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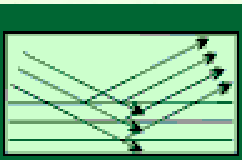
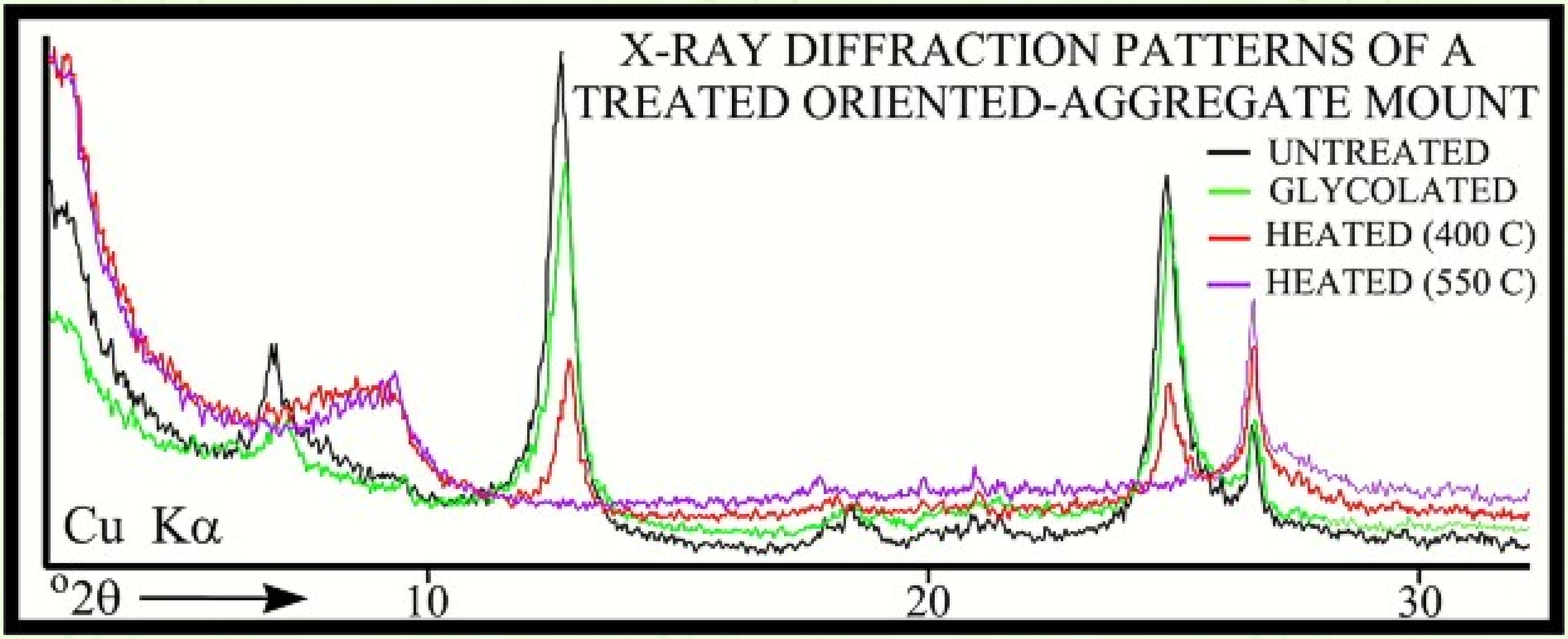


U. S. Geological Survey Open-File Report 01-041

A Laboratory Manual for X-Ray Powder Diffraction

by L.J. Poppe, V.F. Paskevich, J.C. Hathaway, and D.S. Blackwood



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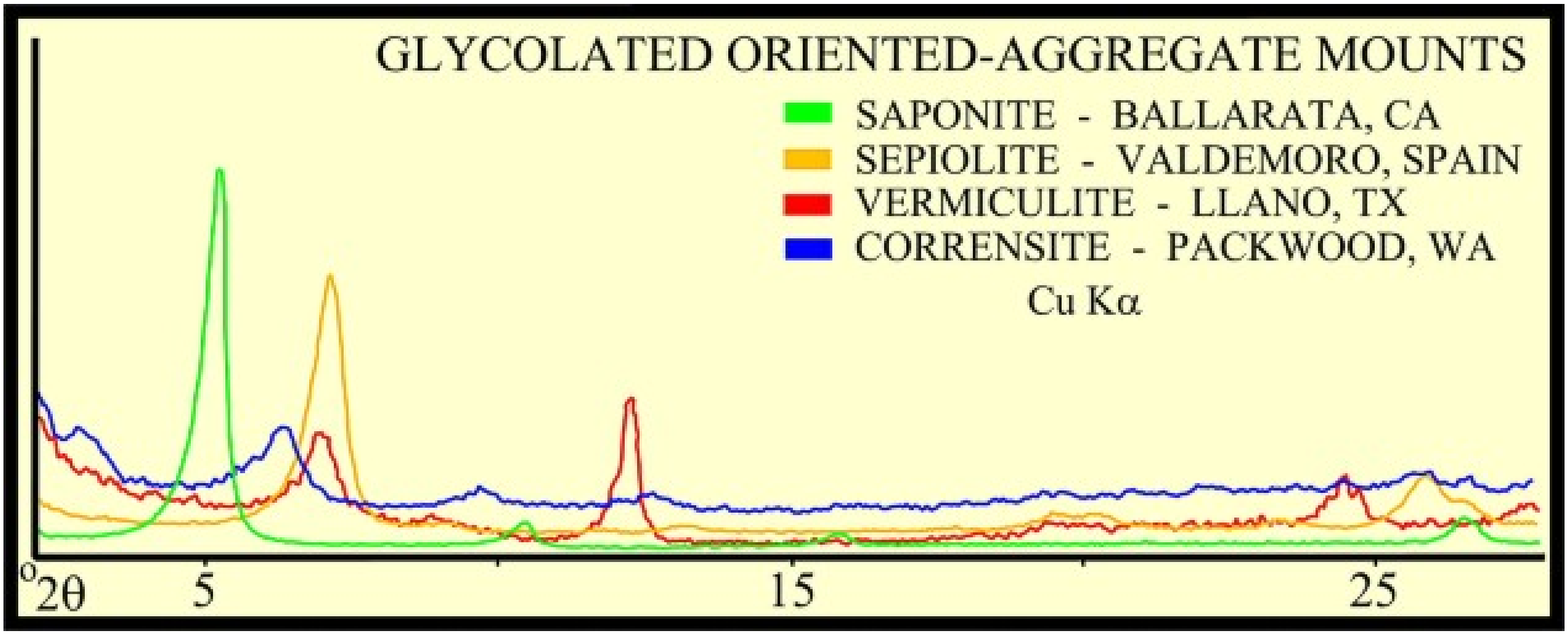
A Laboratory Manual for X-Ray Powder Diffraction



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Introduction

Size and composition are the most fundamental attributes of sediments. Although optical microscopy can be used to readily identify sand and coarse silt-sized crystalline material, X-ray powder diffraction is the most common technique used to study the characteristics of crystalline structure and to determine the mineralogy of finer grained sediments, especially clays. As a method, X-ray diffractometry is attractive because of its speed and ease of performance, and because it requires only small amounts of material, is nondestructive, and can be used to perform semi-quantitative analyses of poly-mineralic mixtures.

This report is presented as an abridged guide for laboratory technicians and students interested in X-ray powder diffraction methodology. The principles of diffractometry and descriptions of clay mineralogy condensed in this report have been discussed in many texts. They are provided here solely to broaden the perspective and understanding of the user. Furthermore, only some of the preparatory and interpretive methods presented herein are original. Users are strongly encouraged to consult the original work cited in the text and in bibliographies associated with each section for a more complete discussion of a method's accuracy and applicability.

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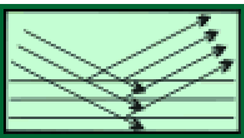

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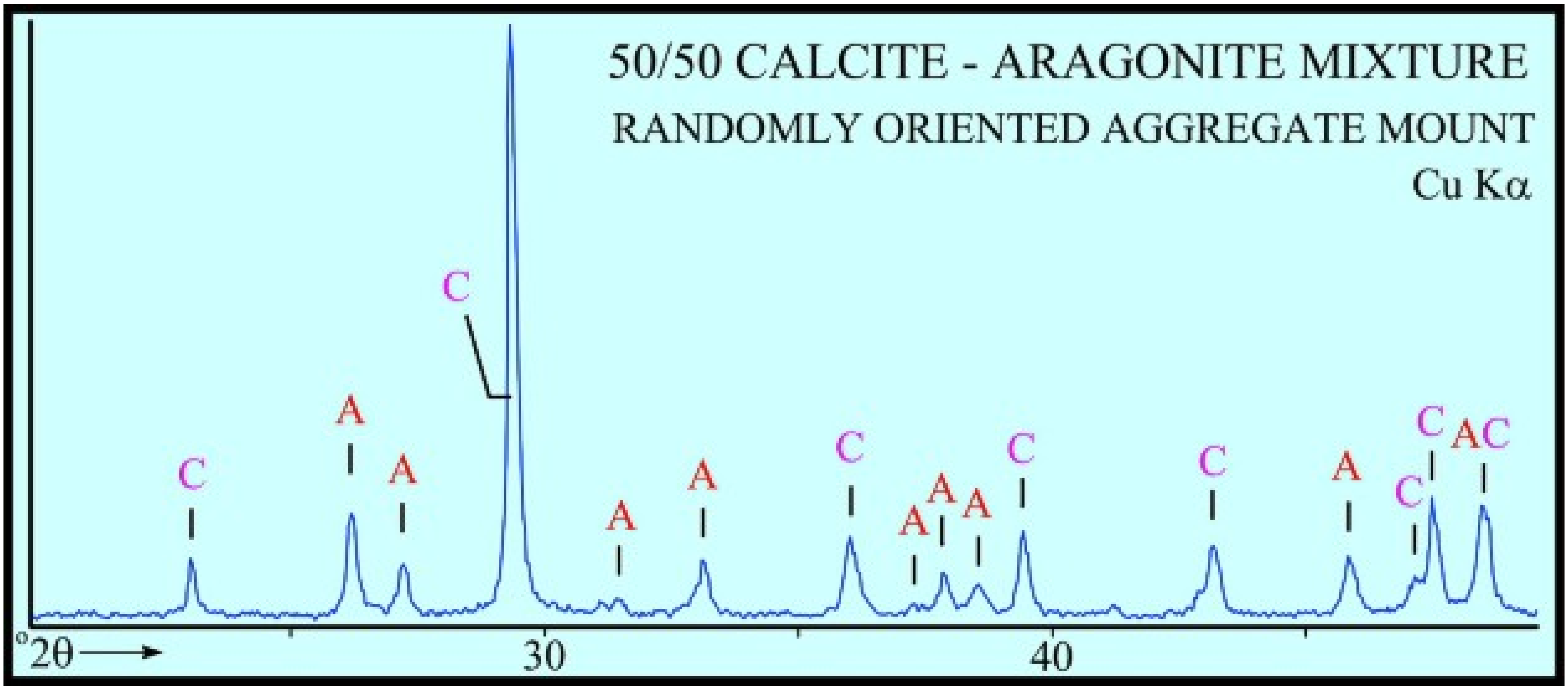

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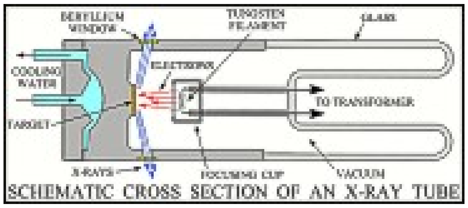
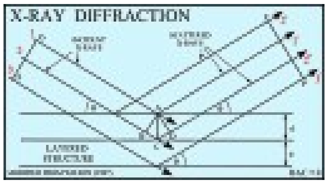
X-Ray Diffraction Primer



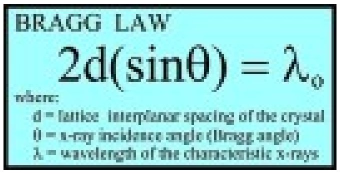
SCHEMATIC CROSS SECTION OF AN X-RAY TUBE

X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength. They are produced when electrically charged particles of sufficient energy are decelerated. In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions. Tubes with copper targets, which produce their strongest characteristic radiation (Kα1) at a wavelength of about 1.5 angstroms, are commonly used for geological applications.

If an incident X-ray beam encounters a crystal lattice, general scattering occurs. Although most scattering



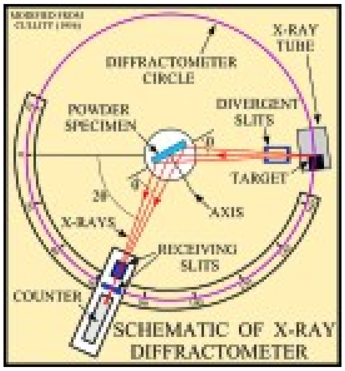
interferes with itself and is eliminated (destructive interference), diffraction occurs when scattering in a certain direction is in phase with scattered rays from other atomic planes. Under this condition the reflections combine to form new enhanced wave fronts that mutually reinforce each other (constructive interference). The relation by which diffraction occurs is known as the Bragg law or equation. Because each crystalline material has a characteristic atomic structure, it will diffract X-rays in a unique characteristic pattern.



BRAGG LAW

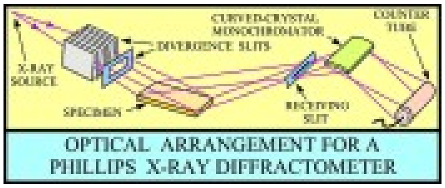
$$2d(\sin\theta) = \lambda_0$$

where:
d = lattice interplanar spacing of the crystal
θ = x-ray incidence angle (Bragg angle)
λ = wavelength of the characteristic x-rays



The basic geometry of an X-ray diffractometer involves a source of monochromatic radiation and an X-ray detector situated on the circumference of a graduated circle centered on the powder specimen. Divergent slits, located between the X-ray source and the specimen, and divergent slits, located between the specimen and the detector, limit scattered (non-diffracted) radiation, reduce background noise, and collimate the radiation. The detector and specimen holder are mechanically coupled with a goniometer so that a rotation of the detector through 2x degrees occurs in conjunction with the rotation of the specimen through x degrees, a fixed 2:1 ratio.

A curved-crystal monochromator containing a graphite crystal is normally used to ensure that the detected radiation is monochromatic. When positioned properly just in front of the detector, only the Kα radiation is directed into the detector, and the Kß radiation, because it is diffracted at a slightly different angle, is directed away. The signals from the detector are filtered by pulse-height analysis, scaled to measurable proportions, and sent to a linear ratemeter for conversion into a continuous current. Common output devices include strip-chart recorders, printers, and computer monitors.



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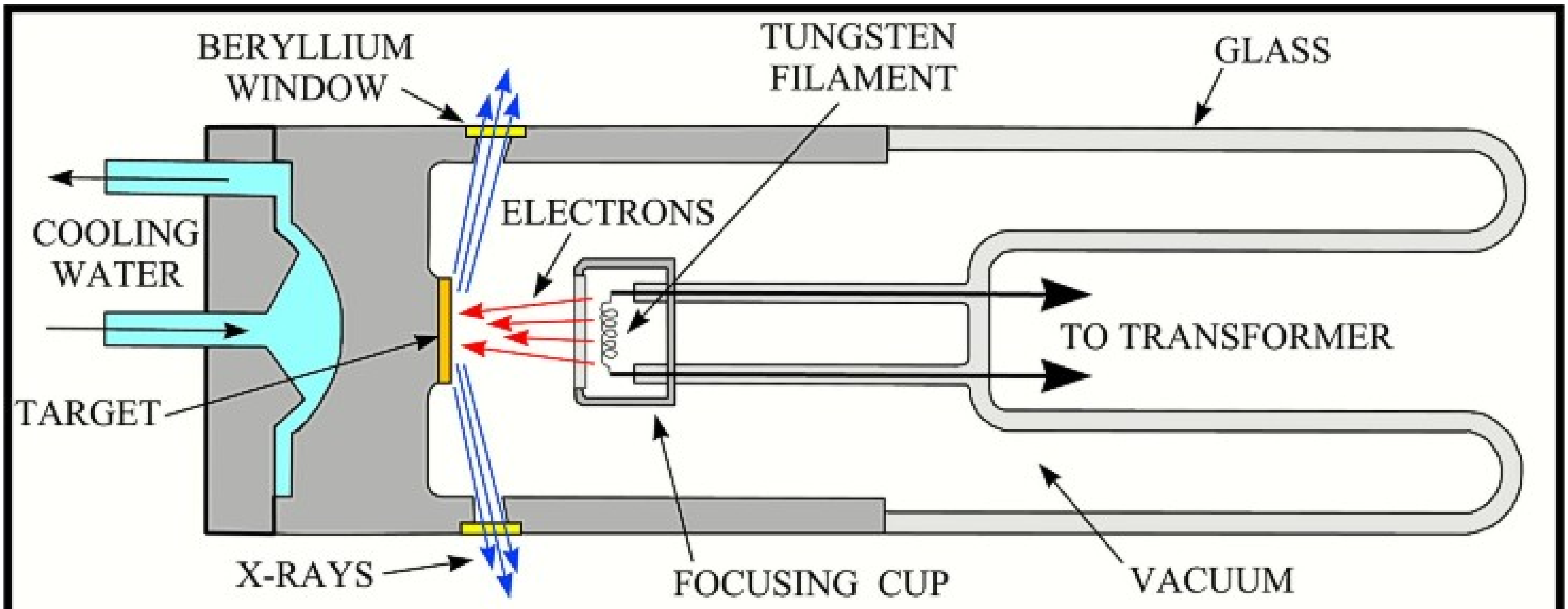
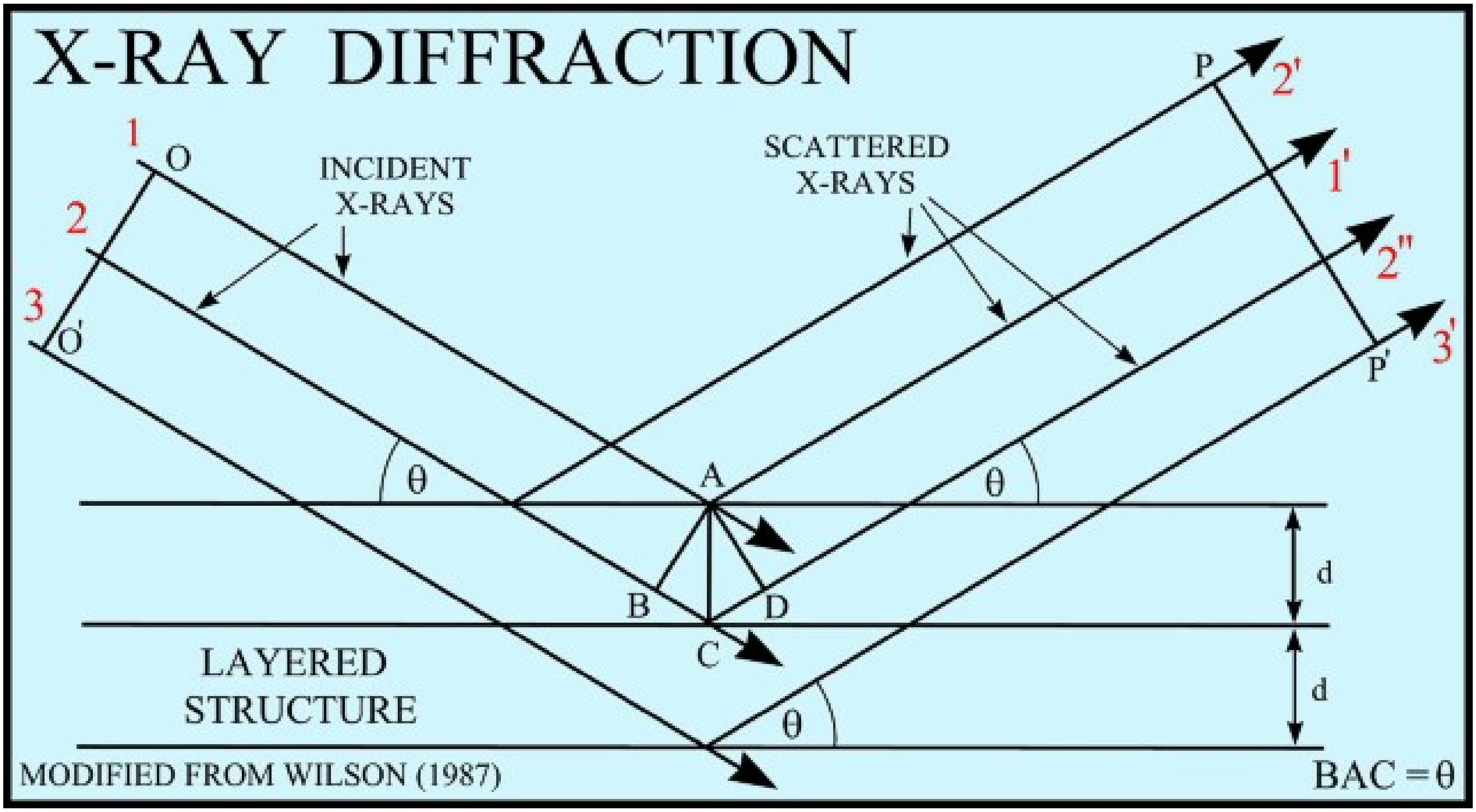
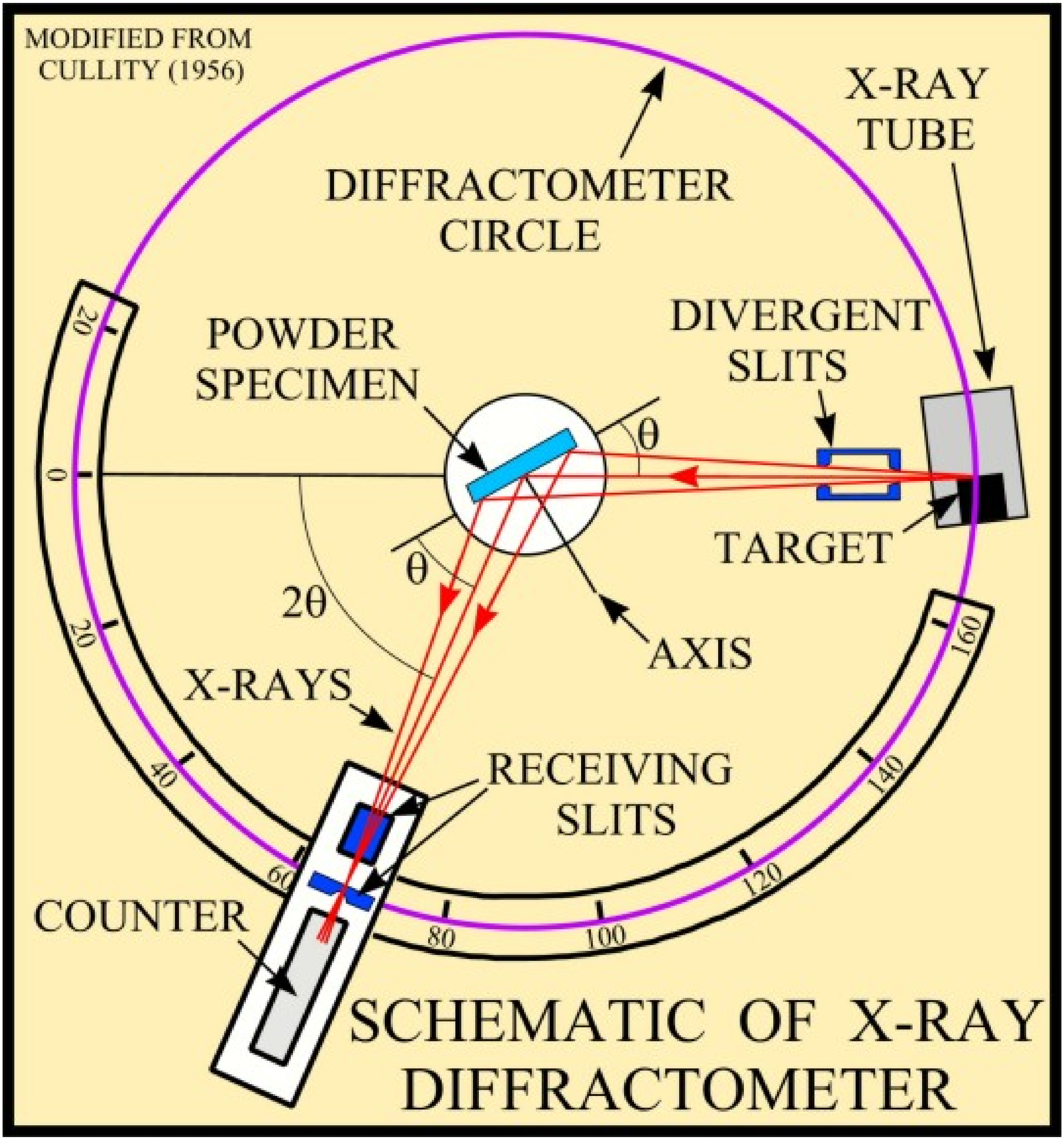
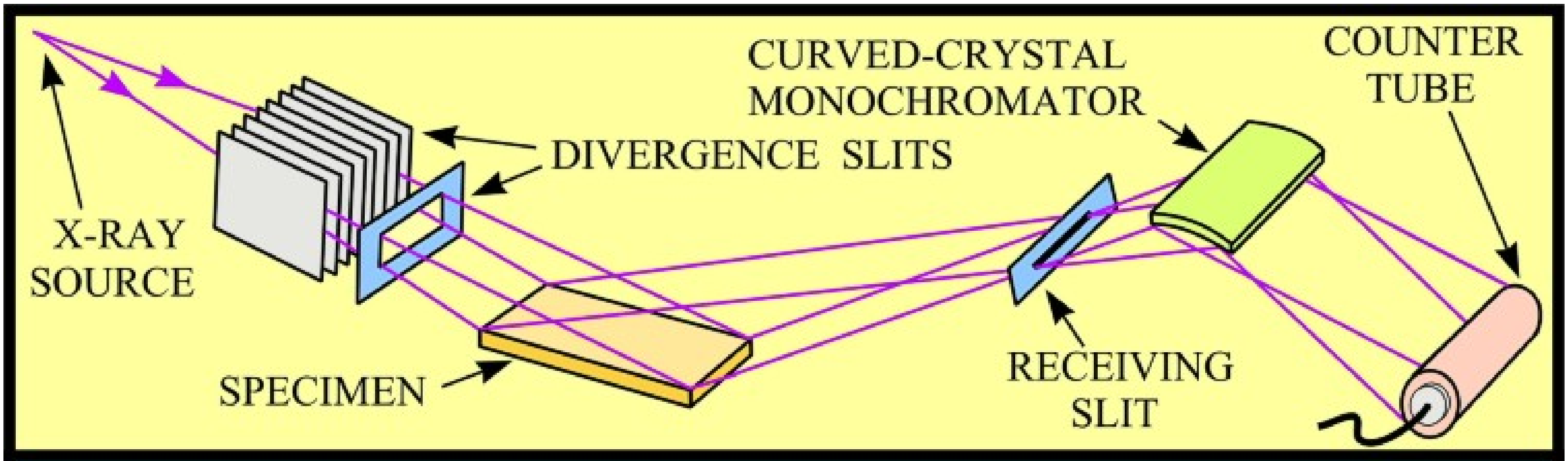


SCHEMATIC CROSS SECTION OF AN X-RAY TUBE


X-RAY DIFFRACTION
1
O
2
3
O'
INCIDENT X-RAYS
SCATTERED X-RAYS
P
2'
1'
2"
3'
P'
θ
A
θ
B
D
C
d
d
LAYERED STRUCTURE
θ
MODIFIED FROM WILSON (1987)
BAC = θ


MODIFIED FROM
CULLITY (1956)
X-RAY TUBE
DIFFRACTOMETER CIRCLE
DIVERGENT SLITS
POWDER SPECIMEN
θ
θ
2θ
TARGET
AXIS
X-RAYS
RECEIVING SLITS
COUNTER
20
0
20
40
60
80
100
120
140
160
SCHEMATIC OF X-RAY DIFFRACTOMETER



OPTICAL ARRANGEMENT FOR A
PHILLIPS X-RAY DIFFRACTOMETER

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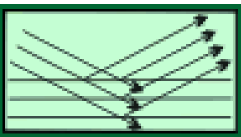

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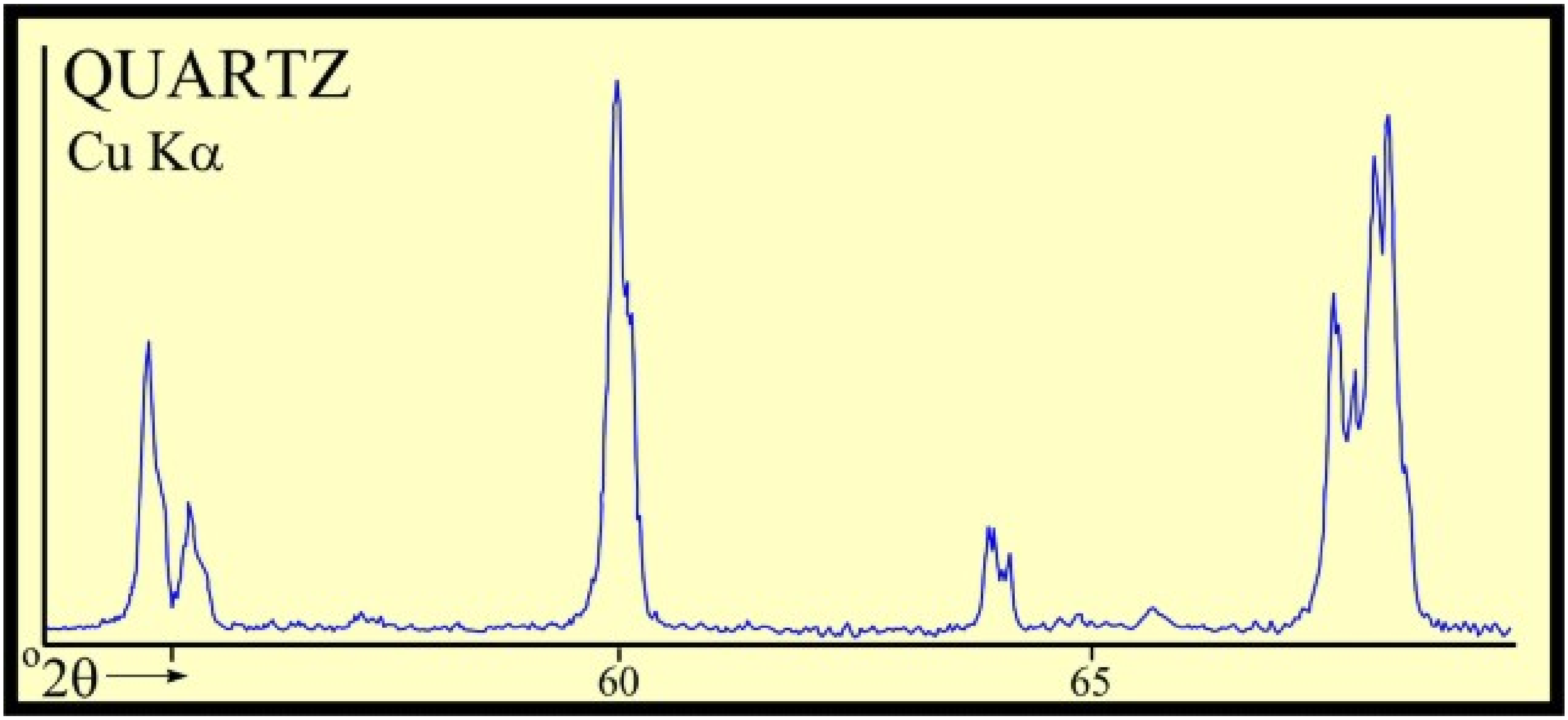

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Intercalation of Kaolinite Group Minerals

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Smear Slides for Optical Microscopy

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ACETIC ACID TREATMENT TO REMOVE CARBONATES

It may be necessary to dissolve the carbonates in some limestones and sediments before the clay minerals can be identified. However, treatment with strong acids to remove carbonate can attack the structure of clay minerals (e.g. trioctahedral minerals are often destroyed by such treatment), and even dilute acid can attack the silicate layers via interlayer regions and exposed edges. Generally, dilute acetic acid is preferred over hydrochloric acid because it less likely to affect clay crystallinity.

PROCEDURE FOR ACETIC ACID TREATMENT

Materials Required:

- glacial acetic acid
- distilled water
- glass graduated cylinder
- glass rod
- marking pencil
- 300-ml glass beakers
- glass pipette with rubber bulb
- siphon or centrifuge

Add 1 part acid to 4 parts distilled water in the graduated cylinder and mix throughly with the glass rod. Caution: acetic acid can cause burns. Wear safety goggles, plastic gloves, and an apron while working with this chemical.

Label 300-ml beakers and add sample.

Add 50-75 ml of the acetic acid solution slowly to avoid foaming and overflow of beaker. A glass pipette may be used to transfer the acid solution. When effervescence subsides, add another 50-75 ml of acid. Stir and allow to stand overnight. Repeat until suspension no longer effervesces.

Allow the suspension to settle and carefully siphon or pour off the supernatant liquid or wash sample by centrifuging. Dispose of acid waste properly. We place it in a 20-liter container of ground-up mollusc shells until neutralized.

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REMOVAL OF ORGANIC MATTER WITH HYDROGEN PEROXIDE

The presence of organics, which causes a broad hump on X-ray powder diffraction patterns, can obscure the diffraction maxima of mineral species. Unfortunately, just about any treatment to clays involves some risk. With hydrogen peroxide, the danger is oxidizing octahedral iron and changing the layer charge. This is most likely with chlorite and vermiculite. However, one has to do something to resolve clay peaks in some organic-rich samples. The general rule (if there is one) is to go ahead with the peroxide treatment, but if you see some strange diffraction patterns that defy interpretation, suspect that iron oxidation has occurred. This is rarely the case under normal circumstances.

PROCEDURE FOR TREATMENT WITH HYDROGEN PEROXIDE

Materials Required:

- hydrogen peroxide (3%)
- glass graduated cylinder
- distilled water
- 300-ml glass beakers
- glass rod
- pencil
- squeeze bottle of distilled water
- lab tissues
- siphon
- safety equipment

If the hydrogen peroxide is laboratory grade (30%), prepare a dilute solution of 3% using a graduated cylinder and distilled water. Caution: hydrogen peroxide is a strong oxidizer that can cause severe burns. Wear goggles, plastic gloves, and an apron while working with this chemical.

Label the beakers with a pencil or marker.

Place a sample in each beaker and add about 50-100 ml of dilute hydrogen peroxide. Stir each beaker with the glass rod to suspend the sample. Rinse the glass rod between each sample and dry with a lab tissue. When bubbling stops or slows, add another 50-100 ml of dilute hydrogen peroxide and restir the suspension.

When the addition of hydrogen peroxide to the samples no longer causes bubbling, the organics have been removed. Allow the suspension to settle and carefully siphon or pour off the supernatant liquid, or wash the sample by centrifuging.

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SEPARATION OF SILT AND CLAY BY DECANTATION FOR X-RAY POWDER DIFFRACTION

Decantation is the gravity settling of particles in a suspension. Although more time consuming than centrifugation, decantation can also be used to separate the clay- and silt-sized fractions for X-ray powder diffraction. For this technique it is assumed that the coarse fraction (sand and gravel) has been removed and that the fine fraction (silt and clay) has been retained as a suspension. After a muddy suspension is dispersed and allowed to settle, aliquots of clay suspension may be withdrawn from above 5 cm in depth at the times and temperatures shown in Table 1.

DECANTATION PROCEDURE

Material Required for Decantation:

- wide-mouth glass jars with lids
- plastic centrifuge tubes with caps
- centrifuge tube rack
- measuring tape or ruler
- marking pen
- labeling tape
- dispersant (sodium hexametaphosphate)
- spatula
- squeeze bottle with distilled water
- ultra-sonic probe
- lab tissues
- thermometer
- timer
- plastic syringe

Label the jars with 0 and 5-cm depths. Sample identifiers should be labeled on the jars and centrifuge tubes with labeling tape for easy removal later.

Add the suspension to be separated to the jar, fill each jar up to the 0-cm water-depth line with distilled water, and add a small amount of dispersant with the spatula (Note: the amount of dispersant should not exceed 0.5% of the suspension by weight). Seal the jar, and shake vigorously to homogenize the suspension.

Disperse the sample with the sonic probe for 15-20 seconds. Rinse off the tip of the probe with distilled water and dry between samples.

Start the timer and check the temperature of the suspension to determine the settling time. If more than one sample is to be separated, record the start and calculated withdrawal times for each sample.

After the appropriate time has elapsed (e.g. 1 hour, 1 minute, and 30 seconds at 20 C) and the silt has settled past the 5-cm mark, use the syringe to withdraw the clay suspension from the interval above this depth and inject it into the centrifuge tube for storage until mounting as an oriented aggregate (any convenient container will suffice). Repeat withdrawals until adequate amount of clay has been isolated, or, if a complete separation is necessary, use larger containers as receptacles for the clay fraction and repeat the analysis until the supernatant liquid is clear after settling. Remember to rinse out the syringe with distilled water between withdrawals to prevent cross-sample contamination.

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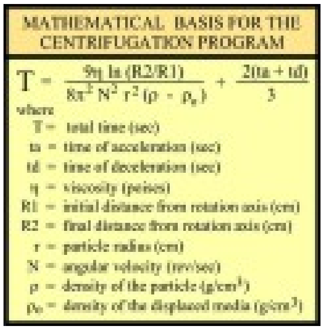
SEPARATION OF THE SILT AND CLAY FRACTIONS FOR X-RAY POWDER DIFFRACTION BY CENTRIFUGATION

Centrifugation is an important research technique with wide applications in the basic sciences. Examples of geological uses include the separation of silt and clay for X-ray powder diffraction analyses and recapture of the entire sample after treatment with acids or oxidizing agents. Decantation may not be an acceptable alternative to centrifugation because normal gravitational methods of particle sedimentation take an inordinate amount of time, and for particles finer than 0.5 micrometers Brownian motion interferes with settling (Folk, 1974).

We have written a program based on Stoke's Law that calculates centrifuge run times and speeds for particles of various diameter and density in media of different temperature, specific gravity, and viscosity (Poppe and others, 1988). The program, which was written in Unisoft C and implemented on UNIX system V, is fast, interactive, allows the user to select all particle- and medium-related parameters, and is not specific to any one piece of centrifugation equipment.



MATHEMATICAL BASIS FOR THE CENTRIFUGATION PROGRAM

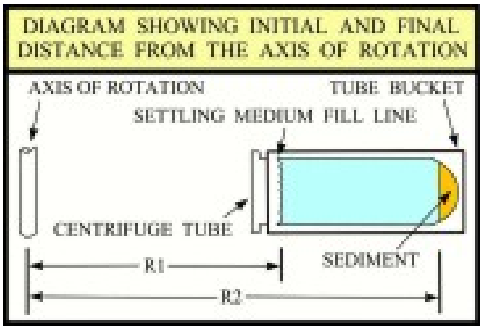
$$T = \frac{9\eta \ln(R2/R1)}{8\pi^2 N^2 r^2 (\rho - \rho_o)} + \frac{2(ta + td)}{3}$$

where

T = total time (sec)
ta = time of acceleration (sec)
td = time of deceleration (sec)
η = viscosity (poises)
$R1$ = initial distance from rotation axis (cm)
$R2$ = final distance from rotation axis (cm)
r = particle radius (cm)
N = angular velocity (rev/sec)
ρ = density of the particle (g/cm^3)
ρ_o = density of the displaced media (g/cm^3)

The program prompts the user for the particle radius in micrometers and the angular velocity in revolutions per minute and then converts these values into the proper units required by the formula. It is important to note that when analyzing non-spherical particles such as phyllosilicates, the value for the radius does not represent the actual radius, but the equivalent radius of a spherical particle of the same material which would settle at the same rate as the actual particle. To obtain the correct results, the user must exercise care to ensure the the other values are in the proper units required by the program and when determining the initial (R1) and final (R2) distances from the axis of rotation. Because of mechanical differences in the designs of individual centrifuges, the user must measure these distances on the specific piece of equipment being used. The units of R1 and R2 are unimportant because they cancel out in the equation.

DIAGRAM SHOWING INITIAL AND FINAL DISTANCE FROM THE AXIS OF ROTATION



Program documentation can be viewed in either a text, Microsoft Word or HTML version. Program source code and include *header* file, program documentation, and a helpful README file are stored in the directory labeled *software* located at the top-level of this CD-ROM.

PROCEDURE FOR SEPARATION OF SILT AND CLAY BY CENTRIFUGATION

Materials Required for Centrifugation:

- marking pencil
- labeling tape
- plastic centrifuge tubes (~50 ml) with
- caps
- centrifuge tube rack
- squeeze bottle with distilled water
- plastic beakers
- dispersant (sodium hexametaphosphate)
- spatula
- ultra-sonic probe
- lab tissues
- thermometer
- timer

If the supplied centrifugation program is to be used, the operator should first determine the necessary information (initial and final distances from the axis of rotation, and the acceleration and deceleration times of the centrifuge for various speeds (rev./min.) and construct a table of run times for common temperatures.

Apply labeling tape to the top edge of the centrifuge tube and label the tape with the marking pencil. Note: the bottom edge of the tape can act as a guide facilitating equal filling of the tubes that will keep the centrifuge in balance. Apply labeling tape to and label the plastic beakers.

Pour enough sample into the centrifuge tubes to fill the rounded part of the bottom of the centrifuge tubes. Note: The powder from the randomly oriented aggregate mounts can be used.

Add a small amount (about 0.25 g) of dispersant to the centrifuge tubes. The dispersant will cover the tip of a narrow spatula as shown.

Add distilled water to the bottom edge of the labeling tape. Place a cap on the centrifuge tube and shake the tube to homogenize the suspension.

Disperse the sample for 15-20 seconds with the ultrasonic probe. Rinse the tip of the ultrasonic probe with distilled water and wipe it dry with lab tissue between sonifications.

Check the water temperature and find centrifugation times in minutes and seconds from the prepared table.

Turn on the power switch and press Stop/Open. This releases the safety latch and allows the cover of the centrifuge to be opened. Place the tubes in the centrifuge. Be sure that the centrifuge is balanced by having opposite tubes filled equally; 2, 4, 6, or 8 tubes may be used. Close cover.

Adjust the speed control, set the machine's timer to hold, adjust the brake, press start on the centrifuge, and start the timer. Note: the timers on most commercial centrifuges are not accurate enough to use for silt and clay fraction separations. When the total run time minus the deceleration time (T-td) has expired on the timer, press stop. The speed should read near zero when the calculated total time is reached.

Remove tubes from the centrifuge, pry off caps, and pour the supernatant liquid into the plastic beakers. Be careful that the sediment on the bottom of the tubes is not poured off. If the silt and clay fractions are to be completely separated, repeat the centrifugation procedure until the supernatant is reasonably clear (4-5 times).

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RANDOMLY ORIENTED POWDER MOUNTS FOR X-RAY POWDER DIFFRACTION

Bulk mineralogy of a sediment sample can be determined by X-ray diffraction with a randomly oriented powder mount. The random orientation insures that the incident X-rays have an equal chance of diffracting off any given crystal lattice face of the minerals in the sample. The use of a powder press to make randomly oriented powder mounts is undesirable because excessive force could cause preferred orientation of the crystallites. Although some orientation is inevitable (platy minerals tend toward some preferred orientation), the method described below is sufficient for most applications.

Sample splits are commonly dried at 60 C prior to the preparation of randomly oriented powder mounts. The mounts are typically X-rayed between the angles of 2 and 70 degrees two theta using copper K alpha radiation at a scanning rate of 2 degrees per minute.

PREPARATION OF RANDOMLY ORIENTED POWDER MOUNTS

Materials Required:

- plastic tape
- weighing paper (4"x4")
- mortar and pestle
- ASTM number 230 (.062 mm mesh) sieve stiff brush
- spatulas
- pencil
- sample holders and clips (the ones pictured hear is for a Phillips diffractometer)
- glass microscope slide
- piece of glass slide cut to a size sufficient to cover the sample holder opening

Tape the glass slide over the opening of the sample holder. Leave tabs on each side for later removal of this cover, but fold the extra tape against itself so that it will not stick to other objects or the sample. Place the holder glass side down on a piece of weighing paper.

Grind the dried sample thoroughly so that it is easily brushed through the sieve. The particles should be much finer than .062 mm to avoid fractionation of the minerals. The sieve is used only to achieve even distribution and to ensure that the grinding is complete.

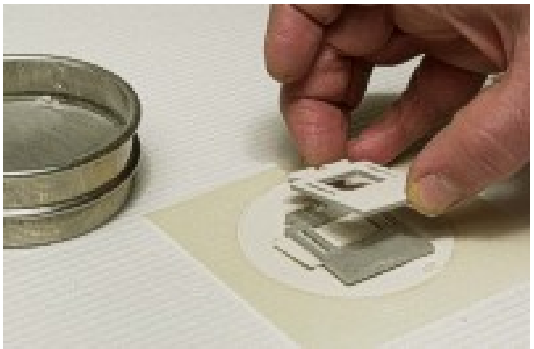
Place a second holder over the first as a mask. This enables the buildup of a thick enough layer of sample for later packing, while maintaining a clean metal surface on the final holder.

Place the sieve over the sample holder and brush the sample from the mortar. (Note: the sample may become contaminated from the sieve and utensils. These contaminants will not affect the x-ray diffraction analysis, but do not plan to reuse this cut of the sample for sensitive chemical analyses.)

Use the spatula to loosen any sample that has stuck to the mortar and brush the material into the sieve.

Brush the sample through the sieve into the cavity of the sample holder. The purpose of the brushing is to obtain an even distribution and to minimize preferred orientation of the particles.

Remove the sieve and mask.



Place the sample holder on a clean piece of weighing paper, tap the powder remaining on the mask onto the first weighing paper, and replace the mask over the sample holder.

Pour the excess powder onto first weighing paper into the sample holder. Distribute the powder evenly.

Use a glass slide to pack the sample into the cavity firmly enough so that it will not fall out, deform, or slide, but not so firmly that preferred orientation will be produced on the opposite surface (which will later become the top surface). The glass slide can also be used to scrape any sample that has flattened onto the holder surface during packing back over the holder opening.

Additional sample can be used as filler if necessary to create a firm pack. This part of the sample need not be as finely ground, as it will become the bottom surface and will not be exposed to the X-ray beam.

Pack as above and then attach a clip to the back of the holder. Alternately, if a generic holder is being used, another cut glass slide can be attached with tape to cover the holder's opening.

Turn the sample holder over and lift the tab of tape. The glass cover is carefully lifted with a slight twisting motion to break and surface adhesion. This will be the surface exposed to the X-rays. It should be smooth, uniform, and flush with the metal surface of the holder. If not remake the mount.

Label the sample holder with the pencil.

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SMEAR SLIDE SAMPLE MOUNTS FOR X-RAY POWDER DIFFRACTION

Samples may be ground and smeared on the surface of a glass slide as a rapid means of preparing samples for X-ray powder diffraction. This mounting method seldom produces acceptable random orientation of the crystallites, resulting in diffraction maxima with relative intensities that are not accurately reproduced. Although not useful for semi-quantitative analysis, this method is useful for rapidly determining bulk mineralogy, especially if the operator knows which mineral phases are likely present.

PREPARATION OF SMEAR-SLIDE MOUNTS

Materials Required:

- weighing paper (4"x4")
- mortar and pestle
- spatula
- glass rod
- marker pen
- glass slide cut to fit the diffractometers's sample holder
- acetone in a squeeze bottle
- lab tissues
- diamond or carbide scribe to cut slides

Grind the dried sample thoroughly with the mortar and pestle. The particles should be much finer than .062 mm to avoid fractionation of the minerals. The finer the powder the greater the opportunity for obtaining an adequate number of particles with random orientation and the less likely that surface roughness will reduce low-angle intensities.

Use the spatula to loosen any sample that has stuck to the mortar and to homogenize the powder.

Place a small amount of sample in the center of the slide and add an amount of acetone sufficient to wet the sample (2-3 drops). Distilled water may be used, but the sample dries quicker with acetone.

Spread the sample into a thin layer with the glass rod. Gently blow on the slide to rapidly evaporate the acetone. Use the spatula or a finger to remove any excess sample sticking to the edges of the slide. Use a lab tissue to remove any sample stuck to the back of the slide.

Label the slide with a marker pen. Brush the sample from the mortar onto the weighing paper and transfer the remaining sample back into a sample vial.

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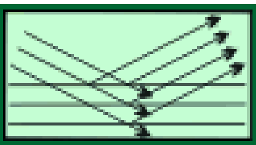

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A Laboratory Manual for X-Ray Powder Diffraction

ORIENTED AGGREGATE MOUNTS FOR X-RAY POWDER DIFFRACTION

The clay fraction can be separated from the bulk sample by centrifugation or decantation and mounted as an oriented aggregate mount for clay-mineral identification. The oriented aggregate mounts force the clay mineral particles , usually plate-shaped phyllosilicates, to lie flat, allowing the operator to direct the incident X-ray beam down the z axis of the minerals and to record the diagnostic basal diffractions. It is the z axis that shows the extent of d-spacing expansion and (or) contraction indicative of certain clay minerals during subsequent treatments. These treatments include: air drying, glycolation with ethylene glycol, heating to 400 C, and heating to 550 C. The material from the randomly oriented powder mount may be used for this analysis.

Commonly used substrates for oriented aggregate mounts include silver filters, ceramic tiles, and glass slides. Silver filters tend to be expensive and react with chloride ions to form crystalline compounds that change the mass-absorption coefficient of the mount and affect peak intensities (Poppe and others, 1989); ceramic tiles tend to contain crystalline material that may complicate the diffraction pattern. Glass slides cut to fit the sample holder of a diffractometer are used in the filter-peel method (Drevers, 1973; Pollastro, 1982) described below.

PREPARATION OF ORIENTED AGGREGATE MOUNTS USING THE FILTER-PEEL TECHNIQUE

Materials Required:

- glass slides cut to fit diffractometer
- carbide or diamond glass scriber
- lab tissues
- vacuum pump
- Millipore filtration apparatus vacuum tubing
- Millipore HA, 47-mm, 0.45-micron nominal pore opening cellulose filters
- pipette or 20-25 cc syringe
- single-edge razor or metal spatula
- cylinder with a 2.5 - 5 cm outside diameter

Cut the glass slides to fit the sample holder and label them with a scriber. Rinse and dry the slides to remove any remaining glass shards.

Assemble the filtration device with the cellulose filter in place. Pour approximately 20 ml of the clay suspension into the assembled filtration device. Exact amount will depend on the density of the suspension, mineralogy, presence of organics, and grain size of the particles.

If the filter clogs, use the pipette or a syringe with a needle attached to remove the excess clay suspension from the filtration device.

As soon as the remaining suspension has been completely drawn into the filter, remove the glass funnel and use a single-edge razor or metal spatula to remove the moist filter from the filtering device.

Wrap the filter membrane tightly around the cylinder with the clay film up and held firmly with the thumb and forefinger.

Membrane filter and clay film are center-positioned near the glass slide and then quickly and smoothly lightly rolled across the slide to transfer the clay film to the slide. Any hesitation or jerky motion during the transfer may cause rippling of the film and disrupt the preferred orientation.

The mounts dry in a few minutes and are then ready for X-ray diffraction analysis. The specimens are subsequently exposed to glycol or heat treatments.

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ETHYLENE GLYCOL TREATMENT

Organic liquids, primarily ethylene glycol and glycerol, are extensively used as an auxiliary treatment to expand swelling clays. Whether or not a mineral expands and the amount of expansion can provide essential supplementary information aiding clay-mineral identification. Swelling clays include smectites (e.g. montmorillonite, nontronite, and beidellite), some mixed-layer clays, and vermiculite.

Two methods are presented here: a vapor treatment and a rapid method. The advantage of the vapor treatment is less disturbance of the sample and less amorphous scattering of X-rays by excess liquid than in the case of the rapid method.

ETHYLENE GLYCOL VAPOR TREATMENT

Materials Required:

- ethylene glycol
- oven
- desiccator
- desiccator shelf

Pour ethylene glycol to about 1 cm depth in base of desiccator.

Place oriented aggregate mounts on the shelf of desiccator. Additional shelves may be stacked if necessary.

Place desiccator in oven at 60 to 70 C for about 4 hours or overnight. Longer times will not hurt samples. Do not remove mounts until they are to be run on the X-ray diffractometer.

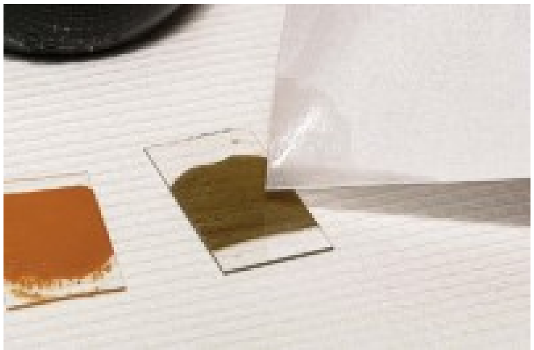
ETHYLENE GLYCOL RAPID METHOD

Materials Required:

- ethylene glycol
- glass rod
- lab tissue

Apply a drop of ethylene glycol directly to the surface of the oriented aggregate mount with the glass rod. Spread the ethylene glycol if necessary.

Mounts are ready to be X-rayed as soon as liquid is uniformly absorbed. Excess ethylene glycol may be gently mopped up with lab tissue.



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HEAT TREATMENTS FOR X-RAY POWDER DIFFRACTION

Heat treatments at various temperatures are commonly used to help identify clay minerals by revealing changes in crystal structure spacings or loss of the structure. Depending on the temperature and the mineral species, these treatments can collapse the structure by dehydration, or in the case of other minerals destroy the crystal structures. However, it is important for the analyst to remember that some of the changes caused by the heat treatments may be temporary, and that partial or complete rehydration may occur during cooling.

HEAT TREATMENT

Materials Required:

- furnace
- tongs
- wire hook

Preheat the oven to 400 C.

Place the oriented aggregate mount in the furnace using the tongs. Leave sample in the furnace not less than one half hour at 400 C.

Remove mount by pulling it forward with the wire hook until the edge of the mount can be grasped with the tongs. Do not remove mounts until they are ready to be run on the diffractometer.

X-ray the sample and repeat the above procedure at 550 C.

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LITHIUM SATURATION OF SMECTITES DURING X-RAY POWDER DIFFRACTION

Lithium saturation can be used to distinguish montmorillonite from beidellite. The method described below was modified by Schultz (1969), but is commonly referred to as the Hofmann-Klemen test. If the smectite present in a Li-saturated sample is beidellite, the basal smectite peak will still expand after treatment with ethylene glycol. If the smectite present in a Li-saturated sample is montmorillonite, this peak will stay collapsed after treatment with ethylene glycol. The filter-peel technique described elsewhere in this report may be used when making the oriented-aggregate mounts for lithium saturation. Readers should note that this test does not distinguish between all montmorillonites and beidellites (Wilson, 1987).

PROCEDURE FOR LITHIUM SATURATION

Materials Required:

- lithium chloride (LiCl)
- distilled water
- graduated cylinder
- balance
- weighing paper (4"x4")
- spatula
- glass jar with lid
- glass rod
- glass petri dishes with covers
- oven
- tweezers
- vacuum pump
- Millipore filtration device
- Millipore 47-mm HA 0.45 micron cellulose filters

Weigh out 9.5 g of LiCl for each 100 ml of distilled water used to make the solution. Dissolve the LiCl in the glass jar by stirring with the glass rod to make up a 3N solution of lithium chloride.

While making oriented aggregate mounts, pour some LiCl solution into the filtering device and draw the solution with suction through the clays on the filter.

Remove the moist filter from the filtration device and allow it to dry. Place the dry filter in a petri dish, and let it soak in some of the LiCl solution overnight.

After soaking, carefully remount the filter in the filtering device and run distilled water through the sample and filter to remove any excess LiCl.

Transfer the clay on the filter to a glass slide as shown in the filter-peel oriented-aggregate mount procedure and keep in an oven overnight at 200 C. Glycolate the samples for at least 4 hours using the vapor-glycolation technique described elsewhere in this report and then analyze the samples by X-ray diffraction. If the 001 smectite peak has expanded, the smectite is beidellite; if the basal peak stays collapsed, the smectite is montmorillonite.

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INTERCALATION OF KAOLINITE GROUP MINERALS

Intercalation complexes have long been used to differentiate between the kaolinite and chlorite group minerals and to identify different members of the kaolinite group (Wada, 1961; Wada, 1965; Wada and Yamada, 1968; Range and others, 1968; Calvert, 1984). The method described below, has been modified from Churchman and others (1984), and uses formamide to distinguish kaolinite from halloysite.

Note: Formamide has a health hazard designation of "3" (severe, life threatening). Use formamide only in a fume hood, avoid contact with skin and eyes, and do not breath vapors. Wear gloves, safety glasses, and protective clothing.

DIFFERENTIATION OF KAOLINITE AND HALLOYSITE BY INTERCALATION WITH FORMAMIDE

Materials Required:

- formamide (CH3-N-O)
- plastic spray bottle
- fume hood
- rubber gloves, lab coat, and safety glasses
- small oven

Prepare an oriented aggregate mount by the filter-peel technique as described elsewhere in this report, and allow the mount to air-dry. Obtain an X-ray powder diffraction pattern covering the 10- to 7-angstrom region and establishing the background on both sides of these peaks.

Spray the sample with an aerosol of formamide. Allow the spray to be absorbed for 30 minutes, and obtain another X-ray diffraction pattern of the 10- to 7-angstrom region. If present, halloysite gives rise to a peak at 10.4 angstroms; kaolinite does not expand beyond 7.2 angstroms. Relative proportions of kaolinite and halloysite can be derived from their respective peak areas.

If the presence of illite is suspected, heat the mount to 110 degrees C for 30 minutes and obtain another X-ray pattern covering the 10- to 7-angstrom region. The heat treatment does not affect the 10-angstrom basal reflection of illite, but causes the halloysite complexed with formamide to collapse to about 7 angstroms. Subtract the area of the 10-angstrom illite peak derived from the heat-treated sample from the area of the 10 angstrom peak derived from the formamide-treated sample. The difference in area is related to halloysite.

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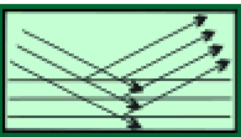

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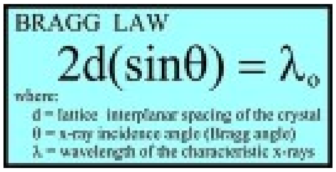
TEMPLATES AND TABLES FOR CONVERTING DEGREES TWO THETA TO D-SPACINGS

Many researchers still generate X-ray powder diffraction data using strip chart recorders. Either templates or conversion tables are then used to convert these patterns from degrees two theta to d-spacings (i.e. interplanar spacings) thereby allowing the Joint Committee on Powder Diffraction Standards (JCPDS) diffraction files to be used to determine which phases are present. Although most X-ray diffraction systems now commercially available are computerized and can automatically perform these conversions, the continued functionality of the older units and cost of the newer systems prevents many researchers and students accessing them.

The templates and conversion tables below were generated for copper radiation. While X-ray tubes with other target materials are available, in practice only copper is commonly used for geological applications. Copper K alpha radiation is preferred because of its relatively high peak energy, intensity, low peak-to-background ratio, convenient wavelength, the high heat conductivity of the target material, and the symmetry of the K alpha 1 and K alpha 2 composite peaks (Commeau and others, 1985).

TEMPLATES

The merits of templates over conversion tables are the time and labor they save. The templates supplied below were generated for Cu K alpha weighted-mean radiation and a 2 degrees 2 theta scale increasing from left to right with an interactive computer program (Poppe and Dodd, 1989). This program utilizes the Bragg equation and was written in C programming language to operate under Unix system 5 or MS-DOS version 2 or later. The weighted-mean wavelengths were calculated using the equation:



BRAGG LAW

$$2d(\sin\theta) = \lambda_0$$

where:

d = lattice interplanar spacing of the crystal
θ = x-ray incidence angle (Bragg angle)
λ = wavelength of the characteristic x-rays

(2(K alpha 1) + (K alpha 2)/3

This equation gives the K alpha 1 lines more "weight" because of their greater intensity relative to those of the K alpha 2 lines.

The templates, which are stored in the graphics directory of this CD-ROM, are supplied in both PDF, JPG, and TIF formats and may be output directly to a plotter fitted with mylar or acetate media. For those without access to a suitable plotter, the shorter templates are designed to fit on standard 8.5 by 11 inch page. Their size allows these shorter templates to be output directly to a standard printer fitted with transparencies, such as those used for overheads. If any slight adjustment for size is necessary, the shorter templates may also be printed on paper and transferred to transparent media and resized with the aid of a reducing/enlarging photocopy machine.

To view and print the PDF version, you must obtain and install the **Acrobat® Reader**, available at no charge from Adobe Systems.

Templates covering 2 degrees 2 theta to 70 degrees 2 theta:

con2_70	**PDF**	**JPG**	**TIF**
con2_21	**PDF**	**JPG**	**TIF**
con20_40	**PDF**	**JPG**	**TIF**
con39_59	**PDF**	**JPG**	**TIF**
con58_70	**PDF**	**JPG**	**TIF**

For best results and proper sizing, exit from your browser and either send the desired images directly to a printer, or activate a graphics application and open the appropriate image file. All format versions of the templates may be found in the directory named *template* at the top-level of this CD-ROM.

CONVERSION TABLES

A table has been generated in Microsoft Excel 97 using the Bragg equation that converts degrees two theta to interplanar spacings for Cu K alpha weighted-mean, K alpha 1, and K alpha 2 radiation. For the purposes of Microsoft Excel, the Bragg equation was rewritten as:

d = lambda/(2.0 * sin(0.5 * twotheta * D2R))

The wavelengths used for copper radiation (lambda) were: K alpha weighted-mean, 1.541838 angstroms; K alpha 1, 1.540562; and K alpha 2, 1.544390. The formula used to calculate the K alpha weighted-mean wavelength is the same as used above for the templates. The conversion factor used to change degrees to radians (D2R) was 0.0174532925199433, and d is in angstroms. The conversion tables that follow show calculated interplanar spacings to 0.01 degrees, and are supplied in **Microsoft Excel** and **ASCII** formats.

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SEMI-QUANTITATIVE ANALYSIS OF CLAY MINERALS

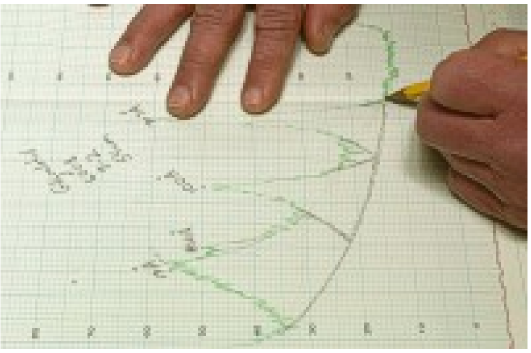
Semi-quantitative assessments make the identification of individual components in polymineralic samples much more valuable. Unfortunately, the intensity of a mineral's diffraction peaks can not be directly used as an accurate measure of abundance because sample mounts and X-ray machine conditions vary, and because different minerals, different atomic planes within a mineral, and different samples of the same mineral do not have the same ability to diffract X-rays (Biscaye, 1965). However, Biscaye (1965) also found that useful semi-quantitative comparisons can be made between samples by means of various ratios of peak areas. These ratios vary in part due to mineralogy and in part due to scattering factors inherent to X-ray diffraction. For example, a 17-angstrom peak will have four times the intensity of a ten-angstrom peak if a two theta compensating device is not used (Borchart, 1989).

The method of weighting basal-peak areas described here, which has been modified from his work, is based on the assumptions that only the less than 0.002 mm fraction is recorded on the X-ray diffractograms and that montmorillonite, illite, kaolinite, and chlorite comprise 100 percent of that fraction. The accuracy of this method increases when replicate x-ray diffraction analyses are performed and the results are averaged, and when the peak areas are not too small.

PROCEDURE FOR ANALYSIS OF CLAY MINERALS

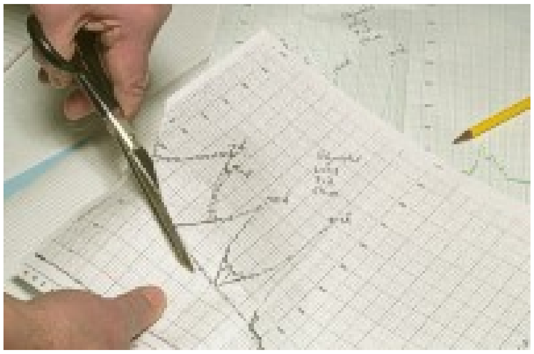
Materials Required:

- photocopy machine
- scissors
- metric balance accurate to four places
- calculator
- pencil and paper



Draw a baseline beneath each of the 17, 10, and 7 angstrom peaks, and the 3.58/3.54 angstrom kaolinite-chlorite doublet.

Photocopy the 2 to 30 degrees two-theta portion of the glycolated pattern.



Using the scissors, cut out each peak and divide the 3.58/3.54 angstrom doublet proportionately.

Weigh the paper copy of each peak and record the weights. Apply the appropriate weighing factor to the weight of each peak, and calculate the ratio of the doublet's parts. The peaks and respective weighing factors are: the weight of the area of the 17 angstrom glycolated peak for montmorillonite; four times (4x) the weight of the 10 angstrom peak on the glycolated pattern for illite; and twice (2x) the weight of the area of the 7 angstrom peak for chlorite and kaolinite. The weighted 7 angstrom peak, common to both chlorite and kaolinite, is divided between the two in proportion to the fraction of each mineral in the total area under the 3.58/3.54 angstrom kaolinite-chlorite doublet.

Normalize the clay mineral distribution by summing the weighted peak-area weights, and dividing the weighted peak-area weight of each mineral times 100 by the sum of the weighted peak-area weights.

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SMEAR SLIDES FOR OPTICAL MICROSCOPY

A split may be taken from each sample to be analyzed by X-ray diffraction and mounted in a optical medium (such as Piccolyte) as a smear slide. These slides are used to check the semiquantitative diffraction techniques, to detect amorphous materials or minerals present in trace amounts, to identify layer-silicate species concentrated in the silt fraction, and to examine the biological debris.

PREPARATION OF SMEAR SLIDES

Materials Required:

- Piccolyte (or other suitable mounting medium) in a dropper bottle
- glass microscope slides
- felt marker pen (water soluble ink)
- spatula
- glass rod
- distilled water in a dropper bottle
- hot plate
- glass cover slips
- glass scriber
- fume hood
- single edge razor
- xylene
- tweezers
- lab tissues

Label the slide temporarily with the felt marking pen. A pen with water soluble ink is used because the labeling is not soluble in xylene which may be necessary later to clean excess Piccolyte from the slide. Place the hot plate in a fume hood and set it at about 150 C (or about 300 F). Exact setting must be determined by experiment. Too hot and the xylene will boil forming bubbles; too cool and the evaporation of xylene will be slow. The cured mounting medium must no longer be tacky or viscous, but not be yellow or brittle.

Place a small amount of sample in the center of the slide.

Add a drop of distilled water and spread the sample into a thin layer with the glass rod.

Place the slide on the hot plate to dry. When completely dry, place one or two drops of Piccolyte on the center of the sample.

After the Piccolyte has been allowed to cook for several minutes (exact time depends on the temperature and amount of xylene used as a thinner), place a glass cover slip over the sample.

Press the cover slip down with a pair of tweezers. The Piccolyte should spread to fill the space beneath the cover glass.

Remove the slide from the hot plate and allow it to cool. If the slide has too much Piccolyte, it can be cleaned with a single edge razor and by washing with xylene.

Xylene is a hazardous chemical and a known carcinogen. If this chemical is used to clean the slides, work under a fume hood and wear protective gloves.

The slide is then permanently labeled with a glass scriber (diamond or carbide tip). This is not done earlier because glass chips may end up in the sample and may be confused with volcanic glass.

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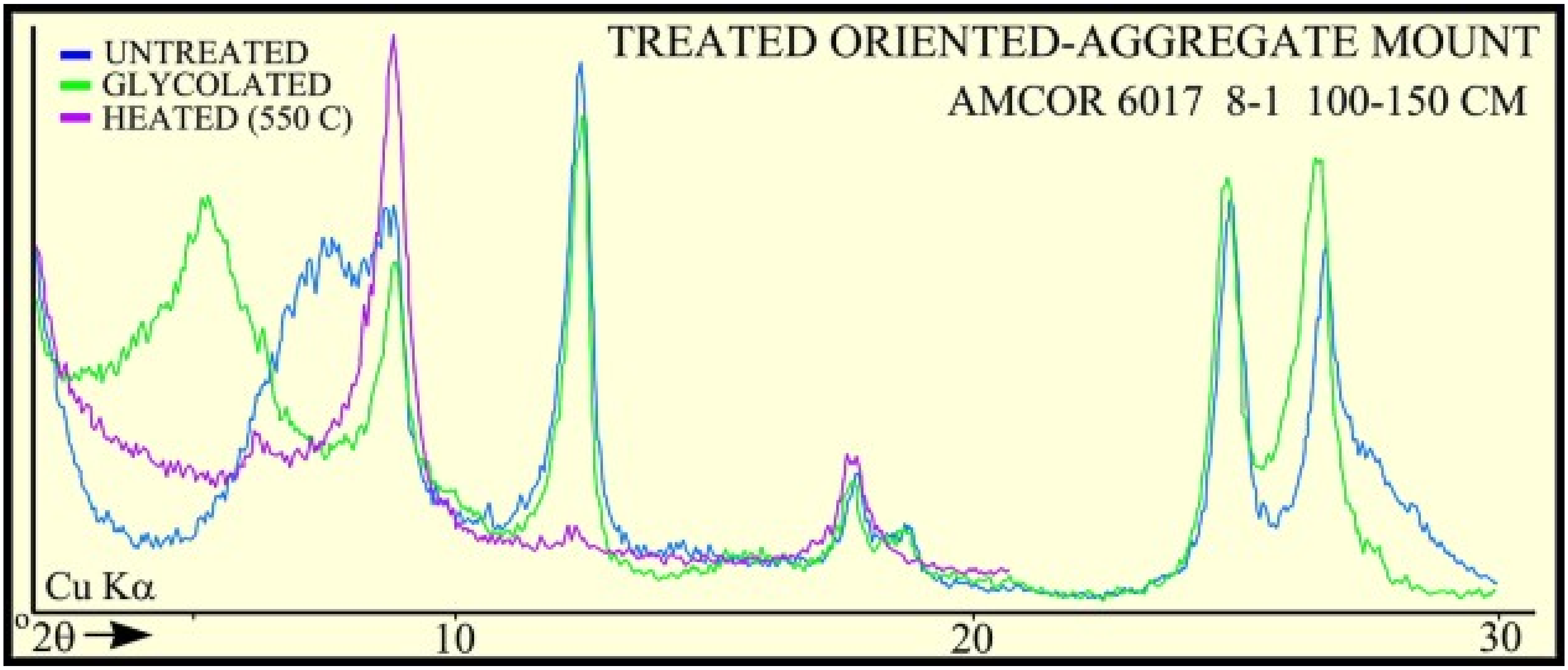

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- **Illite**
- **Kaolinite Group**
- **Mixed-Layer Clays**
- **Smectite Group**
- **Sepiolite and Palygorskite**
- **Vermiculite**

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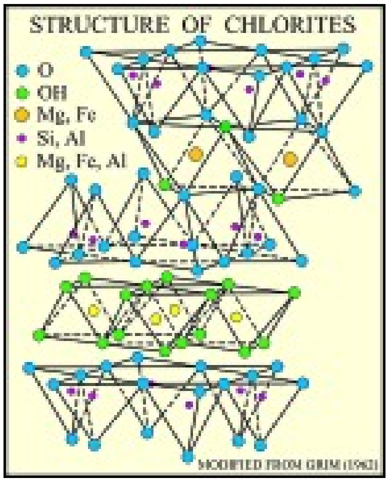
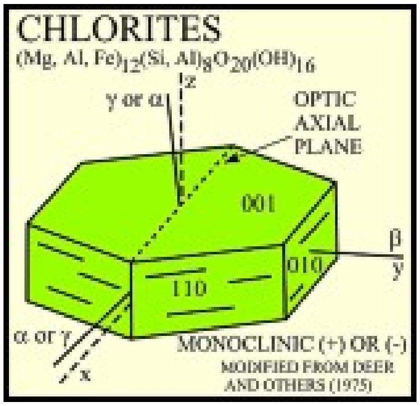
CHLORITE GROUP



The basic structure of chlorites consists of negatively charged mica-like (2:1) layers regularly alternating with positively charged brucite-like (octahedral) sheets (Grim, 1962). Members of the chlorite group include: brunsvigite, chamosite, clinochlore, cookite, diabantite, nimite, pennantite, penninite, ripidolite, sheridanite, and thuringite. The various members are differentiated by the kind and amount of substitutions within the brucite-like layer and the tetrahedral and octahedral positions of the mica-like layer.

The chlorite minerals are common components of low-grade greenschist facies metamorphic rocks, and of igneous rocks as hydrothermal alteration products of ferromanganese minerals (Deer and others, 1975). Chlorites are also common constituents of argillaceous sedimentary rocks where these minerals occur in both detrital and authigenic forms.



Chlorites have their 001 peaks at 14 to 14.4 angstroms, depending on the individual species. Peak positions are unchanged by ion saturation, solvation with ethylene glycol, or heating. However, heat treatments above 500 C alter peak intensities (Barnhisel and Bertsch, 1989; Moore and Reynolds, 1997). Typically, the 001 chlorite peak may increase dramatically and higher-order peaks may be conspicuously weakened. In poly-mineralic samples, chlorites can be distinguished from kaolinite by comparisons of the 3.58 angstrom kaolinite and 3.54 angstrom chlorite peaks, from smectites by the expansion and contraction of the 001 smectite peak after ethylene glycol solvation and heating to 400 C, and from vermiculite by the progressive collapse of the 001 vermiculite peak during heat treatments.

X-ray powder diffraction patterns of oriented-aggregate mounts showing the effects of standard treatments on a chlorite:

- Ripidolite

Selected Bibliography for Chlorite Group

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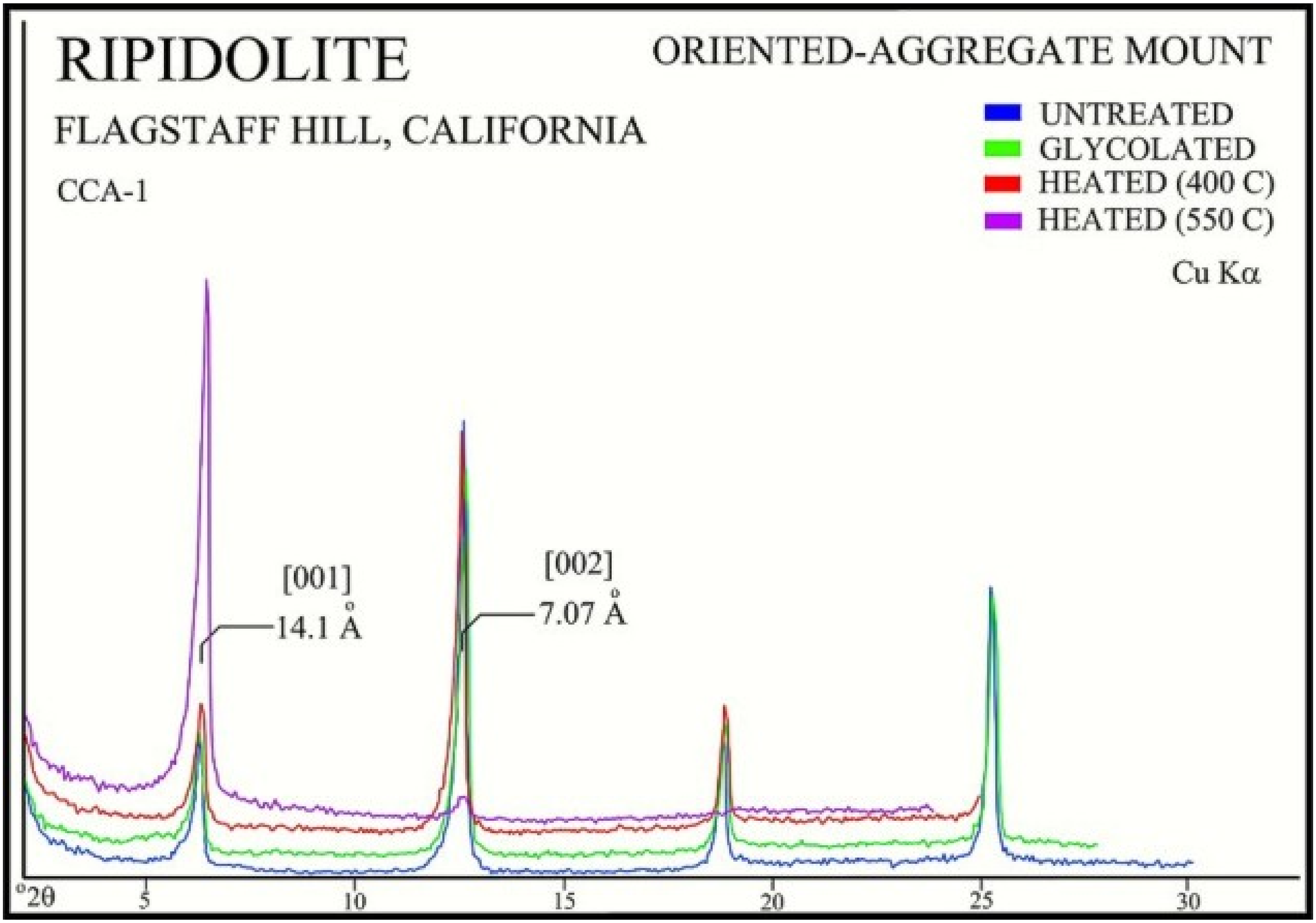
RIPIDOLITE
FLAGSTAFF HILL, CALIFORNIA
CCA-1
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400 C)
HEATED (550 C)
Cu Kα
[001]
14.1 Å
[002]
7.07 Å
°2θ
5
10
15
20
25
30

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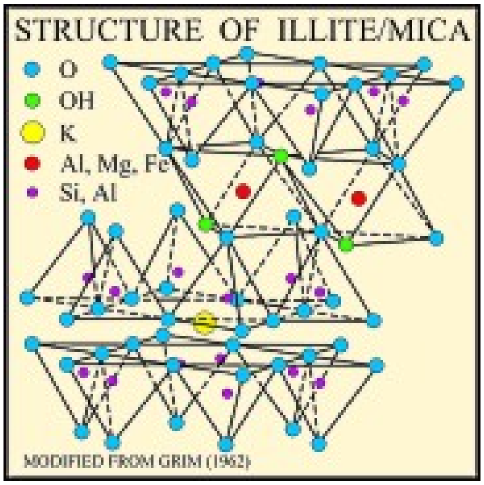
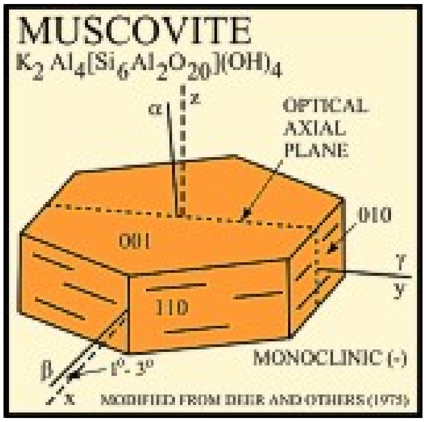
ILLITE GROUP



Illite is essentially a group name for non-expanding, clay-sized, dioctahedral, micaceous minerals. It is structurally similar to muscovite in that its basic unit is a layer composed of two inward-pointing silica tetragonal sheets with a central octahedral sheet. However, illite has on average slightly more Si, Mg, Fe, and water and slightly less tetrahedral Al and interlayer K than muscovite (Bailey, 1980). The weaker interlayer forces caused by fewer interlayer cations in illite also allow for more variability in the manner of stacking (Grim, 1962). Glauconite is the green iron-rich member of this group.



Illites, which are the dominant clay minerals in argillaceous rocks, form by the weathering of silicates (primarily feldspar), through the alteration of other clay minerals, and during the degradation of muscovite (Deer and others, 1975). Formation of illite is generally favored by alkaline conditions and by high concentrations of Al and K. Glauconite forms authigenically in marine environments and occurs primarily in pelletal form.

Members of the illite group are characterized by intense 10-angstrom 001 and a 3.3-angstrom 003 peaks that remain unaltered by ethylene glycol or glycerol solvation, potassium saturation, and heating to 550 degrees C (Fanning and others, 1989). Glauconite can be differentiated from illite by a 1.5- to 1.52-angstrom 060 peak (illite's 060 peak occurs at 1.50 angstroms), and by the presence of only a very weak 5-angstrom 002 peak.

X-ray powder diffraction patterns of oriented-aggregate mounts showing the effects of standard treatments on:

- Illite

Selected Bibliography for Illite-Group Minerals

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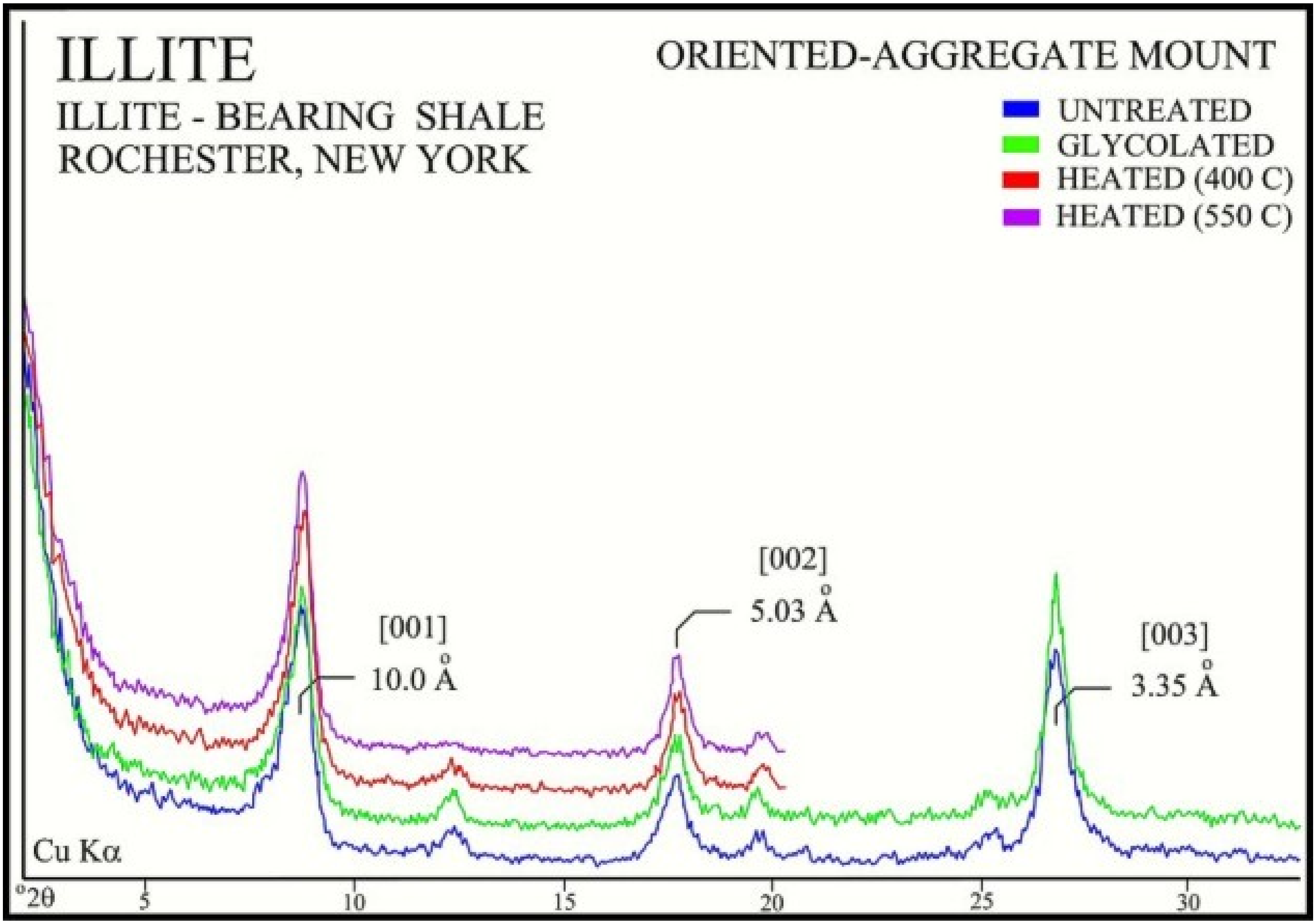
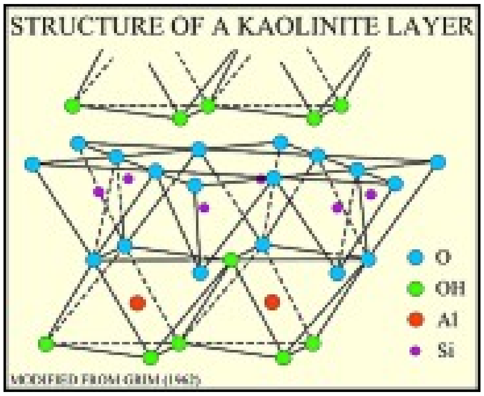

ILLITE
ILLITE - BEARING SHALE
ROCHESTER, NEW YORK
ORIENTED-AGGREGATE MOUNT
🟦 UNTREATED
🟩 GLYCOLATED
🟥 HEATED (400 C)
🟪 HEATED (550 C)
[001]
10.0 Å
[002]
5.03 Å
[003]
3.35 Å
Cu Kα
°2θ
5
10
15
20
25
30

USGS
Coastal and Marine Geology Program

U. S. Geological Survey Open-File Report 01-041

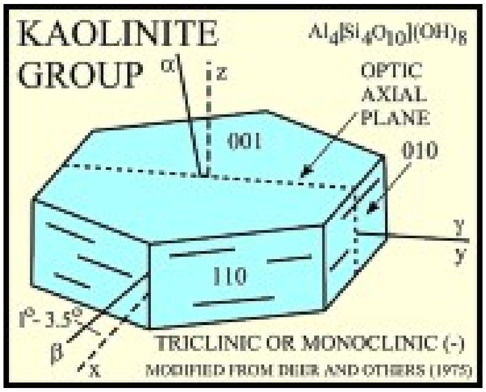
A Laboratory Manual for X-Ray Powder Diffraction

KAOLINITE GROUP



The kaolinite group includes the dioctahedral minerals kaolinite, dickite, nacrite, and halloysite, and the trioctahedral minerals antigorite, chamosite, chrysotile, and cronstedite. The primary structural unit of this group is a layer composed of one octahedral sheet condensed with one tetrahedral sheet. In the dioctahedral minerals the octahedral site are occupied by aluminum; in the trioctahedral minerals these sites are occupied by magnesium and iron. Kaolinite and halloysite are single-layer structures. Although dickite and nacrite have the same basic structure, the stacking sequence of layers is different in these minerals (Dixon, 1989; Moore and Reynolds, 1997). Kaolinite, dickite, and nacrite occur as plates; halloysite, which can have a single layer of water between its sheets, occurs in a tubular form.

All members of the kaolinite group form primarily during hydrothermal alteration or weathering of feldspars under acid conditions; but kaolinite and halloysite are probably the only members formed in soils (Deer and others, 1975; Swindale, 1975). Kaolin minerals are used during the manufacture of ceramics, paper, and paint.



In mono-mineralic samples the dioctahedral members of this group are readily identified because they become amorphous to X-rays after heating to 550 degrees C and their diffraction patterns disappear. Kaolinite, dickite, nacrite, and halloysite can be differentiated from chlorite by comparisons of the 3.58-angstrom kaolin peak with the 3.54-angstrom chlorite peak (Biscaye, 1965), and from chlorite and the trioctahedral members of this group by intercalation with potassium acetate (Wada, 1965). Heating alone will not distinguish the dioctahedral kaolinite group minerals from chlorite because the 002, 003, and 004 chlorite peaks are also weakened by this heat treatment (Moore and Reynolds, 1997). Intercalation complexes can also be used to differentiate individual dioctahedral kaolinite minerals. For example, dehydrated halloysite can be distinguished from kaolinite by intercalation with formamide (Churchman and others, 1984).

X-ray powder diffraction patterns of oriented-aggregate mounts showing the effects of standard treatments on:

- Kaolinite
- Dickite
- Halloysite

Selected Bibliography for Kaolinite-Group Minerals

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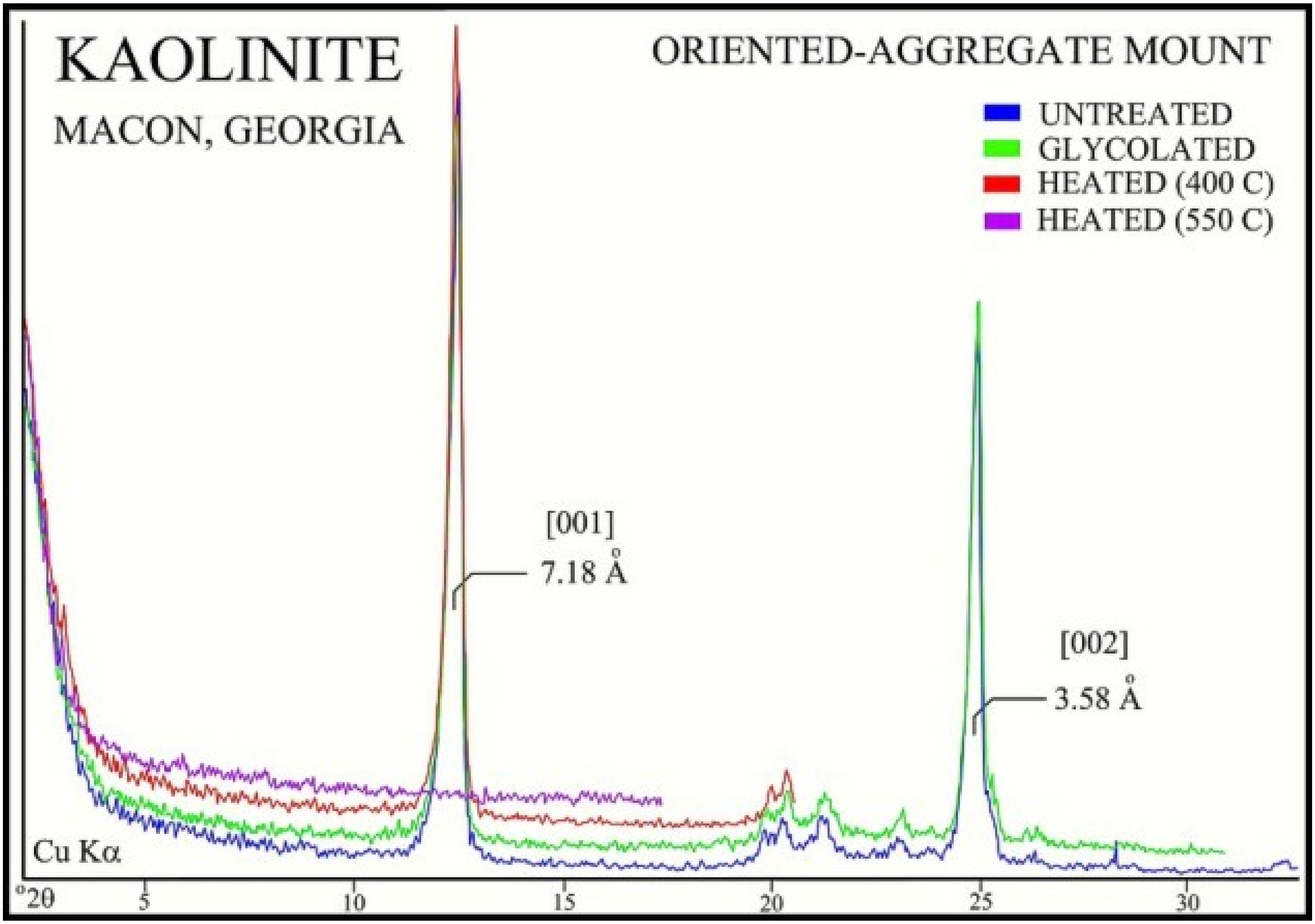
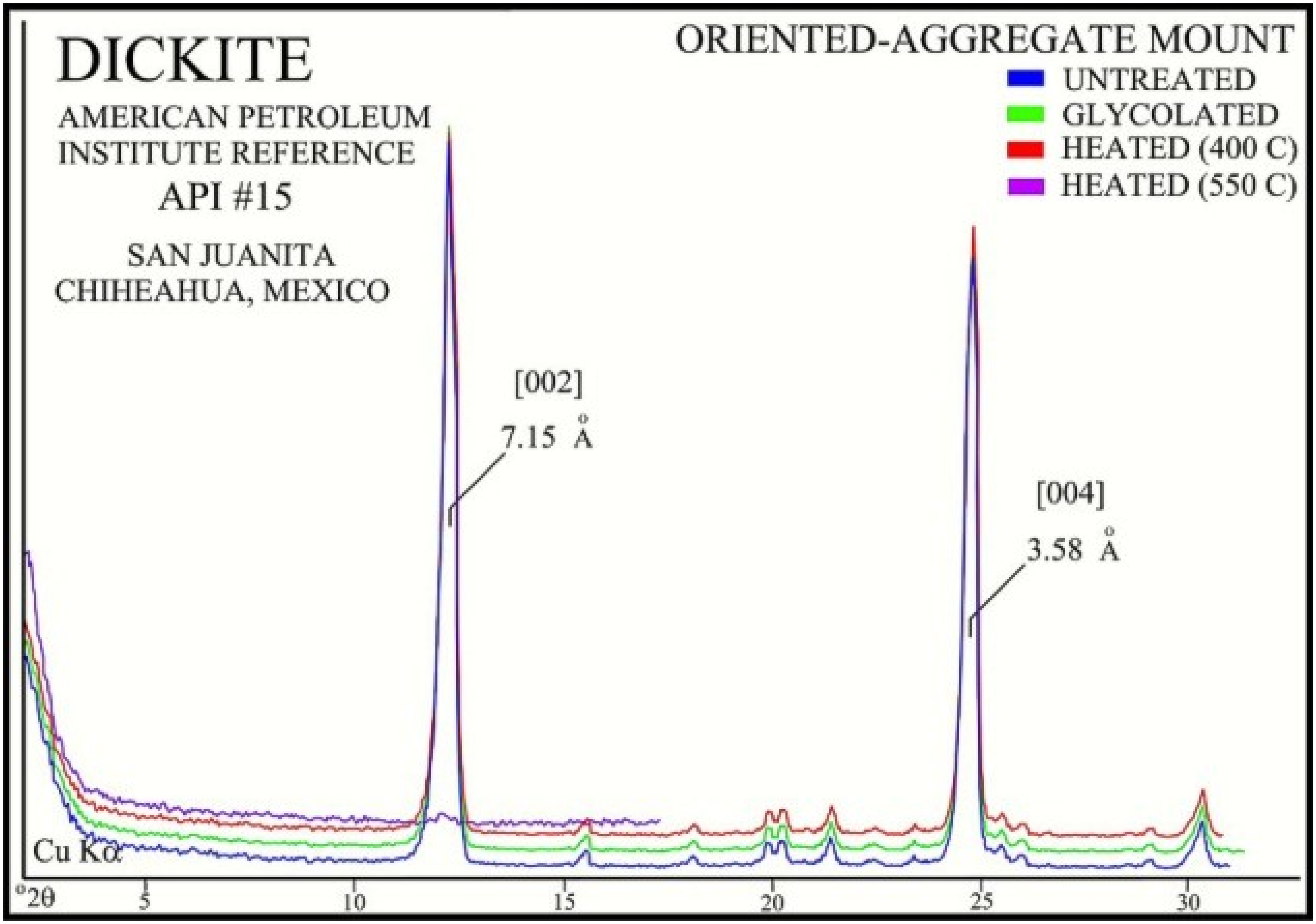
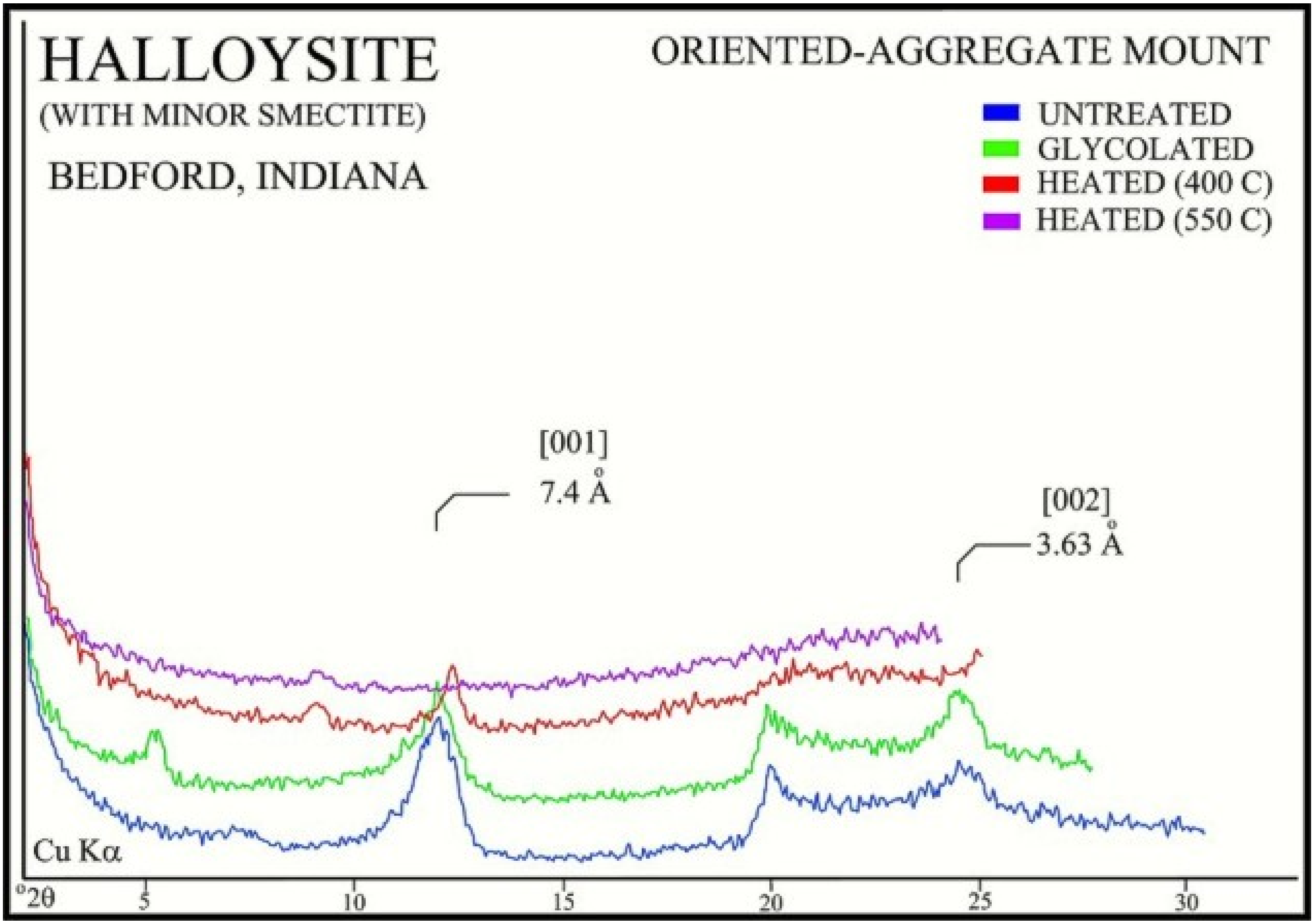

KAOLINITE
MACON, GEORGIA
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400 C)
HEATED (550 C)
[001]
7.18 Å
[002]
3.58 Å
Cu Kα
°2θ
5
10
15
20
25
30


DICKITE
AMERICAN PETROLEUM
INSTITUTE REFERENCE
API #15
SAN JUANITA
CHIHEAHUA, MEXICO
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400 C)
HEATED (550 C)
[002]
7.15 Å
[004]
3.58 Å
Cu Kα
°2θ
5
10
15
20
25
30


HALLOYSITE
(WITH MINOR SMECTITE)
BEDFORD, INDIANA
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400 C)
HEATED (550 C)
[001]
7.4 Å
[002]
3.63 Å
Cu Kα
°2θ
5
10
15
20
25
30

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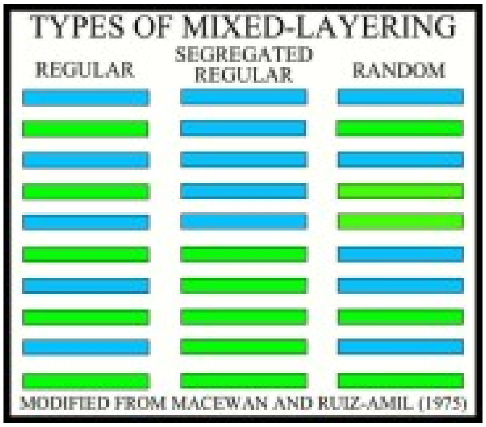
Mixed-Layer Clays

Mixed-layer clay minerals are materials in which different kinds of clay layers alternate with each other. The mixing or interstratification in vertical stacking can be regular (ordered), segregated regular, or random (MacEwan and Ruiz-Amil, 1975; Reynolds, 1980; Wilson, 1987). Commonly described mixed-layer clays include: illite-vermiculite, illite-smectite, chlorite-vermiculite (corrensite), chlorite-smectite, and kaolinite-smectite. Mixed-layer clays can form by weathering involving the removal or uptake of cations (e.g. K), hydrothermal alteration, or removal of hydroxide interlayers, and, in some cases, may represent an intermediate stage in the formation of swelling minerals from non-swelling minerals or visa versa (MacEwan and Ruiz-Amil, 1975; Sawhney, 1989).



Regularly interstratified structures are readily identified by their 001 basal reflection, which corresponds to the sum of the spacings of the individual components, and subsequent peaks of higher integral orders (Sawhney, 1989). For example, regularly interstratified illite-smectite, when Mg-saturated and glycolated, would be characterized by a 001 diffraction peak at about 27 angstroms, corresponding to the sum of the spacings of illite (10 angstroms) and smectite (17 angstroms). Conversely, randomly interstratified structures have non-integral peaks at positions intermediate between the peaks from the individual mineral layers. For example, randomly interstratified illite-chlorite would be characterized by a 001 basal diffraction peak between 10 and 14 angstroms.

X-ray powder diffraction patterns of oriented-aggregate mounts showing the effects of standard treatments on Chlorite-Vermiculite:

- Corrensite

Selected Bibliography for Mixed-Layer Clays

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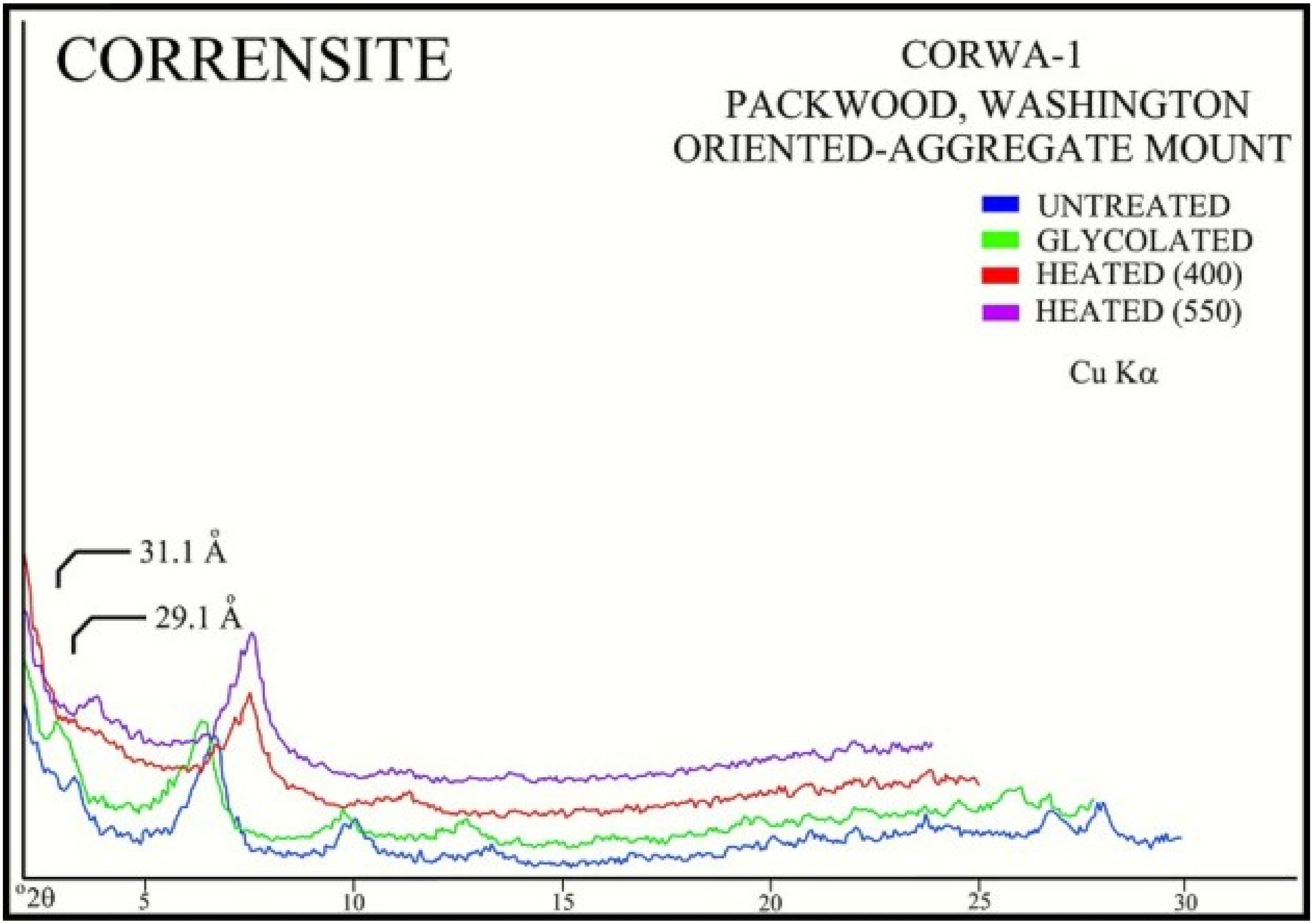
CORRENSITE
CORWA-1
PACKWOOD, WASHINGTON
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400)
HEATED (550)
Cu Kα
31.1 Å
29.1 Å
°2θ
5
10
15
20
25
30

USGS
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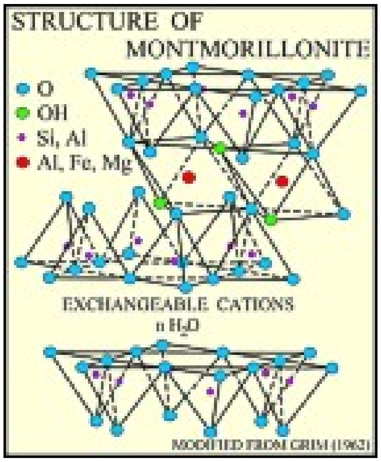
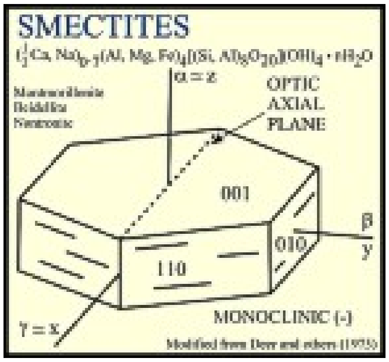
SMECTITE GROUP



Members of the smectite group include the dioctahedral minerals montmorillonite, beidellite, and nontronite, and the trioctahedral minerals hectorite (Li-rich), saponite (Mg-rich), and sauconite (Zn-rich). The basic structural unit is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet. The layers are continuous in the a and b directions, but the bonds between layers are weak and have excellent cleavage, allowing water and other molecules to enter between the layers causing expansion in the c direction (Grim, 1962).

Smectites commonly result from the weathering of basic rocks. Smectite formation is favored by level to gently sloping terranes that are poorly drained, mildly alkaline (such as in marine environments), and have the high Si and Mg potentials (Borchardt, 1977). Other factors that favor the formation of smectites include the availability of Ca and the paucity of K (Deer and others, 1975). Poor drainage is necessary because otherwise water can leach away ions (e.g. Mg) freed in the alteration reactions. Smectites are used in industry as fillers, carriers, absorbents, and a component in drilling fluids (Grim, 1962).



Smectites yield X-ray diffraction patterns characterized by basal reflections that vary with humidity, exposure to certain organic molecules, heat treatment, and exchangeable cations (Wilson, 1987). When saturated with ethylene glycol, the 001 reflection of most smectites will swell to about 17 angstroms (about 17.8 angstroms with glycerol); when heated to 400 C, the 001 reflection will collapse to about 10 angstroms (the exact amount of collapse is often related to the exchange cations present and to the smectite itself). Individual smectites can sometimes be differentiated by their higher-order peaks or by cation saturation. For example, dioctahedral smectites have 060 reflections at 1.50-1.52 angstroms, whereas trioctahedral smectites have 060 reflections at 1.53-1.54 angstroms; and Li saturation can be used to differentiate some montmorillonites from beidellite (Schultz, 1969).

X-ray powder diffraction patterns of oriented-aggregate mounts showing the effects of standard treatments:

- Montmorillonite API 11
- Montmorillonite API 25
- Nontronite
- Saponite

Selected Bibliography for Smectites

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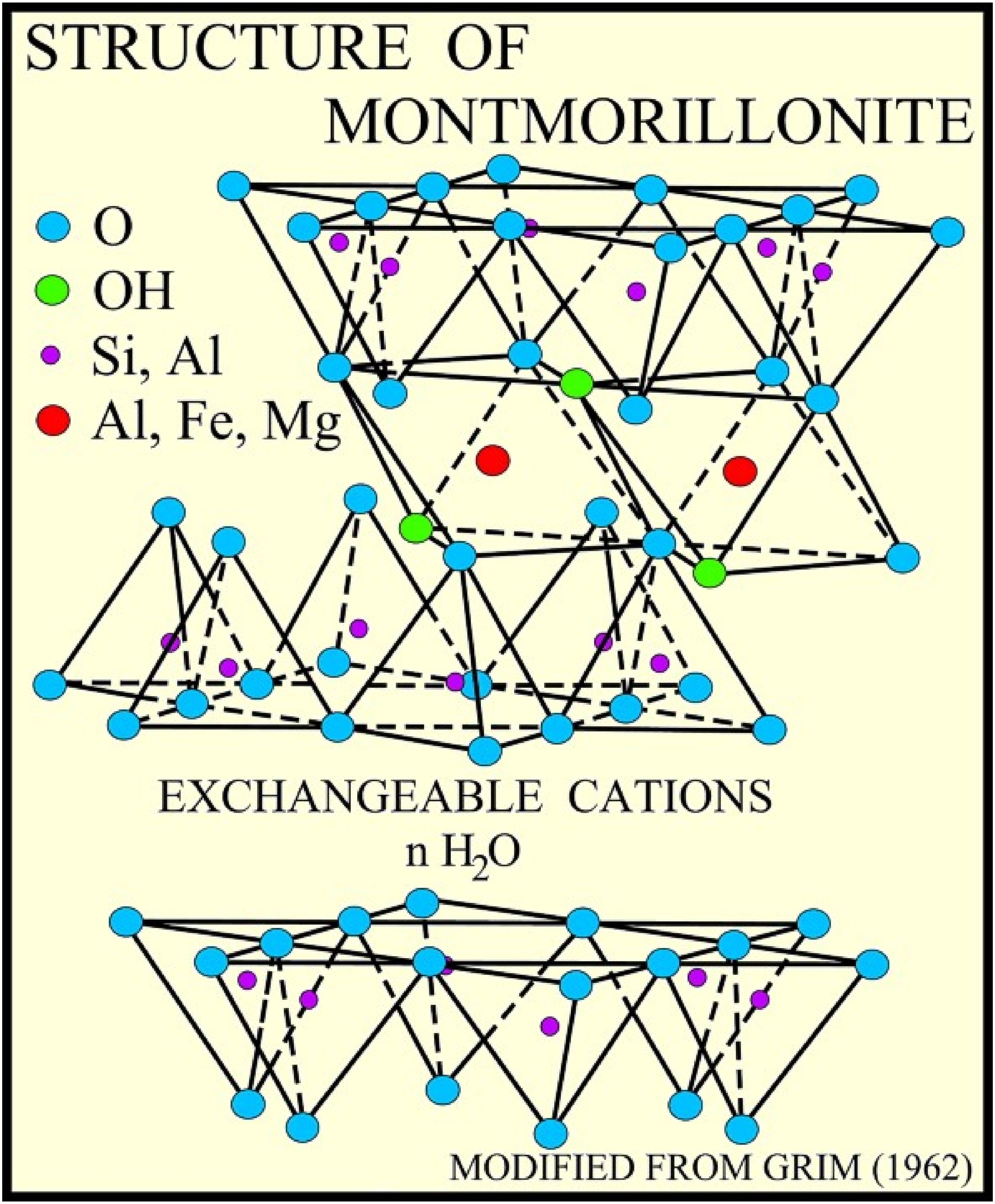

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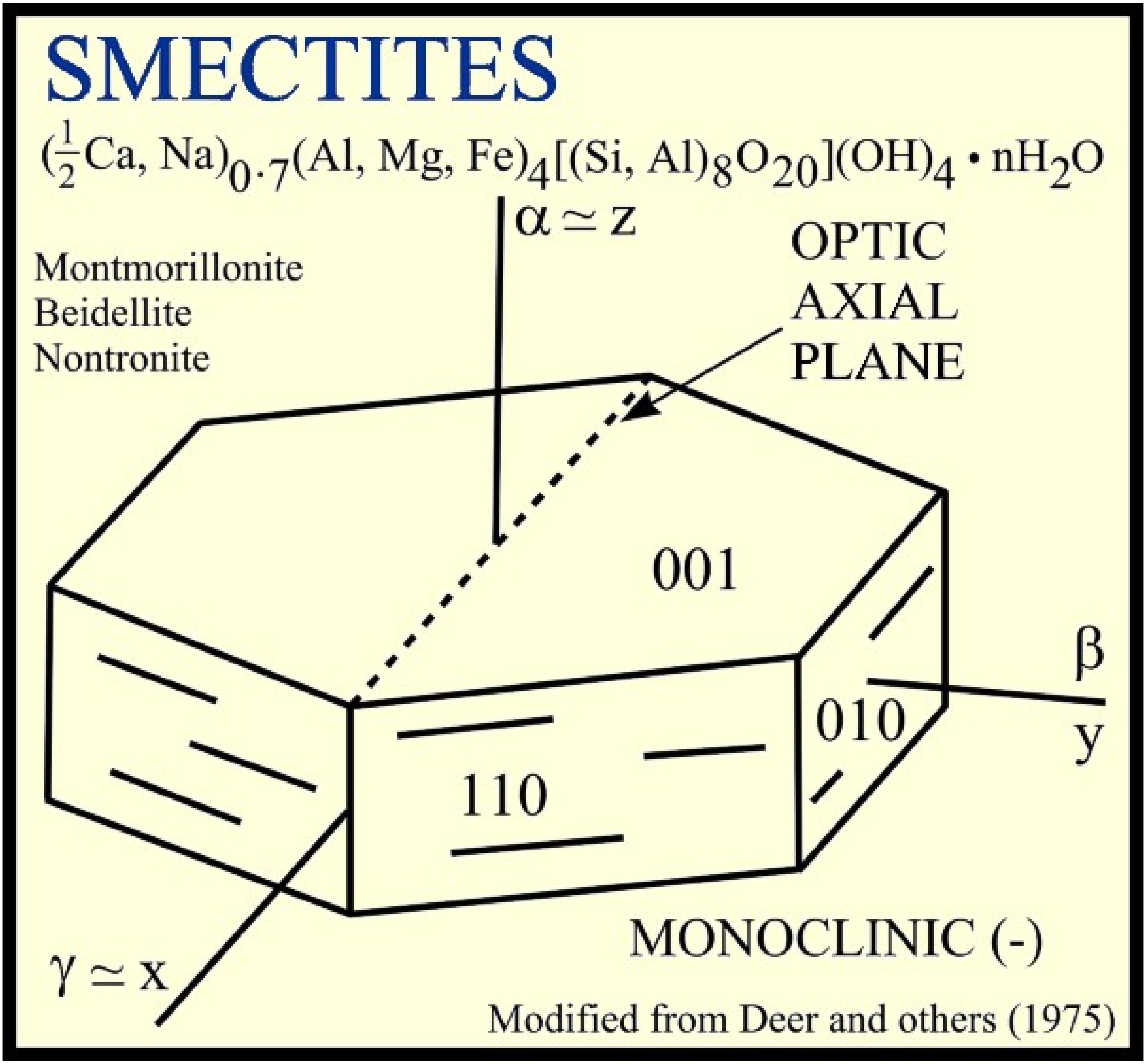
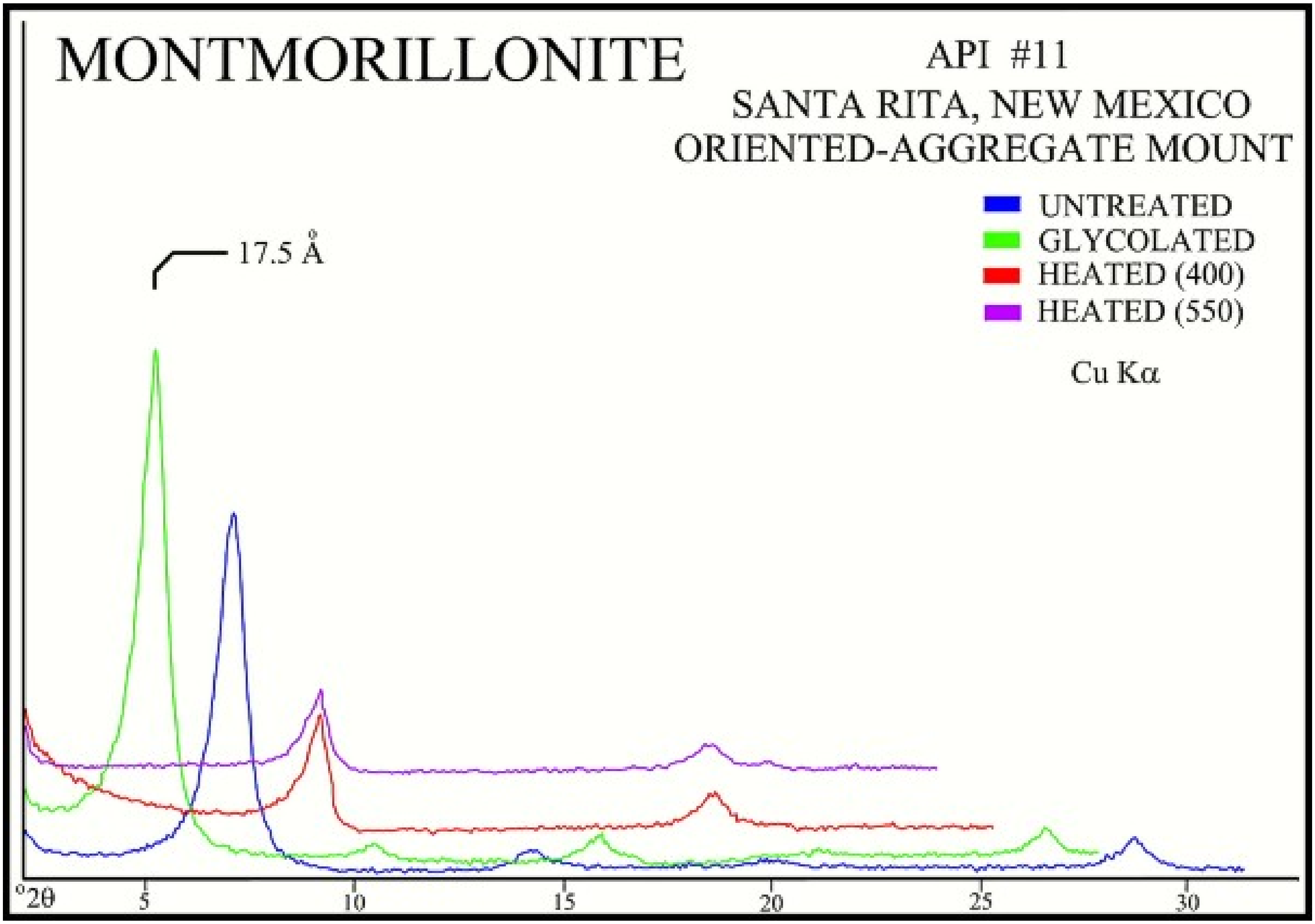
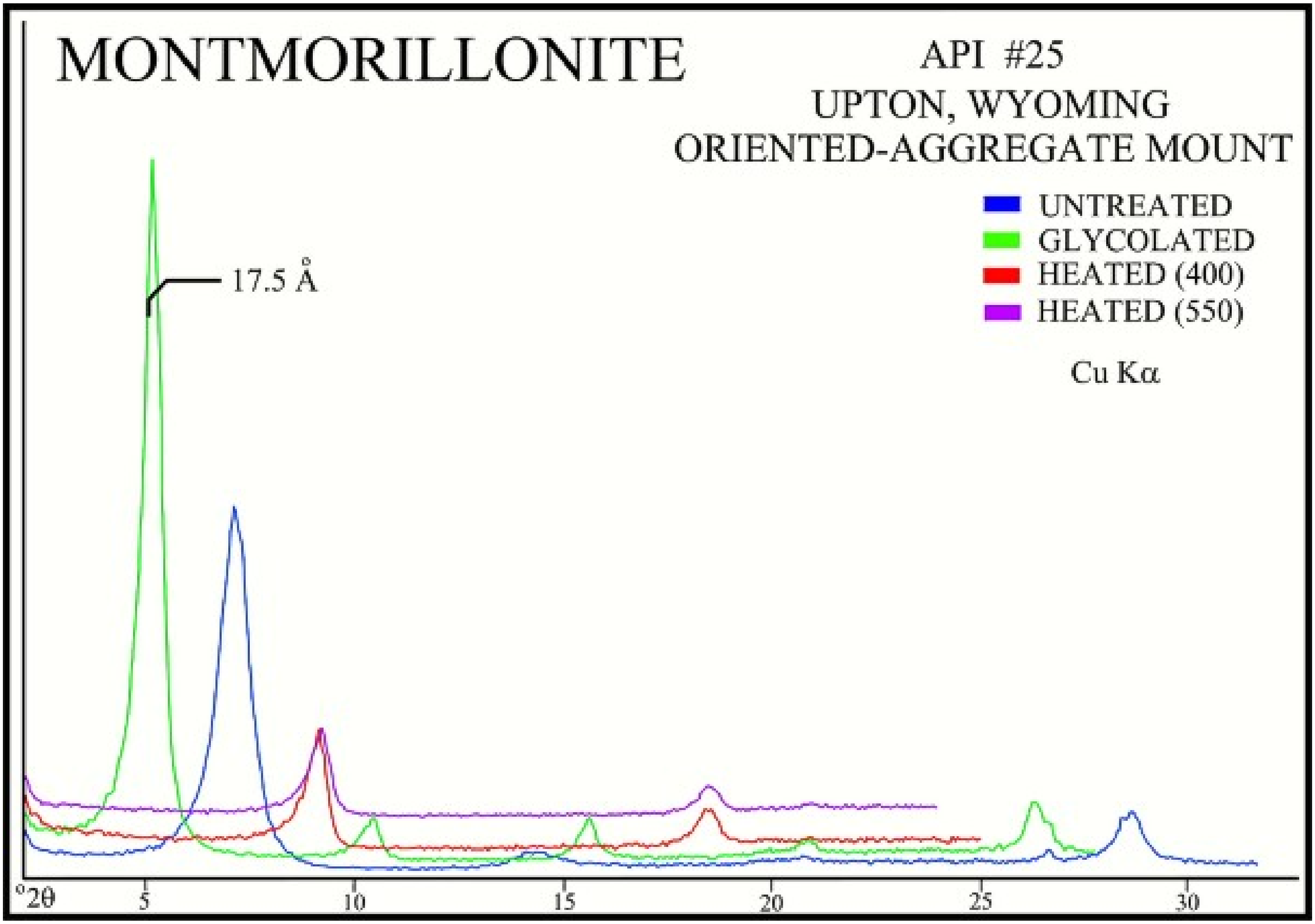
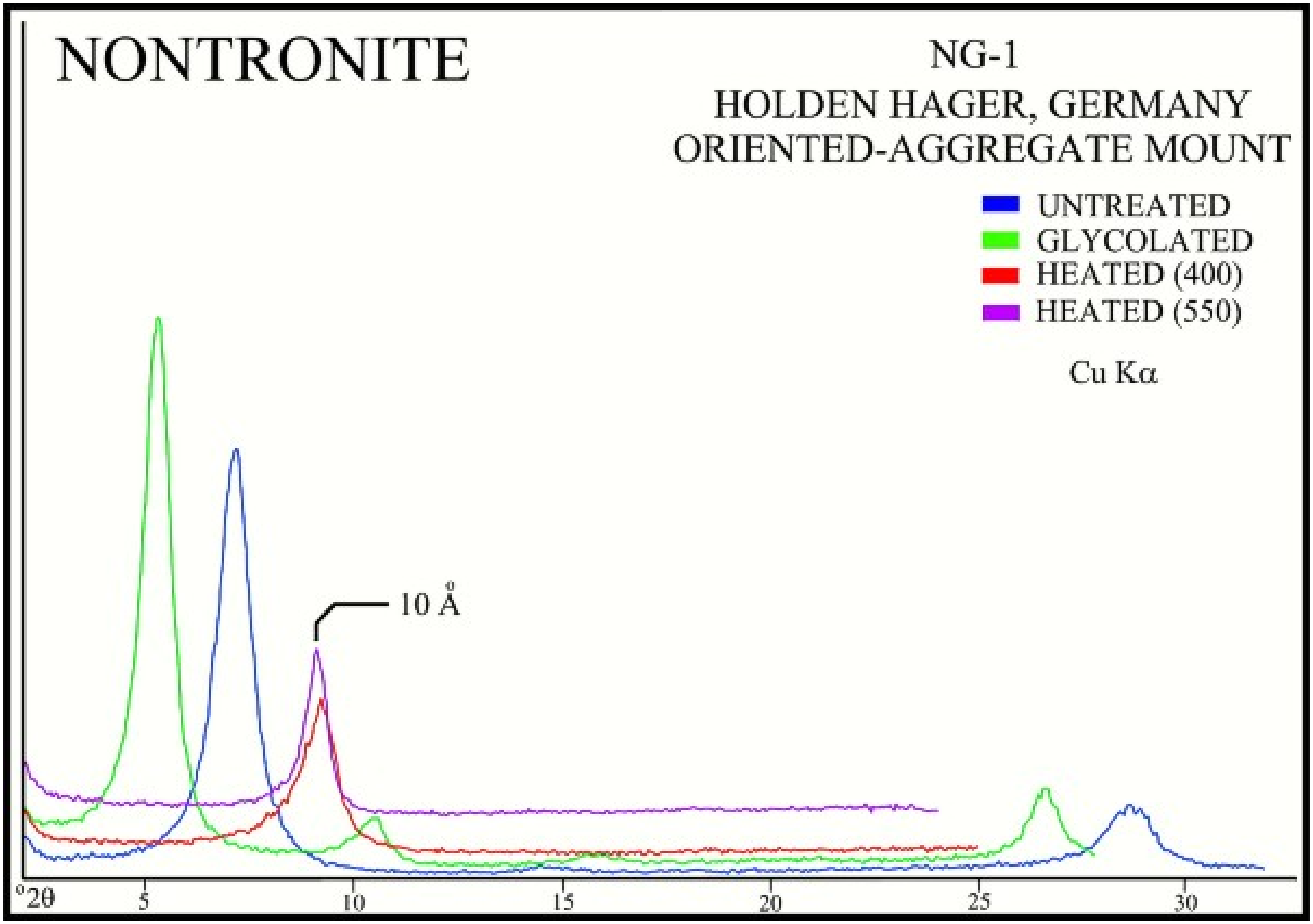
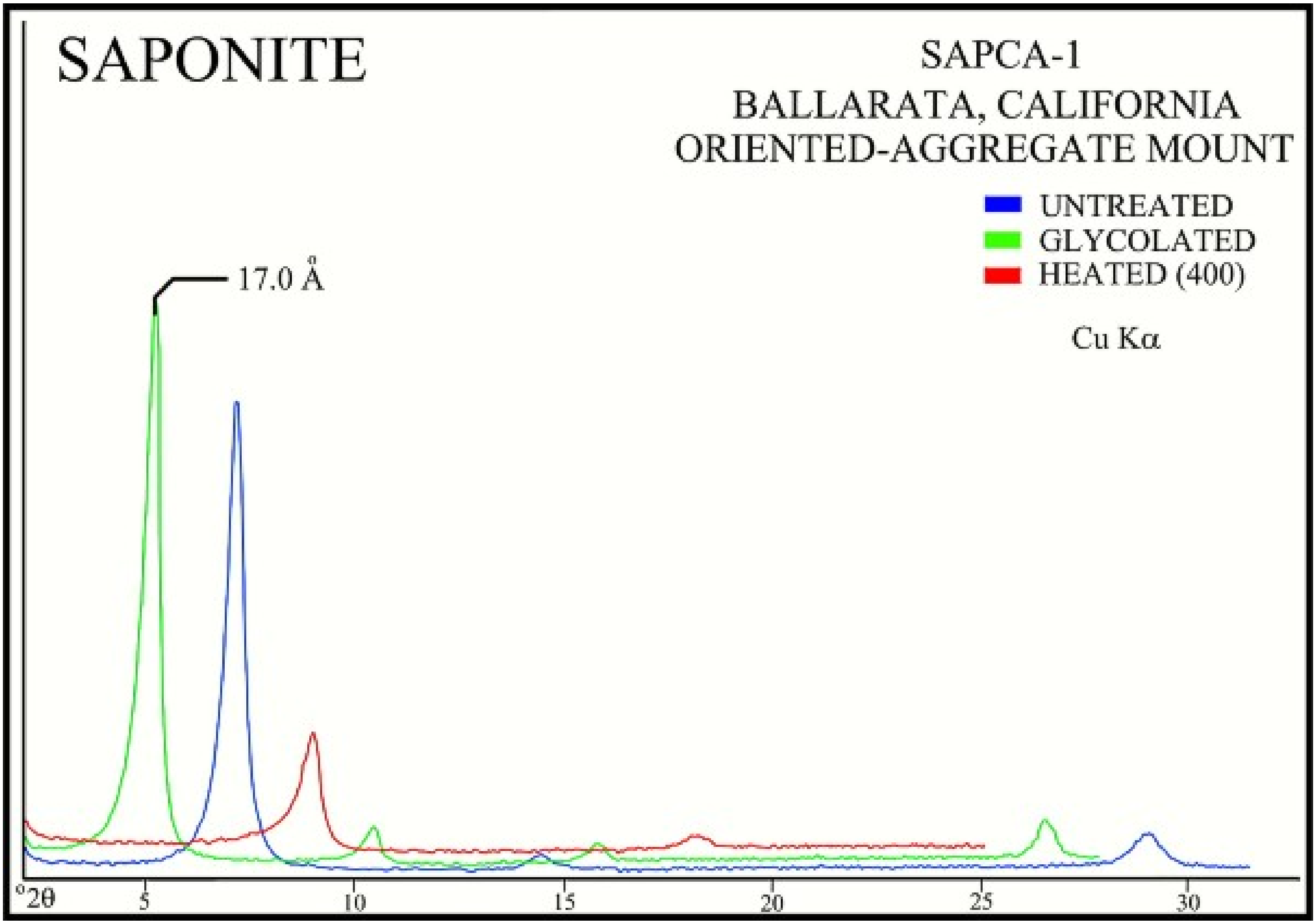

SMECTITES
$(\frac{1}{2}Ca, Na)_{0\cdot7}(Al, Mg, Fe)_4[(Si, Al)_8O_{20}](OH)_4 \cdot nH_2O$
Montmorillonite
Beidellite
Nontronite
$\alpha \simeq z$
OPTIC AXIAL PLANE
001
110
010
β
y
$\gamma \simeq x$
MONOCLINIC (-)
Modified from Deer and others (1975)


MONTMORILLONITE
API #11
SANTA RITA, NEW MEXICO
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400)
HEATED (550)
Cu Kα
17.5 Å
°2θ
5
10
15
20
25
30


MONTMORILLONITE
API #25
UPTON, WYOMING
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400)
HEATED (550)
Cu Kα
17.5 Å
°2θ
5
10
15
20
25
30


NONTRONITE
NG-1
HOLDEN HAGER, GERMANY
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400)
HEATED (550)
Cu Kα
10 Å
°2θ
5
10
15
20
25
30


SAPONITE
SAPCA-1
BALLARATA, CALIFORNIA
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400)
Cu Kα
17.0 Å
°2θ
5
10
15
20
25
30

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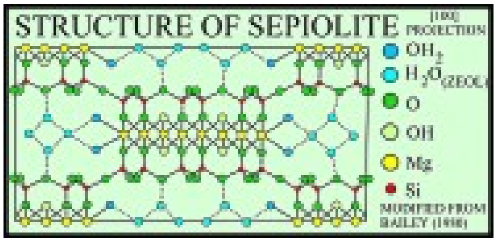
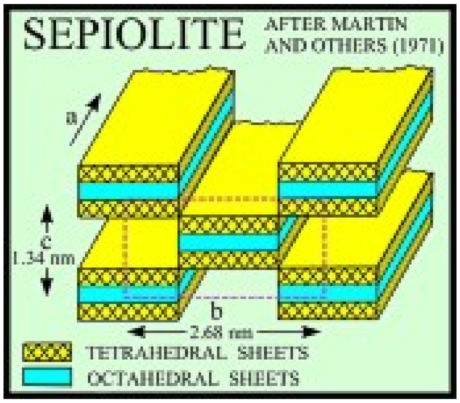
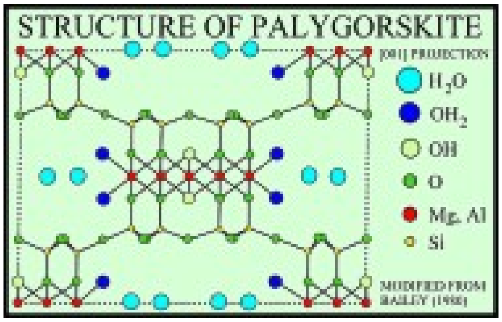
SEPIOLITE AND PALYGORSKITE

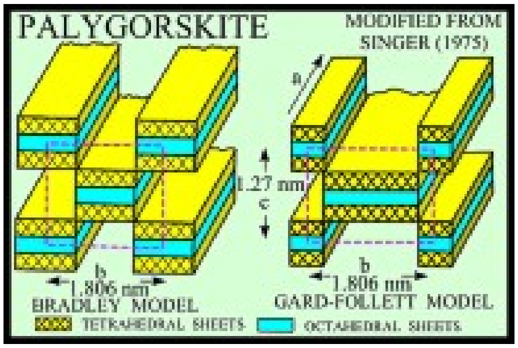




Sepiolite and palygorskite have similar fibrous or lath-like morphologies, but palygorskite exhibits more structural diversity and, although both minerals are Mg silicates, has less Mg and more Al than sepiolite (Caillere and Henin, 1961; Moore and Reynolds, 1997). The structures of both minerals are similar in that tetrahedra pointing in the same direction form 2:1 ribbons that extend in the direction of the a-axis and have an average b-axis width of three linked tetrahedral chains in sepiolite and two linked chains in palygorskite (Singer, 1989). Rectangular channels, which contain some exchangeable Ca and Mg cations and zeolitic water, lie between the ribbons, and molecules of bound water lie at the edges of the ribbons.



Both sepiolite and palygorskite require alkaline conditions and high Si and Mg activities for stability (Singer, 1989). They are also loosely associated with low latitudes and semi-arid climates. Most major deposits were originally formed in shallow seas and lakes as chemical sediments or by the reconstitution of smectites, in open oceans by the hydrothermal alteration of volcanic materials, and in calcareous soils by direct crystallization (Callen, 1984). Owing to their absorptive properties, sepiolite and palygorskite are used commercially as carriers, fillers, clarifying agents, and in used lubricant reclamation.



The fibrous nature of sepiolite and palygorskite precludes the production of oriented aggregate mounts to enhance the 001 reflection for X-ray powder diffraction (Wilson, 1987). However, strong reflections from the 011 planes yield intense peaks at 12.2 angstroms in sepiolite and at 10.5 angstroms in palygorskite. These peaks are unaffected by solvation with ethylene glycol, but change during heat treatments. After heating to 400 C, the 001 peaks of both minerals are reduced in intensity and new palygorskite peaks occur at 9.2 and 4.7 angstroms (Singer, 1989). After heating to 550 C, the original 011 palygorskite and sepiolite peaks are completely destroyed, but now new peaks for sepiolite occur at 10.4 and 8.2 angstroms.

X-ray powder diffraction patterns of oriented-aggregate mounts showing the effects of standard treatments:

- Sepiolite
- Palygorskite

Selected Bibliography for Sepiolite and Palygorskite

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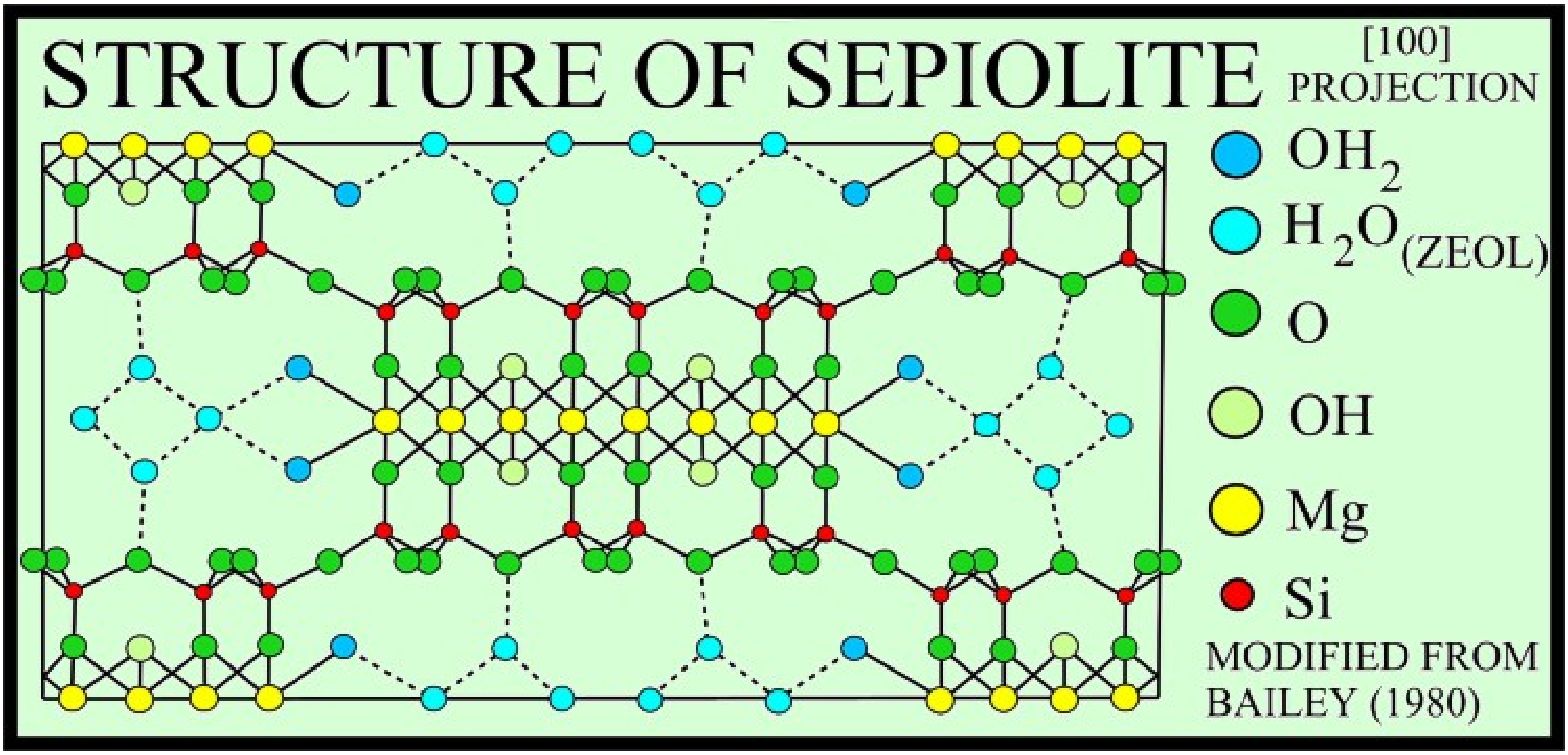
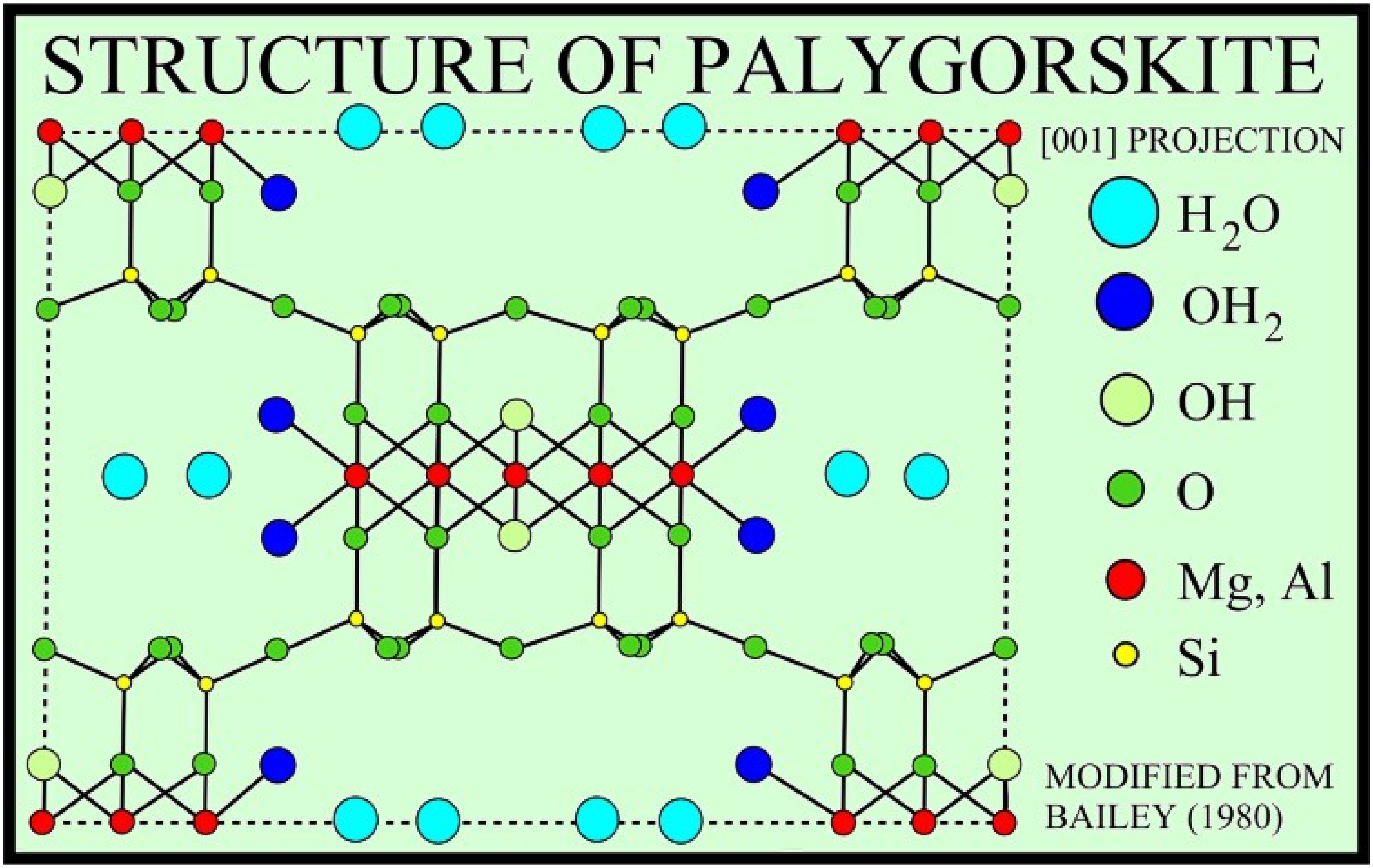
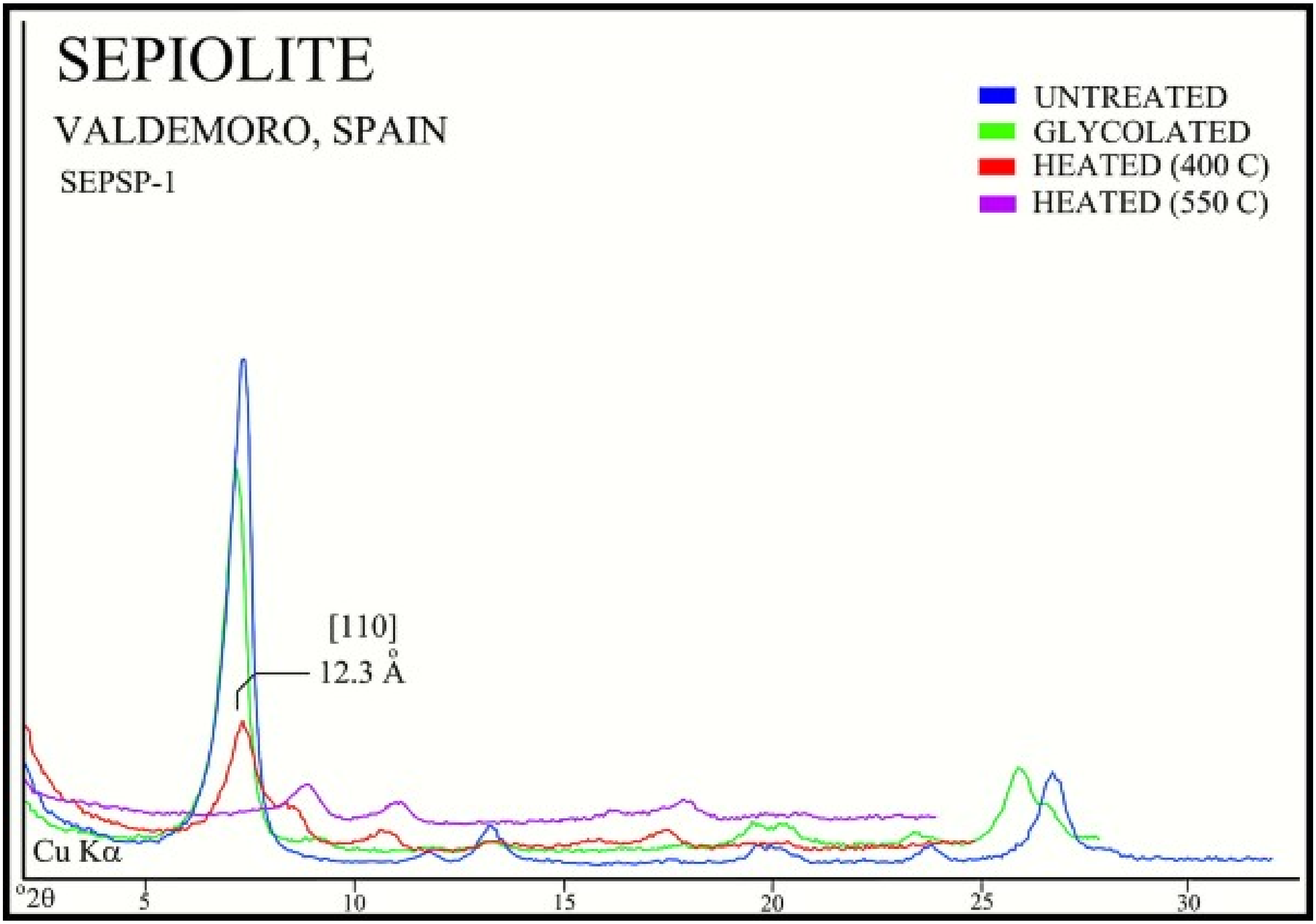
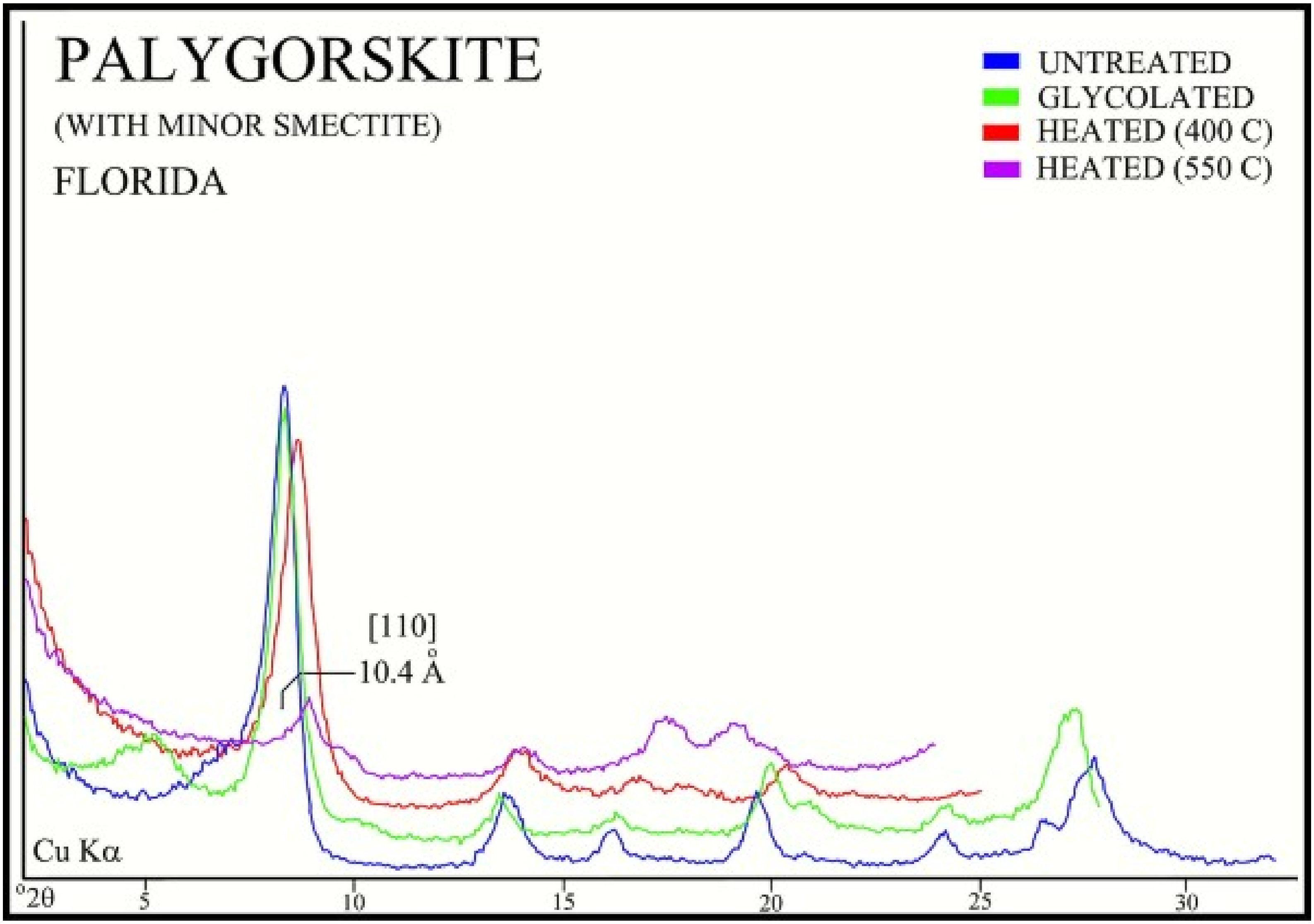

STRUCTURE OF SEPIOLITE
[100]
PROJECTION
OH_2
$H_2O_{(ZEOL)}$
O
OH
Mg
Si
MODIFIED FROM
BAILEY (1980)

STRUCTURE OF PALYGORSKITE



MODIFIED FROM BAILEY (1980)


SEPIOLITE
VALDEMORO, SPAIN
SEPSP-1
🟦 UNTREATED
🟩 GLYCOLATED
🟥 HEATED (400 C)
🟪 HEATED (550 C)
[110]
12.3 Å
Cu Kα
°2θ
5
10
15
20
25
30


PALYGORSKITE
(WITH MINOR SMECTITE)
FLORIDA
UNTREATED
GLYCOLATED
HEATED (400 C)
HEATED (550 C)
[110]
10.4 Å
Cu Kα
°2θ
5
10
15
20
25
30

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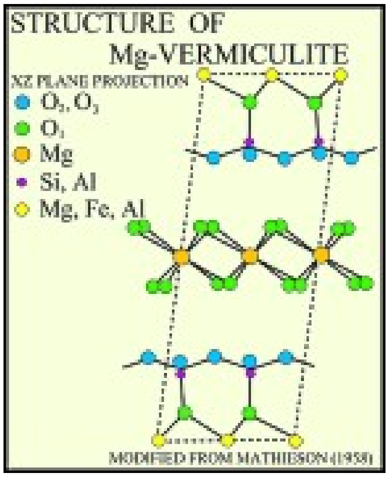
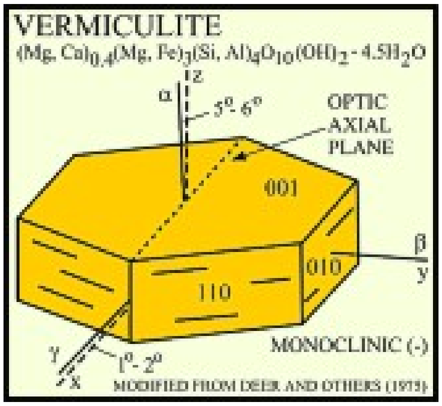
VERMICULITE

The structure of Mg-saturated vermiculite resembles talc in that it contains a central octahedrally-coordinated layer of Mg ions that lie between two inwardly pointing sheets of linked tetrahedra (Mathieson, 1958). These silicate layers are normally separated by two sheets of interlayer water molecules arranged in a distorted hexagonal fashion. Progressive removal of this interlayer water results in a series of less hydrated phases that include the 14.36 angstrom lattice with two sheets of water molecules, a 11.59 angstrom lattice with a single sheet of water molecules, and a 9.02 angstrom lattice from which all water has been removed (Walker, 1975). Inasmuch as the layers are electrically neutral and interlayer cations occupy only about one-third of the available sites, cohesion between the layers is typically weak.





Vermiculites are usually formed in sediments by the alteration of micaceous minerals (biotite and chlorite to trioctahedral vermiculite; muscovite to dioctahedral vermiculite; Moore and Reynolds, 1997). However, vermiculites formed through the alteration mica are comparatively rare in marine sediments because the K of sea water readily contracts them (Deer and others, 1975). Where present, marine vermiculites are probably derived from volcanic material, chlorite, and hornblende.

Although dentification of vermiculite can be problematic because its characteristics vary, most Mg-saturated and hydrated vermiculites yield a 14-angstrom 001 peak that does not expand upon solvation with ethylene glycol. The 001 peak of dioctahedral vermiculite collapses to about 12 angstrom after heating to 400 C and to about 11 angstroms after heating to 550 C. The 001 peak of trioctahedral vermiculite collapses to about 10 angstroms after heating to 400 C, but shows no change or only a slight additional collapse after heating to 550 C. Dioctahedral and trioctahedral vermiculites may also be differentiated based on 060 diffraction lines of 1.50 angstroms and 1.52-1.54 angstroms, respectively (Douglas, 1989).

X-ray powder diffraction patterns of oriented-aggregate mounts showing the effects of standard treatments on:

- Vermiculite

Selected Bibliography for Vermiculite

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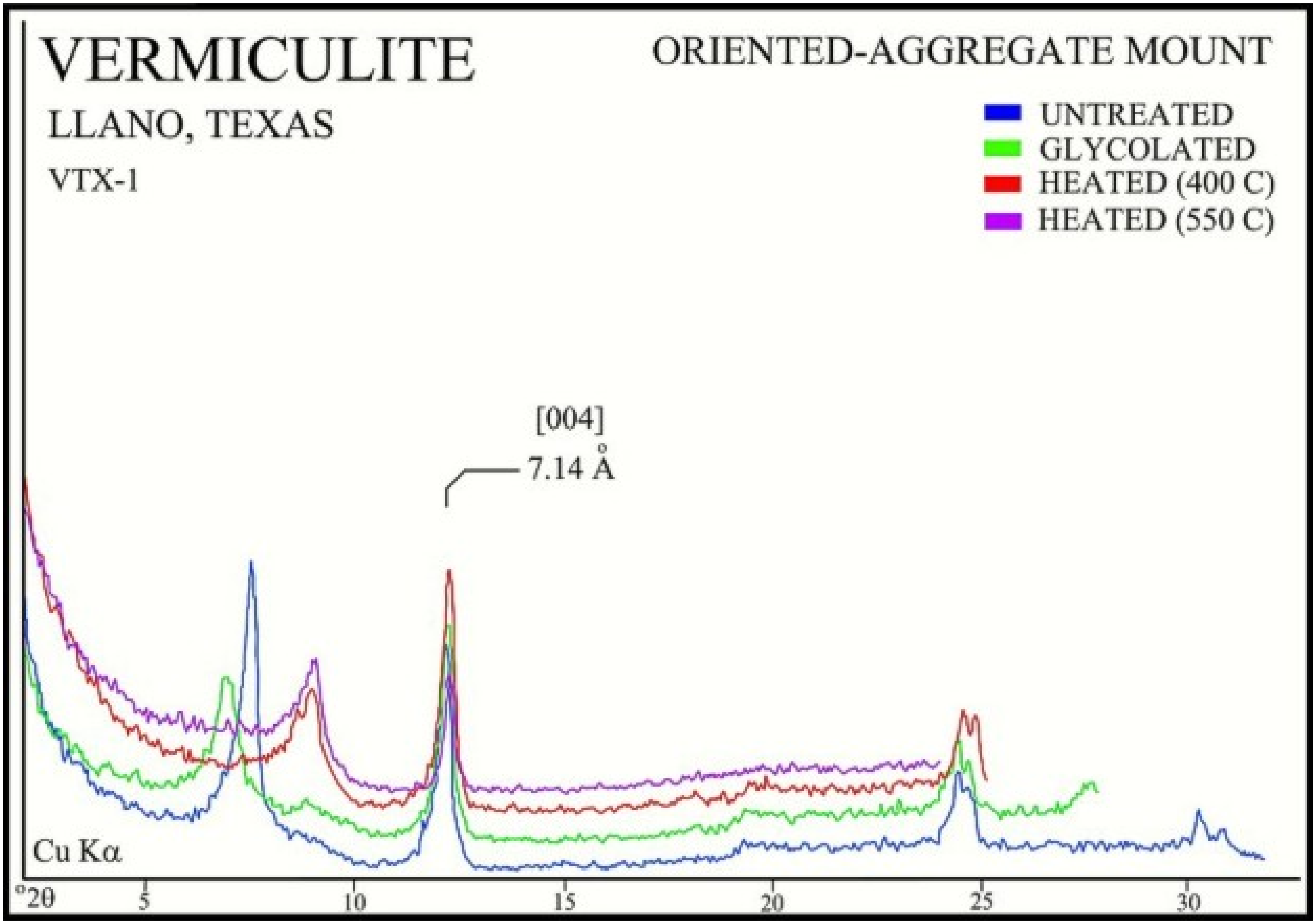
VERMICULITE
LLANO, TEXAS
VTX-1
ORIENTED-AGGREGATE MOUNT
UNTREATED
GLYCOLATED
HEATED (400 C)
HEATED (550 C)
[004]
7.14 Å
Cu Kα
°2θ
5
10
15
20
25
30

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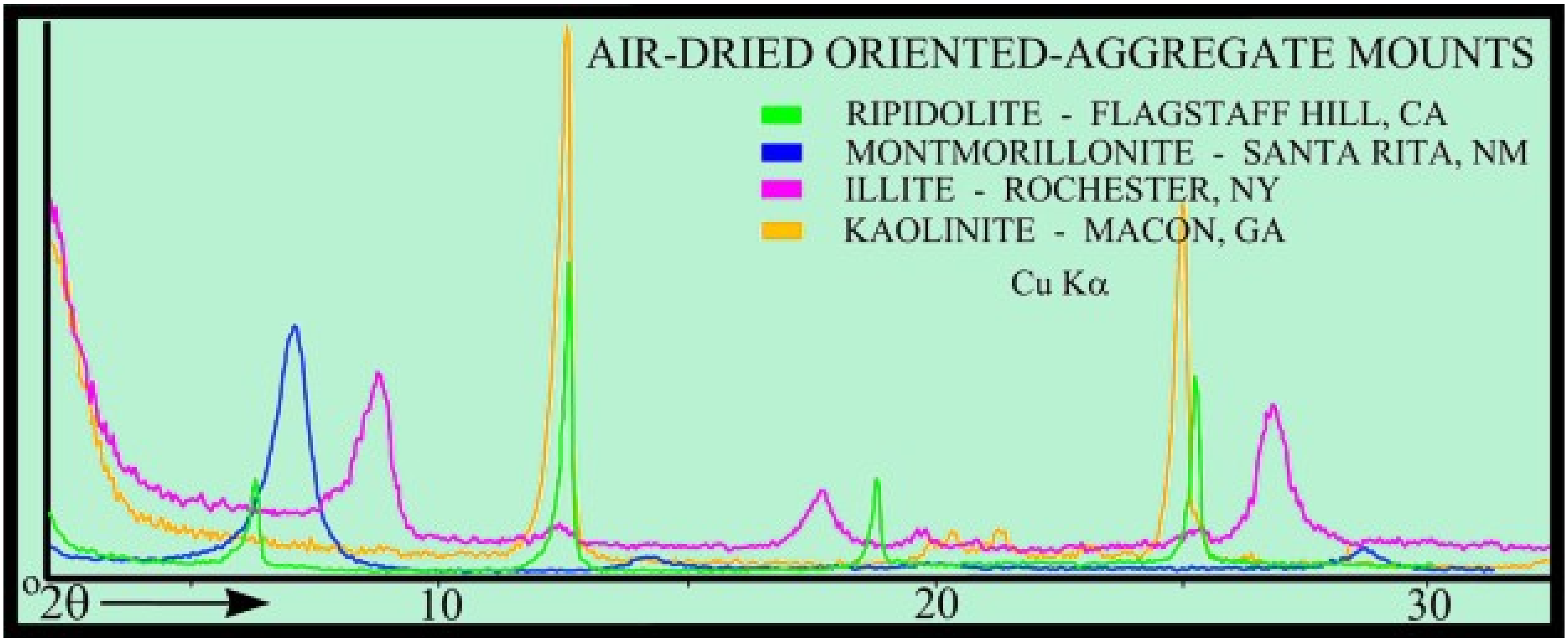

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Clay Mineral Identification Flow Diagram

A clay mineral identification flow diagram is available in 5 formats. Please select the form you wish to view from the table below.

HTML	GIF	PDF	TXT	Microsoft Word Document

When using the HTML formatted pages, please use the up arrow (△)when available from the right column to return to a previous selection. Using the browser's back button will not refresh the pages and the selection process will not operate properly.

To view and print the PDF version of the Clay Mineral Identification Flow Diagram, you must obtain and install the **Acrobat® Reader** **version 4 or later**, available at no charge from Adobe Systems.

U.S. Department of the Interior, U.S. Geological Survey
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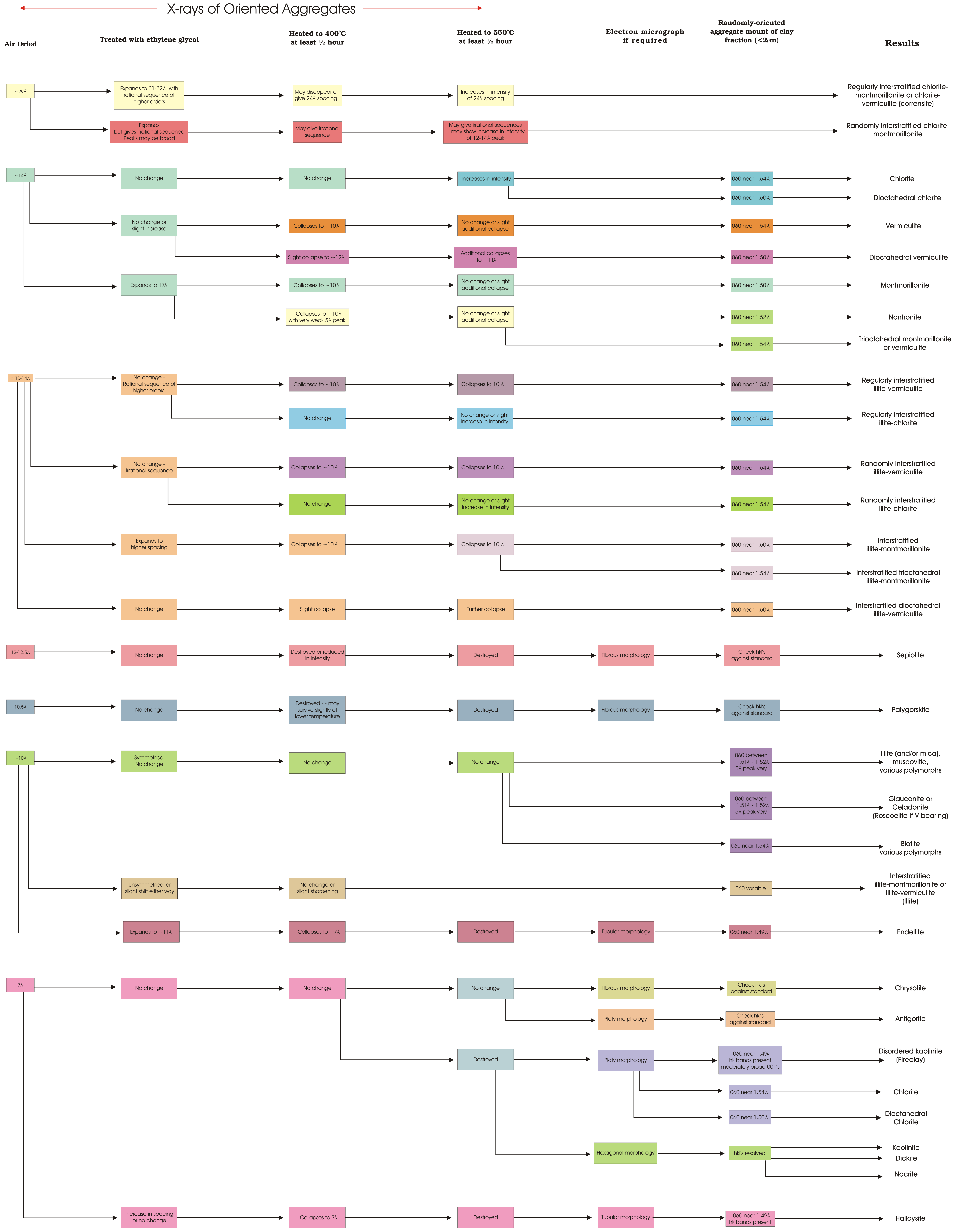
Clay Mineral Identification Flow Diagram



X-rays of Oriented Aggregates

Air Dried	**Treated with ethylene glycol**	**Heated to 400°C at least ½ hour**	**Heated to 550°C at least ½ hour**	**Electron micrograph if required**	**Randomly-oriented aggregate mount of clay fraction (<2μm)**	**Results**
~29Å	Expands to 31-32Å with rational sequence of higher orders	May disappear or give 24Å spacing	Increases in intensity of 24Å spacing			Regularly interstratified chlorite-montmorillonite or chlorite-vermiculite (corrensite)
	Expands but gives irrational sequence Peaks may be broad	May give irrational sequence	May give irrational sequences -- may show increase in intensity of 12-14Å peak			Randomly interstratified chlorite-montmorillonite
~14Å	No change	No change	Increases in intensity		060 near 1.54Å	Chlorite
					060 near 1.50Å	Dioctahedral chlorite
	No change or slight increase	Collapses to ~10Å	No change or slight additional collapse		060 near 1.54Å	Vermiculite
		Slight collapse to ~12Å	Additional collapses to ~11Å		060 near 1.50Å	Dioctahedral vermiculite
	Expands to 17Å	Collapses to ~10Å	No change or slight additional collapse		060 near 1.50Å	Montmorillonite
		Collapses to ~10Å with very weak 5Å peak	No change or slight additional collapse		060 near 1.52Å	Nontronite
					060 near 1.54Å	Trioctahedral montmorillonite or vermiculite
>10-14Å	No change - Rational sequence of higher orders.	Collapses to ~10Å	Collapses to 10 Å		060 near 1.54Å	Regularly interstratified illite-vermiculite
		No change	No change or slight increase in intensity		060 near 1.54Å	Regularly interstratified illite-chlorite
	No change - Irrational sequence	Collapses to ~10Å	Collapses to 10 Å		060 near 1.54Å	Randomly interstratified illite-vermiculite
		No change	No change or slight increase in intensity		060 near 1.54Å	Randomly interstratified illite-chlorite
	Expands to higher spacing	Collapses to ~10Å	Collapses to 10 Å		060 near 1.50Å	Interstratified illite-montmorillonite
					060 near 1.54Å	Interstratified trioctahedral illite-montmorillonite
	No change	Slight collapse	Further collapse		060 near 1.50Å	Interstratified dioctahedral illite-vermiculite
12-12.5Å	No change	Destroyed or reduced in intensity	Destroyed	Fibrous morphology	Check hkl's against standard	Sepiolite
10.5Å	No change	Destroyed - - may survive slightly at lower temperature	Destroyed	Fibrous morphology	Check hkl's against standard	Palygorskite
~10Å	Symmetrical No change	No change	No change		060 between 1.51Å - 1.52Å 5Å peak very	Illite (and/or mica), muscovitic, various polymorphs
					060 between 1.51Å - 1.52Å 5Å peak very	Glauconite or Celadonite (Roscoelite if V bearing)
					060 near 1.54Å	Biotite various polymorphs
	Unsymmetrical or slight shift either way	No change or slight sharpening			060 variable	Interstratified illite-montmorillonite or illite-vermiculite (Illite)
	Expands to ~11Å	Collapses to ~7Å	Destroyed	Tubular morphology	060 near 1.49Å	Endellite
7Å	No change	No change	No change	Fibrous morphology	Check hkl's against standard	Chrysotile
				Platy morphology	Check hkl's against standard	Antigorite
			Destroyed	Platy morphology	060 near 1.49Å hk bands present moderately broad 001's	Disordered kaolinite (Fireclay)
					060 near 1.54Å	Chlorite
					060 near 1.50Å	Dioctahedral Chlorite
				Hexagonal morphology	hkl's resolved	Kaolinite
						Dickite
						Nacrite
	Increase in spacing or no change	Collapses to 7Å	Destroyed	Tubular morphology	060 near 1.49Å hk bands present	Halloysite