PS Using X-Ray Fluorescence to Quantify Clay Content in Mudrock and Sandstone Outcrops*

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Abstract

This study evaluates protocols for collecting X-ray fluorescence (XRF) data on outcrop and using these data to estimate clay content. These protocols were tested on a marine chert - mudrock section (Devonian Woodford Formation, southern Oklahoma) and fluvial sandstone - mudrock section (Castlegate Formation, Cretaceous, central Utah).

Because clay content and bulk mineralogy can be estimated from these major and minor element concentrations, counting times need not be as long and surface preparation need not be as meticulous as in laboratory chemostratigraphic trace element studies. Theoretical x-ray attenuation by a rough surface geometry should affect Al and Si the most and should not significantly affect heavy elements such as Fe and K. Theory was then tested by measuring changes of apparent elemental concentrations measured against sample geometry, surface preparation, and offset from the detector nose. The instrument used for this study showed no significant Al or Si concentration differences up to an offset of 1 mm between a mudrock reference sample and the detector nose and for surface roughness equivalent to a rough-sanded, scratched surface. Battery-powered angle grinders remove most weathering effects, flatten the surface, and leave the surface smooth enough to acquire reproducible data.

Local calibration is necessary to convert measured elemental ratios to mineralogy. Samples were analyzed by x-ray diffraction to calibrate directly the measured elemental ratios to mineralogy. The calibrated relationships can then be used to estimate mineralogy of the other XRF analyses.

The following protocol is recommended for outcrop XRF analysis. (1) Prepare a flat smooth surface using an angle grinder. The prepared surface should cut below the weathering rind. Surfaces should be normal to bedding to minimize heterogeneity problems, especially in laminated shales. (2) Analyze each spot twice to test operator error. Analysis periods of 30 seconds are adequate to characterize elements of interest (depending on the instrument). (3) Elemental trends are evaluated from the data to develop qualitative shaliness indicators and estimate the number of component minerals affecting elemental concentrations. (4) Calibrate elemental ratios to mineralogy using three or more samples analyzed by both x-ray diffraction and XRF.

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Because clay content and bulk mineralogy can be estimated from XRF major and minor element concentrations, counting times need not be as long and surface preparation need not be as meticulous as in laboratory chemostratigraphic trace element studies. Theoretical x-ray attenuation by a rough surface geometry should affect Al and Si the most and should not significantly affect heavy elements such as Fe and K. Theory was then tested by measuring changes of apparent elemental concentrations measured against sample geometry, surface preparation, and offset from the detector nose. The instrument used for this study showed no significant Al or Si concentration differences up to an offset of 1 mm between a mudrock reference sample and the detector nose and for surface roughness equivalent to a rough-sanded, scratched surface. Battery-powered angle grinders remove most weathering effects, flatten the surface, and leave the surface smooth enough to acquire reproducible data.

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One Minute Summary

This poster presents methods for determining clay content of rocks on outcrop by XRF. The key issues are (1) proper preparation of the outcrop surface, (2) counting times appropriate for the problem, and (3) calibration of elemental compositions by a subset of samples analyzed by both XRF and XRD. In detail:

- Surfaces must be ground flat and smooth to remove weathering and surface effects. After grinding, the surface must be dusted.
- Counting times should be as short as possible yet sufficiently long to attain desired compositional resolution for Al, Si, and K.
- XRD mineralogy, XRD elemental composition, and XRF compositions for a subset of samples are used to construct functions that convert elemental ratios into clay contents.

Examples are discussed.

Introduction

Clay content and porosity control many physical properties of rocks. Examples include flow properties of fault rocks and mechanical properties that control fault and fracture development. Typical methods for outcrop mineralogical characterization are poor or expensive:

- Visual inspection and simple tests (acid tests, scratch tests, stains) are all qualitative and ambiguous in many settings.
- Sampling followed by lab analysis (thin section, XRF, XRD, calcimetry): quantitative results, but time consuming and expensive. High cost results in few analyses per study.

Typically, outcrop descriptions of bedding, fault, and fracture geometries far exceed descriptions of the clay content that controls the development of fault rocks and fractures.

One possible clay analysis method suitable for outcrop analysis is x-ray fluorescence (XRF). In the lab, XRF provides quantitative elemental analyses from which clay content can be estimated. However, outcrops present considerable challenges for XRF.

The purpose of this poster is to discuss these limitations, devise preparation and measurement protocols that overcome these limitations, and demonstrate this application with examples.

WHAT IS XRF?

X-ray fluorescence (XRF) results from the interaction of x-rays with electrons of atoms. High energy x-rays interact with electrons from inner electron shells, causing their ejection from that shell (Figure 1). Outer-shell electrons drop into inner shell positions vacated by the ejected electron. The electrons must lose energy to do so. Excess energy is emitted as a secondary, fluorescent x-ray of weaker energy than the exciting x ray.

- The energy of the emitted x-ray indicates the element.
- The count rate (emitted x rays per unit time) of a given energy x ray indicates the concentration of that element.

Detectors measure both the energy and the intensity (count rate), from which elemental composition is determined. Abundances are reported as weight percent or weight ppm.

Figure 1. X-ray fluorescence. Figure courtesy Thermo Fisher.

XRF Attenuation

After secondary x-ray generation, x-rays are attenuated by interaction with material between the target and the detector (Figure 2). The amount of attenuation is controlled by the x-ray energy, the number of atoms along a pathway, and the atomic number of the atoms (Hubbell and Seltzer 1996). Count rate decreases exponentially with distance traveled through the medium. The count rate is therefore a function of both the target composition and the amount of attenuation between detector and source.

"Soft" (low energy) x-rays, which are characteristic of light elements, are readily attenuated by any material in the path, including air. "Hard" (high energy) x-rays, which are characteristic of heavy elements, are attenuated primarily by the rock itself. The attenuation of a particular energy x ray in a material can be described by its half distance, the distance required to reduce the count rate by half. The longer the half distance, the less the attenuation of that material. Attenuation half-distance increases with x-ray energy. The significance of attenuation effects depends on the energy of the x ray and the nature of the pathway. Air is always present on outcrops, so its effects will be discussed first.

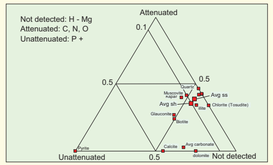


Figure 4. Weight fraction of rocks seen by XRF, as the result of air attenuation. About half weight is not detected, and about 2/3 of the remaining weight is attenuated (Al, Si).

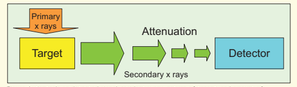


Figure 2. Controls on detected signal: incident x ray, nature of target, and amount of attenuation between target and detector.

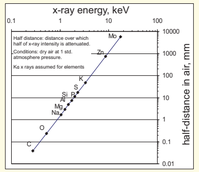


Figure 3. X ray attenuation by air and x-ray energy.

Air Attenuation

For evaluating potential attenuation, the half distance is compared to the typical working distance of field XRF analyzers, which is on the order of 3 mm. Carbon and oxygen kα x-ray half distances are less than half a mm in air (Figure 3). These elements are essentially undetectable by field XRF units. Sodium and magnesium x rays are so heavily attenuated by air as to be unreliable and typically undetectable. Aluminum and silicon count rates are significantly attenuated by air, but sufficient signal reaches the detector so that concentrations can be estimated. X-rays from elements heavier than about phosphorous are not significantly affected by air over the mm-scale travel distances. XRF elemental detection can be divided into 3 groups and plotted on a ternary diagram: not detected (Mg and lighter), significantly attenuated by air (Al, Si), and minor air attenuation (P and greater). A few minerals, mainly sulfides, have compositions entirely unattenuated (Figure 4). Only about 10% of the weight of most aluminosilicate minerals and average shales and sandstones is detected by unattenuated XRF.

Rock Attenuation

Rocks have higher density and heavier elements than air, so attenuation is much greater. The Kα x rays from most elements of interest have half distances less than 1 mm. Half distance of Si and Al are less than 10 microns. The volume from which secondary x rays are generated that can reach the detector is therefore very shallow, on the order of tens to hundreds of microns deep by about 8 mm wide.

The implication for outcrop analysis is that any surface weathering, no matter how shallow, may affect the analysis. Also, any dust on the surface may dominate the XRF analysis, because a thin layer of dust may comprise a substantial fraction of the irradiated volume. Water and dust may also attenuate x rays from the real rock.

Implications for outcrop work are that the analysis is effectively a surface analysis. The surface must be unweathered, dust free, and dry. The surface must also represent the volume for which the analysis is desired.

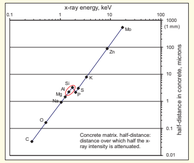


Figure 5. Concrete attenuation of x rays as a function of x-ray energy. Concrete is used an analog for porous rock.

Constraints for XRF Analysis on Outcrop

- The surface being analyzed must be representative of the dust free, unweathered lithology. Few natural outcrops meet these criteria.
- Good Al and Si analyses are needed, yet the counts for these elements will be attenuated by the atmosphere. A constant working distance must be used for all analyses and calibration. This is difficult on natural rock surfaces.
- Analysis duration must be suitable for the problem at hand. If analyzing major or minor elements, this may take only a few seconds. If analyzing trace elements, this may require a few minutes or more, depending on the concentration, element, and detector.

Methodologies to overcome these problems should be addressed prior to analysis. This requires quantification of the effects on the actual instrument that is to be used, because each model has different design and sensitivity. .

XRF Analysis Equipment

A Thermo Fisher Niton XL3t GOLDD+ hand-held XRF Analyzer was used for this study. It approaches the light element problem by using a geometrically optimized large-area drift detector that gives high count rates and light element detection without vacuum pump or He purge. Factory algorithms and autocalibration were used, so elemental weight percents are reported directly. Reported elemental compositions are typically in error, but these are corrected and calibrated after field work (see next sheet). Analyzed spot is about 8 mm across.

The instrument weighs less than 1.3 kg, is water and dust resistant, and the battery lasts for 4 hours + of analyses. These characteristics, combined with operating without vacuum or He purge, makes this instrument easy to use in the field.

This hand-held XRF was loaned to RDR by Thermo Fisher for this study, which is acknowledged for their assistance.

Standardizing Air Attenuation

Air attenuation effects are standardized by maintaining the same working distance for all analyses. Working distance through air is minimized and constant if the surface is flat and smooth (left, Figure 6). If surface is smooth but not flat, an air gap develops as the instrument nose bridges over the analysis location, and air attenuation varies with the degree of curvature of the surface (middle, Figure 6). If smooth but rough, air gaps develop in the surface roughness (right, Figure 6). The rougher the surface, the more attenuation. Rough surfaces also trap more dust that may contaminate the analysis and may cause additional attenuation by the solid.

The degree of flatness and smoothness needed to obtain analyses of sufficient quality for the analytical problem must be determined for the instrument in question and the elements of interest.

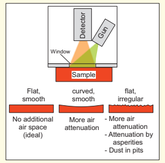


Figure 6. Surface geometry effects on air attenuation.

Lab Determination of Air Attenuation Effects

Air attenuation effects were investigated by increasing working distance from a standard sample in the lab. Analyser working distance was varied by placing shims of known thickness between the nose and the sample, thereby adding to the air gap between the instrument and the sample. Samples of Mexican obsidian, Mecca Shale (Pennsylvanian), and Woodford Shale (Devonian) were used for this analysis. Surfaces were lapped to #600 grit, with shale surfaces following bedding planes. All samples are heterogeneous for the spot size analyzed. Results for the Woodford shale are shown. Attenuation for Al and Si increases with working distance. Attenuation of other elements lies within heterogeneity of the sample surface. At 1 mm working distance, Al shows about 11 % attenuation, and Si shows about 3% (Figure 7).

Given the nature of the problem, an attenuation of 10% or less is considered acceptable, so as long as the surface is flat within an average of 0.5 mm (1 mm maximum depression on a bridged sample) results should be acceptable.

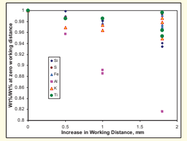
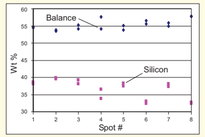


Figure 7. Attenuation reported as ratios vs. working distance. Attenuation is the ratio of the wt% divided by wt % at no added working distance. Where sample heterogeneity causes ratios higher than 1, the inverse is taken.

Sample Heterogeneity

Ultimately, it is the heterogeneity of the material to be analyzed that controls the degree of precision needed for each analysis. If a rock has significant elemental concentration heterogeneity, an analysis at one small spot, no matter how precise, cannot characterize the average concentration of the rock. Because high precision analyses take longer than low precision analyses, the best strategy to characterize the average composition is to take many short analyses at different spots and average. Of course each short analysis must be long enough to get statistically significant count rates. This is judged by duplicating the analysis at each spot and comparing reproducibility of concentrations in duplicate analyses vs. concentrations at different spots.

To assess how to best analyze mudrocks, a sample of faintly laminated Woodford Formation was analyzed in the lab. The sample was cut, and a large piece with a natural bedding plane was prepared for analysis by grinding and by hand (Figure 8). Two smaller pieces of the same sample were lapped to #600 grit for a smooth surface. Results were compared to understand both effects of surface preparation and sample heterogeneity. Analysis times are 10 seconds each for main, low, and light element spectra settings, giving a total analysis time for each spot of 30 seconds. With duplicate analyses, total analysis time per spot is 1 minute.



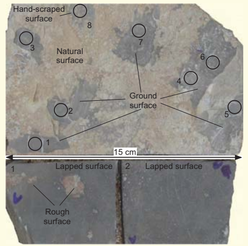


Figure 8. Woodford Fm sample used to evaluate surface preparation and heterogeneity. Side "A", shown here, was prepared by both grinding with the angle grinder and lapping to a smooth surface. Areas of rough surface were avoided for these analyses.

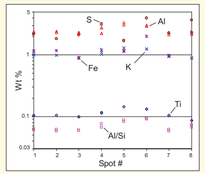


Figure 9. Compositions of spots on natural Woodford Fm bedding surface (Figure 8). Each spot has duplicate analyses. All spots except #8 were prepared by angle grinder.

Figure 9 shows both reproducibility at each spot and heterogeneity between spot analyses of the prepared natural bedding plane. Duplicate analyses for iron, potassium, sulfur and titanium practically overlap in most analyses. Silicon analyses show somewhat lower reproducibility whereas aluminum shows lowest reproducibility. Excepting Al, other elements average reproducibility is within 2% of their reported value. Average Al reproducibility is 8% of reported value, but this is caused by one poor analysis (#4), which also has the poorest reproducibility of other analyses. The Al/Si ratio shows better reproducibility (6% of reported value) than the Al analysis because both Al and Si are affected.

Variation between spots prepared by grinding the surface is much greater than the variation between duplicate analyses at each spot. Fe and S show highest heterogeneity because of variable distribution of large pyrite crystals. Potassium, titanium, and Al/Si ratio covary, indicating that the cause of heterogeneity is clay content. Clay variation is related to the nature of the surface (Figure 10). Although the Al and Al/Si has low reproducibility, reproducibility at each spot is better than variation between spots.

The lapped surface is the same bedding plane as the natural surface analyzed above (Figures 8). Its elemental concentrations (Figure 11, surface A) fall within the range of the ground surface analyses (Figure 9), indicating that the moderate surface roughness on the ground sample does not significantly alter the analysis reproducibility or average concentrations (Figure 11). Both lapped surfaces A and B are heterogeneous. Measurements made normal to bedding show greater reproducibility between spots (excepting pyrite). This measurement orientation averages compositional variations on the lamina level and better represents the average concentration in the rock.

<u>To summarize</u>: (1) Al concentrations show relatively lower reproducibility, but the variation between duplicate analyses are still much less than variation between different spots on the same surface that is being characterized. (2) The quality of the surface prepared by the angle grinder is sufficient to obtain reproducible analyses within the range of heterogeneity expected in organic shale samples.

Figure 10. Cross-section of Woodford sample showing that Side "A" irregularly cuts a thin argillaceous laminae. Different positions on the slab will expose different positions within the argillaceous lamina and thus may have different elemental composition. Most of sample is faintly thickly laminated siliceous mudstone. White specks are recrystallized radiolaria.

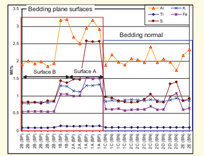


Figure 11. Analyses of lapped surfaces. Surface A is the same surface characterized by the grinder prepared spots discussed above.

Surface Preparation

As shown by lab tests, battery-powered angle grinders flatten and smooth outcrop surfaces sufficiently for XRF clay content analyses, with composition and reproducibility similar to that of the lapped surfaces. The angle grinder proved effective on all tested rock surfaces except the hardest cherts. With practice, it is easy to make a flat, smooth surface large enough for analysis (1 cm + across). Grinding is battery intensive, so pneumatic grinders may be more effective for larger jobs.

Grinding the surface also removed surficial weathering rinds. Ground surfaces must be dusted after grinding.

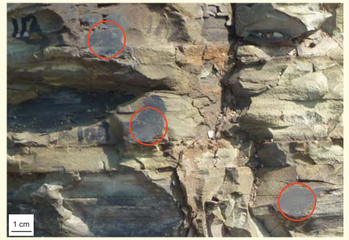


Figure 12 Woodford Fm outcrop surface showing analysis locations (red circles) prepared by the angle grinder. It is most efficient to grind small protuberances on a rough outcrop such as this, because the grinder can cut deeper to remove weathering more effectively. The analyzer nose is significantly wider than its window, so the analyzer can fit flush against a flat surface on a protuberance, but may not sit flush against a flat surface on a thin recessive bed or salient on the outcrop surface.

Analyzing protuberances alone may introduce a bias towards harder lithologies, so recessive beds must also be analyzed to characterize the outcrop. Recessive beds can be analyzed by flattening a larger area in situ on the outcrop or by excavating a small sample from the outcrop, and grinding a surface on the small sample flat.

The importance of surface preparation can be demonstrated by comparing analyses of ground and lapped surfaces (Figure 13A) with those analyzed on surfaces flattened with a hammer and chisel (Figure 13B). Both data sets come from the same measured section on outcrop at close to the same depths, but analysis locations are not identical. Surfaces prepared by grinding in the field and lapped in the lab show more systematic elemental variation than seen in hand-prepared surfaces. The balance (a measure of the unanalyzed light element content of the rock) is also significantly lower in ground or lapped surfaces than on the rough surfaces.

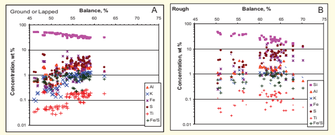


Figure 13. Comparison of a Woodford Fm outcrop analyzed on ground or lapped surfaces (A)with analyses of surfaces prepared by hammer and chisel (B). Analyses are from the same outcrop and approximately the same depths. Lapped samples in the left figure are hard cherts lapped in the lab due to inability to flatten the surface by the grinder. These samples have the lowest Al and highest Si.

A side benefit of grinding the outcrop surface for analysis is that visualization of fine-scaled fault-rock fabrics are much easier on the prepared rock surface. Where rock is soft, large surfaces can be quickly prepared with the angle grinder and features not evident on the weathered surface can be identified and analyzed (Figure 14).

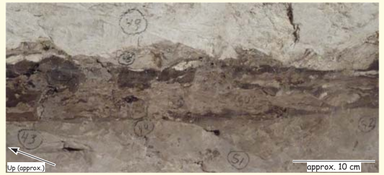


Figure 14. Surface of the Salina Tunnel fault (Utah) prepared by the angle grinder. The surface more clearly shows textural complexity of the fault core. This helps understand origin of the fault rock as well as guiding selection of analysis locations on the fault rock. Pencil circles with numbers are analysis stations.

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Recommended Analysis Protocol

SURFACE PREPARATION

- Surface over the 1 cm² analysis area needs to be flattened to within 1 mm relief with a roughness equivalent to a coarse-sanded surface or better. Any weathering rind should be removed. This is best achieved by an angle grinder or similar power tool. Small-scale roughness and small fractures/imperfections have little effect on analysis as long as the surface is properly dusted.
- If necessary, flatten an area about 2.5 cm across around the analyzed spot so that the analyzer will fit flush against the surface to be analyzed. A natural convex surface is OK for this area.
- Dust surface after flattening to remove potentially contaminating dust.
- If representative analysis of bulk rock is desired, measure a surface oriented normal to bedding. Many bedding planes have thin argillaceous layers that may not reflect the bulk composition of the rock.

ANALYSIS

- Make sure analyzer is flush and flat against surface to be analyzed and the detector window centered over the spot to be analyzed prior to analysis (Figure 15). The analyzer must be held steady and flush to the outcrop surface during detection to keep air x-ray attenuation constant. From experience, it is difficult to hold the detector steady against the outcrop surface for long analysis times, especially where the detector is held above head high or far from the analyst. Select the shortest analysis time that gives sufficient counting statistics for the desired analysis.
- Select analysis periods for a minimum of 10 seconds for each spectral band (main, low, light). This time is sufficient for counting statistics for the minor elements needed to identify clays and major minerals. It is not sufficient for trace elements used for chemostratigraphy. For rocks with lower clay content, the light element spectral analysis time should be doubled to 20 seconds for better Al and Si resolution. Counting times for other instruments may be different.
- Take two analyses at each sampling spot (station). Move the detector slightly between analyses if room permits so that effects of any surface defects can be detected. Samples with poor reproducibility indicate surface defects, improper positioning of the detector against the surface, or wobbling of the analyzer during analysis.

DATA DOCUMENTATION

- Mark the analysis location on the outcrop surface and label with the station number. Photograph the surface after completion of analyses for future reference.
- Excluding preparation time, total time per station is about 2 – 3 minutes per station. Most of this time is spent positioning the analyzer over the spot of interest and marking the analysis location.

Figure 15. Analyzing the rock surface, Salina Tunnel fault rock. Detector should be held braced between the body and the rock surface to steady the detector and minimize wobble during analysis.

Why Reported Analyses are Wrong

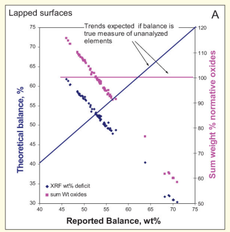
Sample XRF analyses are reported in weight percent. For porous sedimentary rocks, the reported values are almost certainly wrong. XRF response is calibrated against non-porous standards. Pore space in rocks take volume from the x-ray excitation volume, thus changing interaction between the rock and secondary x-rays in the samples vs. the standards.

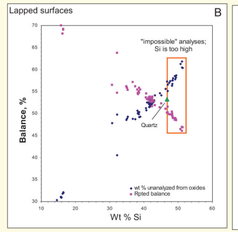
This effect is best illustrated using the "balance" reported with analyses. Balance is the weight fraction of the rock which does not generate detectable x-rays. In silicates, most of this weight is oxygen. A "theoretical" balance can be estimated by converting the reported elemental concentrations to element oxides. Sodium, another undetected element, is estimated by assuming all Cl is NaCl. The wt. fraction of oxygen in the element oxides plus Na in NaCl is the theoretical balance, which can then be compared to reported balance.

Average theoretical balance is approximately the same as the wt% unanalyzed elements, but the trend is opposite of that expected (Figure 16A). The higher the reported balance, the lower the theoretical balance. Sum of element oxide weight in samples with low reported balance exceeds 100%. Because of balance problems, Si in Si-rich samples exceeds the maximum possible Si concentration in silicate rocks (quartz; Figure 16B). Problems with balance invalidates reported elemental weight percentages reported from the analyzer for these types of porous rocks.

The cause of this behavior is not clear. The behavior is present in both lapped rock surfaces measured in the lab (Figure 16A) and in-situ ground surfaces on outcrop (Figure 16C), so it is not a surface preparation problem. It is probably an effect of porosity, hydrogen, and carbon content (from kerogen, hydrated minerals, and sorbed water). If so, correction for better balance estimates requires better estimates of bulk dry density and attenuation factors than can be routinely measured on outcrop.

The way around this problem is to convert weight percentages to weight ratios. Misestimation of balance affects all weight percentages in an analysis, so the ratios should remove some of the error introduced by the balance problem. Complete correction requires local calibration.





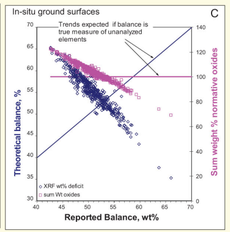


Figure 16. (A) Comparison of reported balance and theoretical balance of lapped samples. (B) measured and theoretical balance as a function of reported wt % Si. Balance decreases with increasing Si. Due to balance problem, some Si wt % exceed the theoretical maximum Si possible in an aluminosilicate mineral. (C) Comparison of reported balance and theoretical balance of samples with in situ surfaces prepared with angle grinder.

Which Elements Can Be Believed?

Before using elemental data to estimate clay content, the data should be reviewed for its significance and general trends. Figure 17A shows all elemental data above limit of detection (LOD) reported for a Woodford Formation outcrop. 20 elements are detected in at least 1 analysis. Some trace elements (Al, K, V, Zr) correlate to Ti (a detrital clay indicator) whereas others (Cl, S) do not. Some (As, Cr, Cu, Ni, Pb, P, Rb, Zn) are reported for only a few samples; in other analyses, these elements are below LOD.

Of more importance is the concentration divided by LOD (Figure 17B). The higher the value, the more reliable the analysis. Al, for example, has moderately high concentration, but concentration/LOD is only about 3 to 15. Other elements at low concentration have higher concentration/LOD, such as Fe and Ti. Some elements with low concentrations (Zn, Sr, and V) approach the detection limit. Longer counting times improve concentration/LOD by decreasing LOD.

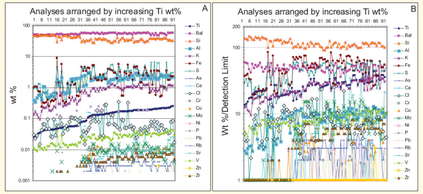


Figure 17. Analyses of a Woodford outcrop arranged by increasing Ti. (A) reported, uncorrected concentrations. Right: Concentration/LOD. Many trace or minor elements were detected, but relatively few have high concentration/LOD.

Calculating Clay Content

Two approaches will be discussed, a clay index approach and an elemental correction approach. Both require XRD calibration data.

The clay index approach identifies elemental ratios that correlate to clay content and uses these elements to estimate clay content by direct calibration to the clay content of XRD calibration samples. This method is more appropriate for settings with mixed or complex clay mineralogy or where clay minerals are not distinguishable from their XRF-detectable major and minor elements.

The elemental correction approach estimates elemental ratios of major and minor elements in the XRD calibration data from the reported mineralogy. These are used to develop correction equations for the XRF elemental ratios. The corrected XRF elemental ratios are then converted to clay contents This approach is best for simple systems with distinct elemental concentrations, such as the illite - kaolinite - quartz system. For the second approach,

Calibration by Clay Index

The clay index approach will be illustrated using analyses from the Devonian part of the Woodford Formation cropping out in the Lawrence Uplift and Lake Anticline in southern Oklahoma. Woodford strata are interbedded siliceous laminated mudstone, argillaceous chert, and chert, all of which have elevated TOC. Quartz (chert) dominates Woodford mineralogy. Phyllosilicate minerals in the Woodford formation include muscovite and illite with minor kaolinite and chlorite. Pyrite is abundant, and feldspars are sparse.

The element concentration plots (Figure 17A) show that some elements covary with titanium, for example, Al, K, V, Fe, S. These elements have been found on a worldwide basis to correlate to shale content (Turekian and Wedepohl 1961). Although elements like Fe, S, V, and Ti are not stoichiometric components of clay minerals, they occur in higher abundance in clay-rich rocks relative to quartzose rocks. They can be used collectively to quantify the clay content once calibrated.

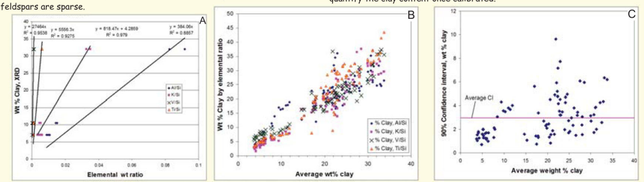


Figure 18. Quantification of bulk clay minerals by correlation to an XRD calibration data set. (A, left) Plots of Al/Si, K/Si, Ti/Si, and V/Si against weight percent total phyllosilicates as determined by XRD. Similar plots can be made for other element ratios. (B) Clay content predicted by each element ratio as a function of average predicted clay content. Scatter of predicted clay content gives uncertainty of the clay content estimate. (C, right) plot of standard deviation (SD) against the average clay content. Most samples show low SD, but a few samples have high SD.

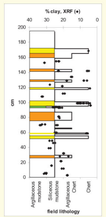
Calibration requires an x-ray diffraction (XRD) calibration data set. Three samples were selected and their mineralogy determined by XRD. The XRD weight percent of phyllosilicate minerals was regressed against the elemental ratios (Figure 18A). Least-square fit of the elemental ratios to the wt % phyllosilicates was calculated, assuming a zero intercept. The regression equations were then used to calculate the wt% phyllosilicates in all XRF analyses. The clay content predicted by each elemental ratio is plotted against the average of the clay contents (Figure 18B). Some analyses have narrow ranges of clay contents whereas others have high scatter. The average 90% confidence interval of the % clay is 2.94. Most samples have CI in range of 1 to 4 wt% clay, with some outliers as high as 9.6 wt%. (Figure 18 C). The confidence interval can be used to judge the validity of the clay content estimated from the elemental analyses.

Other element ratios can also be used. This will increase n, thereby decreasing the confidence interval. As the explained variance (R^2) of each individual elemental ratio regression to wt% clay decreases, the weighting of the elemental ratio should be reduced so that elements with low correlation to clay content do not distort the average estimates.

Results can be compared to field interpretations of lithology (Figure 19). In general, rocks classed as cherts have lowest clay content, argillaceous cherts have slightly higher clay content, and siliceous mudstones have the highest clay content. There is significant scatter in the wt% clay in each stratigraphic unit due to the laminated, interbedded nature of the Woodford shale.

Figure 19. Comparison of field lithology interpretation to weight percent clay estimated by XRF in a 2 meter section of middle Woodford Formation from the Hunton Quarry, Oklahoma. In general, there is a good general agreement between lithology and XRF clay content. Significant variation in % clay within field units is related to the laminated nature of the rock. The rock originally interpreted as an argillaceous mudstone (green) is actually a microporous siliceous mudstone similar to other siliceous mudstones.

Because of calibration to XRD, the weight percent is relative to the mineral matter only and does not include the kerogen.



Calibration by Correcting Elemental Ratios

The second approach for calibration of XRF elemental concentrations to clay content utilizes the XRD data to correct XRF elemental ratios. The corrected XRF elemental ratios are then used to estimate the amount and kind of clay minerals present. This approach works only where elemental ratios can be interpreted from the XRD data. The elements of interest should be stoichiometric or near stoichiometric components of the minerals. For example, calcium in smectite varies significantly as it substitutes for Na, so smectite would be difficult to quantify using Ca. The clay minerals to be identified must also have unique XRF-detectable elemental ratios. Dickite cannot be distinguished from kaolinite, for example, because the only XRF-detectable elements are Al and Si and they have the same ratio.

These constraints are rather severe, so this method is best applied for mineralogically simple systems with two clay components with well constrained elemental concentrations that can be detected by XRF. The advantage of this approach is that two or more clay components can be identified under favorable circumstances.

Example Application: Castlegate Sandstone, Utah

The Cretaceous Castlegate Sandstone at the Salina Tunnel in central Utah was evaluated to determine the origin and composition of fault rocks along the Salina Tunnel Fault. See Spieker and Baker (1928) or Tabet, et al. (2009) for stratigraphic and setting background information and Covault (2006) for detailed description of the fault.

Castlegate sediments are quartzose sandstones, conglomerates, and silty mudstones with rare, discontinuous claystones. XRD analysis finds only three major mineral components: quartz, kaolinite, and illite. Traces of k-feldspar, anatase, and chlorite are also present. Conceptually, the Al/Si and K/Si can distinguish these three major mineral components.

The work flow is as follows: (1) estimate elemental ratios from mineralogy in the XRD calibration samples. (2) Compare XRD elemental ratios to XRF elemental ratios and use the XRD ratios to correct the XRF elemental ratios. (3) Use corrected elemental ratios to determine the three mineral components quartz, illite, and kaolinite.

Clay minerals typically have variable compositions. The weight Al/Si of kaolinite is very close to the stoichiometric value, with atomic Al/Si uniform in different samples and size fractions, and all very close to 1 (Jepson and Rowse 1975). Measured weight K/Si in natural illites average about 0.242 (Rosenberg and Hooper 1997) as compared to the stoichiometric value of 0.2388 used for elemental ratio correction. The elemental ratios (and therefore the illite concentrations) are similar, so illite concentration estimates are robust. Weight Al/Si measured in illites is somewhat more variable and averages 0.586 (Rosenberg and Hooper 1997). This is significantly different from the theoretical value of 0.357 used for conversion in this study. Fortunately, the illite Al/Si is not used to determine illite content, but it does affect the estimated kaolinite content at the expense of quartz. For example, a sample with typical analysis with 25 % total clay changes to 27 % total clay if the empirical Al/Si ratio is used instead of the theoretical value.

The XRF elemental ratios were corrected using the following relationships. Corrected and uncorrected ratios are shown on Figure 20.

- corrected XRF K/Si = 1.27* uncorrected XRF K/Si.
- corrected XRF Al/Si = 0.44*XRF Al/Si + 0.0058*exp(7*XRF Al/Si) - 0.0055

The non-linear Al/Si correction was necessary due to the large range of Al/Si ratios in the sample. At the lower concentrations, the correction equation is almost linear with a slope of 0.54; that is, corrected Al/Si is about half that of the uncorrected XRF Al/Si (Figure 21).

Kaolinite (K) and illite (I) content of XRF analyses were calculated from the following relationships. Because the K/Si correction was linear, the illite content was calculated from the uncorrected K/Si.

$$K = \frac{\left(\frac{Al}{Si}\right)_{xrf} - 0.3568I}{0.9606(1-I)} \qquad I = \frac{1.27\,K_{Si}}{0.2388}$$

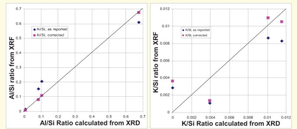


Figure 20. Elemental ratios of the four XRD calibration samples. Plots show XRF ratios before (blue) and after (magenta) correction. The K/Si ratio plots (right) show high scatter after correction due to the low K content of these rocks. Longer counting times might improve the correlation, but it is possible that heterogeneity within the calibration samples is responsible for the scatter.

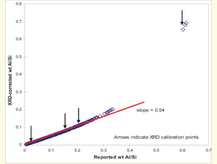


Figure 21. Comparison of corrected and uncorrected Al/Si ratios showing the effect of a non-linear correction. Most samples have low clay contents and the corrected values are slightly greater than half the uncorrected values.

Weight fraction illite and kaolinite for XRF analyses show two dominant trends (Figure 22). Most data form a trend with relatively constant illite/kaolinite ratio. Some samples on this trend mix with a high kaolinite end member. These compositional trends may indicate mixing of a detrital clay with early diagenetic (pedogenic) clay. Most samples are mixtures of detrital quartz and detrital clay with a relatively uniform clay mineral ratio that is probably detrital in origin. The variation towards higher kaolinite may be related to early diagenetic kaolinitization of the illite by weathering of the detrital clay in soil zones on the floodplains.

The rock is assumed to be a mixture of quartz, illite, and kaolinite, so the quartz fraction is 1 - K - I. Quartz dominates the vast majority of samples, and illite is a minor component compared to quartz and kaolinite. This conclusion is made from clay contents interpreted from both "as received" and corrected elemental ratios (Figure 23). Correction reduces the amount of total clay in most samples by about half, forcing most analyses closer to the quartz point.

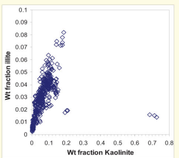
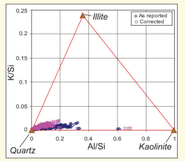


Figure 22. (Left) Illite and kaolinite weight fractions calculated from XRF analyses of the Castlegate Sandstone, Salina Tunnel, Utah. Illite axis greatly expanded to show linear variation of illite and kaolinite present in most samples.

Figure 23. (right) Comparison of mineral fractions calculated from uncorrected and corrected elemental ratios. Correction decreases clay content by almost a factor of 2 for most low clay samples. However, most samples are characterized by low clay contents regardless of correction.



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