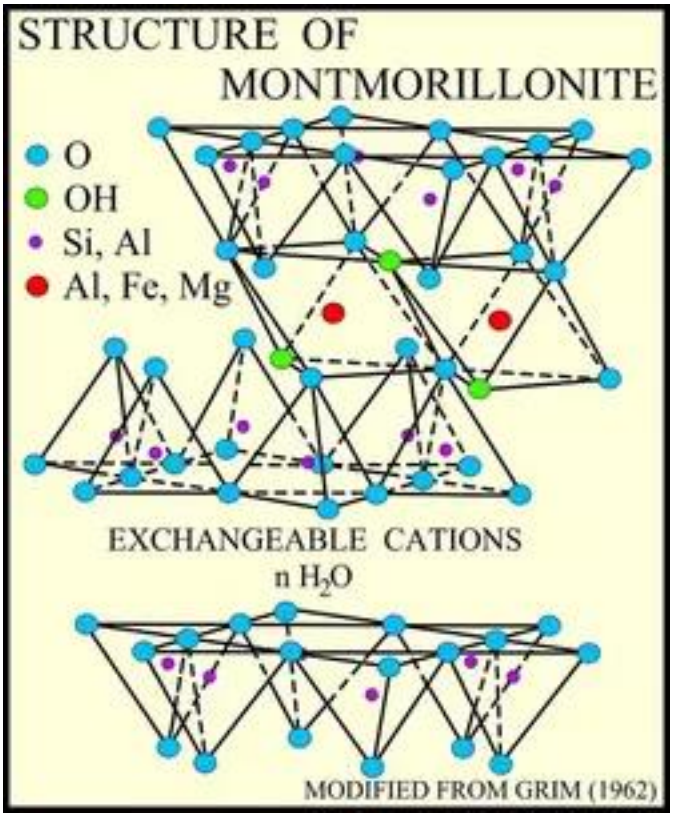
ICAL Technical Report: Clay Mineralogy USING X-ray Diffraction (XRD)

David W. Mogk, Professor of Geology (Emeritus)
Dept. Earth Sciences, Montana State University

Clay minerals are common in many natural environments (soils, weathering products of rocks, alteration of ore bodies, in sedimentary rocks in shales and as cements in sandstones) and also as important industrial materials (e.g., kaolins in ceramics, insulating materials such as spark plugs, as the sorbent in kitty litter). Clays have important physical properties (e.g., swelling, cohesion), chemical properties (cation exchange capacity, sorptive properties, bipolar charge distribution on grains), and affect the properties of host rocks (e.g., porosity and permeability). Given this diversity of physical and chemical properties and applications, it's important to accurately identify clay minerals. Note: there can be some confusion regarding the use of the term "clay" as a) a type of phyllosilicate mineral or b) a clay-sized particle (regardless of mineral type or composition) that is smaller than 2 microns.



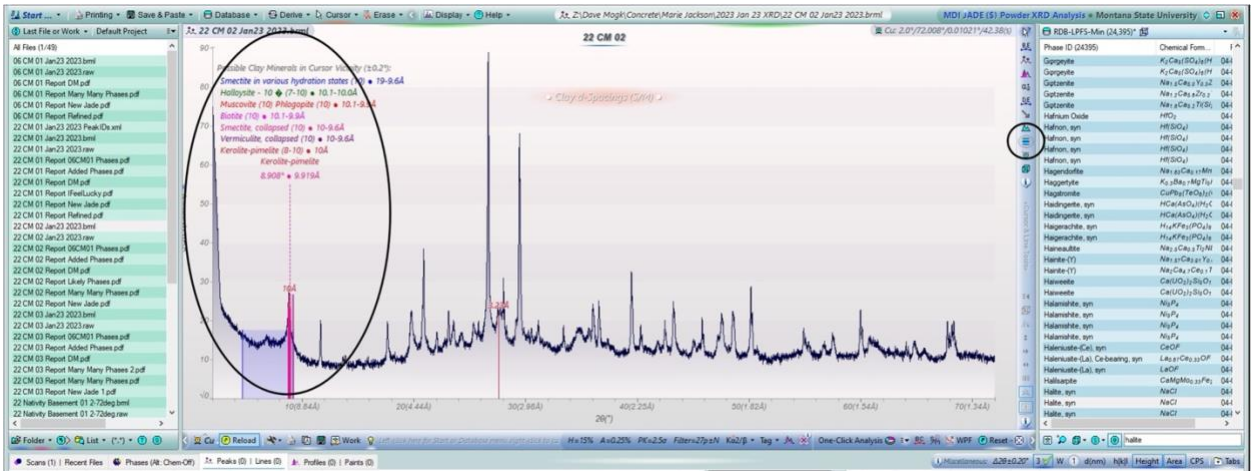
Clays are members of the phyllosilicate class of minerals or "sheet silicates". The basic crystal structure is alternating planes of tetrahedral-octahedral (T-O) or tetrahedral-octahedral-tetrahedral (T-O-T) sheets. The tetrahedral layers are predominantly Si and Al, the octahedral sheets are typically metals (Al, Fe, Mg), and larger alkalis (Na, K) or alkali earth elements (Ca, Sr) may occupy interlayer sites. One series of phyllosilicates has 2 trivalent cations (Al^{+3}), the dioctahedral micas, such as the mica muscovite $KAl_2(Si_3Al)O_{10}(OH)_2$ and related minerals kaolinite (clay) and vermiculite. A second series is the trioctahedral micas with 3 divalent cations (Mg^{+2}, Fe^{+2}) in the structural formula such as biotite $KMg_3(Si_3Al))_{10}(OH)_2$ and related chrysotile (serpentine) and talc. All phyllosilicates are hydrous with structural hydroxyl, and the group of swelling clays can also sorb variable amounts of molecular water H_2O in interlayer sites.

There are three main types of clay minerals that can readily be identified using XRD methods based on the d-spacing of the prominent basal {001} crystallographic orientation: 1) the 7 Å clays (kaolinite and related halloysite, dickite), the 10 Å clays (muscovite, illite), and the 14-20 Å "swelling clays" (montmorillonite, smectite). All of the clay minerals will have a strong basal {001} reflection due to the strong preferred orientation of the planar sheet structure. It gets more confusing as it is possible to have mixed layer clays (illite-smectite), and the d-spacing of the

clays may change considerably due to cation exchange particularly if alkali or alkali earth elements are involved. See the USGS overview of clay mineralogy groups and their basic characteristics: https://pubs.usgs.gov/of/2001/of01-041/htmldocs/clay.htm

The analytical routines used for XRD determinations will depend on the type of information that is required to address your research question:

1. **If you simply want to determine if clay minerals are present, and a general identification is sufficient:**
    a. Prepare a standard random grain mount.
    b. Run the XRD spectrum as is customary over a broad range of two theta angles (e.g., 2 to 75 degrees), but we will only be interested to see if there are peaks present for 14 Å (~3°), 10 Å (~9°), or 7 Å (~13°), clays.
    c. Start your XRD scan at 2 or 3 degrees to be sure to catch any peaks associated with swelling clays with large d-spacings. Note this may be a broad, ill-defined peak if the clays have variable amounts of sorbed water.
    D. The JADE software has a built-in function that helps identify clay minerals based on additional peaks in the entire XRD spectrum. Access this application using the link on the vertical task bar with horizontal dashes (small circle below). Hovering over the primary {001} peak and using this function will deliver a list of possible clay minerals (large oval on the right, below). This will help you identify the general type of clay mineral(s) that may be present. You will need to apply other contextual information (e.g., composition, type of sample, geological occurrence, etc.) to make an informed identification of the clay.



2. Advanced Clay Mineral Identification Using Powder XRD

There are many geological and engineering applications that require a more precise identification of clay minerals. This can only be done using powder X-ray Diffraction or transmission electron microscope methods. For XRD clay determinations, a series of sample preparation steps is used to systematically identify or rule out various clay minerals. These methods are fully described in:

- Moore, D. M. and R. C. Reynolds, Jr. 1997. X-Ray diffraction and the identification and analysis of clay minerals. 2nd Ed. Oxford University Press, New York. (A copy is available to refer to in ICAL)
- Poppe, L.J., Paskevich, V.F., Hathaway, H.C., and Blackwood, D.S., A Lab oratory Manual for X-Ray Powder Diffraction, U. S. Geological Survey Open File Report 01-041. Access at: https://pubs.usgs.gov/of/2001/of01-041/index.htm

Sample preparation is critical. To help you prepare your experiment, you will need to be aware of the following steps:

- To focus on the clay minerals, you will want to remove other possible phases in the sample. This may require an acetic acid treatment to remove carbonate minerals or a hydrogen peroxide treatment to remove organic material.
- You will want to separate and concentrate the <2-micron clay fraction from other grains (i.e., silts and larger) using either gravity settling and decantation or centrifuge methods. A Waring Blender can be used to get the clay minerals into suspension, and sodium hexametaphosphate (detergent) can be added to the solution as an anti-flocculant to disperse the clay minerals. Formula for settling times or centrifuge settings is in the above references.
- You will need to prepare at least 4 oriented grain slides for each sample, unlike standard XRD which requires random grain mounts. This method looks specifically at the d-spacings of the basal {001} planes of the clays and their response to multiple treatments.
    - Using the suspended clays from the above step, the solution will be poured into a receptacle in a vacuum system, and the solution will be pulled through the vacuum system and grains will be pulled deposited on a 0.25 micron filter.
    - The clay minerals will be transferred to the glass slide using the filter-peel method. The filter is placed upside down on a glass slide, pressure is applied (roll a glass tube over the filter and glass slide), and the clays are transferred onto the slide.
    - One analysis will simply use an air dried oriented sample.
    - The next step is to use a new slide that will be glycolated. This is done by placing ethylene glycol in a shallow pie pan and suspending the glass slide over the fluid (a simple wire stand can be used). The covered glycol should be heated to 60-70^{o}C for at least 4 hours (or overnight) to expose the sample to glycol fumes. A drying oven is used to heat the pie plate with cover and sample, and one is available in the Mineralogy teaching lab, Gaines Hall, Dept. of Earth

Sciences. This step displaces inter-layer water that is common in many swelling clays and normalizes the d-spacing to full saturation of the glycol molecule.
    - A third preparation involves heating another oriented sample to 400^{o}C and the fourth preparation is to heat another oriented sample to 550^{o}C for at least a half hour at temperature. This determines whether or not there is a collapse of the interplanar layers due to dessication of the clay minerals. This preparation can be done in a calibrated muffle furnace, also available in the Mineralogy teaching lab.
- It is also necessary to prepare a "smear mount" with random grain orientation, as detailed tests will require measurement of the (060) peak between 1.50-1.54 angstroms for some clay determinations.
- Clay powders may also have to be examined by SEM imaging. Sprinkle a few dispersed grains onto a carbon sticky dot. It may be necessary to also add a conducting coat (C, or Ir) as clays are subject to large charging problems. Grain morphology may be needed to determine certain forms of the kaolinite family (e.g., tabular, hexagonal, platy, fibrous, tubular).

The USGS Clay Mineralogy Identification Flow Chart is appended in a separate document.

Finally, look critically at all your clay XRD spectra. There is tremendous variation in composition and structure of the clay minerals. Is your determination of clay mineral(s) consistent with geologic environment, prior literature, etc.?