Standard Operating Procedure No. 29

Clay Mineralogy

REVISION LOG		
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29.0	Original SOP	10/23/03
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1. PURPOSE AND SCOPE

This Standard Operating Procedure describes the method for determining clay mineralogy.

2. RESPONSIBILITIES AND QUALIFICATIONS

The Team Leader and Characterization Team will have the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate staff to implement this SOP and for ensuring that the procedures are followed.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP, and receive specific training regarding these procedures, if necessary.

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the Team Leader.

3. DATA QUALITY OBJECTIVES

Determine how the clay-mineralogy influences the rock pile stability.

4. RELATED STANDARD OPERATING PROCEDURES

The procedures set forth in this SOP are intended for use with the following SOPs:

1 Data management (including verification and validation)
2 Sample management (chain of custody)
4 Taking photographs
5 Sampling outcrops, rock piles, and drill core (solid)
6 Drilling, logging, and sampling of subsurface materials (solid)
7 Decontamination of sampling equipment

The procedures set forth in this SOP also are intended for use with the drill plans and sampling plans.

5. EQUIPMENT LIST

The following materials are required for prepare sample for XRD-Clay Mineral Analysis:

- Oven
- Jaw crusher
- Jones splitter
- Weighing balance (up to 400gm with accuracy of 0.02gm)
- Volumetric beakers (100, 500, 1000mL)
- Pipette or eye-dropper
- Glass slides
- Centrifuge with sample vials
- Indelible marker
- Mixer

The following materials are required for analyzing samples in the X-Ray Diffraction (XRD) machine:

- XRD machine
- Disk, computer and spreadsheet software

6. COLLECTION OF SAMPLES

Fine-grained size samples will be collected according to SOP 5.

7. PROCEDURES

These are the simplified instructions from the attached clay manual.

1. Add approximately 20gm of sample to a 100ml beaker and fill with distilled water.
2. Mix and wait 5 min. Remix, wait 15 sec, and pour suspension into a properly labeled beaker. Allow the beaker and its content to stand for 10 minutes.
3. If the entire sample does not stay in suspension for 10 minutes, stir the sample and pour it into a centrifuge vial.
4. Place four centrifuge vials in the machine to balance the load. Set the speed to the maximum and the time to 5 minutes.
5. Once the centrifuge has turned off, decant the water from the sample into a waste water bucket or beaker.
6. Add more DI water to the vial to wash the sample. Stir the sample until the clay sample is in solution.
7. Repeat steps 4 and 5 for a total of 5 sample washing cycles.
8. After the final washing cycle, add DI water and pour into a small beaker. Wait 10 minutes to see if the entire sample stays in suspension.
9. If the sample does not stay in suspension add 3 to 5 drops of Calgon® to the sample and re-stir the sample. Wait 10 minutes.
10. If the sample does not stay in suspension repeat steps 4 – 9 again for another 5 cycles and add a few more drops of Calgon®.
11. Label two glass slides with the sample number and. After the sample has remained in suspension for 10min touch the eye-dropper or 2ml pipette to the surface and draw off enough material to cover a glass slide.
12. Slide should be allowed to air dry.
13. Four runs on the XRD machine are required for clay-mineral identification. Air-dried, oriented, glycolated for 24-hours, and heated at 375 ºC for 30 minutes at two different angles.
14. The scan angle, speed, and rate for the XRD machine for each run is listed below

Run	Scan angle (2 Θ)	Speed (2 Θ degree / minute)	Step rate (counts/ 2 Θ degree)
Oriented air-dried	2 – 45 °	2 º / minute	0.3
Glycolated	2 – 15 °	2 º / minute	0.3
Heated 1	8 - 10 °	2 º / minute	0.3
Heated 2	2 – 15 °	2 º / minute	0.3

15. Save data to a MDI file.
16. Produce printouts using the appropriate MDI file and be sure to include proper sample-number and mineral-identification labels.
17. Diffractograms are interpreted by measuring the heights and positions of the peaks they contain. The peak position data are compared with the known positions of peaks for the clay-mineral groups.
18. The peak heights are used to calculated the clay mineral groups in parts per ten using the equations listed in the Clay Mineralogy manual attached to this SOP.

8. QUALITY ASSURANCE/QUALITY CONTROL

Check for flocculation(particles sticking together and acting as larger particles; this is what Calgon® prevents). It is important because flocculation destroys the preferred orientation of the clay particles. Duplicate samples will be run.

9. DOCUMENTATION

Diffractograms will be stored electronically and available upon request. Clay mineral analyses in parts per ten will be compared with the bulk chemistry and petrographic analyses to determine if they are reasonable. Data are recorded in the database.

10. REFERENCES

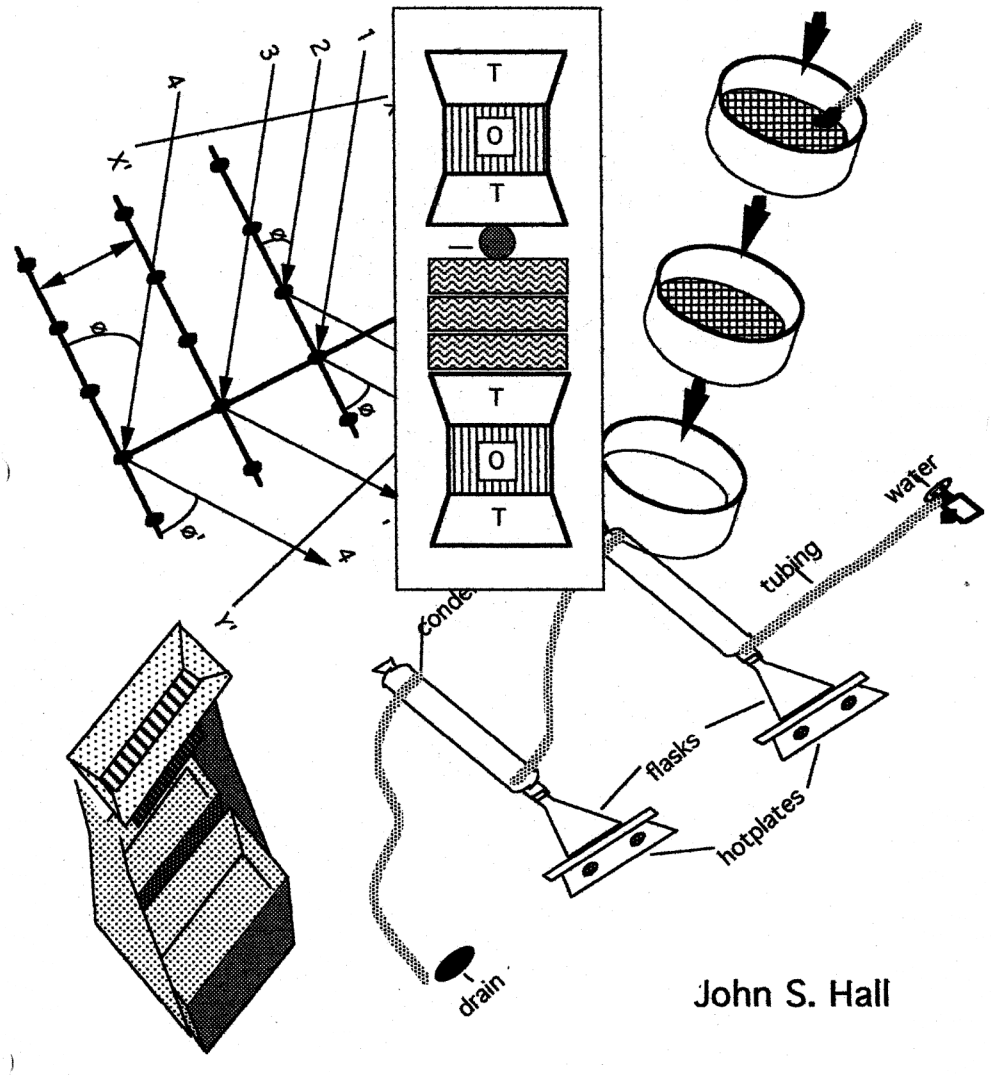
Hall, J. S., New Mexico Bureau of Mines and Mineral Resource's Clay Laboratory Manual

APPENDIX 1. FORM

APPENDIX 2. Mineral Resource's Clay Laboratory Manual

New Mexico Bureau of Mines and Mineral Resource's Clay Laboratory

Manual



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Acknowledgments

It must be recognized that all human endeavors are made possible by the experiences made available to, and sought out by, us collectively and individually; therefore, it is appropriate that I thank those who provided me with the opportunity to make this manual possible.

My first acknowledgment goes to Tanya Baker (Brickle) who wrote the first version of the Clay-lab manual, Without her help, I don't think I would have gotten past my first set of particle-size analyses. I thank George Austin for his help and patience in reviewing this manual and for making many opportunities available to me throughout my undergraduate studies. I am also indebted to many of the staff of the New Mexico Bureau of Mines and Mineral Resources as well as the student workers (Lab Rats) for their suggestions and assistance on various projects as well as this manual. Also, I must thank the New Mexico Bureau of Mines and Mineral Resources for funding me to write this manual.

John S. Hall

Introduction

This manual is intended for student employees and clay-mineralogy students working at the New Mexico Bureau of Mines and Mineral Resource's clay laboratory. It will describe the standard analyses, procedures, and techniques, as well as the principles behind them that are used in the Clay Lab. Additionally; it will give variations to these analyses, procedures, and techniques for dealing with special circumstances and difficult samples.

This manual is divided into five major chapters based on the general type of analysis being made or general-sample-preparation procedures. Chapter 1 deals with general sample preparation procedures used in some or all of the following chapters. Chapter 2 describes particle-size analysis for determining the percentages of clay, silt, and sand-sized particles in a sample. Chapter 3 is concerned with the three types of leaching analyses performed to remove organics and determine the amounts of carbonate and sulfate minerals in a sample. Chapter 4 deals with XRD (x-ray diffraction)-clay-mineral analysis, which is used to semiquantitatively determine the amounts of the five major groups of clay minerals. Chapter 5 describes XRD-bulk- mineral analysis for the determination of the nonclay mineral phases contained in a sample. Each of these chapters will be further divided into sections on theory standard-analysis procedure, and special procedures (where necessary).

This manual is designed to provide step-by-step-standard procedures for each of the types of analyses described. These can be followed nearly verbatim for perhaps the small majority of samples encountered in the Clay Lab. However, many samples will be encountered for which this basic procedure will prove inadequate and modifications will have to be made. The reason for this is usually the nature and characteristics of the sample

involved of even the quantity of sample provided. When the standard procedures and techniques prove inadequate, workers will find that they must rely on their creativity and ingenuity to modify the procedure in a manner that allows results to be obtained that are both reproducible and have a reasonable degree of validity. Some of the procedures in this manual, in addition to the alternate procedures and suggestions given, are the result of modifications that have been used in this lab to deal with difficult samples. Clay-lab workers will find them useful; however, these modifications are not completely comprehensive and they have their limitations. With this in mind, workers will be able to come up with additional modifications and improvements to the procedures as required.

Clay-lab work has been described as being both an art and a science. This is due to its heavy reliance upon techniques in which skill must be developed in order to perform them adequately. Additionally, there are numerous instances when one must use his or her judgment to determine the best course of action. Experience is often your best guide to know if an experiment has reached completion or if it is practical to perform a given analysis on a particular sample. A further purpose of this manual is to help workers gain this experience and develop an understanding of the limits of the procedures and techniques presented as well as those that they may create and modify on their own.

Chapter 1: Basic Procedures and Sample Preparation

THEORY

All of the analyses presented in this manual have the following requirement:

The sample fraction used in the analysis must be representative of the entire sample delivered to the lab. Additionally, the sample will be subjected to a gravimetric-analysis procedure in the cases of particle-size analysis and leaching. Because these requirements are so basic to the successful outcome of the analyses, the procedures used to achieve them will be discussion separate from the analyses. These procedures are the splitting, drying, and weighing of samples.

SPLITTING

The basic objective of splitting samples is to take a smaller representative sample for analysis from the larger sample that is delivered to the lab. In turn, the larger sample is assumed to be representative of the site from which it was taken. The smaller representative sample is obtained by a process of homogenization through blending and then systematically splitting the sample into smaller fractions in a manner that maintains the homogeneity of the sample down to the size required.

Particle or fragment size is a major factor to consider. A sample with sand-sized particles can be split down to a smaller size than a sample with larger particles (i.e. pebble sized) and still be representative. The reason for this is statistical with a weight of sand-sized particles having a larger sample population size of grains compared to an equal weight of larger particles. Similarly, a sample with a small average grain size but containing a scattering of larger particles or fragments also requires a greater

weight of sample to be representative. Larger particles or fragments scattered throughout a sample act as outliers that will bias the sample splits. This makes reproducibility difficult as one split may contain one or two pebble-sized particles and the other has none. A larger sample split must be used to get a representative amount of these scattered particles or fragments.

DRYING

Drying will be required for samples that undergo a gravimetric analysis procedure as part of the lab analysis (i.e. particle size or leaching tests). It is necessary to remove the pore water from the sample split before the initial weighing. This is more accurate because the pore water would interfere with the gravimetric analysis that requires dried products from the lab analysis. This also creates consistency between analyses of different samples and between duplicate analyses of the same sample because all samples will be run with essentially zero pore water.

WEIGHING

Weighing is a straightforward procedure theoretically; however, there are a few considerations that need to be recognized when using a precision analytical balance that will make measurements to +/- 0.0002g. The first is that objects that are above (or below) the ambient room temperature will generate convection air currents within the weighing chamber that will cause the balance's readout to drift erratically. To prevent this, samples should be cooled to room temperature in a desiccant chamber before weighing. Samples that have been previously dried will pick up moisture from the atmosphere and therefore should be kept in the desiccant chamber until it is time to weigh them. It is normal for the weight of the sample to increase slowly when it is sitting on the balance pan picking up moisture, however

this is usually just a few ten thousandths of a gram in the 10 to 20 seconds it takes for the balance to stabilize. If the weight decreases slowly, this is an indication that volatiles are being released from the object being weighed. This can be the result of small water droplets evaporating on an improperly dried beaker; therefore, it would be a good idea to investigate the situation if a decreasing weight is encountered.

The mass of what is being weighed is also a factor that should be considered. For masses of one gram and above, small variations and errors that may occur due to fingerprints on a beaker or minute bits of debris being unwittingly added to or removed from the object being weighed will have little significance. These changes would only be a few parts in 10,000 or perhaps 1000. However, a minute induced error could easily be a few percent when only a few hundredths of a gram are weighed.

SAMPLE PREPARATION

The only initial sample preparation required to perform normal laboratory analyses is crushing and containerizing. Then, providing the sample is adequately dry so it will not stick, it should be passed through a small jaw crusher set to break the sample into pieces no larger than 0.5 inch in the longest direction. If the sample is damp then it will have to be dried in an oven or under a heat lamp prior to crushing. The crushed sample should be put into the appropriate labeled container. If the volume of sample is too large for one container, use two or three as necessary.

STANDARD PROCEDURE

The following standard procedures will be used predominantly for splitting, drying, and weighing; however, there are situations in which modifications must be made. The following section will describe a couple of circumstances where this is necessary.

SPLITTING

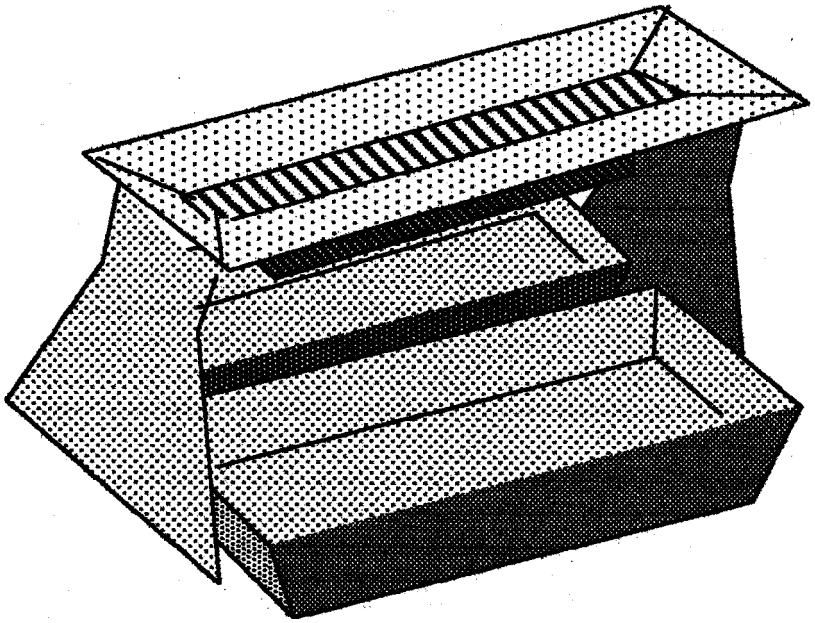

Fig. 2.1. Jones splitter (riffle box).

1. Pour entire sample from lab storage container(s) into rectangular pan.
2. Place two rectangular pans under Jones splitter (riffle box; Fig. 2. 1)
3. Pour sample, in rectangular pan, through Jones splitter making sure that sample goes through all slot openings of splitter simultaneously-not just a few in the middle. The best way to do this is to evenly distribute the sample in the rectangular pan and pour into splitter over the widest side of the rectangular pan that is no wider than the width of the Jones splitter This ensures an even split and helps maintain homogeneity.
4. Reject one of the two splits by pouring it back into the lab storage container.
5. Take the remaining split and continue to repeat steps 3 and 4 until the two splits are of appropriate weight for the analysis being performed (both splits of the final splitting process will be used where samples are run in duplicate).

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It is useful to retain the last split that would normally be rejected in a separate pan in case the final two splits are too small. This way the entire sample need not be resplit again.

Note: Several different sizes of Jones splitters are available. The one in the Clay Lab is adequate for most splitting operations, but for very small samples of sand-size grains or smaller, it is best to use a microsplitter. Generally samples with fragment sizes up to 0.5 inches in the longest direction should not be split to a weight less than 20gm. If these fragments are highly heterogeneous (i. a. different types of primary particles), It is best to increase the size of the last split(s) to 30 to 40gm.

DRYING

The drying procedures used in the Clay Lab are simple and straightforward. Two procedures are used depending on whether the entire uncrushed sample requires drying, or crushed and split samples are prepared for a gravimetric analysis procedure.

In the first case the entire uncrushed sample will require drying because it is too damp, plastic, and sticky to go through the jaw crusher. Usually a few hours in an oven or under a heat lamp will do.

In the second case, virtually all the pore moisture must be removed. The crushed and split samples are placed in an oven at 105°C for at least one hour. One hour is sufficient because of the small size of the sample split and the relatively small size of the fragments with their surface areas for evaporation.

WEIGHING

The balance that you use will depend on the weight of the sample to be weighed and the accuracy required. For all gravimetric analyses performed in the clay tab, the analytical balance (up to 180 gm. with accuracy of +/- 0,0002 gm.) is the best choice. For weighing out samples in bulk or balancing centrifuge tubes, the courser balance (up to 400 gm. with accuracy of 0.02 gm.) is used. If necessary, heavier balances for weighing bulk samples are available in other locations in the Bureau of Mines, The procedure is the same in all cases:

1. Check to make sure balance is level (by looking at leveling bubble if so equipped) and that balance pan is clean.
2. Turn balance on and wait for 0.0000 readout, If read" is different, press the tare bar to reset.
3. Place weighing container in center of balance pan and wait for reading to stabilize (usually 10 to 20 seconds).
4. Record weight and remove weighing container with sample.

Note: Never exceed the maximum weight limit of the balance, place sample directly on balance pan, or leave object to be weighed on the balance for extended periods of time. Always make sure balance is clean, level, and turned off after use. It is a good idea to periodically calibrate the balances; follow the instructions in the appropriate instruction manual.

SPECIAL PROCEDURES

A few deviations from the basic procedures and sample preparation above may be required. Elemental contamination is a concern for samples that will undergo trace element analysis. The trace elements being analyzed for will define what is considered a contaminant.

This is to say that it a sample undergoing a trace-metal analysis includes Fe (iron), the sample should not come into contact with any material or equipment made of Fe, especially in a crushing or grinding operation. This idea holds for all trace elements being tested for. It would not be a concern for major-element analyses since any contamination would be insignificant when compared to the concentrations of the major elements in the sample.

SAMPLE PREPARATION

Preparation for samples undergoing trace-element analysis will be similar to conventional samples, except one must be conscious of the types of materials used in the process. For instance, a sample that requires drying before trace-element analysis for Fe should be dried in an aluminum pan or a pan lined with aluminum foil rather than a steel pan. Additionally, the steel jaw crusher would not be used and the sample would have to be crushed by hand with a mortar and pestle to the appropriate size, or for softer samples, a rolling pin with the sample placed on a piece of waxed paper can be employed. Another reason to avoid the jaw crusher when a trace-element analysis is being performed is that it is difficult to got the crusher entirely clean and thus possibly contaminating samples with the residue of previously crushed samples.

SPLITTING

The example of the trace-element analysis that includes Fe also can be used to modify the process of splitting. Once again the steel of the Jones splitter (riffle box) makes it unsuitable for use and an alternate method will be needed. The alternate method that works well is the con-and-quarter method (Fig. 2.2, Head, 1980) as follows:

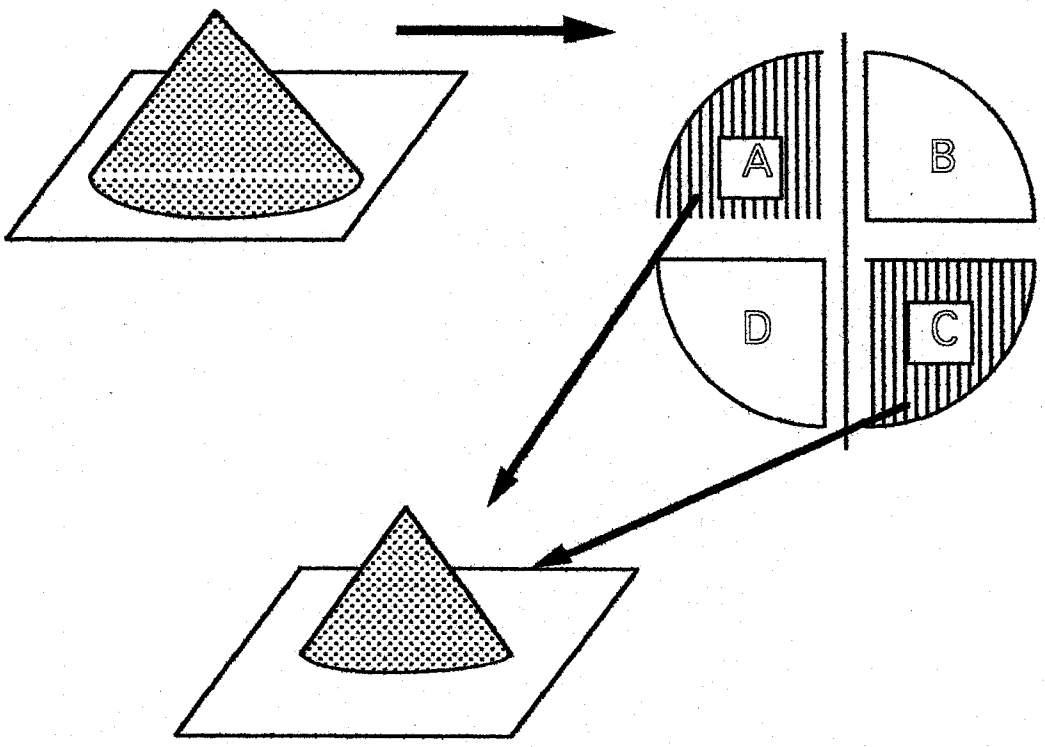

Fig. 2.2. Cone and quartering.

1. Mix sample thoroughly in pan.

2. Pour sample onto clean surface (i.e. waxed paper) to form a circular conical heap (if fragments are small enough, poring samples through a large plastic funnel held by a ring stand is helpful).

3. With a straight edge, divide cons into four equal portions (Fig. 2.2)

4. Reject portions 8 and D-placing them in their lab sample container.

5. Mix portions A and C together and repeat steps 2 to 6 until last group of portions are of appropriate size for the analysis being performed.

Chapter 2: Particle-size Analysis

The primary objective of performing particle-size analysis in the Clay Lab is to measure the weight percent of sand-and-larger-, sift-, and clay-size particles in a sample. The size of the particles are agreed upon by the geological community and by definition are set at the following values: sand and larger size is >63 um (micrometers), silt-size is 163 um to 2 um, and clay-size is <2 um. This chapter will cover the theories and practices concerned with the separation of a sample into its primary-particle sizes.

THEORY

Two techniques are used for the separation of the different particle sizes in the Clay Lab. Sieving is used to separate the sand-and-larger size particles from the whole sample and a sedimentation technique is used to separate a fraction of clay- sized particles from the remainder. The theories behind these two techniques are discussed below.

Sieving theory is simple. It is based on passing particles through precision-size- square openings in the wire screen of the sieve. The condition under which this happens is usually that of shaking/vibrating of the sieve(s) for an appropriate length of time. This allows particles, smaller than the size of the sieve openings, to pass through the screen. It is typically performed dry for clean-course sands and gravels. A wet- sieving procedure must be used for samples that contain silt and clay-sized material to wash them off the surfaces of courser particles.

Sedimentation theory is not quite as straight forward as sieving theory because it describes phenomena in the microscopic as well as the macroscopic realm. Furthermore, the phenomenon of particles settling is described by Stoke's Law in which a number of assumptions are made that are listed below (Head, 1980).

The following formulas (Stoke's Law) can be used to determine the terminal velocity of spherical particles failing freely through a liquid or the diameter of a particle failing a certain distance in a given amount of time:

$$v = \frac{D^2 g (\rho s - \rho l)}{18n}$$

$$D = \sqrt{\frac{18n}{g T (\rho s - \rho l)} \frac{H}{}}$$

Where:

D = diameter of particle.

ρs = mass density of the solid particle.

ρl = mass density of the liquid.

n = dynamic viscosity of liquid.

g = acceleration due to gravity.

v = terminal velocity.

H = distance particle falls.

T = time.

Assuming:

(1) The condition of viscous flow in a still liquid is maintained.

(2) There is no turbulence: that is, the concentration of particles is such that they do not interfere with one another.

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(3) The temperature of the liquid remains constant.

(4) Particles are small spheres.

(5) Their terminal velocity is small.

(6) All particles have the same density.

(7) A uniform distribution of particles of all sizes is formed within the liquid prior to the start of settling.

Of course, all of these assumptions will not be met when processing real samples.

Assumptions numbers 3 and 5 will essentially be met, given the small particle size that is being sampled (clay sized) and the constant temperature of the laboratory over a period of time. The water temperature is considered to be about room temperature because the distilled water used in the procedure is stored in the same building or room where the sedimentation procedure is performed.

Assumptions numbers 4 and 6 affect the sedimentation procedure to varying degrees depending on the makeup of the clay-and silt-sized particles. Physically, this means clay particles settle slower than most other minerals of the same diameter due to their plate-like nature. Also, Stoke's Law assumes a perfect spherical shape that presents the least surface area for a given mass. Therefore, particles, given their imperfect shapes, will settle slower than this ideal particle. In terms of size, this means that the particles sampled will always be somewhat larger than the size calculated using the formulas given. A similar situation exists for particle densities that are assumed to be equal for all particles. In real samples, there will be some variations in particle densities due to the variations in mineralogy Therefore; an estimated- representative density of the particles anticipated is used. The difference between this estimated value and the actual value can vary either positively or negatively, but is assumed to be reasonably small. While assumptions 4 and 6 are entirely characteristics of the sample, assumptions 1, 2, and 7 are all very much affected by the actions of the worker.

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Assumption number 1 states that viscous flow will be maintained in a still liquid. This requires the sample be undisturbed by vibrations or other movements. Assumption number 2 states that there will be no turbulence. Turbulence occurs when the concentration of the suspension reaches a point where particles interfere with each other.

For a clay material, flocculation is reduced by keeping the concentration of particles in the suspension below a certain amount. Assumption number 7 states that a uniform distribution of particles sizes is formed within the liquid prior to the onset of settling. The lab worker ensures this through ample stirring and/or agitation of the sample just prior to settling. It should be clear that consideration of all these assumptions is important to the interpretation of data collected and that these last three assumptions should be of particular importance to the Clay-lab worker.

STANDARD ANALYSIS PROCEDURE

1. Label and weigh four 100 ml beakers (one each for the whole-sample/sand- and-larger-size fraction and clay-size fraction for both the A and B splits/runs).
2. Record these weights on the particle-size data sheets for both the A and B runs. 3. Split, dry, and weigh sample as described in Chapter 1. Record whole-sample weights on data sheets.
4. Disaggregate sample further by placing it in a Waring® blander with about 200ml of distilled water. Distilled water is always used in sample analyses in the Clay Lab because it has the dissolved solids removed, which would remain as an impurity in the samples after evaporation. Blend for 1min on the lowest speed.
5. Check sample for complete disaggregation. Use a spatula to obtain

some of the courser grains (those not in suspension) at the bottom of blender to see if they are individual primary (non-aggregate) particles or aggregates of smaller particles. If they are individual primary particles, then place the sample in an ultrasonic cleaner, if available, for 10min to aid the disaggregation of smaller particles that adhere together or to larger particles (Johnson and Moston, 1976). This disaggregation also occurs in the sieving process during particle-size analysis. Ultrasonic energy commonly has no affect on larger-well-cemented aggregates of particles. If the particles are still an aggregate of smaller particles, pour sample from blender to a 1000ml beaker (making sure to wash all remaining grains into the beaker with distilled water) and allow it to stand overnight. Return sample to blender and blend for 1min on the third-speed setting. Again, check to see if larger particles are primary or aggregates. If they are primary, then proceed to step 6. If not, pour liquid portion (suspension) from blender into the 1000ml beaker.

Wash the remaining part of the sample into a mortar and wet grind until sample is disaggregated into its primary particles. It may be very difficult to determine when this has occurred. Several indicators or ways that may help the worker make the determination are: look at grains with a hand lens or microscope to see if they are primary particles. Stir sample in mortar and pour resulting suspension into the 1000ml beaker. Add more distilled water. Continue grinding sample and removing the suspension (pour it in the 1000ml beaker). Continue until a significant decrease in the amount of suspended material (cloudiness) occurs. (Note: The assumption here is that the primary particles are harder than the aggregate as a whole and will be released relatively intact. However, it is necessary to realize that primary grains will be broken and that grinding should be kept to the minimum necessary for effectively complete disaggregation. In cases where a lot of grinding is necessary and/or the point of completion is not clear, this should be noted on the data sheet.)

6. Wet sieve sample through two 230-mesh sieves (Fig. 2.1). An older-

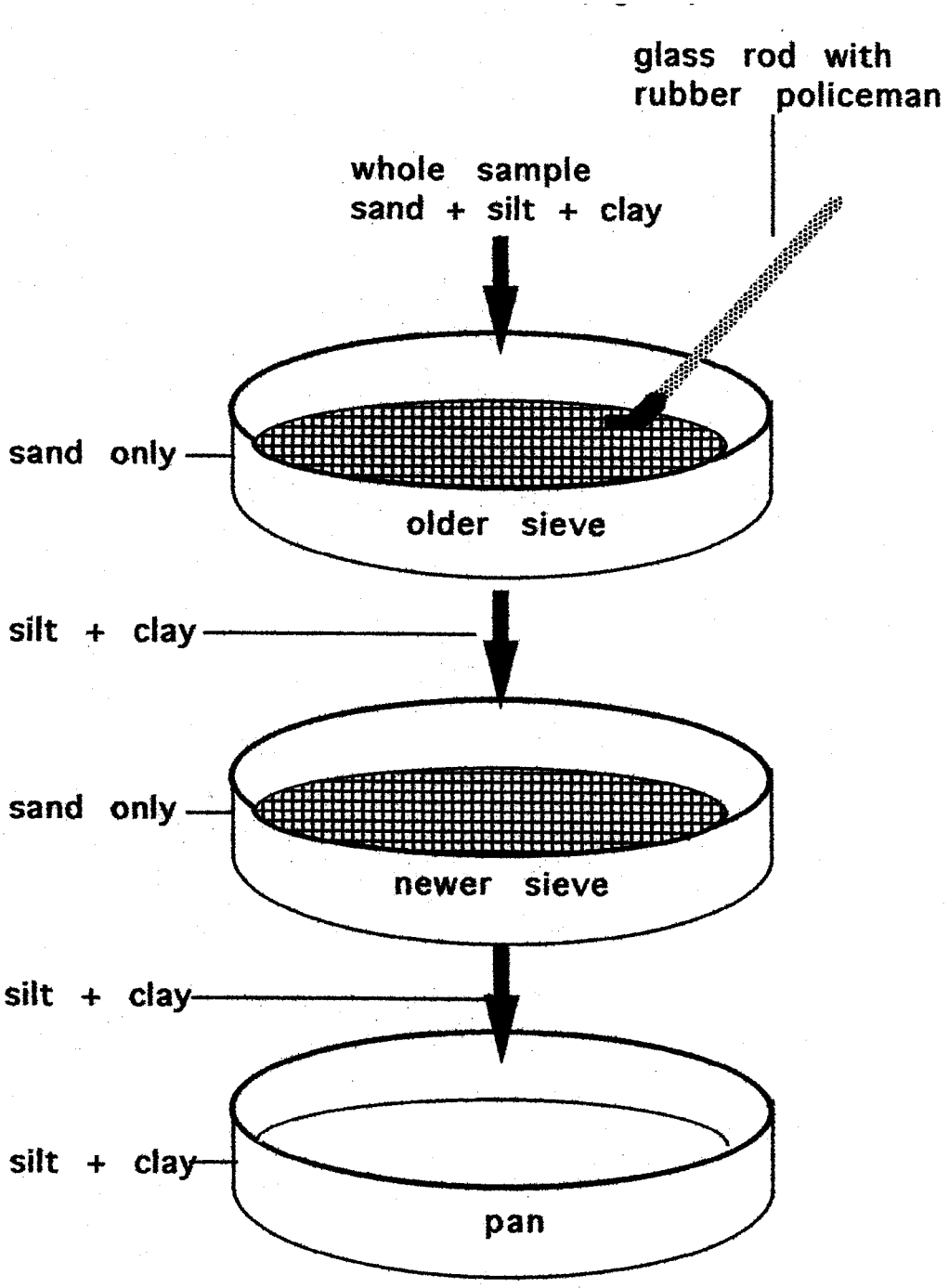

Fig. 2. 1. Sieve arrangement and locations of size fractions.

worn sieve is placed on top so that further disaggregation can be performed, if necessary, by rubbing the sample on the screen with a rubber policeman. A newer sieve is positioned Wow the older and is never rubbed with the rubber policeman. This arrangement allows additional mechanical disaggregation of the sample on the old sieve while maintaining the precision calibration of the screen on the newer sieve. Sieving can be performed manually by placing the sieves into a pan and alternating between rubbing the sample on the top sieve and washing the disaggregated particles through the sieves with distilled water. The process is complete when essentially only clear water passes through the sieves.

The preferred method of wet sieving is to put sieves on the sieve shaker designed for wet sieving operations and shake for a minimum of 5 minutes. While the machine is operating, the lab worker should alternate between washing the sample through the sieves with distilled water via the water inlet tubing and removing the suspension by applying a vacuum to the tubulated flask connected to the water outlet hose. A hand-operated-bildge pump is usually adequate for this purpose. The vigorous shaking of the machine is often enough to finish disaggregating samples, but for difficult samples, it may be necessary to rub the sample on the top sieve to break it up further. Then, proceed with shaking until at least 5 min of shaking has elapsed or sample is thoroughly sieved, whichever is longer. The sample is considered to be finished when the suspension passing through the clear outlet tubing is clear.

7. After the sieving process is complete, transfer the >63 um fraction from the two sieves into the previously weighed and labeled beaker (Stop 1).

8. Transfer the <63 um fraction from the tubulated flask (or pan ff doing particle size manually) into the I 000 ml beaker. If I 000 ml has been exceeded, the volume of liquid must be reduced by centrifugation (the preferred method) or by adjusting the calculation to reflect the larger

volume of liquid. (Note: keep in mind that if more than one volume measurement is made to get total volume, the maximum possible error becomes the sum of each individual measurement's error. For example, if two beakers are used to measure the total volume, the maximum possible error of each beaker, 5 wt %, adds to 10 wt % for the combined measurement.)

9. Before taking a volume measurement, thoroughly mix and check for flocculation. It appears as a graininess of the suspension or as a uniform distribution of irregular particles that swirl around within the suspension (they even move in the upward direction, This would not occur with particles that are not floccules). If no flocculation is detected, fill beaker to 1000 ml or other appropriate mark (if the calculation is to be adjusted). If flocculation has occurred, add 10 ml of dispersant. Sodium hexametaphosphate (Calgon®) in a solution of 50gm/l of distilled water is commonly used. Mix and check for flocculation again. If flocculation persists try another 10ml. If flocculation persists or it the worker is uncertain about its occurrence, go to the next section of this chapter, Special Procedures, that covers flocculation problems.

10. If flocculation is not or is no longer a problem, fill beaker to 1000ml, or appropriate mark, mix thoroughly and allow suspension to stand for 30min.

11. Using a pipette, extract 40 ml of the suspension in the 1000ml beaker from just below the surface (the tip of the pipette is not submerged more than 0.5cm in depth). Place the suspension from the pipette into the previously weighed and labeled 100ml beaker (Step 1) and heat to dryness in a 105°C oven. The depth of the clay and clay-silt suspension interface below the surface of the suspension after 30 minutes is as follows:

Temp. °C	Depth in cm*
16	0.53
20	0.59
24	0.65
28	0.71
32	0.77

*-for e.s.d. particles of 2 cm for the longest dimension and specific gravity of 2.50

12. Remove beakers with sample fractions from oven, cool in desiccator, weigh, and record data on data sheet.

13. Perform calculations on data sheet for both A and B runs of sample. If A and B are within 211/o of each other for the sand, sift, and clay fractions, report results. If not, perform a third trial, C, and I necessary a fourth, 0, until a pair of trials are within 20/.*. If after the fourth trial none are within 20/o but the results are reasonably close (i. a. within 5% and the sand, silt, and clay values show the same trend for each trial) report results: they will be averaged. If the results are erratic, consider making some reasonable changes to this procedure to mitigate the problem, or perhaps it is impractical to perform a particle-size analysis on the particular sample.

SPECIAL PROCEDURES

This section contains additional information and suggestions for dealing with difficult samples and special requirements. This information either modifies or adds to the standard procedure in the preceding section. This section, along with the standard procedure, provides adequate

directions for performing successful particle-size analyses on the majority of samples encountered. On occasion, samples will be encountered for which the information in this manual will be inadequate. It is then up to the lab workers to use other resources (personnel, material, and informational on and off campus) to find a solution to the difficulty encountered.

PARTICLE-SIZE ANALYSES IN WHICH TRACE ELEMENT ANALYSIS WILL BE PERFORMED ON ONE OR MORE OF THE SIZE FRACTIONS

This situation is a continuation of the special procedures outlined in Chapter 1: Basic Procedures and Sample Preparation. The concern is still elemental contamination and the elements being analyzed for define what is considered a contaminant. After following the special procedures for sample preparation in Chapter 1, the lab worker must consider the particle-size apparatus being used and eliminate, where possible, all components that can be a source of contamination. It should be kept in mind that sieves and sieve accessories are commonly made of brass, an alloy of copper and zinc. Additionally, the screens are soldered in place. Solder is an alloy of lead and tin. Stainless-steel sieves are available but are very costly and their screens may also be soldered in place. It is not known how significant a source of contamination the sieves and accessories may be for copper, zinc, tin, and lead. A certain source of copper and zinc contamination is the brass-bilge pump attached to the top of the tubulated flask used with the sieve shaking machine. Occasionally it sucks small amounts of water into its pump chamber and then occasionally drips a dark liquid back into the tubulated flask. A remedy for this is to attach the pump with a longer line that includes a liquid trap. These are just a couple examples of potential sources of contamination. It is up to the lab worker to look for and eliminate any potential sources of contamination that may be applicable to the trace element(s) analyses being made.

SAMPLES THAT PERSISTENTLY FLOCCULATE

Flocculation in most samples is remedied by adding sodium hexametaphosphate as described in the Standard Procedure. However, some samples will require more extensive attention. If sodium hexametaphosphate does not work, then wash the sample using 250ml centrifuge bottles and the super-speed centrifuge set at 10,000 rpm for 5min. Resuspend the sample with distilled water (pour into a glass beaker if necessary to see better) and check for flocculation. Repeat this washing up to 4 times. If flocculation persists then try other dispersants such as ammonium hydroxide (especially useful for samples with high concentrations of kaolinite) or other phosphates (Head, 1980). For a brief discussion on flocculation and dispersants, read Moore and Reynolds, 1989 p. 187-188. Another method of controlling flocculation is to decrease the concentration of the suspension by adding distilled water (i.e. increase volume from 1000ml to 2000ml).

If it is difficult to determine if flocculation is occurring, try looking at the sample through the side of the glass beaker with a 10X hand lens in strong light. Another way is to treat one sample run (A) by washing and with dispersants and comparing it with the untreated sample run (B) after stirring and allowing to settle for 30 minutes.

These methods can be very time consuming, however a large majority of samples with flocculation problems can be effectively dealt with by these means.

WELL-INDURATED AND/OR CARBONATE CEMENTED SAMPLES

Well-indurated sandstones, and especially siltstone-s, can be nearly impossible to analyze for particle size by the standard procedure alone. This is because the amount of mechanical disaggregation required to free the primary particles is excessive and can result in the destruction of those primary grains.

Additionally, a large amount of time can be spent wet grinding with the mortar and pestle, as well as rubbing on the sieve screen. Further, in the case of siltstone when grinding and rubbing is finished, one is often not sure that the sample is broken into its primary particles or just to small enough aggregates to fit through the sieve opening.

A modified EDTA leaching procedure is very helpful in these situations. First, prepare sample as for standard particle size, but only use about 12 to 15 gm. Further crush sample in mortar until no pieces are larger than 114in. in diameter in the longest direction. Perform EDTA leaching procedure as in next chapter, except do not grind and pass through 70-mesh sieve. It is advisable to use magnetic stirrers during leaching to further break up sample and to prevent the beaker from bumping. After leaching is done, perform a particle-size analysis by the standard procedure on the insoluble residue.

CHEMICALLY-TREATEID SAMPLES

Samples that are extremely hydrophobic may have been treated with commercial sealers or other compounds. It would be advisable to find out what was used to treat the sample in order to decide on possible solvents to remove the chemical in question. Some solvents used in the Clay Lab are alcohols, acetone, and carbon tetrachloride. Many organic solvents volatilize readily and produce toxic fumes; therefore, treatment of samples in these solvents should be done under a fume hood. It may also be useful to get suggestions from the Chemistry Lab before preceding.

SAMPLES THAT CONTAIN SULFUR

If a sample contains enough sulfur to produce an odor, flocculation problems are almost certain. Repeated washing in distilled water using the centrifuge has solved this problem for some samples, while others have

defied every attempt. Additionally, when adding dispersant (either sodium hexametaphosphate or ammonium hydroxide) a dark precipitate may form in a number of these samples. When precipitation occurres, the samples may never be cured of flocculation.

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Chapter 3: Leaching Analyses

Three different leaching analyses are performed in the Clay Lab. These are EDTA (ethylenedinitrilotatraacetic acid tetrasodium salt), HCI (hydrochloric acid), and NAOCI (sodium hypochlorite). The objective of all three is to remove, in solution and as a gaseous phase, certain groups of materials and to leave the remainder behind as an insoluble residue. The relative weight percents of the soluble and insoluble portions are calculated and reported. This chapter will present the theory and the standard procedures for each different leaching analysis.

THEORY

EDTA

EDTA leaching is the preferred method for determining the relative weight percents of insoluble and soluble materials in a sample as well as separating clays and other silicates from carbonate rocks. This is because EDTA causes less undesirable damage and alteration to some of the silicate phases when compared to conventional-acid-dissolution techniques (Bodine and Fernalid, 1973).

EDTA is a chelating or complexing agent that forms multiple-covalent bonds with the alkaline-earth-metal cations as well as transition-metal cations. When the metal cations complex with the EDTA, their concentrations in the aqueous solution decrease resulting in further dissolution of the carbonate and/or sulfate minerals. Carbonate and sulfate minerals are preferentially dissolved because of their higher solubilities in water than silicates. For this reason, silicates and other highly insoluble minerals will be little affected by the EDTA and will be left behind as insoluble residue.

The standard volume (100 ml) of 0.25 M EDTA boiling for 4 hr was found, experimentally, to dissolve the following amounts of carbonate and sulfate minerals (Bodine and Fernaild, 1973):

Gypsum	4.3 g
Anhydrite	3.4 g
Calcite	2.3 g
Dolomite	2.1 g
Magnesite	1.9 g
Apatite	0.1 g

These dissolution amounts are the basis for the Clay Lab's EDTA leaching procedure.

HCl

HCl can also be used to leach carbonates and sulfates, but it can damage and/or alter other phases. Because HCl creates a strong ionic reaction, it can react with minerals that are otherwise highly insoluble in aqueous solutions.

HCI leaching is included here because of its low cost. It should be used with samples that have high concentrations of carbonates and/or sulfates for which the standard volume of EDTA (100ml) is inadequate to completely leach the sample. This is discussed further in the standard procedure section.

The standard volume and concentration of HCl used in the Clay Lab to finish an incomplete EDTA leach analysis is 100ml of 1.0 M. Experiments performed in the Clay Lab have shown that 100ml of 1 M HCl will dissolve 4.5 gm of calcite. 1.0 M HCl is also used for other carbonate and sulfate minerals dissolution; however, experiments using these other mineral phases have not been run in the Clay Lab. A further literature search and/or experiments would be useful to establish the dissolution amounts for these other minerals.

NAOCl

NAOCl leaching is used to remove organic materials when they exist in quantities large enough to interfere with XRD (x-ray diffraction) patterns or particle- size-analysis results. NAOCl is a strong oxidizing agent and removes organics by converting organic molecules to gaseous and soluble forms. It can also alter clay minerals by oxidizing ferrous iron in octahedral sites (Moore and Reynolds, 1989) and may affect other minerals as well. For this reason, it should be used only if considered necessary; however, it has been shown that this method, while altering XRD peak positions somewhat, has little affect on relative peak heights for samples containing a mixture of illite, smectite, mixed-layered illite/smectite, and kaolinite. For these treated samples, there is virtually no difference in the results reported using the New Mexico Bureau of Mines and Mineral Resource's semiquantitative clay minerals analysis technique when compared to untreated samples (Hall, unpublished).

This technique, like the H_2O_2 (hydrogen peroxide) technique (Head, 1980), could also be used for determining organic content. It would be a good idea to run experiments comparing the two reagents to demonstrate that similar results are obtained.

The standard concentration used is 5 % to 6 % NAOCl (common household bleach); however, the volume used varies depending on the amount of organics in the sample. It is not known what amount of organics is removed for a given volume of NAOCl solution used; therefore, completion is based on a color change of the sample.

STANDARD PROCEDURES

EDTA

1. If necessary, prepare a 0.25M EDTA solution with a pH of 10 to 12. Weigh out 104.0 gm of EDTA (ethylonedinitrilotetraacetic acid tetrasodium salt) powder. Mix powder in a graduated container with about 900ml of distilled water. A hot plate with a magnetic stirrer works best. Heat and stir until powder is dissolved and solution is clear. Add distilled water until solution volume is 1000 ml. If you used the tetrasodium salt of EDTA named above, the pH will be between 10 to 12 and no other adjustments will be necessary.

2. Split the sample as described in Chapter 1, but only keep one 25 to 30gm split.

3. Grind the split in a mortar and pass through a 70-mesh sieve.

   Any sample that does not pass through the sieve should be returned to the mortar for further grinding. Repeat the sieving and grinding until entire sample is passed through the sieve.

4. Thoroughly mix ground sample, and split once more. Place one split into a small 1 oz bottle (it can be used later for bulk-mineral analysis and/or third and fourth leach runs if necessary). The remaining split will be passed through the Jones splitter once more and the resulting splits will be placed in two properly labeled and pre-weighed 100 ml beakers (one beaker is the A run and the other is the B run). Dry, cool, and weigh beakers with samples as described in Chapter 1. Record weights on leach data sheets.

5. Pour samples from beakers into two properly labeled erlenmeyer flasks. Add 4 glass beads and 1 00 mi of EDTA solution to each.

6. Place flasks on hot plates and connect condensers to their tops (Fig. 3.1). Turn on the water, at a modest volume, to the condensers (make sure water is flowing through all condensers). Turn hot plates on high (do not leave unattended) until boiling starts. Reduce hot plate setting to maintain moderate boiling. Check condenser; condensation should stop

about half -way up the condenser. If not, adjust water accordingly

7. After the sample has boiled for 4 hr, turn off the hot plates and water and allow flasks to cool.

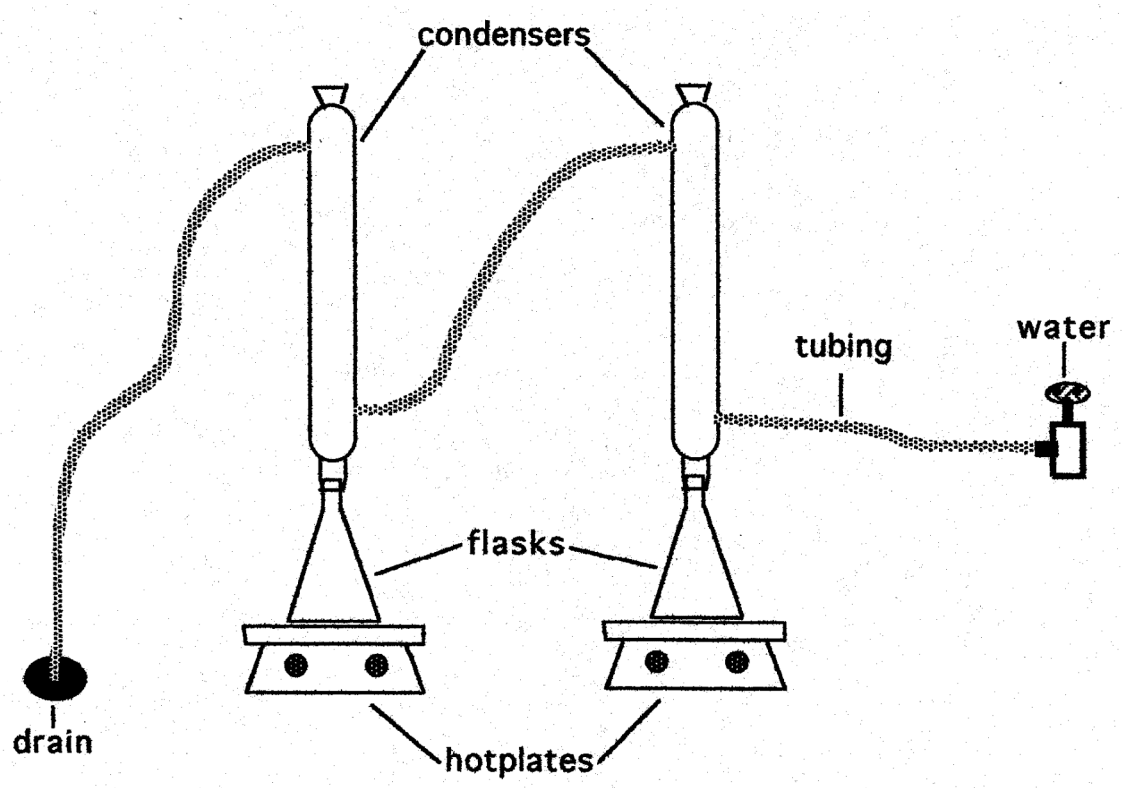

Fig. 3.1 Leaching apparatus.

8. Wash sample 3 times: First, pour the sample into centrifuge tubes. Balance centrifuge tubes to within 0.1 gm. Centrifuge for 5 min at maximum speed in small centrifuge or 5,000 rpm in super-speed centrifuge. Pour off supernatant (clear or nearly clear liquid above solid sample) and resuspend sample by adding distilled water and stirring. Recentrifuge and pour off supernatant as described above. Again fill centrifuge tubes with distilled water, resuspend sample, balance, centrifuge, and pour off supernatant.

9. Recover sample, both A and B runs, into their appropriate pre-weighed and labeled beakers. Dry samples in I 05'D 0 oven, cool in desiccator, weigh, record weights on leach data sheets, and calculate results. If the amount of insoluble residue is <80%, the EDTA may not have been in excess and the leaching may not be complete. Therefore, go to the HCI leaching procedure in the next section. If the amount of insoluble residue is >80 %, then report results. The results should be within 2%. If not, perform a third and if necessary a fourth run until a pair are within 211/a. Unlike particle-size analysis, there is no reason why a reproducibility within 211/o can not be achieved; therefore, if results are erratic, recheck technique and be sure no sample is being lost in any of the steps.

HCl

1. Pour about 50ml of 1.0 M HCl into the beaker with insoluble residue from EDTA leach. If the sample effervesces, this is a sure indication that the EDTA leaching was incomplete. Wait until effervescence slows and pour in the remainder of 100ml of 1.0 M HCI.

2. When effervescence slows again, place beakers in a boiling-water bath for about I hr (Fig 3.2). Make sure the reaction does not precede too rapidly, as sample loss may occur.

3. After I hr, turn off the hot plate and allow beakers to cool.

4. Wash sample 3 times: First, pour the sample into centrifuge tubes. Balance centrifuge tubes to within 0.1 gm. Centrifuge for 5 min at maximum speed in small centrifuge or 5,000 rpm in super-speed centrifuge. Pour off supernatant (clear or nearly clear liquid above solid sample) and resuspend sample by adding distilled water and stirring.

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Recentrifuge and pour off supernatant as described above. Again fill centrifuge tubes with distilled water, resuspend sample, balance, centrifuge, and pour off supernatant.

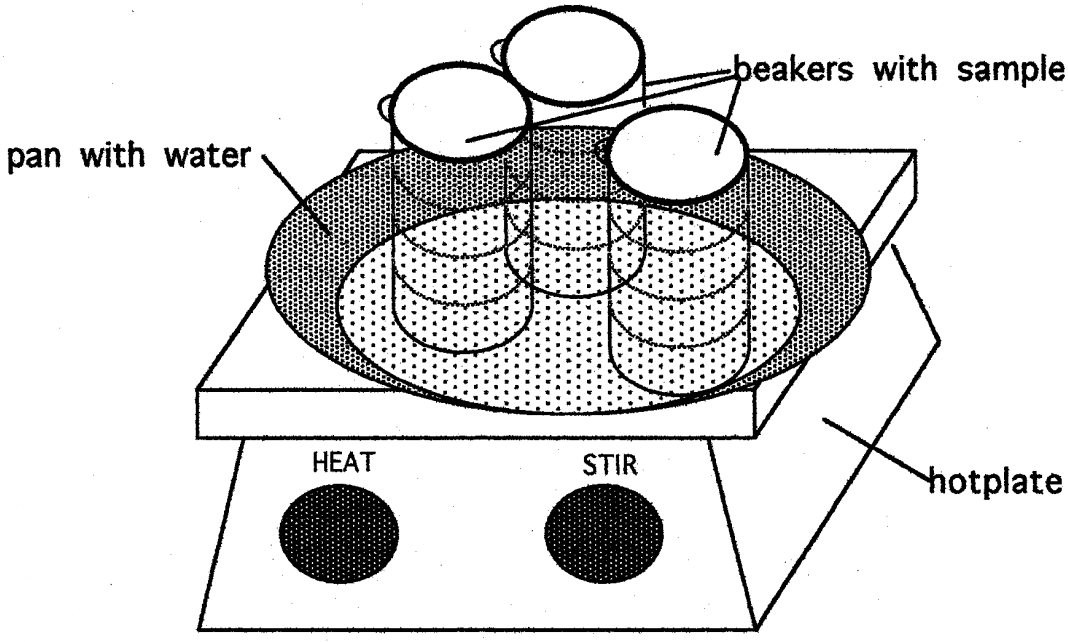

Fig. 3.2. Boiling-water bath.

5. Recover sample, both A and B runs, into their appropriate pre-weighed and labeled beakers. Dry samples in 10510 0 oven, cool in desiccator, weigh, record weights on another set of leach data sheets, and calculate results. The results should be within 4%. If not, perform a third and if necessary a fourth run until a pair are within 410/o. Note: A reproducibility of within 4% was chosen because the amount of handling the sample is subjected to is doubled when this procedure is added to the previous EDTA leaching procedure.

Additionally, this procedure may be scaled up and used for samples with known high carbonate and/or sulfate contents without performing the EDTA leach first. It may also be scaled up and used where larger volumes of carbonate or sulfate materials must be leached prior to particle-size analysis.

NAOCl

1 Use household bleach for the NAOCl solution. Adjust to pH 9.5 with HCl just prior to treatment.

2. For each 10gm of sample being leached, pour 50ml of NAOCl into the beaker containing the sample.

3. Place beakers in a boiling-water bath for about 15 min (Fig. 3.2).

4. After 15 min, turn off the hot plate and allow the beakers to cool.

5. Wash sample and check for completeness of leaching: Pour the sample into centrifuge tubes. Balance centrifuge tubes to within 0.1 gm. Centrifuge for 5 min at maximum speed in small centrifuge or 5,000 rpm in super-speed centrifuge. Pour off supernatant (clear or nearly clear liquid above solid sample). Repeat steps 2 through 5 until organic material is removed as evidenced by a change in sample color to white, gray, or red (Moore and Reynolds, 1989). When color change occurs, precede to step 6.

6. Wash sample: Centrifuge for 5 min and pour off supernatant as described above. Resuspend sample by adding distilled water and stirring. Recentrifuge and pour off supernatant. At this point, the sample should have been washed 3 times after the last leaching.

6. Recover sample into a labeled beaker. Dry samples in 105°C oven and cool in desiccator. If data on the amount of organics is desired then weigh, record weight on a leach data sheet, and calculate result.

Because this technique, for determining the amount of organics in a sample, has not been adequately verified in the Clay Lab, no reproducibility error has been established. Therefore, the sample does not need to be run in duplicate and any data collected should be considered only a rough estimate of organic content. If data on the amount of organics is not desired, simply use the leached material as the input to a particle-size analysis or an x-ray analysis.

Chapter 4: Clay-Mineral Analysis

Clay-mineral analysis at the New Mexico Bureau of Mines and Mineral Resource's Clay Lab is intended to identify the major clay-mineral groups and give a semiquantitative indication of the relative amounts of the illite, smectite, kaolinite, I/S (mixed-layered illite/smectite), and chlorite groups. In some cases, where characteristic XRD (x-ray diffraction) patterns are produced, more specific identifications of particular species can be made. This chapter will cover the theory necessary to interpret XRD patterns and the procedure for identifying and estimating the amounts of the clay-mineral groups illite, smectite, kaolinite, I/S, and chlorite.

THEORY

In order to interpret XRD patterns of clay minerals, the lab worker must have an understanding of the structure of clay minerals and the nature of XRD. This section will look at both of these topics in a rudimentary fashion. Additionally, the theories behind making oriented-clay slides will also be discussed.

CLAY-MINERAL STRUCTURE

Clay minerals are hydrous-aluminum silicates and are classified as phyilosilicates, or layered silicates. Most have in common a plate-like morphology and perfect (001) cleavage (Moore and Reynolds, 1 989). The (00 l) is one of the (hk l) or Miller indices that defines the orientation of an internal crystal plane. In this case, the (001) represents the plane perpendicular to the c-axis in which clay-mineral layers often stack (Fig.4.1). For a further explanation of this system, consult an introductory mineralogy text.

The clay-mineral layers that form the stack in Fig. 4.1 can be further

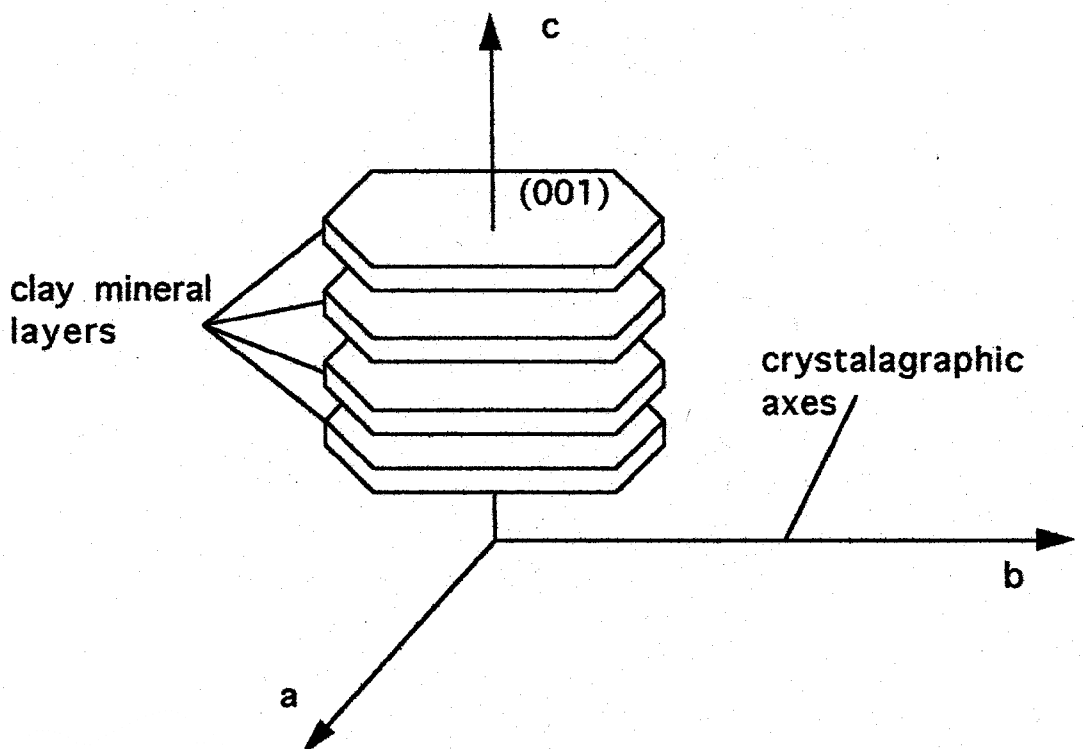

Fig. 4.l. Clay mineral layers on crystallographic axes.

broken down into tetrahedral sheets (corner-linked tetrahedra of Si^{4+} or Al^{3+} with attached oxygens) and octahedral sheets (edge-linked octahedra of $A1^{3+}$, Mg^{2+}, Fe^{2+}, Fe^{3+}, or less commonly, other transition elements with attached oxygen). The octahedral sheet can have two types of structure; trioctahedral containing 3 Mg^{2+} cations and having a cation-to-anion ratio of 1:2 (brucite-like) or dioctahedral containing 2 $A1^{3+}$ cations and having a cation-to-anion ratio of 1:3 (gibbsit8-like) (Moore and Reynolds, 1989).

The tetrahedral and octahedral sheets are joined together in an alternating fashion to form the layers illustrated in Fig. 4. 1. These layers are of two types. The first has one tetrahedral sheet (T) joined to an octahedral sheet (O) and is called a 1:1 layer-silicate structure.

The second type has two tetrahedral sheets with an octahedral sheet in between (Fig. 4.2) and is called a 2:1 -layer-silicate structure (Moore and Reynolds, 1989). The 1:1-layer-silicate structure most often corresponds to the kaolin- group-clay minerals (Al-rich) which are identified as kaolinite in the Clay Lab. It also corresponds to serpentine (Mg-rich) which is not a clay minerals and is not identified as such in the Clay Lab. The most basic 2:1 -layer-silicate structure corresponds to the minerals pyrophyllite (Al-rich) and talc (Mg-rich) which are not clay minerals and are not identified as such in the Clay Lab (Fig 4.2).

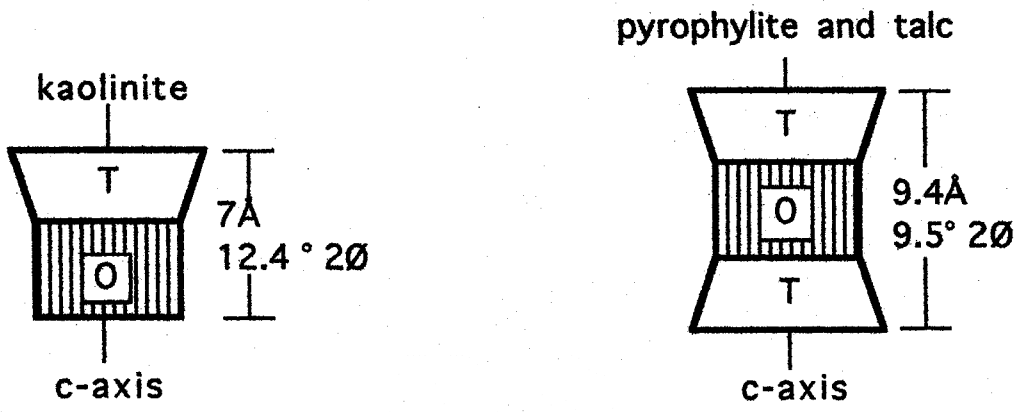

Fig. 4.2. The 1:1- and 2:1-layer-silicate structures of kaolinite, pyrophyilite, and talc with c-axis and d-spacing.

The 2:1-layer-silicate structure clay minerals are illite, glauconite, vermiculite and smectite; chlorite will be dealt with later. Illite, glauconite, vermiculite and smectite have interlayer cations. Vermiculite and smectite can also accommodate varying amounts of water into their interlayer spaces (Fig. 4.3 a & b). It can be seen that several different combinations of d-spacings can be obtained for these hydratable minerals.

The differences between these 2:1-layer-silicate structure clay minerals is the result of different layer charges that are caused by substitutions in the tetrahedral and octahedral sheets. Illite has a layer charge of x ≈ 0.6, vermiculite x ≈ 0.6 to 0.9, intermediate between illite and smectite, and smectite x < 0.6. The lower the layer charge, the more readily the clay mineral will accommodate water into its interlayer space, whereas, higher-layer-charge minerals accommodate more cations in the interlayer space (Moore and Reynolds, 1989).

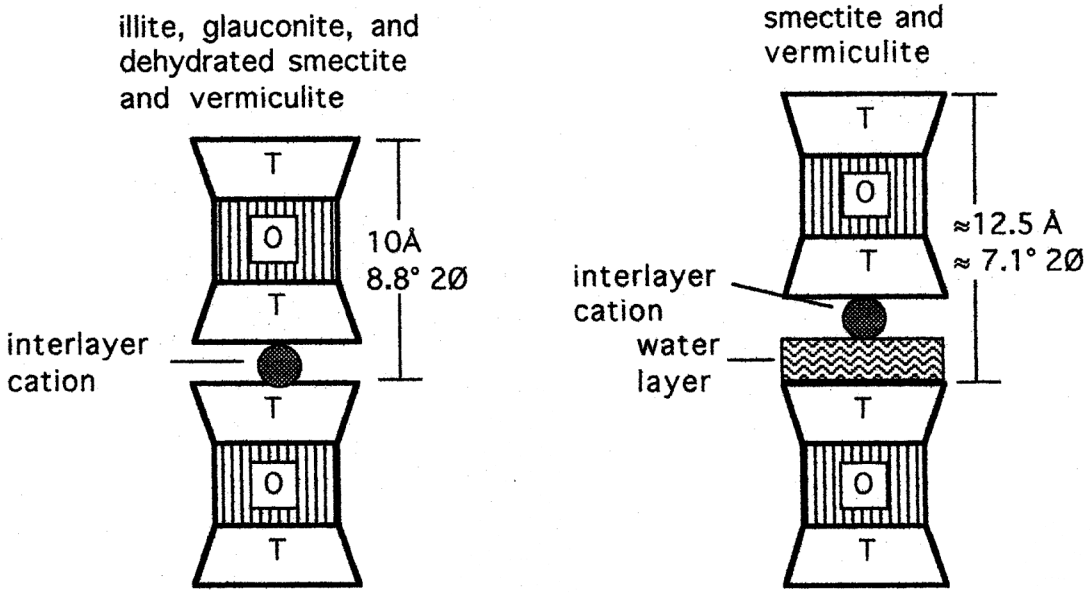

Fig. 4.3 a. Illite, vermiculite, and smectite structures.

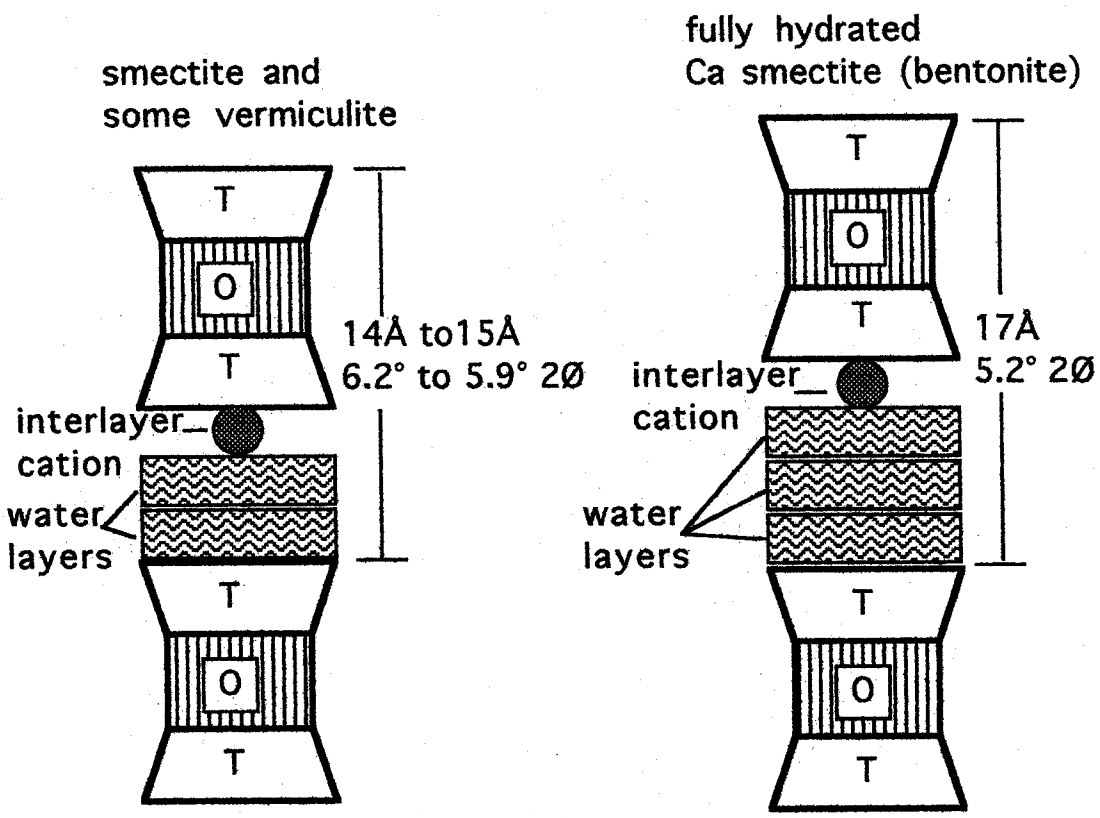

Fig. 4.3 b. vermiculite, and smectite structures.

Chlorite can be considered a 2:1-layer-silicate structure with a positively- charged-octahedral sheet instead of a cation (Fig. 4.4), This results in a d-spacing of 14 Å. The structure, like that of illite, will not accommodate water in its interlayer.

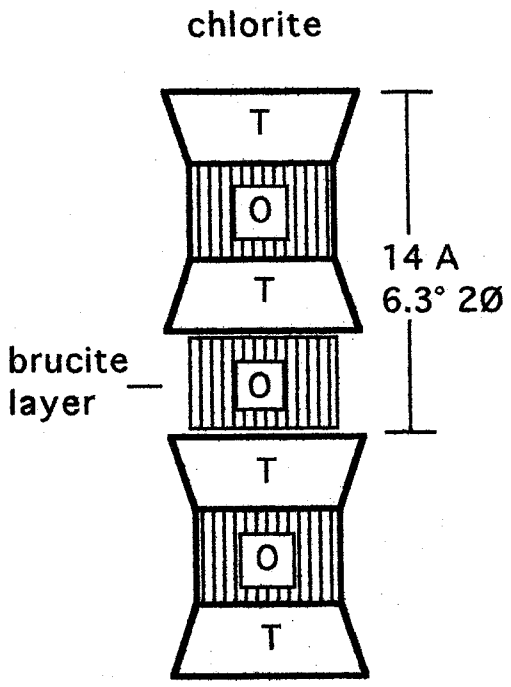

Fig. 4.4. Chlorits structure.

Mixed-layered-clay minerals are clay minerals formed of two or more types of clay layers, however, mixtures of more than two components are quite rare (Moore and Reynolds, 1989). Of all the possible types, US is the most common and is found in the majority of samples analyzed in the Clay Lab. Corrensite, an ordered chlorite/smectite, has also been seen on occasion.

The layers are stacked along the c-axis or perpendicular to (00,0. They can be arranged in an ordered, partially ordered, or random sequence (Fig. 4.5). This interlayering results in clay particles with larger d-spacings that depend on the ordering arrangement (s) of the two different types of clay layers.

In the case of the ordered-mixed-layered-clay minerals, the effective d-spacing, for this particular ordering pattern, becomes the sum of the illite and smectite d-spacings or 20A to 27A, depending on the hydration state of the smectite.

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For random-mixed-layered-clay minerals this is not the case, because no one ordering scheme is followed.

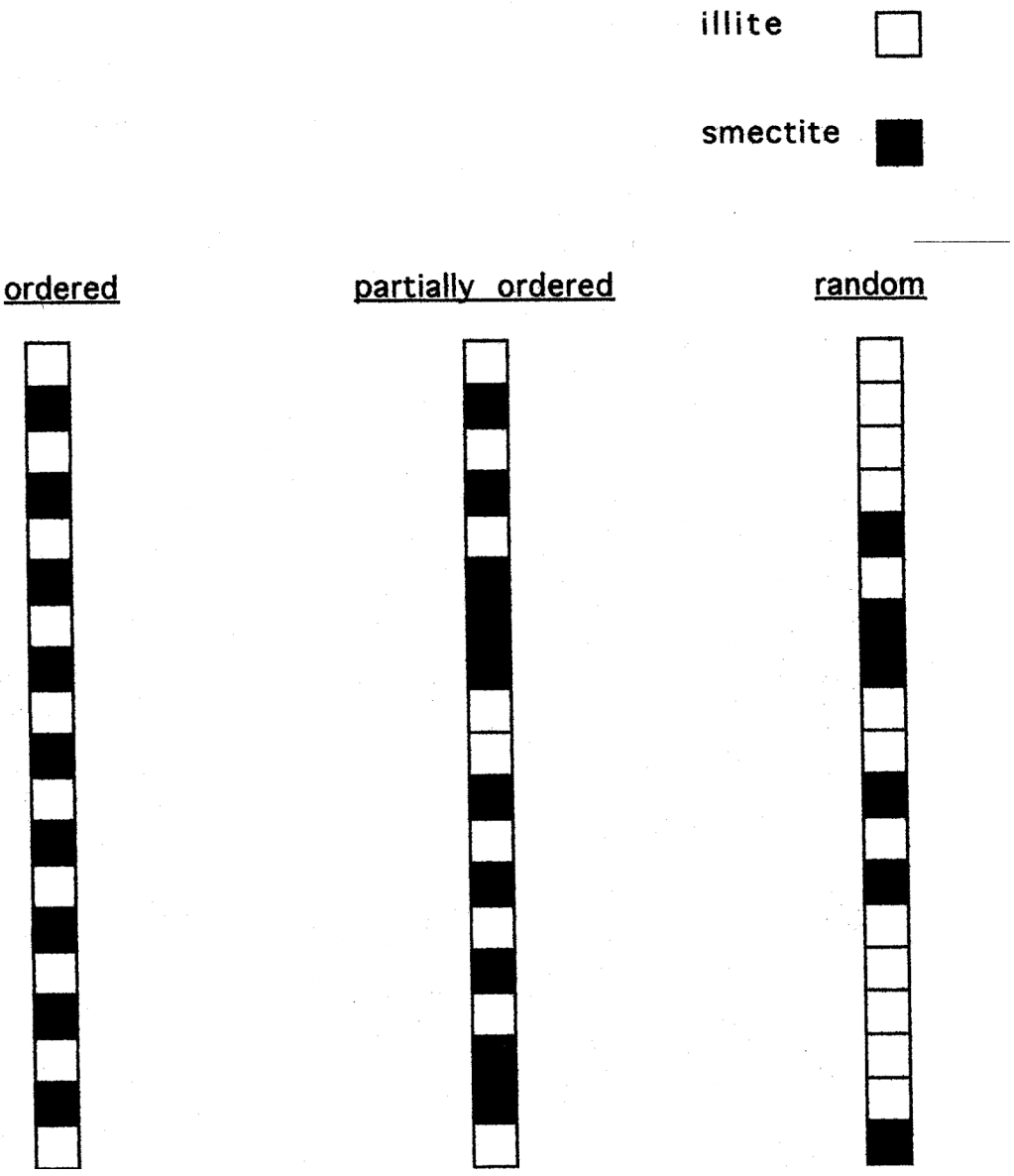

Fig. 4.5. Ordering of mixed-layered-clay minerals.

X-RAY DIFFRACTION THEORY

Diffraction of x-rays is usually referred to as reflection. This is probably because the angle of reflection or diffraction is equal to the angle of incidence. Diffraction of x-rays is different than reflection of Visible light because it only occurs at specific angles as determined by the clay mineral's d-spacing and Bragg's Law whereas visible light is reflected at all angles. Also, unlike visible light, it is essential that the distance between scattering centers be about the same as the wavelength of the x-rays being scattered (Moore and Reynolds, 1989).

When scattering centers (atoms) interact with incident x-rays, they reradiate in all directions at the same wavelength of the incident beam. Wherever many of these reradiated wavelengths are in phase, and therefore constructively interfering, diffracted or reflected beams will result. Consider Fig. 4.6, in which incident rays 1, 2,3, and 4 interact with 4 scattering centers to produce reflected rays 1', 2', 3', and 4'. The scattering centers (black dots) are located on internal crystal planes (heavy lines) that are spaced a distance (d) apart: this is the d-spacing of the clay mineral's unit cell along the c-axis. The angle of incidence is ∅ and is equal to ∅' in all cases. If rays 1, 2, 3, and 4 of the incident beam are in phase, X-X' represents a wavefront. It is easily seen that the paths traveled by rays 1 and 2 from X-X' to Y-Y' are of equal length; therefore, these rays will still be in phase at Y-Y' and will constructively interfere. This will occur for any angle of ∅. The paths for rays 3 and 4, that travel below the surface, are successively longer than rays 1 and 2 at the surface. If these paths are longer by a whole number multiple of the rays' wavelength, rays 3 and 4 will also be in phase with rays 1 and 2 leading to maximum constructive interference. When this occurs, a diffracted x-ray beam will be produced. Under what conditions does this occur? The reradiated wavelengths from the atoms making up the internal planes beneath the surface will all be in phase when Bragg's Law ($2d \sin\varnothing = n\lambda$) is satisfied.

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It can be seen from the formula that the angles (∅), where diffraction occurs, is a function of the d-spacing of the mineral and the wavelength of the X-rays that is dependent upon the equipment used, Chapter 4 of Moore and Reynolds (1989) provides a more rigorous geometrical explanation of XRD and derivation of Bragg's Law.

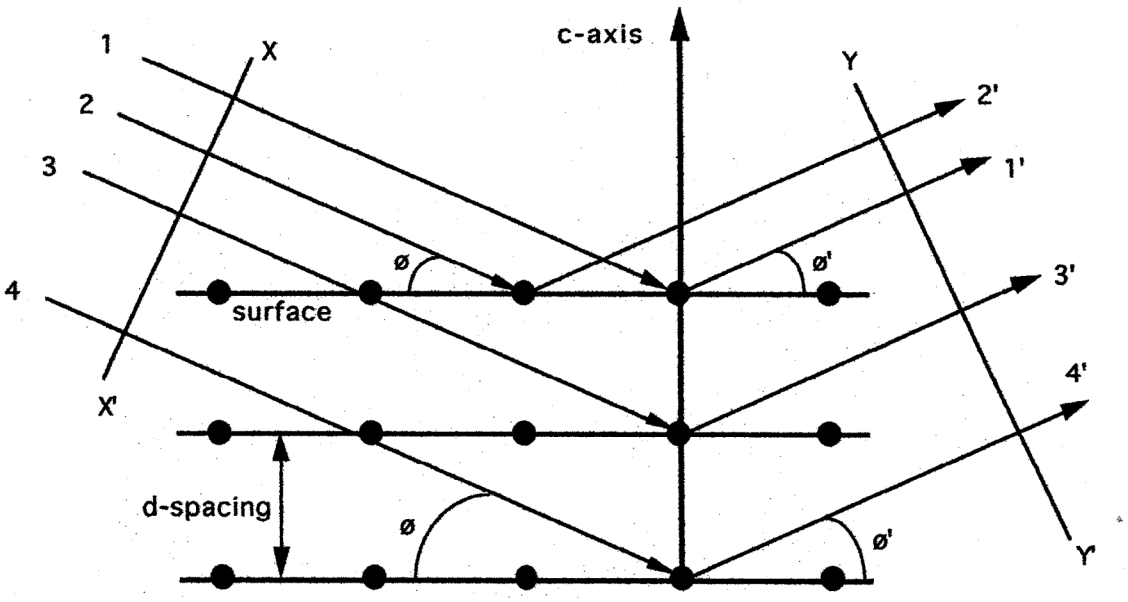

Fig. 4.6. Diffraction in multiple planes of scattering centers.

SEDIMENTATION IN MAKING SLIDES

Sedimentation theory in making slides is the same as in collecting a clay fraction in particle-size analysis (Chapter 2); however, some of the details are changed. The settling time is 10 min instead of 30 min because less material is required (usually about 4 ml for two slides). It must be kept in mind that the depth of the interface is less with a settling time of 10 min, therefore, it is very important that the suspension is drawn off the surface and that the tip of the pipette or eye dropper is not submerged more than about 2 mm.

The material, when placed on a slide, undergoes settling again. The plate-like clay particles settle in an oriented fashion with the c-axis perpendicular and (001) parallel to the surface of the slide. This orientation is important because it is the (001) that is diagnostic in the semiquantitative method and must be measured. Flocculation is the primary difficulty in obtaining this orientation because the clay particles agglomerate in a variety of orientations and then settle onto the slide. The elimination of flocculation will be discussed in the Standard Procedure Section.

STANDARD PROCEDURE

The Standard Procedure is divided into 3 parts: 1.) Making Slides; 2.) Running The Slides; 3.) Interpreting Diffractograms and Performing Semiquantitative Calculations. This is because each one of these parts is distinct and is completed before moving on to the next. Additionally, samples are usually run in batches of 3 to 10 in the Clay Lab.

MAKING SLIDES

1. Place about 20 gm of sample in a 100 ml beaker and fill with distilled water. Mix and wait 5 min. Remix, wait 15 sec, and pour suspension into a properly labeled beaker.
2. If clay flocculates (for description of flocculation, go to Chapter 9, p. 18), wash in centrifuge (for description of centrifugation, go to Chapter 3, p. 28) up to 5 times.
3. If flocculation still persists, remix and pour 1/2 of suspension into another beaker. Add a few drops of concentrated ammonium hydroxide (NH_4 OH) to one of the beakers and remix. If clay is still not dispersed, wash in centrifuge up to 3 times.

4. If clay still flocculates, Fill both beakers up to 100ml; remix the one treated with ammonium hydroxide, and check for flocculation. If it flocculates, add a few drops of sodium hexametaphosphate solution (Calgon®) to other beaker and mix. If flocculation persists wash in centrifuge up to 3 times.

5. If clay is still not dispersed and its concentration is still high enough, try further dilutions by pouring off suspension and adding more distilled water. If flocculation still persists go to the Curlers and Peelers/Flocculation Part in the Special Procedures Section of this chapter.

6. Once the clay is dispersed, remix and allow the beaker and its contents to stand for 10 min. Label two glass slides with the sample number and one as A and the other as B using a diamond stylus. At the end of 10 min touch the eye dropper or 2ml pipette to the surface and draw off enough material to cover a glass slide. It is desirable to make two slides of each sample at this time. Make the second slide (B) a bit thinner than the first in case the sample turns out to be a curler and peeler. Slides should be allowed to air dry. If clay flocculates on slide while drying (this rarely occurs), remake slide after washing sample several times using the centrifuge and distilled water. This is important because, as already discussed, flocculation destroys the preferred orientation of the clay particles.

RUNNING SLIDES ON THE XRD MACHINE

Four runs on the XRD machine are required for clay-mineral identification and to perform the semiquantitative determination of the amounts of these clay minerals. The basic instructions and parameters are contained in the following procedure, however, the specific instructions

for setting up and using the XRD machine, as well as generabng the appropriate diffractograms, are contained in the Talk® and Jade® programs' instruction manuals. The X-ray Lab Supervisor can also be of help if questions or problems arise.

1 The first (air-dried) run is carried out from 35° to 2° 2∅ at a scan rate of 2° 2∅ /min (set count rate to 1.0 and step size to 0.3 on Talk® program). An example of the desired diffractogram output is given below (Fig. 4.7). If chlorite is seen or suspected, carry out an additional run from 39° to 37° 2∅ to get the kaolinite 003 reflection. Additionally, do a slower run at 0.5° 2∅ /min from 26° to 24° 2∅. Save data to a MDI file.

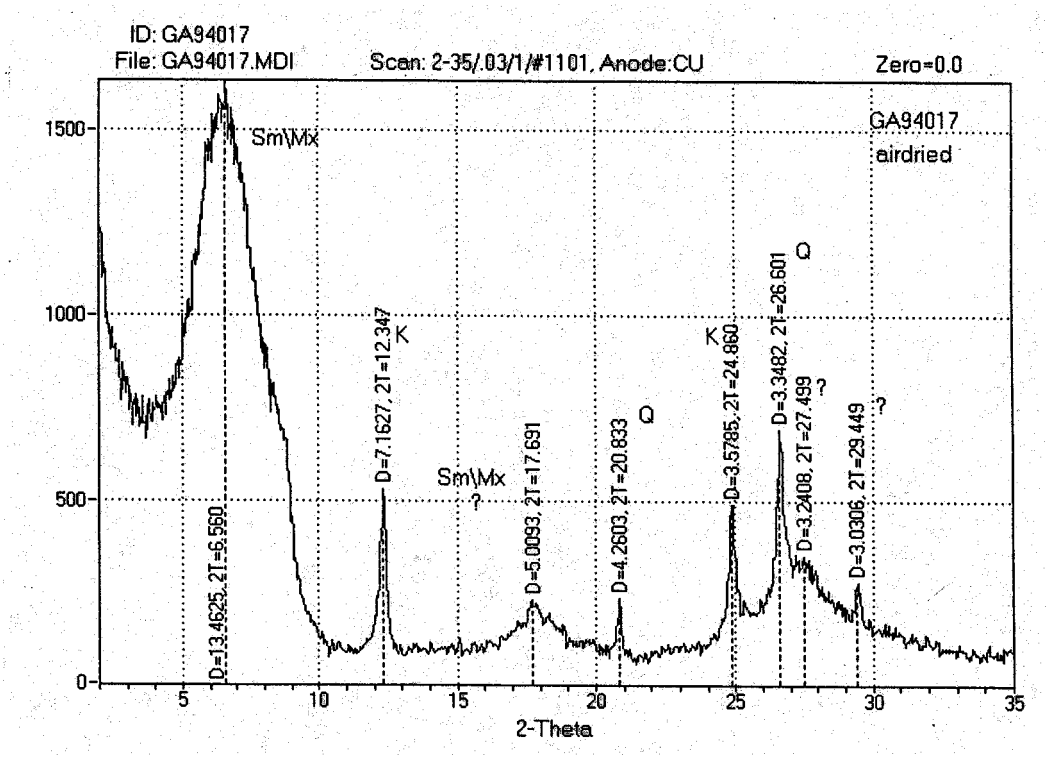

Fig. 4.7. Air-dried diffractogram.

2. The second (glycolated) run is carried out from 15° to 2° 2∅ at 2° 2∅/min. An example of the desired diffractogram output is given below (Fig. 4.8). To glycolate the slides, either place them in an ethylene glycol

chamber at ambient temperature for at least 24 hr (3 days may be necessary for thicker slides) or place in a heated (low setting on a hot plate) chamber for about 30 min. Save data to a MDI file.

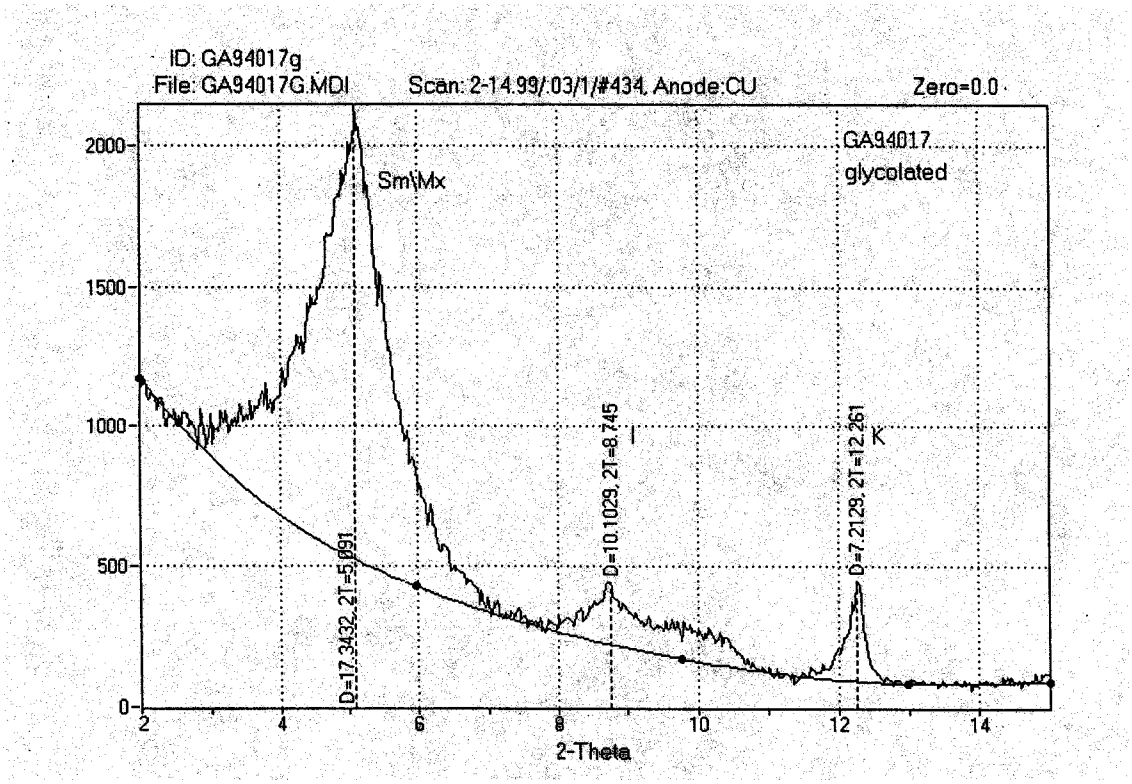

Fig. 4.8. Glycolated diffractogram.

3. The third and fourth (heated) runs are carried out successively An example of the desired diffractogram output is given below (Fig. 4.9). First, heat slides for 30 min at 375°C in a furnace. While hot, carry out run from 9.5° to 7.5° 2∅. Lastly, carry out run from 15° to 2° 2∅. These runs will be carried out successively with no operator intervention if programed into Talk® in the order given and followed by an undefined program. Save data to an MDI file.

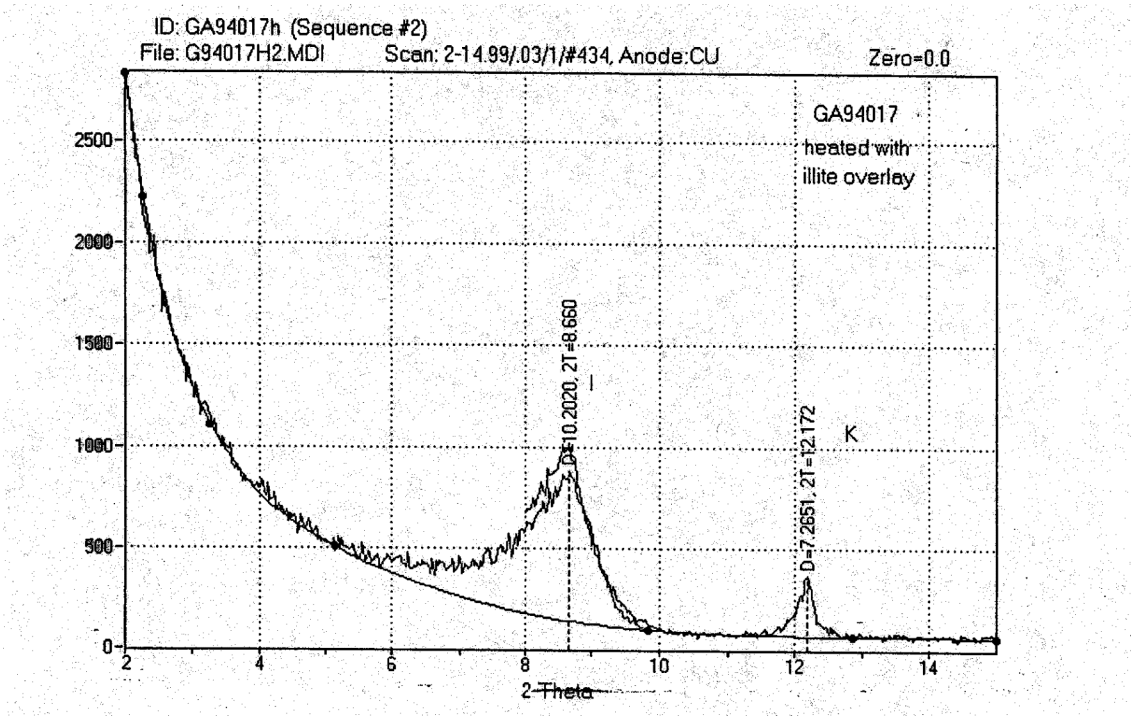

Fig. 4.9. Heated diffractogram.

4. Produce printouts using the appropriate MDI file and the Jade® program for runs 1, 2, and 4 (run 3 will be overlaid onto run 4). Be sure to include proper sample-number and mineral-identification labels as well as a designation of airdried, glycolated, or heated. A background curve should be included on the glycolated and heated runs. Also, lines further dividing the computer-generated divisions in halves, fourths, and possibly eighths is useful to measure counts later. Save diffractogram to a SAV file and print a hard copy of the three runs for calculations.

INTERPRETING DIFFRACTOGRAMS AND PERFORMING SEMIQUANTITATIVE CALCULATIONS

Diffractograms are interpreted by measuring the heights and positions of the peaks they contain. The peak position data are compared with the known positions of peaks for the five clay-mineral groups, The positions of the peaks are dependent upon the d-spacing of the unit cell in the c-axis direction and is related to the angle 20 by Bragg's Law as described in the theory section. The d-spacings are different for some of the clay-mineral groups, and behave in distinctly different ways for others, allowing for their identification. The peaks, that are observed, are of the first-order, 001 reflection, second-order, 002 reflection, third-order, 003 reflection, and fourth-order, 004 reflection. The first-order peak is an actual measurement of the minerals d- spacing and the rest are usually multiples of this first-order angle. The exception to this is the disordered or random-mixed-layered-clay minerals. For these, the peaks are broader and their positions lie at irregular intervals. Their positions are between the normal positions of the closest peaks of the constituent clay minerals: this is Mering's principle (Moore and Reynolds, 1989).

The heights of the peaks are a measurement of the diffracted x-ray beam's intensity and are taken to indicate the relative abundances of the different clay-mineral groups. It should be noted that the height, or intensity, of the diffracted-x-ray beam increases significantly at the lower angles (less than about 8° 2∅) due to polarization as described by the Lorentz-Polarization Factor (Moore and Reynolds, 1989). This is taken into account when performing the calculations for the semiquantitative method. (Note: Peak heights can no longer be compared directly from one run to another or between samples because of the autosealing feature of the Jade® program. It is now necessary to compare the count values whose scale is located on the vertical axis of the diffractogram.)

The semiquantitative method used at the New Mexico Bureau of Mines and Mineral resources indicates the presence and estimates the amounts of the clay mineral groups illite, smectite, kaolinite, chlorite, and I/S. The method does not differentiate between specific clay-mineral species and it does not distinguish vermiculite from other clay minerals.

1. Measure and record the following peak heights (counts on the vertical axis of the diffractogram) above the background line.

If chlorite is present:

Mineral	Order	Symbol*	Run	Position 2∅
kaolinite	1	K1	air dried	12.35°
illite	2	I2	air dried	17.6°
chlorite	3	C3	air dried	18.4° to 18.9°
kaolinite	2	K2	air dried	24.9°
chlorite	4	C4	air dried	25.1°
Smectite/mixed	1	S1g	glycolated	5.2°
illite	1	I1g	glycolated	8.8°
illite	1	I1h	heated	8.8°

*The Symbols (i.e. S1g) are interpreted as follows: The letter, in the first position, indicates the mineral type; the number, in the second position, is the peak order; and the letter, in the third position, indicates the particular run the peak comes from (airdried = no designation, g = glycolated, and h = heated).

It may be necessary to perform a slower run over the C4 chlorite peak to differentiate chlorite from kaolinite as previously described. Also compare the kaolinite peaks (K1) on the glycolated and heated runs, They should have about the same count values above background. If not, this may indicate a fluctuation in the XRO machine or degradation of the clay slide. If the difference is > 20%, compensate for any corresponding changes in the illite peaks between the glycolated and heated runs by applying the following correction, 1 h corrected = 1 h X (K1g/K1h).

If chlorite is not present:

Mineral	Order	Symbol	Run	Position 2∅
smectite/mixed	1	Slg	glycolated	5.2°
illite	1	I1g	glycolated	8.8°
kaolinits	1	K1	glycolated	12.35°
illite	1	I1h	heated	8.8°

Compare the kaolinite peaks (K1) on the glycolated and heated runs. They should have about the same count values above background. If not, this may indicate a fluctuation in the XRD machine or degradation of the clay slide. If the difference is > 20%, compensate for any corresponding changes in the illite peaks between the glycolated and heated runs by applying the following correction: I 1 h corrected = I 1 h X (K1 g/K1 h).

Plug the values obtained in step I into the following formulas where appropriate. Calculate the amounts of the clay-mineral groups and round off to the nearest part in 10. All of the clay- mineral group's amounts together should add 10 parts in 10.

With no chlorite present:

$$\text{Illite} = \frac{\text{I1g}}{\text{T}} \times 10$$

$$\text{Smectite} = \frac{\text{S1g/4}}{\text{T}} \times 10$$

$$\text{Mixed} - \text{layerI/S} = \frac{\text{I1h} - \text{I1g} - \text{S1g/4}}{\text{T}} \times 10$$

$$\text{Kaolinite} = \frac{\text{K1}}{\text{T}} \times 10$$

Where T is equal to "Total Counts"

$$\text{T} = \text{I1h} + \text{K1}$$

With chlorite present:

$$\text{Illite} = \frac{I1g}{T} \times 10$$

$$\text{Smectite} = \frac{S1g/4}{T} \times 10$$

$$\text{Chlorite} = \frac{C3}{I2} \times \frac{I1g}{T} \times 10$$

$$\text{Mixed} - \text{layerI/S} = \frac{I1h - I1g - S1g/4}{T} \times 10$$

$$\text{Kaolinite} = \frac{K2}{(2)C4} \times \frac{C3}{I2} \times \frac{I1g}{T} \times 10$$

Where T is equal to "Total Counts"

$$T = I1h + \frac{C3 \times I1g}{I2} + \frac{K2 \times C3 \times I1g}{(2)C4 \times I2}$$

3. List any non-clay minerals that are present (i.e. quartz, calcite, or feldspar) and report results in part in 10.

At this point, a brief explanation of the basis of the formulas is appropriate. The simpler case without chlorite will be covered. The formulas for each of the clay- mineral suites are fractions of the total, and as such, should always add up to 10 parts in 10. The total intensity count (I1h + K1) theoretically includes all the counts of all the clay-mineral suites involved. The term K1 is the counts for kaolinite. The term I1 h contains the counts for illite, smectite, and I/S. This is because the smectite structure, in both the pure smectite and I/S, collapses to 10 Å when heated due to the expulsion of water from its interlayer space, Under this condition, no distinction can be made between illite and smectite with XRD because their d-spacings are identical. The peak intensity (count) is raised by the added diffraction contributed by the collapsed smectite at the angle corresponding to I 1 h.

The individual clay-mineral formulas use peaks that are the result of the specific clay mineral being calculated. The intensities (counts) of these peaks are divided by the total to give ratios that are the relative proportions of the individual clay minerals. The only exception to this is I/S in which the proportion is found by calculating a remainder, or difference, by subtracting the known intensities (counts) form I 1 h. This leaves only the mixed-layer fraction to account for the remaining intensity (count).

It should be noted that S1 is divided by 4. The reason for this is that peaks at low angles of 2∅ have exaggerated intensities due to polarization as described by the Lorentz-Polarization Factor. This adjustment works well for the large majority of samples analyzed, but occasionally fails when the sample contains a large amount of pure smectite and virtually no mixed-layer illite/smectite. When this happens, the mixed-layer illite/smectite calculation gives a negative value that is physically impossible. In this case, I 1 g and S 1 /4 combined are larger than I I h from which they are subtracted.

SPECIAL PROCEDURES

CURLERS AND PEELERS/FLOCCULATION

On occasion, particularly recalcitrant flocculation and curlers and peelers (material that delaminates from the glass slides) may be encountered. These are considered together because their remedies beyond the Standard Procedure are similar.

First, as already mentioned in the Standard Procedure, dilution should be tried. Continue diluting samples until either flocculation or curling and peeling stops, or until the slides are too thin (have too little clay) to obtain a usable diffraction pattern. (Note: it is possible to do some dilution on the slide by placing less material on it. If necessary to cover the entire slide, put distilled water on it prior to adding the clay suspension.

The water and suspension should be mixed with the tip of the dropper or pipette. This is particularly useful for curlers and peelers.)

There is another technique that may be helpful for dealing with curlers and peelers. If dilution alone does not solve the problem, consider making two slides that are as identical as possible. Use one for the air-dried and glycolated runs and the other for the heated run. Because the one used for the heated run is not expanded as far as when glycolated, less contraction occurs, therefore, there is less chance of curling and peeling. It is not desirable to use two different slides for one analysis, but in this case, it may be the best that can be done. The smear method for dealing with curlers and peelers, mentioned in Chapter 5 of Moore and Reynolds (1 989) does not solve the problem of curling and peeling on the heated run where it occurs most. Therefore, it will not be considered here.

MAKING SLIDES WITH SMALL AMOUNTS OF SAMPLE

If slides must be prepared from only a few grams of sample and/or only a small amount of clay exists in a sample, the standard procedure may produce slides that are too thin. This is remedied by wet grinding the sample, if necessary, to release as much clay as possible. The sample should be collected into a 100 ml beaker and filled with only a small amount of distilled water. The beaker should be filled to 10 ml to 20 ml. If necessary, a larger volume can be reduced to this amount by centrifugation.

ALTERNATE METHOD FOR PREPARING SLIDES

It has not been necessary to use other methods of preparing slides in the Clay Lab, However, one method is worth mentioning and has its benefits. It is the Millipore® Filter Transfer Method. The method requires collecting clay suspension with particle sizes of < 2um and filtering the clay out of suspension onto a paper filter. The clay film on the filter is then transferred to a glass slide. The benefit of this method over the conventional glass slide method is that the clay surface presented to the x-ray beam is more representative of the actual amounts of the various clay minerals. This method is preferred for quantitative analysis. The drawback is that the method is time consuming and requires a lot of practice to perfect. The procedures for this method and other methods are given in Chapter 5 of Moore and Reynolds, 1989.

ADDITIONAL HELPFUL TECHNIQUES USED FOR CLAY MINERALS.

There are some situations in which it may be difficult to distinguish between two clay-mineral groups or more detailed information is desired. Additional techniques may be required to resolve the problem. Two techniques that can be useful are heating and cation saturationlexchange (or both).

Heating clay minerals can do several things. At temperatures lower than 500°C interlayer water, ethylene glycol, or glycerol are removed with resulting changes in the diffraction patterns.

At temperatures higher than 500°C, the clay-mineral structures can be altered or destroyed completely. Different clay minerals undergo these changes at different temperatures and in different ways allowing for additional or further identification. For example, heating a sample suspected of having a mixture of chlorite and kaolinite to 550°C for 1hr will destroy the kaolinite structure leaving behind chlorite. The result of heating will be seen on the diffraction pattern. This technique, depending on the outcome, may not be definitive, but it may help. Heating can also differentiate between vermiculite and chlorite. By heating a sample suspected of containing vermiculite and chlorite to 3000 for 1 hr, the vermiculite structure will collapse to IOA leaving the remaining chlorite peak at 14A. Heating is also used to distinguish between Fe-rich and Mg-rich chlorite. If heating a chlorite sample at 5000' C for 1 hr increases the peak intensity at 14A, the sample is Fe-rich. If heating the sample at 60011 C for 1 hr increases the peak intensity at 14A, the sample is Mg-rich (Austin and Leininger, 1976).

Cation exchange/ saturation is important because it can be used in some cases for further identification, and for determining/controlling other physical properties that are related to interlayer cations. Cations can be exchanged, and a clay mineral can become saturated, by exposing it to a salt solution rich in a particular cation. In general, the ease with which one cation can be replaced by another is as follows (Moore and Reynolds, 1989):

$Na^{+} < K^{+} < Ca^{2+} < Mg^{2+} < NH_4^{+}$

i.e. ca2+ is held more firmly in the interlayer space than Na+. An interesting property of expandable-clay minerals is a positive correlation between cation

exchange capacity and layer charge. Working backwards, it is possible to estimate layer charge based on measured cation-exchange capacity.

Cation saturation before using XRD identification techniques can make them more effective by reducing the diffuseness of the diffraction maxima. For example, using a 1 N solution of Mg^{2+} will make the distinction between smectite, vermiculite, and chlorite more pronounced.

Chapter 5: Bulk-Mineral Analysis

Bulk-mineral analysis in the Clay Lab is primarily intended to identify non-clay minerals using randomly-oriented-sample-mounting techniques, however, peaks of clay-mineral phases can sometimes be seen. This chapter will cover the theory of randomly-oriented-sample preparation and how peaks are produced from these orientations. Additionally, the standard procedure for running these samples on the XRD machine and interpreting the diffractograms will also be presented. With the addition of newer equipment, it is also necessary to provide a special procedure for using this equipment to take advantage of its beneficial features.

THEORY

In order to interpret bulk-mineralogy-XRD patterns, the lab worker must have an understanding of both mineralogy and XRD. This section will add to the information already presented in Chapter 4 by extending it to all crystallographic dimensions. It will also consider the production of peaks (x-ray-reflection maximums) using randomly- oriented-powder-mounting techniques.

MINERAL STRUCTURE.

A mineral is a naturally occurring inorganic element or compound having an orderly-internal structure and characteristic-chemical composition, crystal form, and physical properties (Bates and Jackson, 1987). Dimensions related to the crystal form of a mineral are measured using XRD and are used for the identification of mineral phases in bulk-mineral analysis.

The primary difference between bulk-mineral analysis and clay-mineral analysis is that bulk-mineral analysis uses XRD to measure the

distances between internal crystal planes of all orientations rather than just those perpendicular to the c- axis (Fig. 5-1). Unlike clay minerals, in which the (001) is most diagnostic, other minerals often require all indices to be examined to make an identification. An example of a cubic mineral (not a clay mineral) is given in Fig. 5. I. For further explanation, consult an introductory mineralogy text.

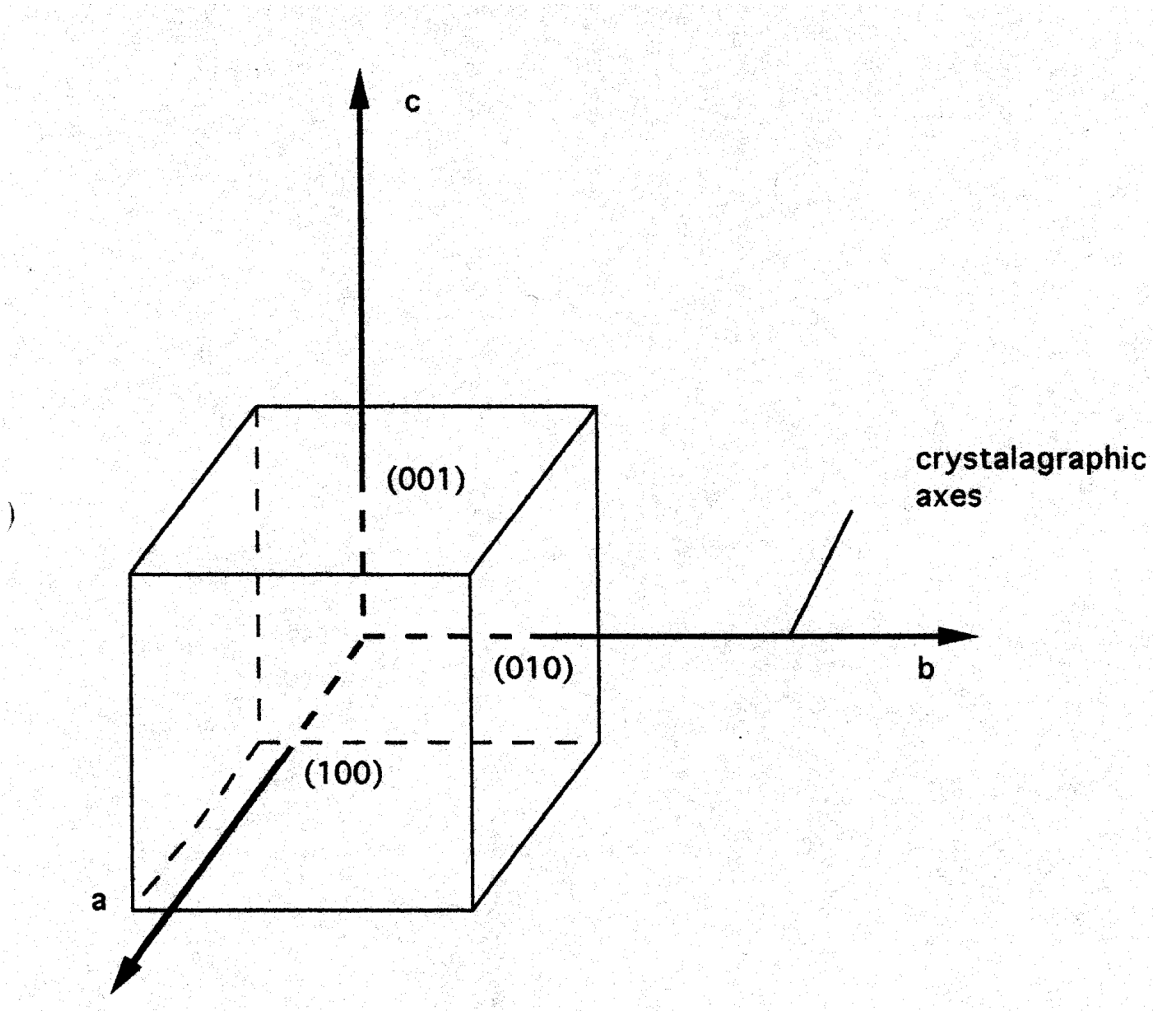

Fig. 5.1 Cubic mineral on crystallographic axes.

XRD USING RANDOMLY ORIENTED POWDER MOUNTS

The powder mounts used ideally have perfect-random-oriented-crystal grains. This is accomplished by grinding the sample to < 70 mesh and pouring them into a sample holder in a manner that does not align the crystals preferentially along their faces. When exposed to an incident x-ray beam, certain crystal grains, with the appropriate orientations, will produce a reflected (diffracted) beam in accordance with Bragg's law. These reflected beams show up as peaks on the diffractogram. The explanation of how these peaks are produced at the specific angles is very complex and beyond the scope of this manual. For a simplified case of XRD, refer to the Theory Section in Chapter 4 of this manual. For a further explanation of this phenomenon, see Klug and Alexander (1974).

STANDARD PROCEDURE

The standard procedure is in two sections. The first covers sample preparation and running samples on the XRD machine (Norelco@ with a horizontal-sample-mount goniometer: the axis of rotation is also horizontal). The second covers interpreting diff ractograms.

SAMPLE PREPARATION AND RUNNING SAMPLES ON THE XRD MACHINE

1. If available, use remaining sample from EDTA leaching procedure that was split, crushed, and passed through a 70-mash sieve. Go to step 4. If not available, precede to step 2.

2. Split the sample as described in Chapter 1, but only keep a 20-gm split. 3. Grind the split in a mortar and pass through a 70-mesh sieve.

Any sample that does not pass through the sieve should be returned to the mortar for further grinding. Repeat the sieving and grinding until entire

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sample is passed through the sieve. Mix sample thoroughly.

4. Attach the glass slide to the aluminum sample well with a clip. Slowly pour sample into sample well using the special-design-funnel device (Fig. 5.2). It is preferable to pour the sample by lightly tapping the sample container and allowing the sample well to fill slowly than pouring the sample rapidly into the funnel in one fast shot. This causes the sample to stick in the funnel, and if tapping is used to free it, there is a tendency to orient the sample grains along the plane of the glass slide.

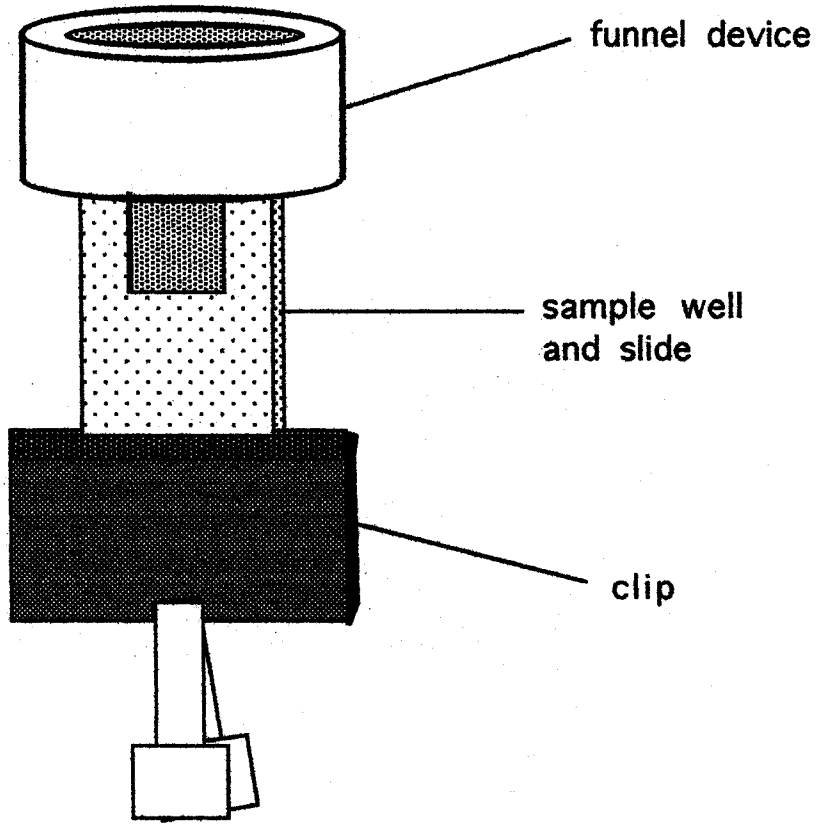

Fig. 5.2. Sample well loading equipment.

5. load sample onto Norelco® XRD with a horizontal-mount goniometer

6. Set the following parameters on the XRD machine (See X-ray Lab Supervisor for specff ic instructions and safety items before using XRO machine for first time); kV = 40, mA = 25, TC = 1 0*, CFS = 1 000*, chart speed -- 0.5 in/min, scan speed 211 20/min.

   *These are initial settings and will need to be changed depending on the sample being run.

7. Run sample in accordance with XRD Lab Procedures. An example of the output diffractogram is given below (Fig. 5.3)

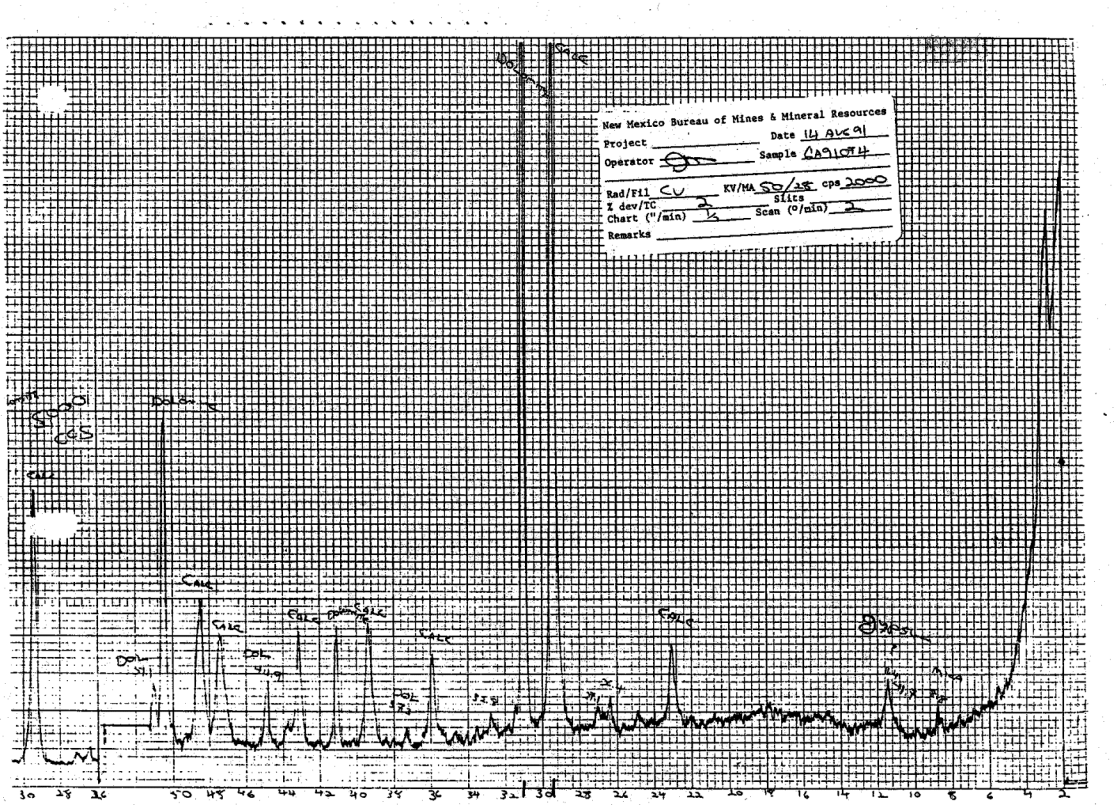

Fig 5.3. Bulk mineral diffractogram.

INTERPRETING DIFFRACTOGRAMS

Diffractogram analysis can be very easy, in cases where only one or two common minerals are to be identified, or it can be extremely difficult when a sample contains numerous uncommon minerals. The following procedure has evolved over time in the Clay Lab as a means of analyzing most diffractograms. If this standard procedure proves insufficient, go to the special procedure that employs a computerized search of the Powder Diffraction File (PDF).

1. Compare diffractogram with pre-prepared traces of common minerals. Both the Clay Lab and the X-ray Lab have collections of these. If minerals are identified, label the associated peaks as those minerals.

2. Look up the identified minerals in the PDF and search for peaks (paying attention to intensites) that may be missing on the pre-prepared traces. label any that are found.

3. The remaining peaks (or all the peaks if none were eliminated in step 1) should be checked using tables in Walker and Renault (1972). If minerals are identified, label the associated peaks as those minerals.

4. Look up the identified minerals in the POF and search for peaks (paying attention to intensities) that are not listed in Walker and Renault (I 972).

5. All remaining peaks should be looked up in the determinative table in Brindley and Brown (I 980). It is best to make a list of possible minerals (with intensities) next to each peak. When this is done for each peak, likely minerals will show up in several of the lists. Check to see that the relative intensities of the peaks reasonably match those given in the table for each mineral identified.

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6. Look up the identified minerals in the PDF and search for additional peaks (paying attention to intensities) that were not listed in the determinative table in Brindley and Brown (1980).

7. By now, most of the peaks should be accounted for. If just a few peaks remain, it is not likely that their identities will be found. Label them with a question mark. If more than a few peaks remain or if this method did not work, go to the Special Procedure Section of this chapter.

SPECIAL PROCEDURE

This special procedure uses the search/match function contained in the Jade® XRD analysis program. This function searches the PDF, according to parameters set by the operator, to find matches with the data being analyzed. The specific instructions for using Jade® will not be discussed here, but they are available in the Jade®- Instruction Manual. Also the X-ray Lab Supervisor can be of some help.

The biggest obstacle to using this procedure is entering the data into the Jade®-XRD-analysis program. There are several ways of doing this. The first way, and the most impractical in terms of time, is to set up a numerical data file that approximates the data (peaks) obtained from the Standard Procedure; this has not been done by Clay-lab workers to date.

The second method is to graphically create a blank scan (see Jade® Instruction Manual), This allows you to graphically create a copy of the diffractogram obtained from the Standard Procedure. This method has met with some success, but has the drawback of loosing precision of peak heights and positions. The third procedure, which will be presented here, is to prepare the sample to be run on the XRD machine connected to the computer containing Jade®. The sample preparation is different because this XRD machine has a vertical-mount goniometer.

1 - There are three sample preparation techniques for running samples on the vertical- mount goniometer. They are as follows:

a. Prepare the sample and load it into the sample well as in the standard procedure. Cover the sample in the well with x-ray-transparent film to keep the sample from coming out of the well. Use tape to attach the film.

b. Grind the sample to a much finer size and press it into a sample well with a glass slide. The smaller size is much more likely to stay in the well when placed in a vertical position and will become less oriented when pressed.

c. Grind the sample to a much finer size and press into a rotating mount. See the X-ray Lab Supervisor for details.

2. Run samples on the XRO machine using parameter settings analogous to the standard procedure (refer to the Jade@ and Talk@ Instruction Manuals).

3. Analyze resulting data using the Search/Match function of the Jade@ program (refer to the Jade@& Instruction Manual).

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