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Title: AN ULTRASONIC METHOD FOR ISOLATING NON-CLAY COMPONENTS FROM CLAY-RICH MATERIAL.

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KEYWORDS: heavy minerals, clay, laboratory, geochronology, microfossils

ABSTRACT

We present an efficient method for high-volume heavy mineral separation from clay-rich rocks using an ultrasonic probe. The ultrasonic clay separator (UCS) is an easily constructed device that allows for the recovery of high density minerals, as small as 10 microns, with a minimum of sample preparation. Recovery of heavy minerals from clay-rich material with the UCS is approximately twice that of gravity settling and decanting. Despite development with heavy mineral recovery in mind, the UCS should suitable for recovering small grain size geologic materials from flocculating clay-rich material.

INTRODUCTION

Clay-rich rocks often contain minerals and other particles that are of interest to earth scientists studying stratigraphy, paleontology, and bolide impacts. Glacially derived marine clay, deep sea pelagic sediments, and altered volcanic rocks are examples of clay-rich rocks that are commonly studied (Bowring et. al. 1998; Connemau et. al. 1991; Kyte 1995). Separation of non-clay material from large volumes of clay-rich rocks, usually involving the dilution of the clay fraction with water, has traditionally been time consuming, messy, and difficult. Poor recovery of small particles in clay-rich samples is probably due to their entrapment in dense networks of flocculating clays. The polar nature of clay minerals, especially smectites, allows them to form a van der Waal bonded network of grain clumps, or flocs, that develop immediately after mechanical dispersing stops, leading to the thixotropic behavior of aqueous clay slurries. There are two common approaches to overcoming flocculation and thixotropy: use of surfactants (Galehouse 1971; Ingram 1971) to create an overall negative charge in the aqueous slurry, or physical interruption of the bonding process with agitation or ultrasonic disruption.

Many minerals and particles of interest to earth scientists are small (10-500 microns), and thus susceptible to entrapment in a network of flocculated clays leading to their eventual loss among the clay-sized material that is removed from the sample. Concerned primarily with the recovery of zircon crystals 20 microns and larger, we experimented with several different methods, notably wet sieving (Commeau et. al 1991), grain settling by gravity (Galehouse 1971), and water table concentration using a homogenized slurry (Söderlund and Johansson 2002). These methods proved inefficient for four reasons: 1) flocculation and thixotropy during both gravity settling and water table concentration; 2) long and repetitive periods of decanting during gravity settling of samples in the required 0.1-1.0 kg range; 3) loss of high aspect ratio prismatic grains (typical for zircon) during wet sieving; 4) the inability to properly "load" the riffled platform with silt- to sand-sized particles during water table concentration. To overcome these difficulties we have developed an efficient method to liberate mineral grains from suspension by continuous flow dilution of the thixotropic slurry, simultaneous ultrasonic interruption of flocculation, and gravity separation of particles under mechanical stirring. This method and the associated ultrasonic clay separator (UCS) device allows recovery of heavy minerals such as zircon, apatite and pyrite, as small as 10 microns and it is used regularly in the Geochronology laboratories at MIT and Boise State University (Davydov et al., 2010; Schmitz and Davydov, 2012). While UCS method and device were developed expressly for the recovery of zircon from bentonitic ash beds, they may easily be adapted to the recovery of other small particles in clay-rich materials.

ULTRASONIC PROBES

Ultrasonic probes (also referred to as sonicators, ultrasonic liquid processors, or ultrasonic cell disruptors) use high voltage electricity to excite a piezoelectric crystal that causes it to vibrate at very high frequencies (20 kHz). This high frequency vibration is then focused at the tip of the probe. The

vibration causes the generation of small bubbles in water that rapidly implode causing a shock wave to transmit through the liquid. This phenomena is referred to as cavitation; the same principle is used in ultrasonic baths although in the latter case the transducers operate at much lower power. The clay separator employs cavitation to disrupt the weak van der Waal bonds that attract and loosely bind clay minerals together. Ultrasonic disruption separates mineral grains from the clay, allowing them to fall to the bottom of the vessel. Ultrasonic methods are far more effective than, and eliminate the need for, the addition of surfactants as a deflocculating agent.

DESCRIPTION OF DEVICE

The ultrasonic clay separator (UCS) is a simple device that allows separation of clay material (mineralogy and grain size) from larger minerals and particles of interest (Figure 1). The UCS consists of two water filled containers, referred to here as the primary and secondary separators. In both containers "floating" magnetic stirbars are used to continuously agitate the sample. The stirbar rate is fast in the primary separator (>200 rpm) and slow (50-60 rpm) in the secondary. The primary separator is elevated relative to the secondary to facilitate gravity feed between them. The clay separation process occurs in two phases. In Phase I separation, the prepared sample (mud slurry) and additional water added to fill the primary separator are suspended by a rapidly rotating magnetic stirbar and subjected to continuous, high power disruption using the ultrasonic probe. During this approximately hour-long phase, flocculated clay particles are broken up; the largest and heaviest suspended grains concentrate just above the turbulent layer created by the magnetic stirbar. In Phase II separation the ultrasonic disruption is pulsed at a lower power setting, the stirbar speed is reduced in the primary separator, and a continuous flow of water is introduced at a fixed rate into the primary separator. The ultrasonic probe continues to interrupt flocculation during phase II while allowing more grains to settle in the primary separator. The speed of the magnetic stirbar is set to suspend clay-size particles while silt and sand are

retained in the bed load at the bottom of the primary separator. As clay-rich water flows from near the top of the primary to the bottom of the secondary separator via a tube (Figure 1), any silt-sized grains accidentally suspended in the primary separator settle out as they enter the second separator, which is set to a lower stirbar speed than the primary. The clay-rich water again exits the top of the secondary separator through a tube to a sediment trap and drain. Phase II can proceed unattended until the clay fraction is removed from both primary and secondary separators, e.g. when the water runs clear. The residual mineral fraction retained in both separators is then transferred to a glass beaker, decanted, and dried for further processing.

MATERIALS

Outfitting a laboratory with an ultrasonic clay separator will cost approximately $5,500 USD (2013 prices), however the time saved and unparalleled recovery quickly makes up for the investment. The 500-watt ultrasonic probe is the most expensive component of the setup, listing at ~ $4,500 USD. Disaggregation of soft samples is quick and simple using a heavy-duty laboratory blender retailing for ~$600 USD. 'Floating' magnetic stir-bars are best suited for this apparatus and retail for approximately ~$330 USD/pair. A needle valve is necessary in order to regulate the flow of water through the system at about $50 USD. The remaining components can be obtained from hardware or laboratory supply houses, and include: (2) magnetic stirplates, (1) ringstand, (1) large finger clamp, (3) 5000 ml plastic pitchers or beakers, (2) 20 mm O.D. sink spray hose guides, (4) 20 mm I.D. rubber O-rings, 20 mm I.D. plastic hose (~1 m), 9.5 mm" O.D. plastic tubing (~1 m), (1) 500 ml squirt bottle, and (1) neoprene grommet from a filtering flask.

SPACE NEEDS AND MATERIAL MODIFICATIONS

The clay separator is easy to build and requires about 0.6 m^2 (6.5 square feet) of counter space. The apparatus is best located at or near a sink for both water supply and drainage. A sound dampening enclosure is important in the working laboratory, and can be easily and inexpensively constructed using a large cardboard box and carpet underlayment for sound absorption. The plastic pitchers (separators) will need to be modified with a hole saw for the exit hose guides and tubing out of each pitcher; these ~22 mm (7/8") O.D. holes should be located as high up on the containers as possible, centered between the spout and handle. The tap water input hole into the primary separator should be an 11 mm hole drilled at the 2000 ml graduation near the base of the handle, such that the neoprene grommet fits snugly in the hole. For high-volume usage, the collar and discs of the floating stir bar can be replaced with stainless steel copies that are more resistant to wear from the abrasion of mineral grains. We recommend a platform 6 inches high be constructed for the primary separator and stirplate to rest on (See figure 1 for schematic illustrations of modifications).

SAMPLE PREPARATION FOR UCS

Water should be added to samples until a mud slurry forms. Depending on the hardness of the sample, disaggregation can be achieved with either a lab blender, disc mill or a mortar and pestle. An alternative, and quite effective chemical method for disaggregation of kaolinite-bearing, relatively indurated samples has been described by Triplehorn (2002). In our experience a blender is often the easiest and quickest method, using a water to clay ratio of 3:1. When mixing with the blender add water first; incrementally add the clay sample until the proper ratio is achieved. The sample should be similar to whipped cream in consistency. A mortar and pestle is sometimes necessary for samples that are too soft for conventional disc milling and too hard for blending. Place $\leq$1 cm^3 pieces of sample in the mortar, add enough water to just cover the sample, and then grind the sample gently. After 30 minutes add ground material to the separator. Disc milled samples should be agitated in the blender with water

before addition to the clay separator to ensure that the sample is completely wetted. Because sample properties vary widely, experimentation is the most effective way to perfect these initial sample disaggregation techniques.

CONSUMABLES, CLEANING AND CONTAMINATION HAZARDS

The UCS breaks down into several easily cleaned components to avoid potential cross contamination of samples. Every component can be cleaned using soap and water with a sponge and brush. Special care should be taken when cleaning the floating stirbars. The water feed tube usually traps grains from the sample, it is important to flush out the tube between samples to avoid contamination. To ensure all components are clean, a procedural blank should be performed occasionally to inspect for contamination. The procedural blank consists of simply going through the clay separation procedure outlined in the appendix to catch any contamination problems. Expect to find small round fragments of titanium (50-150 microns) that spall off the tip of the probe. The only significant consumables are ultrasonic probe tips and replacement parts for the floating stir bars.

RECOVERY AND YIELD

Recovery of mineral grains 30 microns and larger is routine for all non-platy or non-bladed minerals, such as sanidine, while high density minerals ($r > 2.81$) as small a 10 microns are commonly retained. Systematic sampling of the exhaust water from the second pitcher during separation of grains from a bentonitic ash bed revealed the loss of light mineral grains ($r < 2.81$) in the 10 to 30 micron size range, however, no zircon or pyrite fragments >10 microns were observed. Samples were taken 30, 60, 90 and 120 minutes after the beginning of phase II separation. The number of >10 micron light mineral grains observed declined over time due to the dilution of the clay component in the mixture.

Experimentation with flow rates of up to 300 ml/min appears to only slightly decrease the overall 10-30 micron grain size yield. The increased flow rate reduces the total time necessary to process a sample. In our laboratory a conservative flow rate of 200 ml/min is used, but this can be adapted to particular applications. Experimentation with varying the rotational speed of the stirbars suggests that it is the most influential factor in determining the minimum size of the mineral grains recovered. Increasing the speed of the primary pitcher stirbar (>250 rpm) during phase II separation leads to more accumulation in the secondary pitcher. Adjusting the stirrer's rpms (± 60 rpm) in the secondary pitcher will ultimately affect the minimum grain size recovered during separation.

COMPARISON OF METHODS

A trial mineral separation for zircon was performed with a sample of the Ordovician Deicke K-bentonite bed (Kolata et al., 1996). The sample was prepared for mineral separation with a jaw crusher and pulverized in a disc mill. The pulverized sample was split into two equal parts with weights of 415 g. One part was processed by gravity settling and hand decanting while the other was treated in the clay separator following the procedures outlined in the appendix, with the exception of decanting twice at 7 minutes to be consistent with the gravity-settled split. The gravity-settled split was decanted once at each of the following time intervals: 3 hours, 2 hours, 1 hour, 30 minutes, 15 minutes, 10 minutes and 7 minutes. Both samples were dried down under heat lamps and weighed; the hand washed sample was 398.8 g while the clay separated sample had a weight of 339.3 g. After heavy liquid separation the sample's heavy mineral splits were passed through a Frantz at 10° forward tilt and 1.4 amperes, sieved down with 100 mesh sieve cloth to remove large fragments of white unidentified heavy minerals and the less than 100 mesh fractions were weighed. The UCS separated sample had double the mass of the hand washed sample. Visual inspection of the grains in a petri dish with a binocular microscope

confirmed that the UCS sample had at least twice the number of zircons contained in the hand washed portion. Zircons from the UCS fraction ranged from maximum of 350x70x70 microns down to small stubby grains 15x10x10 microns in size. The hand washed split contained zircons in the same size range, however the smaller grains were far less abundant than those observed in the UCS fraction.

CONCLUSIONS

High-volume heavy mineral separation from clay-rich rocks can now be performed quickly and easily using the ultrasonic method outlined above. The method has proven to give excellent recovery of both heavy and light mineral grains >30 microns in size and heavy minerals >10 microns. Comparison trials have shown that material yield is substantially higher using the UCS. The UCSC can easily be adapted to suit the needs of many different investigations dependent on recovery of particles from clay-rich rocks

APPENDIX:

Procedure

This procedure assumes the sample slurry has already been prepared and is ready for introduction to the clay separator.

1. Flush out water supply line to remove any residue from previous samples.
2. Readjust needle valve to 100-200 ml/min flow, turn off until phase II separation.
3. Clean all other parts with soap and water to remove possible contaminants.
4. Assemble as shown in figure 2 and connect water supply, place stirbars in each pitcher.
5. Set primary stirbar to 200 rpm, secondary stirbar to 50-60 rpm.
6. Completely fill secondary separator with water.
7. Fill primary separator with 2000 ml of water, then add 500-1000 ml of sample. The volume of sample processed at one time is dependent primarily on the percentage of grains to clay in the mixture; 500 ml is a typical sample size.
8. Top off Primary separator with water being careful not to over fill.
9. Place ultrasonic probe in primary separator and connect to ultrasonic generator

Phase I clay separation

10. Turn Ultrasonic generator “on”. Sonicate the sample at the highest power setting for 45 Minutes.

Phase II separation

11. Turn on water.
12. Adjust primary pitcher stirbar to 150 rpm.
13. Set Ultrasonic generator to pulse at 3 seconds on, 8 seconds off, and adjust power setting to 60%. Program generator for approximately 8 hours running time.

Processing time varies from sample to sample.

14. When water in both containers is clear, 6-8 hours later, the sample is finished. Turn off stirrers and water. Allow any suspended grains to settle.

15. Transfer sample from both pitchers into a 4000 ml glass beaker. Fill with water and allow to settle.

The decanting times given for this decanting scheme assume a 4000 ml beaker. When filling up beakers be sure all material is mixed using a turbulent stream of water. While decanting, pour off water slowly and be careful not to pour off the migrating front of grains that forms on the side of the beaker as it is tipped forward.

16. Decant after 10 minutes. Refill with water, allow to settle.

17. Decant after 4 minutes. Refill with water, allow to settle.

18. Decant after 3 minutes, and dry down residue under a heat lamp.

FIGURE CAPTIONS

Figure 1. Schematic drawing and photographs of the UCS at Boise State University. Clockwise from upper left: Schematic drawing of UCS; UCS without separators installed, illustrating ultrasonic generator and horn, magnetic stirplates, and ring-stand; assembled UCS prior to installing floating stirbars and filling with sample; assembled UCS in Phase II separation (the separation between suspended silt and clay sized particles can be seen midway up the primary separator on the right); assembled floating stirbars prior to insertion into separators; disassembled separator pitchers, illustrating the hose guides, o-rings and large-bore tubing used to connect the pitchers in series.

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Sonicator
to ultrasonic generator
to second container
inlet
Exhaust to drain
stirrer
Magnetic stirplate
Stand

Figure 1.