

A Widespread Challenge: Differentiation of Illite Clay from Muscovite Mica for Resource Exploration and Development

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Summary

We present the results of investigations into methods for differentiation of illite clay from muscovite (and biotite group) micas, with proportional mineralogy output. Several analytical methods were investigated, with the intention of devising a new approach for commercial and industrial purposes. This approach is intended to be reliable, widely applicable, and efficient in terms of time and cost.

After research and testing, a new approach has been largely simplified to XRD alone. The new approach is based on existing routine approaches for clay differentiation, but involves a moderately more complex preparation including additional stages of heat treatment. The principle revolves around the structural transformations of illite, muscovite, and biotite during dehydroxylation at particular temperature ranges.

Theory / Method / Workflow

The phyllosilicates are a large group of silicate minerals, including clays and micas, which crystallize in parallel sheets of silicate tetrahedral groups. They are hydrated phases, including hydroxyl groups and/or water. The water, hydroxyl groups, and ionic species can occupy ion sites in the nanoscale spaces between layers, the interlayer sites. Some phyllosilicates have fairly well defined and consistent chemistries. Muscovite, a mica, is generally considered such a mineral, with potassium occupying most of the interlayer cation sites and limited substitution. Others can have quite variable chemistries, with multi-dimensional solid solution series and high cation exchange capacity (the ability to substitute ions readily). Illite, a clay, has similar chemistry to muscovite but has less potassium, more hydration, and usually includes substitutions of alternate ions into the interlayer sites. Pure illite is virtually unknown in nature, and the mineral is sometimes defined in different ways depending on the context.

There are well-known challenges in differentiating various phyllosilicates from one another. Identifying the mineralogy and mineral proportions effectively is of significant importance to a number of industries, including resource exploration and production and geotechnical engineering. There exist several approaches for this, but the most widely used involve X-ray Diffraction (XRD) analysis with a clay separation step, and treatment of the clay-enriched fraction in multiple ways to allow differentiation of the clay phases. The separation step is typically based on settling (often accelerated by centrifugation), and yields a clay-enriched (“clay”) fraction of <2µm particle size, and a clay-depleted (“bulk”) fraction of >2µm. Treatments for clay differentiation include glycolation, acid treatment, and heating (most commonly to 400°C and 550°C). These processes can allow differentiation of illite, smectite, kaolinite, chlorite, mixed layer species, and more.

However, a persistent challenge for this testing is that the X-ray diffraction patterns of muscovite, biotite, and illite, are essentially indistinguishable under any of these treatment conditions. It is sometimes simply assumed that illite, being a clay, will concentrate in the clay fraction during separation, and muscovite will remain in the bulk fraction. However, this is not necessarily the case, as clays within detrital rock fragments will not necessarily enter the clay fraction, and it is possible for muscovite to be small enough to be collected in the clay fraction (especially if the sample has been crushed during preparation).

Biotite and muscovite are also nearly indistinguishable by XRD, except in samples that have very high mica content. Other species are also indistinct in their X-ray diffraction patterns, such as lepidolite, but this is not the focus of this study. The IR spectral properties of muscovite and illite are also so similar as to be indistinguishable in natural systems, although it may be possible to differentiate pure standards.

There are several potential methods that allow differentiation of illite and muscovite. A method that is known to be effective is acid dissolution treatment. This method involves moderate crushing of the sample followed by treatment with concentrated hydrochloric acid. The treatment requires several weeks, during which illite will be broken down but muscovite will not. XRD analysis before and after the treatment will reveal the illite content. The method is not without problems – detrital illite contained within rock fragments will require finer crushing of the rock, this can yield very fine mica flakes that can behave more like illite. The long time period required, risks of handling concentrated/fuming HCl, and uncertainties mean that this method is seldom used.

Illite, like most clays, has naturally higher cation exchange capacity (CEC) than micas. Hypothetically, obtaining a complete mineralogy (without differentiation of mica and illite), and CEC data, with known CEC values for mica and illite, could allow the extraction of the proportions of mica and illite present in a sample. In practice this is impracticable due to the levels of uncertainty in the CEC methods available, and the variability of various clays (including illite) in their CEC properties.

Bulk geochemical analysis, for instance by WD-XRF, cannot substantially help with illite-mica differentiation, even when used to help refine XRD interpretations. This is because the compositions are too similar, and because the degree of hydration cannot be determined precisely enough. With pure standard samples this might be possible, but in natural rock systems it is not effective.

Since illite partitions additional cations into its interlayer sites, while muscovite does not, it could be possible to find elemental associations for illite for given formations. While not a general solution this could be made to work for specific formations or locations. However, it would require thorough validation of the elemental associations that are to be used. Many of the elements that might be tracked are likely to be present in multiple phases, not just illite, making them unusable as simple guides to illite content. In addition, it cannot be said that a consistent proportion of a given element will always partition into illite. In most cases there is likely to be a maximum possible partitioning factor for a given element or ion, and the amount partitioned may range up to that maximum. The amount that will substitute into illite will depend on the amount available more than the amount possible, unless the species is considered to be always in excess.

A more promising method for rapid, efficient, and reliable differentiation of illite from mica revolves around dehydroxylation, which occurs at high temperatures (up to 1000°C). As phyllosilicates are hydrated phases, almost all include hydroxyl groups which are part of the mineral crystallographic structures. Often water is present as well, and may be structural (in clays), or bound by hydrogen-bonding to the hydroxyl groups (bound water). Bound water is lost at relatively low temperatures, but the hydroxyl groups, being structurally part of the crystal lattices, are more resistant. At more elevated temperatures, dehydroxylation reactions occur, during which the hydroxyl groups are lost, and the mineral structures are changed. This results in shifts in peak positions and relative heights on X-ray diffractograms, when comparing before and after dehydroxylation.

Illite and muscovite behave differently at high temperatures. Illite, depending on its structural arrangement, experiences dehydroxylation at temperatures between 550°C and 700°C. Muscovite, on the other hand, experiences dehydroxylation at temperatures between 800°C and 900°C. The minerals also experience different effects on their diffractogram patterns due to dehydroxylation. This provides the basis for a relatively simple XRD-based approach to differentiation of illite from micas.

Biotite also experiences changes due to high temperature treatment, including structural alterations at 400-500°C and 800°C, with dehydroxylation at >1000°C. The temperatures and peak shifts in biotite differ again from those of muscovite and illite, making thermal treatment a potentially robust approach for differentiation of these phyllosilicates.

Results, Observations, Conclusions

Illite, muscovite, and biotite can be differentiated by XRD using relatively simple steps additional to the routine methods for differentiation of clay phases. The interpretation process is more complex, and may be supported by geochemical analysis (as is the case for most XRD interpretation).

The proposed XRD preparation and analysis method is an extension of the more routine clay differentiation process. This process includes the following steps:

- Clay separation (concentration), by settling and/or centrifuge
- Analysis of the bulk fraction (micronize, single dry run, Rietveld suitable)
- Analysis of the clay fraction:
 - Dry
 - Glycolated
 - Acidized (10% HCl, 12hrs)
 - 400°C
 - 550°C
- New steps to allow differentiation of mica and illite:
 - 600°C
 - 750°C
 - 950°C
 - 1100°C

The resulting diffractograms are then interpreted together, looking at peak height changes and location shifts particular to the dehydroxylation changes that impact the micas and illite.

Testing is continuing as the specific temperatures and number of temperature steps are optimized to maximize reliability and minimize the duration of the process.

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