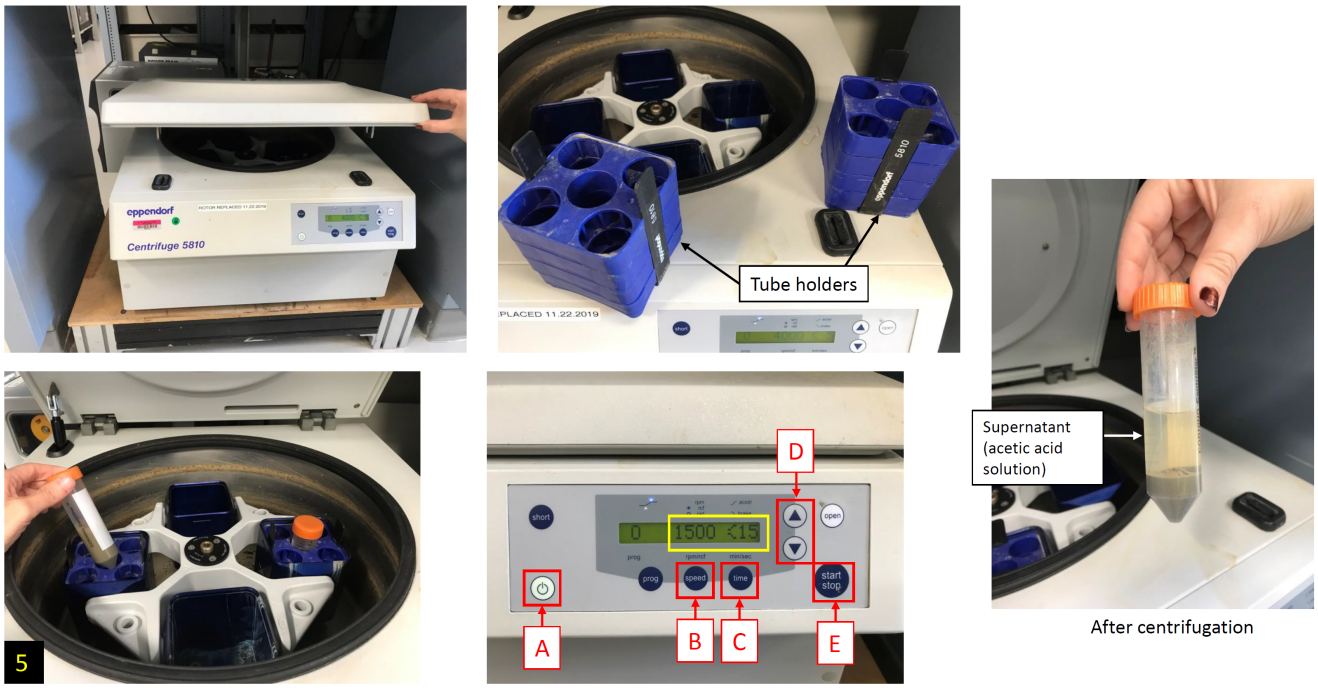
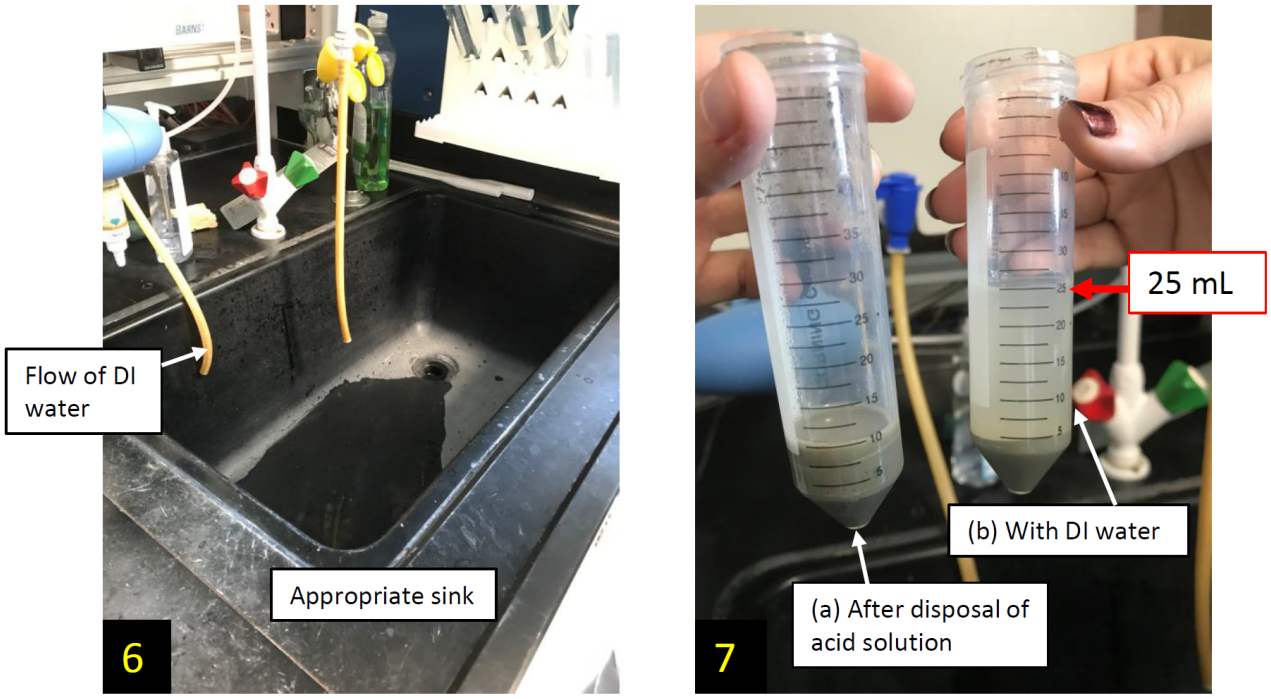


Figure 6. Using the shaker to help decarbonation reaction.



5. Spin sample in the centrifuge

Figure 7. Setting the centrifuge.



6. Dispose the acid solution properly

7. Add ~25 mL DI water

Figure 8. Disposal of acid solution and DI washing cycle.

Hydrochloric Acid Treatment

HCl is the simplest method for removing carbonate from sediment but does have severe drawbacks. Strong acids damage the mineral structure, especially within trioctahedral minerals. Before proceeding, be aware that this treatment may affect clay crystallinity.

1. Place undried sample on a glass slide or quartz disk.

2. Using a Pasteur pipette, slowly drop 2M HCl on the sample until bubbling/fizzing stops.
3. Desiccate and transfer sample to sample holder for analysis.

Separating Clay

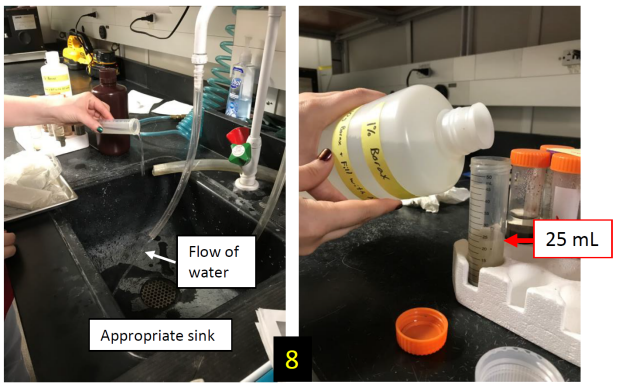
There are various methods for separating clay from coarser material involving a series of centrifuging or gravity settling. Those listed below are methods used on-board. If you removed carbonates first, start here after your water washes are finished and the water has been decanted. If you did not remove carbonates, take approximately 5 mL of sample material and put into a centrifuge tube.

Suspending Material

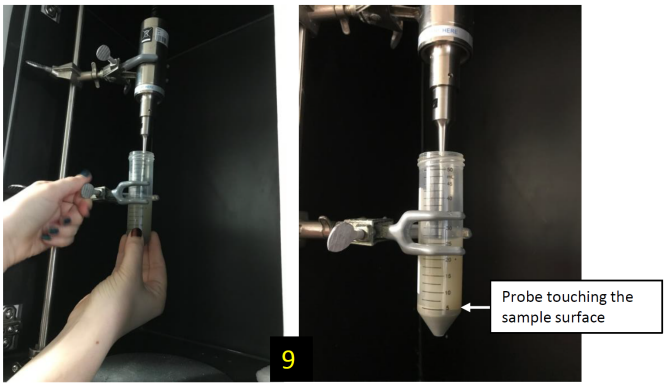
Get the sonic dismembrator case and probe power source (either in the Thin Section Lab or Chemistry Lab). Using the dismembrator is a very effective way to fully and randomly suspend the material. Suspended material can then separate out according to size, with the largest grain size on the bottom and the very small clay size fraction on top.

The dismembrator setup is shown in *Figure 10*. The power source is connected to the probe. The probe fits into the case through a hole in the top.

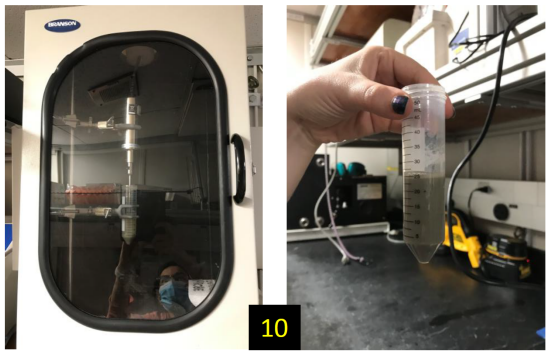
1. After removing the supernatant (after the last wash), add ~25 mL of a 1 % Borax solution to the centrifuge tube (*Figure 9, Step #8*). Borax prevents the sample from flocculating. Too much Borax however will increase flocculation.
2. Position the sample with the sonicating probe abut half-way into the sample material. Use the clamp to hold the tube in place (*Figure 9, Step#9*). The probe should not be touching the sides of the tube or the release of energy from the probe will melt the plastic tube.
3. When satisfied with the positioning, flip the "ON" Switch (*Figure 10, arrow A*). The settings are already set to our needs: **Mode = Continuous, Amplitude = 65** (*Figure 10*). To run as is, press the "Test" button (*Figure 10, arrow D*), the screen will display 'rdy' when it is ready for use. Alternatively, if you select Mode = Time (min/sec), the probe will stop automatically after 1.5 minutes. If you need to change a setting, press the "Mode" button (*Figure 10, arrow B*) and then the "Set" button (*Figure 10, arrow C*). From these two panels, you have access to the power, time, and displayed units. For more information, reference the Manufacturer Manual located in the side pocket of the dismembrator case (*Figure 10*).
4. Press the "Start" button on the probe power supply (*Figure 9, Step #10* and *Figure 10, arrow E*). If the material does not appear to be circulating throughout the whole tube or the tube is heating up, adjust the probe position and start the dismembration over. Allow the sample to circulate for at least 1 minute, then press the "Stop" button (*Figure 10, arrow E)*. Remove the sample from the clamp. Wipe the probe with a Kimwipe, then clean with isopropyl alcohol and dry with a Kimwipe.
5. Leave the sample to settle for about 12 hours on the benchtop (*Figure 9, Step #11*).



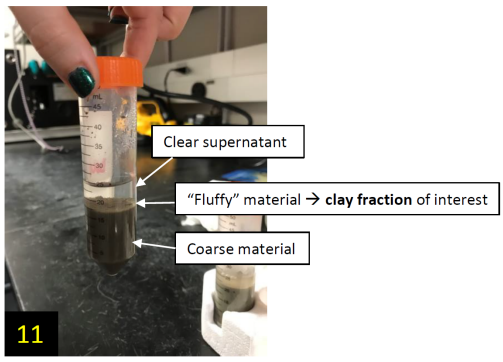
8. After the washing cycle, add ~25 mL Borax



9. Setting the tube in the dismembrator



10. Resuspended material



11. After ~12 hours of rest time

Figure 9. Adding Borax and Suspending Material with the dismembrator. Make sure to adjust the probe half-way into the sample material

Figure 10. Dismembrator set up and Probe with power source. Dismembrator power source control Panel. (A) On/Off switch (B) Start button (C) Set button (D) Mode button (E) Start/Stop button

Standard IODP Clay Separation Method: Not for Semi-quantitative Analysis

1. In a centrifuge tube, mix a small amount of bulk sample (~5 mL; fresh, not dried) with 1% Borax solution. Use the shaker (in the cold room of the Chemistry Lab) or the dismembrator, if necessary to suspend particles.
2. Centrifuge the Borax solution/sample mix at 750 rpm for 4 minutes to remove the >2 µm size fraction
3. Decant the supernatant liquid (containing suspended clay) into a new centrifuge tube
4. Centrifuge the <2 µm fraction for 15 mins at 1500 rpm to remove the Borax solution
5. Decant the Borax solution and add 25 mL of nanopure (DI) water to wash the clay
6. Repeat Steps 4 and 5 as necessary to remove the Borax (USGS recommends repeating up to 4-5 times)

Alternative method from Exp. 379

1. Add 25 mL of 1% Borax solution to the clay plug
2. Dismembrate the sample (machine is auto set on time), to remove the >2 µm clay fraction
3. Centrifuge for 4 mins at 750 rpm, decant the supernatant liquid into a separate centrifuge tube (you should end up with a ~full centrifuge tube of suspended clay)
4. Repeat steps 1–3 on the remaining >2 µm fraction
5. Centrifuge the <2 µm fraction for 15 mins at 1500 rpm to remove the Borax solution
6. Decant and add 25 mL of nanopure water
7. Centrifuge for 60 mins at 3000 rpm, the liquid is decanted before loading onto a zero background silica disk.

Preparing the Mount

Clay mounts are different either you are using the D4 Bruker or the Aeris for the analyses.

Clay Mount to use with the D4 Bruker

Clay mounts are put onto a zero-background silicon disk that fits into a 2 mm steel sample holder (*Figure 11*). Only put the disks into sample holders that have a hole drilled in the bottom (*Figure 11*). The hole allows the disks to be taken out, otherwise they are stuck inside the holder.

The disk should sit flush with the sample holder. Some of the zero-background silicon disks are at different depths, so a quartz insert disk (*Figure 11, Step #1*) can also be put in the bottom of a sample holder with the silicon disk on top (*Figure 11, Step #2*). Do not force the zero background disks into the holder, it may break.

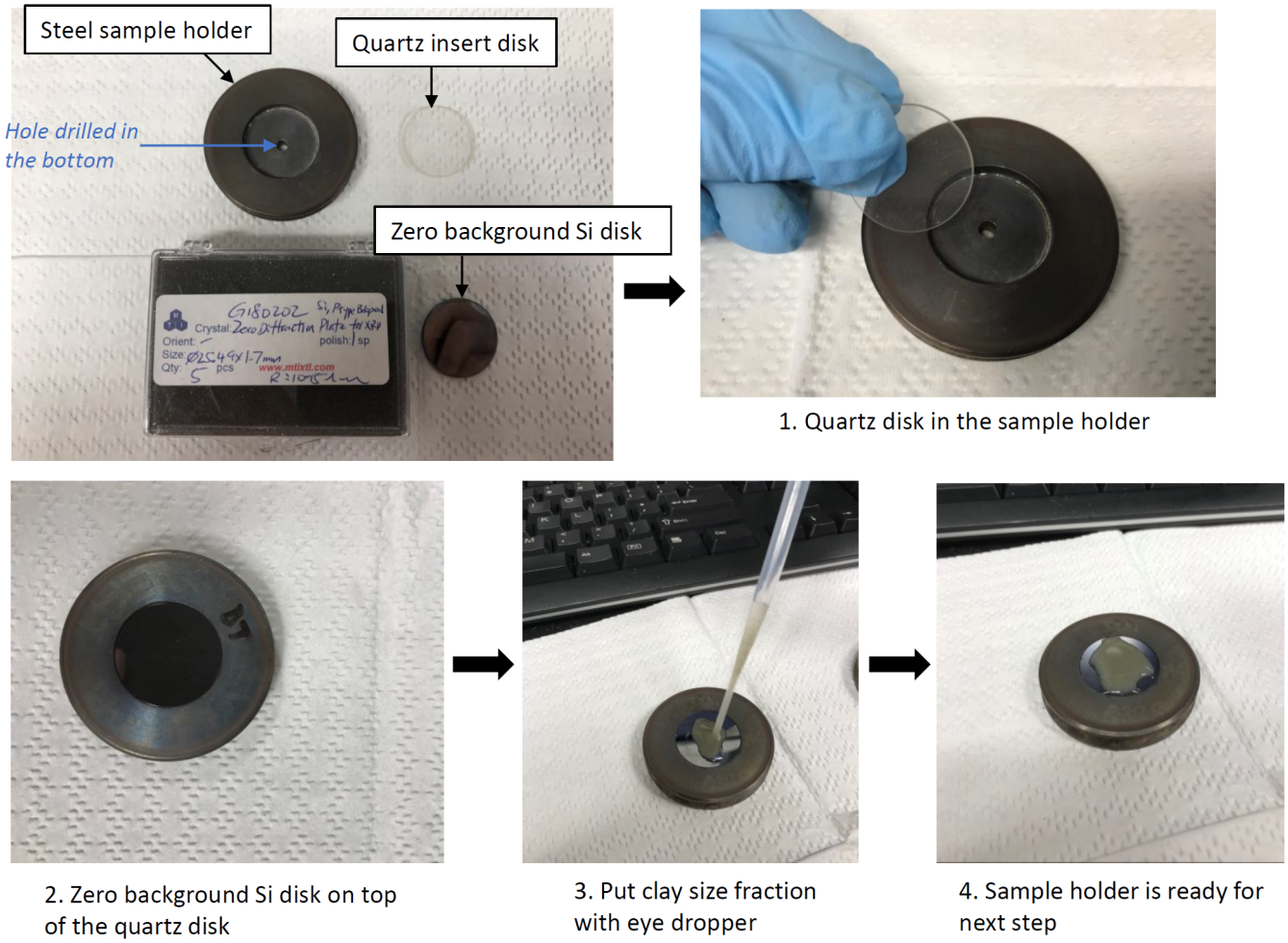


Figure 11. Steel sample holder with quartz insert disk and zero-background silicon disk. Clay Mount for the D4 Bruker.

Clay Mount to use with the PANalytical Aeris

Insert a zero-background silicon disk in a sample holder in a 'back loading' way (*Figure 12, Step #1*). Add on top of it an Aluminum spacer disk (*Figure 12, Step #2*) and clip the whole thing (*Figure 12, Step #3*). Flip the sample holder (*Figure 12, Step #4*).

The zero-background silicon disk can be heated up to 550ºC, which makes it suitable for further clay treatments as described below. However, the rest of the sample holder assembly must not be heated (magnetic part of holders). Please remind to dismantle the mount and put only the Silicon disk in a muffle furnace for additional clay treatment (*Figure 14*). Only the treatment with Ethylene Glycol is not 'destructive' because the temperature does not exceed 70ºC.

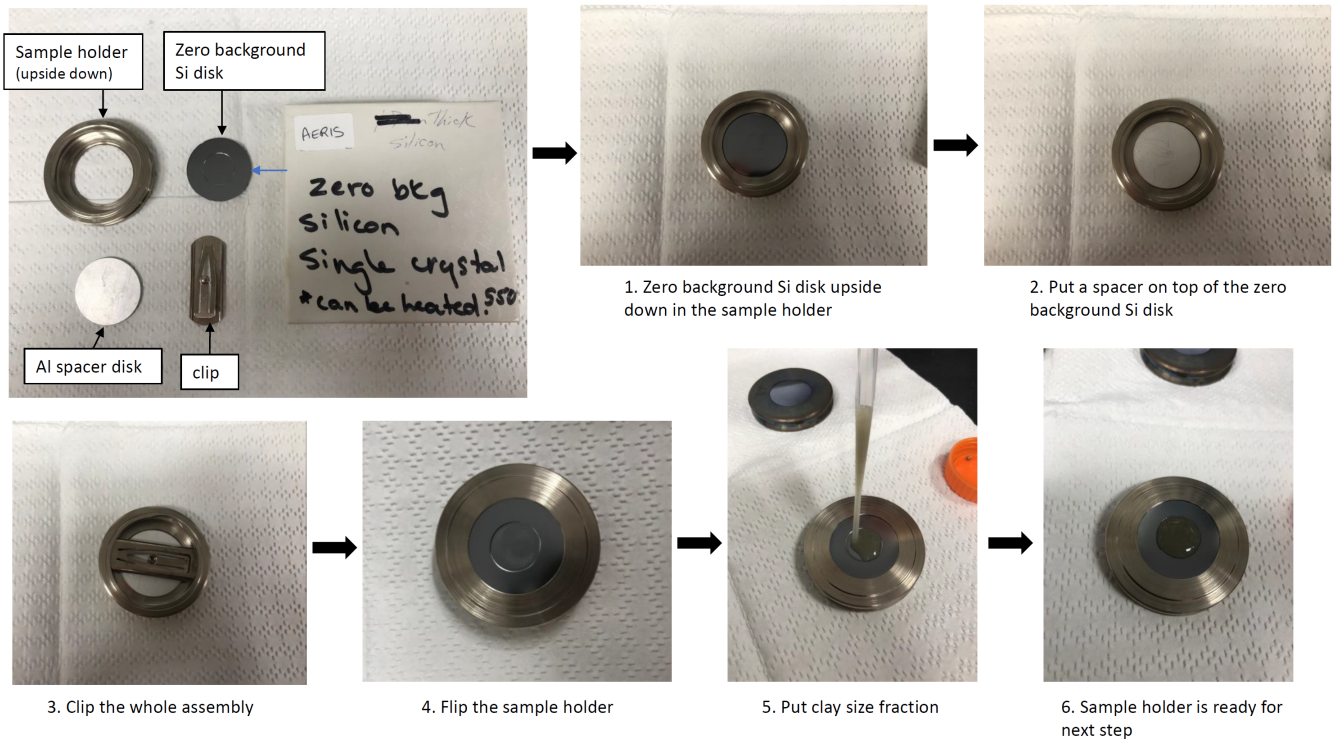


Figure 12. Clay Mount with Aeris Sample Holders.

Putting Material on Mounts

1. Remove the <2 µm size fraction by collecting the uppermost 1 cm of solution with an eye dropper (*Figure 13*). It helps to add a little isopropanol. If necessary, resuspend flocculated clay particles using the dismembrator and add more Borax solution.
2. If material is still very suspended, try centrifuging the samples for 4 minutes at 750 rpm. In this instance, the >2 µm size fraction will be the only fraction suspended in the liquid and all the larger grains will be packed in the bottom. Take the suspended material with an eyedropper and put it on the quartz disk.
3. Make an oriented clay mount by placing 2–3 drops (enough to cover the disk) of clay suspension directly onto the silicon disk (*Figure 11, Step #3* and *Figure 12, Step #5*). If the material is not spreading evenly, add a drop or two of 70% isopropanol and spread the material around with a small glass rod (*Figure 11, Step #4* and *Figure 12, Step #6*). Once spread, let the sample dry in the desiccator (*Figure 14A*).

The clay particles orient themselves as the solution dries on the disc. Note that it can be difficult to determine if there is enough material on the disc for a scan. Sometimes it may appear as if there is no sediment in the upper 1-2cm and thus nothing on the disk. Try scanning in the XRD before assuming there is nothing in the water drops added to the silicon disk. It is surprising what the XRD will return with very little sample. If the scan is not satisfactory add a few more drops from a bit deeper in the test tube and re-scan.

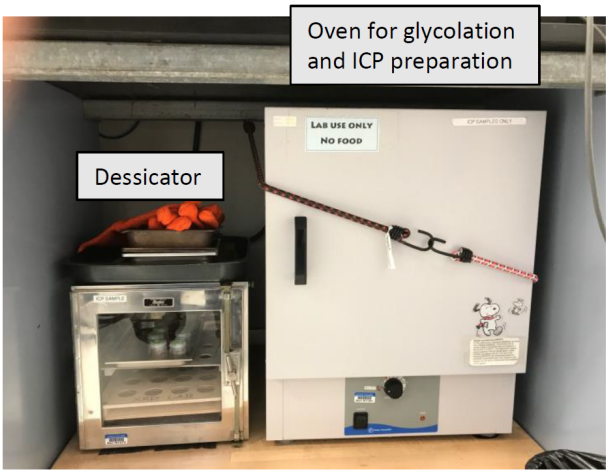
4. Once the sample is dry (*Figure 14B*), you are ready to run it through the D4 or the Aeris. If there are additional treatments requested, continue to the sections below after running the samples through the X-Ray diffractometers.

Collecting solution with an eye dropper

Approximate amount to put on disk

Figure 13. Collecting the suspended material with an eye dropper. Make sure to have enough clay material.

A.



B.

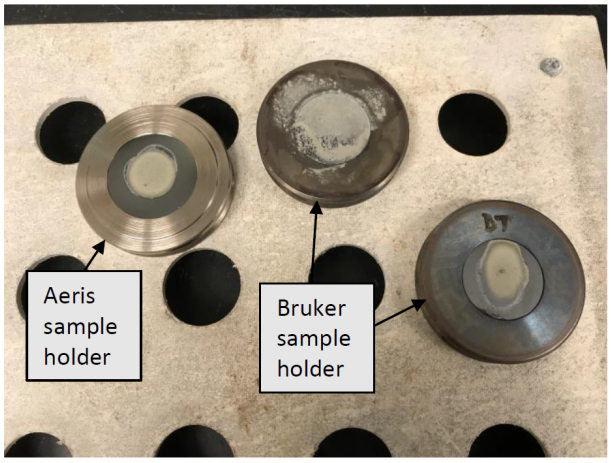


Figure 14. A. Dessicator and oven for glycolation. B. Dried sample preparation after dessication.

Additional Clay Treatments before Scanning

Treating with Ethylene Glycol

The following techniques are modified from the *U.S. Geological Survey Open-File Report 01-041, A Laboratory Manual for X-Ray Powder Diffraction* (hard copy available in the X-Ray Lab Library). Ethylene glycol can be used to expand swelling clays (e.g., smectites, montmorillonite, nontronite, and beidellite), some mixed-layer clays, and vermiculite as an aid to mineral identification. There are two ethylene glycol treatment methods:

1. Vapor Treatment (recommended)
2. Quick Treatment (aggressive)

Vapor Treatment

The advantage of the vapor treatment is less disturbance of the sample and less amorphous scattering of X-rays by excess liquid than in the Quick method (below).

1. Find the "glycolator" container stored in the ICP preparation oven below the Aeris (*Figure 14A).*
2. If empty, pour ethylene glycol to a depth of ~1 cm in the bottom of the container (*Figure 15A*).
3. Take off the lid and place the samples on the rack inside the glycolator (*Figure 15B*).
4. Place glycolator in an oven (60°–70°C) overnight (~12 hours) (*Figure 15C*).

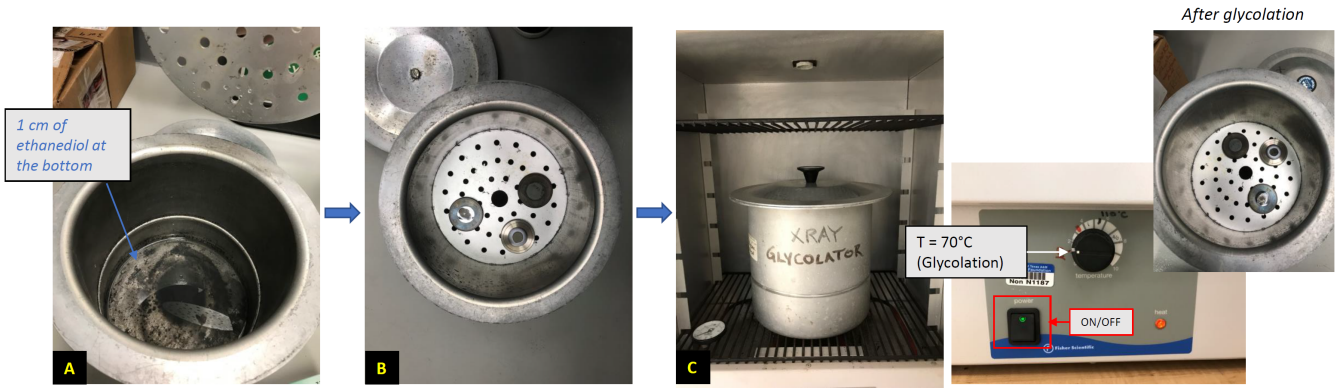


Figure 15. Glycolation: Vapor Treatment

Keep samples in the glycolator until ready to run through the XRDs. **Glycolation only lasts for 4 hours after the samples are removed from the glycol atmosphere.**

Before placing samples in the XRDs, wipe all sides of the sample holder with a Kim Wipe to remove any ethylene glycol. Ethylene glycol is sticky and can damage the grabber arm and sample spinner.

Quick Treatment

1. Using a glass rod or eye dropper, apply a drop of ethylene glycol directly to the surface of the sample mount.
2. Samples are ready to be analyzed as soon as the glycol is uniformly absorbed on the sample mount. Excess ethylene glycol may be gently mopped up with a Kim Wipe.

Heating Samples

Several clays have intensity peaks at very similar angles making it difficult to distinguish one clay from another. Heating clays is a way to work around this. We can run a sample through one of our XRDs, heat the sample in the muffle furnace, run again, and then compare the scans. For example, kaolinite and chlorite have overlapping peaks, making it hard to differentiate one from another. Heat morphs kaolinite, and it develops an amorphous signal, essentially removing its presence in the scan and leaving only the chlorite signal. The amount of kaolinite and chlorite can be determined by comparing these scans.

1. Prepare an oriented clay mount by adding several drops onto a zero-background Si disk in a sample holder and spreading it out evenly with a glass rod or eye dropper. See 'Preparing the Mount'.
2. Put the clay mount in the desiccator until it dries.
3. Put the sample in the muffle furnace in the Chemistry Laboratory (*Figure 16A*). Do **not** forget to dismantle the Aeris sample holder assembly - they must **not** be heated !! Only the Si disk should be put in the muffle furnace (*Figure 16B*). Different temperatures (at 400ºC and at 550ºC, following USGS Methods) and heating times (~1-2 hours) are used when trying to identify different minerals. Confer with your scientist to determine the parameters.

When the muffle furnace has finished its program and is cooling down, wait until the temperature reaches between 100° and 200°C before removing the sample (*Figure 16C*). The sample can be placed in the desiccator until it reaches room temperature. Once it has completely cooled down it can be run in the XRDs.

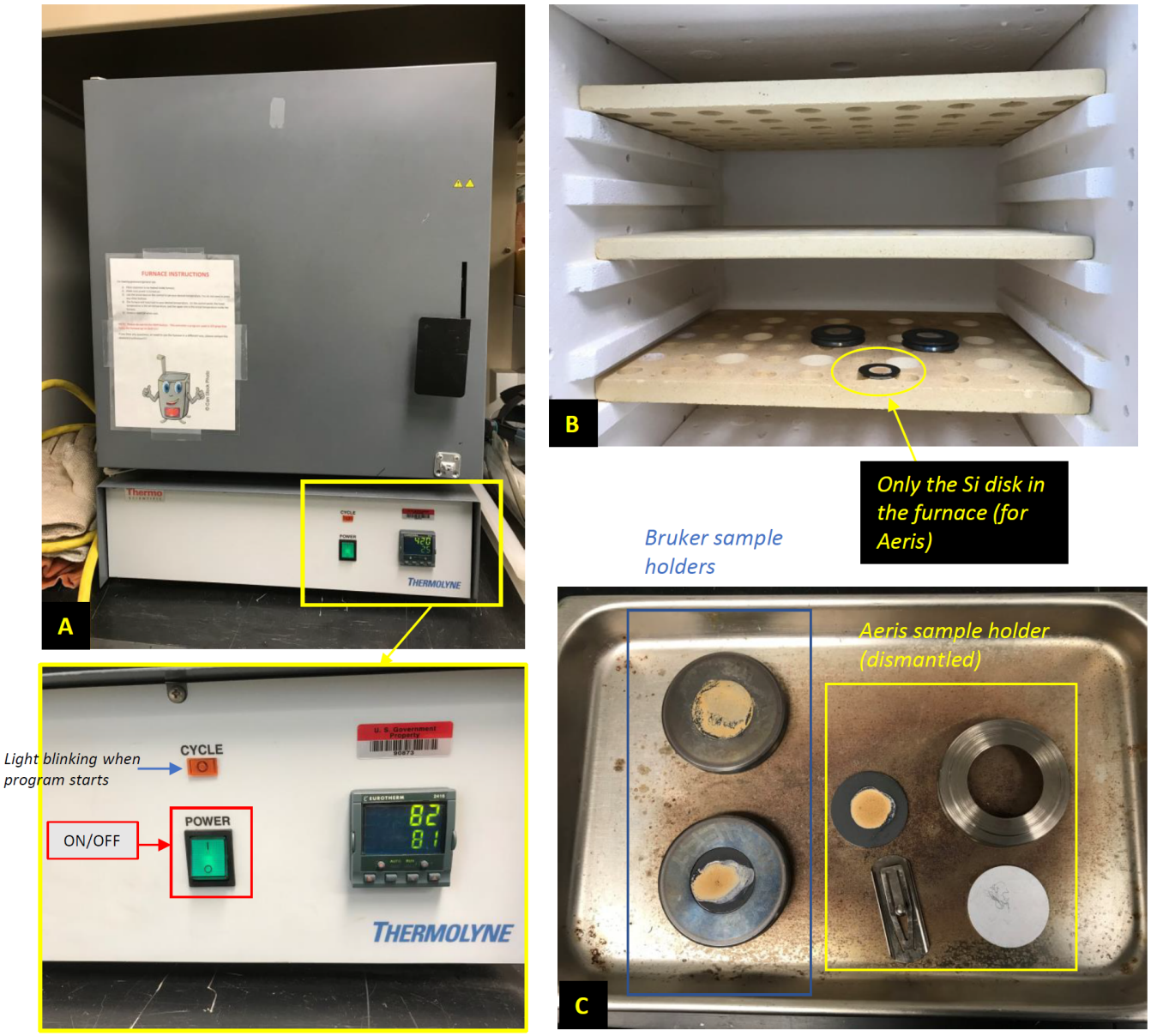


Figure 16. A. Muffle furnace in the Chemistry Lab. B. Clay Mount in the muffle furnace. Note that only the Si disk of Aeris sample holder is put in the furnace. C. After heating.

Clay Separation Method for removal of Chlorite (not recommended onboard the JR)

For the double peaks of Kaolinite and Chlorite, heating the sample only suggest that one of the minerals is present, it will not give final and complete results for a sample that contains both Kaolinite and Chlorite. In order to determine which mineral is present, an additional treatment is necessary.

1. Take the <2 µm clay fraction, this should be rinsed and free of any treatments.
2. In centrifuge tube, add ~20 mL of 1N HCl.
3. Vortex the sample to completely dislodge all material before pouring sample into a 100 mL beaker, add stir bar once sample is in place.
4. Set hotplate to 300°C (boiling point of HCl is ~101°C, but in order to maintain a continuous boil the hotplate needs to be much hotter)
5. Set the stir RPM below 100, this is only to keep the material suspended within the HCl
6. Start time once the samples have come to a complete boil, leave for 2 hours — add more HCl as necessary (DO NOT let the sample go dry and burn)
7. Once the sample has boiled for 2 hours, turn off the hot plate and allow sample to return to room temperature before pouring beaker contents back into a clean centrifuge tube. Rinse beaker with DI water to collect all material
8. Centrifuge down for 15 mins at 1500 rpm, decant acid and rinse with 25 mL nanopure (DI) water. Repeat the washing cycle 3 times.
9. After samples has been washed 3 times and is free of HCl, centrifuge for 60 mins at 3000 rpm

Troubleshooting

If the dismembrator does not start the program after pressing the button "Start", i.e., if the screen still displays 'P 0' (Power=0) and not 'rdy' (Ready), press the "Reset" button, then press "Test" and finally "Start". The dismembrator should clear the error and start the program normally. Power on the display screen should be 'P 11' when a sample is vibrating. The cause of this error is unknown and happens when the dismembrator is turned on.

References

Jackson, M.L., 1956. ***Soil Chemical- Analysis Advanced Course*** by Hsueh-Wen Yeh, Hawaii Institute of Geophysics, 1980.
Moore, D.M., and Reynolds, R.C., Jr., 1989. *X-ray Diffraction and the Identification and Analysis of Clay Minerals*: New York (Oxford University Press).