

Dual-Range FT-IR Mineralogy and the Analysis of Sedimentary Formations

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ABSTRACT

Fourier transform infrared spectroscopy (FT-IR) has been successfully used as an alternative to X-ray diffraction in the analysis of sedimentary minerals. Many common minerals exhibit unique absorbance spectra in the mid-IR range, which extends from 400 cm^{-1} to 4000 cm^{-1} . Several authors have shown that the mineral concentrations of an artificial mixture can be quantitatively derived from the mixture spectrum and the spectra of the mineral standards using the mid-IR. There are some limitations to the use of FT-IR that can result in errors in such an analysis, particularly for real sedimentary rock samples as opposed to laboratory mixtures. A new procedure was developed that combines mid-IR and far-IR into a single spectrum covering the range 300 cm^{-1} to 5200 cm^{-1} . The inclusion of the far-IR enables a better analysis of carbonate minerals since the metal-oxygen bond energies are included. Other improvements include compensation for variable light scattering by potassium bromide pellets, wavelet-based weighting of spectra, and use of end-member feldspar standards. Analysis of over 1000 oilfield samples shows that for many minerals, available library mineral standards have appreciably different FT-IR spectra than are found in oilfield samples. As a result, the mineral standard set has been expanded and now includes 49 mineral species of 29 distinct sedimentary minerals including 5 calcites, 4 dolomites, 5 kaolinities and 4 illites. The sample's FT-IR spectrum is solved as a linear combination of the standard spectra, so the individual mineral species' concentrations are available. The accuracy of the analyses is confirmed by comparing chemical concentrations measured on a split of the samples with concentrations reconstructed from the mineral concentrations. The new level of quantitative analysis has already resulted in a quantitative lithology analysis for total clay, carbonate, anhydrite and sand that is implemented for open- and cased-hole geochemical log analysis.

INTRODUCTION

Mineralogy is a fundamental part of formation description yet the analytical capabilities for accurate mineral analysis lag behind those of other parameters. Matteson and Herron¹ presented results for a quantitative mineral analysis system based on Fourier Transform Infrared (FT-IR) spectroscopy measurements with special sample preparation and signal processing steps. Comparison of known mineral compositions in artificial mixtures with values determined from FT-IR showed errors of better than ± 2 wt. %. In that study, it was observed that for several minerals, different specimens had slightly different FT-IR spectra such that quantitative analysis could be perturbed. However, the samples and the standards were constructed from the same mineral specimens so the degree of natural variability outside the standards set was not specifically addressed.

Since that report, our laboratory has analyzed over 1000 oilfield samples for mineralogy. Making such analyses quantitative has necessitated a number of developments to account for mineral variability and to produce accurate mineral assessments. This report

details several of the developments as well as adopted quality control procedures. Finally, some of the mineral surprises that have occurred during this time period will be mentioned.

EXPERIMENTAL METHODS

The fundamentals of sample and KBr pellet preparation are unchanged from Matteson and Herron¹. Cleaned oil-free samples are crushed and split with a microsplitter into two identical fractions, one for chemical analysis and one for mineralogical analysis. The chemistry fraction is sent to X-ray Assay Laboratories for multi-element analysis. The mineralogy fraction is ground with a Micronizing Mill, mixed with KBr using an auto-mixer, and pressed under vacuum into a clear pellet. The infrared absorbance of the pellets is measured using a Perkin-Elmer System 2000 FT-IR Spectrometer with a SpectraTech autosampler. Absorbance is recorded on a PC and ASCII files are compared to mineral standard spectra using custom MATLAB programs. All mineral standards have been analyzed mineralogically by x-ray diffraction (XRD) as well as chemically for over 50 elements². A number of changes have been implemented and they are detailed in the following.

1) *Merger of mid-IR and far-IR*. Both the mid-IR (500-5200 cm^{-1}) spectrum and the far-IR (300-710 cm^{-1}) spectrum are collected and merged into a single spectrum. Figure 1 shows two calcite spectra and two dolomite spectra from the standards set. There is a great deal of variance in the large carbonate peak between about 1350 cm^{-1} and 1550 cm^{-1} , so much so that the calcite and dolomite peaks are not easily separated in this region. On the other hand, in the 300-500 cm^{-1} region, the calcite and dolomite peaks are fairly strong and the different minerals are well separated.

2) *Wavelet-based weighting of spectra*. Stark et al.³ used the data base of Matteson and Herron (1993a) to develop an innovative procedure to weight the FT-IR spectra. This procedure involved performing a wavelet transform of spectra of mineral standards and artificial mixtures of known composition. Wavelet coefficients which changed a great deal for replicate analyses were unweighted since they most likely represented analytical errors. Coefficients which didn't change much across the entire training set were also unweighted since they are not very diagnostic. The results showed that the errors in estimating mineral percentages in the training set could be dramatically reduced. Those portions of the spectra found not to be diagnostic have been similarly unweighted for subsequent rock analysis.

3) *Expansion of mineral standard data base*. The number of mineral standards has been increased from 14 to 29 to account for additional minerals observed in the oilfield samples. The mineral set currently includes: quartz, chert, opal-A, opal-CT, K-feldspar, Na-feldspar, Ca-feldspar, calcite, dolomite, ankerite, siderite, sideroplescite (Mg-rich siderite), magnesite, aragonite, high magnesian calcite, fluorite, illite, smectite, kaolinite, chlorite, glauconite, muscovite, biotite, pyrite, gypsum, anhydrite, celestite, hematite and barite. The total number of mineral standards including multiple species is currently 49. There are also spectra for CO_2 and H_2O contaminants that may be present in the sample chamber atmosphere despite purging with dry CO_2 -free gas. Multiple mineral species standards exist for quartz, calcite, dolomite, illite, smectite, kaolinite, and chlorite. An example of the need for multiple standards is shown in Figure 2 which shows the combined mid-IR and far-IR spectrum of the five calcite samples in our standards set. Several of the more recent mineral species standards have been constructed from oilfield samples rather than from conventional sources.

4) *End-Member Feldspar Standards.* Natural feldspar minerals are almost always some mixture of the Na-, Ca- and K-feldspar end members; end-members are virtually unknown. Matteson and Herron⁴ constructed mid-IR spectra for feldspar end-members using the combined chemistry and FT-IR data. They found that the compositional data could be accurately estimated from an unknown feldspar's spectrum and the end-member spectra. Use of three end-member standards is a preferred way to deal with natural mineralogical diversity compared to increasing the number of feldspar species in the standards set. For our current analytical procedure, combined mid- and far-IR spectra for the end-member feldspars have been similarly constructed.

5) *KBr pellet light scattering.* KBr pellet (blank) spectra exhibit absorbance slopes due to scattering by grain boundaries or impurities. Figure 3 shows the mid-IR spectra of fourteen blank KBr pellets. Note the variability in slopes of these spectra caused by scattering. The portion of the spectrum from 4000-5200 cm^{-1} shows the effects of the scattering but has no apparent mineral absorbance. For a rock spectrum, the slope over the 4000-5200 cm^{-1} region is matched to that of the closest KBr blank pellet before the appropriate blank is subtracted. In addition, the standard mineral spectra include a diagonal line as recommended by Brown and Elliott (1985).

6) *Offset optimization.* KBr pellet spectra also exhibit variable offsets due to imperfect optical alignment (Figure 3). The magnitude of this uncertainty can produce errors of several weight percent in a mineralogical analysis. A novel iterative procedure has been developed whereby after the sample spectrum is analyzed for mineralogical content, the total mineral content is computed along with the goodness of fit between the measured and reconstructed spectra. The difference of the total from 100% provides a possible spectral offset estimate. The sample spectrum is given the offset and the mineralogy is recomputed. If the goodness of fit is improved, the offset estimate is adopted.

RESULTS AND DISCUSSION

Analytical Validation

The accuracy of the FT-IR analysis of natural sedimentary materials is difficult to verify. Other methods such as x-ray diffraction have large relative errors when clay minerals are involved and clays are too small for accurate thin section analysis. Note that FT-IR detects total illite and smectite independent of any interstratification. Two validation tests were invoked. First, the training set of Matteson and Herron¹ with known mineralogy was re-analyzed using the current procedure. Second, measured chemistry was compared to concentrations expected based on the FT-IR mineralogy. This type of test implies constant chemical composition and can be slightly perturbed by the nature of the adsorbed cation on clay surfaces but is nevertheless very useful for quality assurance.

Table 1 contains summary information about the analysis of the training set of Matteson and Herron¹. Column A lists the average absolute errors in fifty experiments between the actual mineralogy and the computed mineralogy reported by Matteson and Herron¹. Column B gives average absolute errors for the restricted frequency range of the current spectrometer, 500-4000 cm^{-1} , using the same 19 standards as did Matteson and Herron¹. On average, this results in about a 0.5 wt % additional error for most minerals. Column C gives the results when the H₂O and CO₂ standards are added. The errors are reduced to, for many minerals, about the value for the original expanded frequency range. Column D shows that the addition of the far-IR to extend the range to 300 cm^{-1} significantly reduces errors for calcite, dolomite, illite, smectite and chlorite.

Column E in Table 1 gives the average absolute error for the expanded standards set. These results are shown graphically in Figures 4 and 5. For most, but not all minerals, the errors are lowest for this set. This is somewhat of a surprise since the actual minerals used to make the mixtures are part of the 19 standard set. Further, many of the additional standard minerals bear some resemblance to the test minerals and so might be expected to interfere with the proper analysis.

The second test for the new FT-IR processing is a comparison of measured chemical concentrations with values estimated from the mineralogy. Estimated concentrations are computed by summing the product of a mineral concentration and the elemental concentration in the end-member mineral. Performing this calculation requires a table of end-member concentrations and there is little consensus regarding many entries in such a table, particularly for clays. Table 2 gives end-member concentrations used in our laboratory. The values are generally either calculated from simplified formulae (e.g. quartz) or from the mineral composition study of Herron and Matteson². Note, for example, that calcite has a slight Mg concentration despite its absence from the ideal chemical formula.

Figures 6 and 7 show comparisons of measured and estimated elemental concentrations for 45 samples from a well in Europe. The well contains sandstones, limestones and shales and a wide variety of minerals within those lithologies. Concentrations of silicon, calcium, potassium, and magnesium all reconstruct extremely well. From the graph (Figure 6e), it might appear that core aluminum concentrations regularly exceed the reconstructed values, but the mean difference is only 0.09 wt. % Al. There is also a slight underestimation of the total sulfur, but the average difference is only 0.3 wt. % S.

In the usual case, the concentrations of Ti, Gd, Th and U are either reconstructed satisfactorily or are underestimated because of the presence of organic matter or trace heavy minerals such as rutile, zircon, monazite and tourmaline, which contribute substantially to the chemical abundance of these elements but which are undetected by the FT-IR method. This is essentially the case for the European well data. Concentrations of Ti reconstruct unusually well. Concentrations of Th, Gd and U generally greatly exceed the reconstructed values.

The very good agreement between measured and estimated major elements provides a second powerful indication that the mineralogy data are of high quality.

Additional Observations

In the course of FT-IR analysis of over 1000 samples from oilfields around the world in the last few years, a few characteristics have been noted that are of interest.

1) *Kaolinite speciation*. There are five kaolinite species in our current standards set. They span the essential range of degree of internal order as defined by the Hinckley Index⁶ from very well ordered (Hinckley Index = 1.5) to very poorly ordered (Hinckley Index = 0.1). When well ordered or very well ordered kaolinite is found in the FT-IR analysis, invariably well defined booklets are observed by scanning electron microscopy. These booklets are assumed to be authigenic. In contrast, poorly ordered kaolinites are assumed to be detrital. Figure 8 shows the kaolinite speciation and total kaolinite for the samples from the Europe well. Over some intervals, all the kaolinite is either very poorly ordered or poorly ordered and thus assumed to be detrital. In other intervals, a substantial fraction is well ordered. The identification and quantification of these kaolinite forms is of use in the

energy industry since well ordered kaolinite can have a significant impact on well productivity and completion design.

2) *Illite speciation*. Illite is the most commonly observed clay mineral in our experience so far. There are four illites in the standards set, one from Fithian, Illinois, one from Silver Hill, Montana, and two we have constructed from Oklahoma and Texas. The 300-1200 cm^{-1} portion of the standard spectra is shown in Figure 9. The Texas sample stands out as having the best developed peak at about 1020 cm^{-1} and is the most common species in our analyses. Fithian illite is the type locality and perhaps the best studied of all illite specimens. Yet for the oilfield samples studied so far, Fithian represents only about 15 % of the total illite concentration.

3) *Muscovite abundance*. For the oilfield samples studied so far, muscovite concentrations average 19 % of illite concentrations. This is an amazingly high number. The experiments shown in Figures 4 and 5 clearly show that the FT-IR procedure is able to quantitatively distinguish illite from muscovite even when present in the same sample. This is not likely to be the case for XRD. In a common XRD procedure, the 19.8° two-theta peak in a bulk scan is assumed to be proportional to total clay. Muscovite, a non-clay, has a large peak within this range, so results using this procedure are likely to have been skewed. For clay identification, the < 2 micron fraction, which presumably has excluded any muscovite, is analyzed and results are normalized to the 19.8° clay content. Any muscovite in the sample is likely to have been overlooked by this common XRD procedure.

SUMMARY AND CONCLUSIONS

A new procedure has been developed for the quantitative analysis of sedimentary minerals by FT-IR. The mid-IR and far-IR spectra have been combined into a single spectrum that is more diagnostic than the mid-IR spectrum alone. The portion of the spectrum above 4000 cm^{-1} is used to find a blank KBr pellet with similar scattering. The spectra are weighted following the experience of Stark et al.³. The number of mineral standards has been increased to 29 and the total number of mineral species has been increased to 49 to account for natural variability in infrared spectra. Feldspar end-member spectra were computed following Matteson and Herron⁴. The procedure has been shown to be accurate to about ± 1 wt. % for most minerals using the test data of Matteson and Herron¹.

There are no alternate procedures for comparison which have the same quantitative capabilities as the FT-IR method. So, to attempt to validate the results, the FT-IR mineralogy is used to compute expected chemical concentrations and these are compared with concentrations measured on splits of the same sample. Expected concentrations of most major elements agree with measured concentrations within measurement error. On the other hand, concentrations of Ti, Gd, Th, and U usually exceed reconstructed values due to organic matter and trace minerals which contribute chemically but are not detected by the FT-IR procedure.

The development of a quantitative mineralogy means that possible links between elemental concentrations and mineral abundances can be explored. Herron and Herron^{7,8} examined chemistry and FT-IR mineralogy data from over 400 sand and shaly sand samples and found that total clay, total carbonate, evaporite and sand lithology fractions can be derived from concentrations of Si, Ca and Fe that are available from open- and cased-hole logging services.

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Table 1. Average absolute difference (wt. %) between the composition of the mineral mixtures and the composition derived from the mixture FT-IR spectra.

Mineral	A	B	C	D	E
	19 Stds ¹ 400-4000	19 stds 500-4000	21 stds 500-4000	21 stds 300-4000	52 stds 300-4000
Quartz	1.5	1.9	1.8	1.7	1.2
Opal-A	0.9	1.5	1.4	1.4	1.1
Oligoclase	0.7	1.1	0.7	0.9	1.1
Orthoclase	0.7	0.8	0.7	0.8	0.6
Calcite	1.8	1.7	1.7	1.4	1.0
Dolomite	1.4	1.5	1.5	1.2	1.7
Pyrite	0.2	0.2	0.2	0.2	0.1
Illite	2.6	3.4	3.3	2.8	1.6
Smectite	2.2	2.9	2.5	1.7	1.1
Kaolinite	1.0	0.9	1.0	0.9	0.6
Chlorite	1.3	2.7	1.3	0.8	1.0
Biotite	0.6	0.5	0.6	0.2	0.1
Muscovite	0.4	0.8	0.9	1.2	0.6
Glauconite	1.3	0.5	0.5	0.8	0.7

Table 2. End-member mineral compositions used to generate estimated chemical concentrations from FT-IR mineralogy for comparison with measured concentrations.

Mineral	Element (wt. %)	Si (wt. %)	Al (wt. %)	Na (wt. %)	K (wt. %)	Ca (wt. %)	Mg (wt. %)	S (wt. %)	Fe (wt. %)	Ti (wt. %)	Th (ppm)	U (ppm)
Quartz		46.74										
K-Feldspar		30.27	9.69		14.05							
Na-Feldspar		32.13	10.29	8.77								
Ca-Feldspar		20.19	19.40			14.41						
Calcite						39.54	0.37					
Dolomite						21.27	12.90					
Ankerite						10.40	12.60		14.50			
Aragonite						40.04						
Siderite									48.20			
Sideroplescite							5.80		38.60			
Magnesite							28.80					
HMC						34.88	3.20					
Illite		24.00	12.00	0.40	4.00		1.20		4.00	0.80	12.00	4.80
Smectite		21.00	9.00	0.50	0.50	0.20	2.00		1.00	0.20	26.00	7.10
Kaolinite		21.00	19.26	0.24	0.10	0.10	0.10		0.80	1.18	21.00	3.30
Chlorite		17.90	9.00	0.30	0.90	1.60	2.50		16.40	2.37	16.00	4.20
Glauconite		23.10	4.40	0.10	5.90	0.50	2.10		15.50	0.10	3.00	5.40
Muscovite		21.15	20.32		9.82							0.70
Biotite		18.20	6.00	0.40	7.20	0.20	7.70		13.60	1.50	1.50	0.70
Pyrite								53.45	46.55			
Opal		29.20										
Gypsum						23.28		19.00				
Anhydrite						29.44		24.00				
Barite								13.74				
Hematite									69.94			

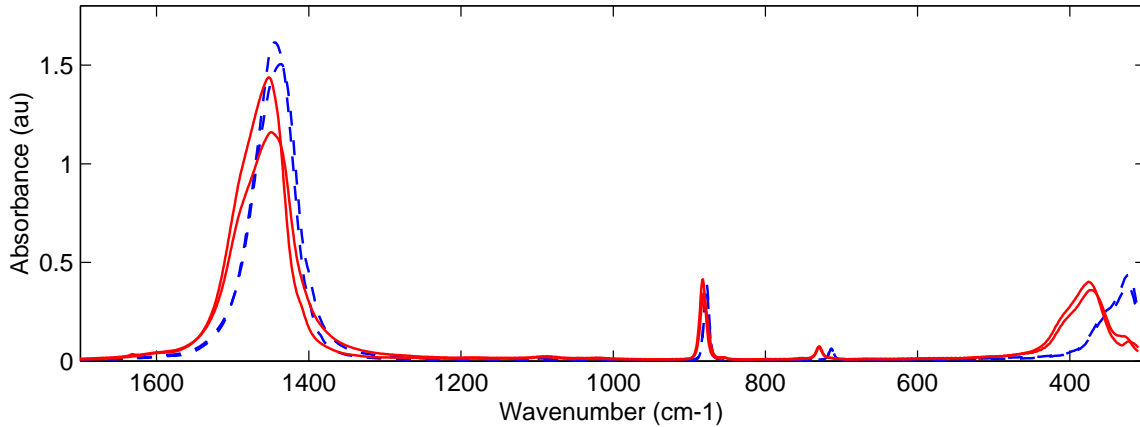


Figure 1. Portion of the dual-range (mid-IR plus far-IR) absorbance spectra for two calcites (dashed) and two dolomites (solid). The far-IR portion of the spectrum below 500 cm^{-1} is a powerful addition for discrimination of carbonate minerals.

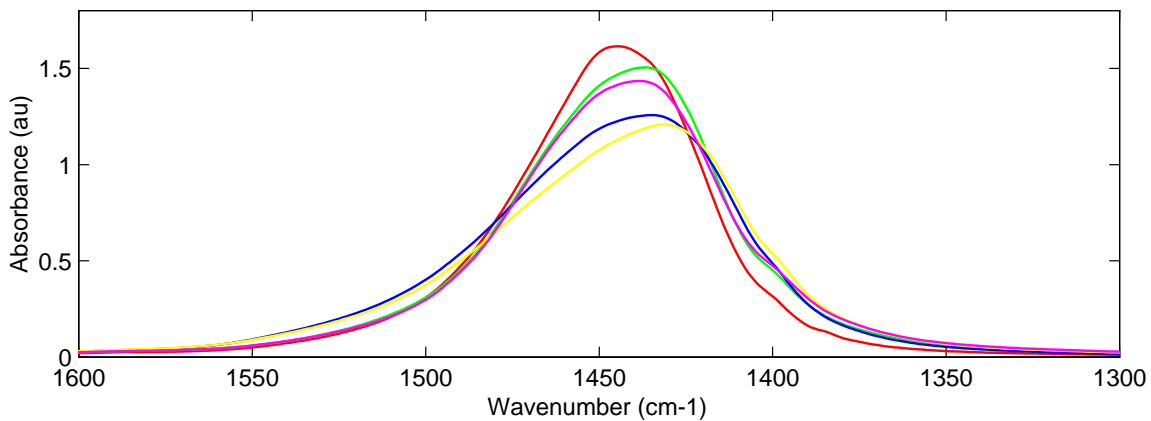


Figure 2. Mid-IR absorbance spectra for five calcites. Note the variability in peak position, peak height, and in full-width at half maximum for these five samples.

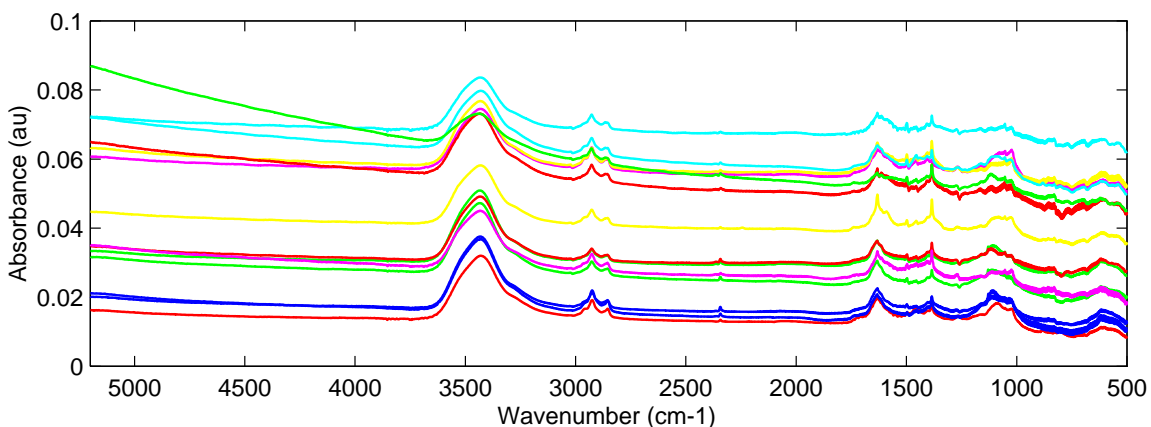


Figure 3. Absorbance spectra for fourteen blank KBr pellets show variable offset from imperfectly aligned optics as well as variable slopes from grain boundary scattering. The 4000-5200 cm^{-1} range is free of mineral absorbance and can be used to match a sample spectrum's scattering with the closest KBr blank's scattering before the blank absorbance is removed.

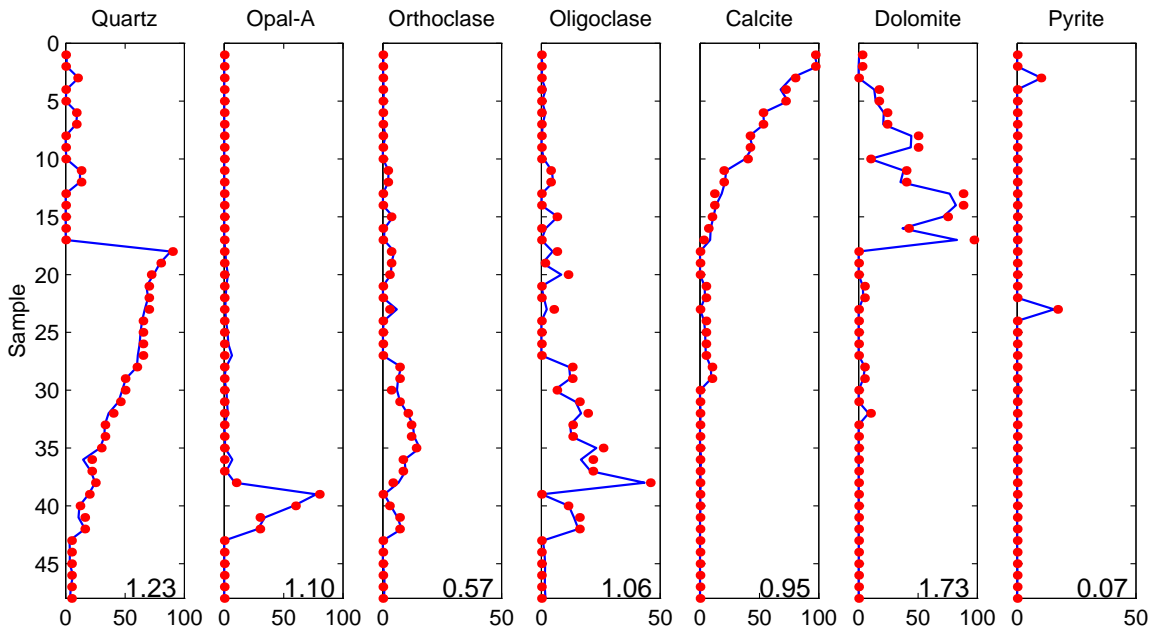


Figure 4. Known (filled circles) and estimated (solid lines) mineral compositions for seven of the minerals in the Matteson and Herron¹ test set using the 52 mineral standard processing. Each row represents one experiment. The first experiments were constructed to resemble carbonate lithologies; the lower experiments represent sands and shaly sands. Number in each block is the average absolute difference between known and estimated mineralogy.

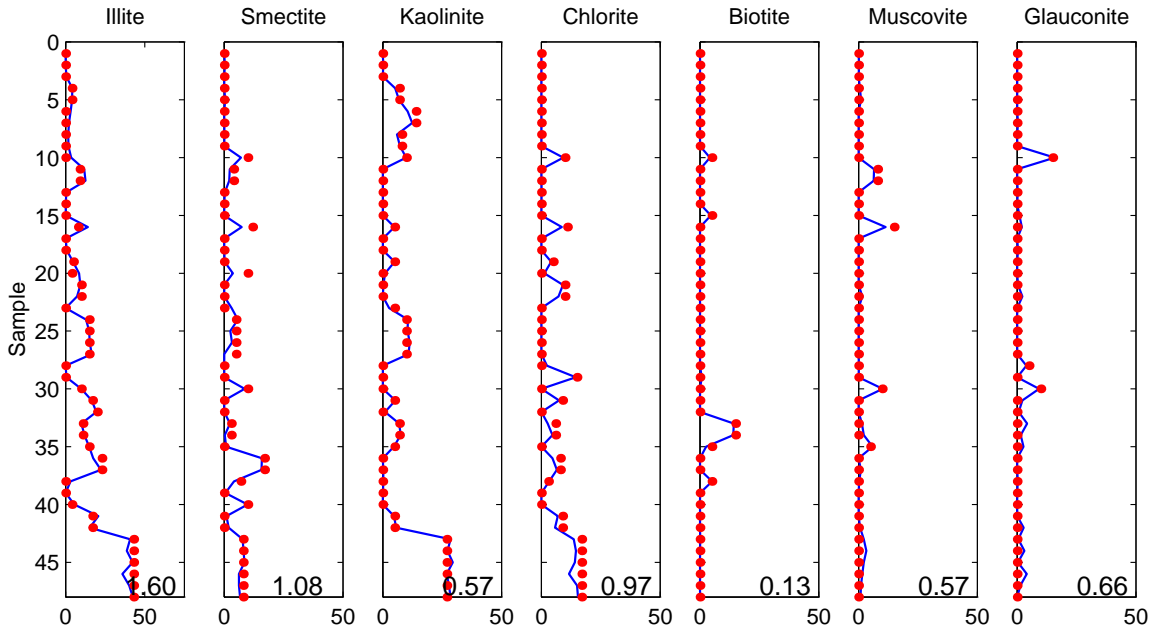


Figure 5. Known (filled circles) and estimated (solid lines) mineral compositions for seven of the minerals in the Matteson and Herron¹ test set using the 52 mineral standard processing. Each row represents one experiment. The first experiments were constructed to resemble carbonate lithologies; the lower experiments represent sands and shaly sands. Number in each block is the average absolute difference between known and estimated mineralogy.

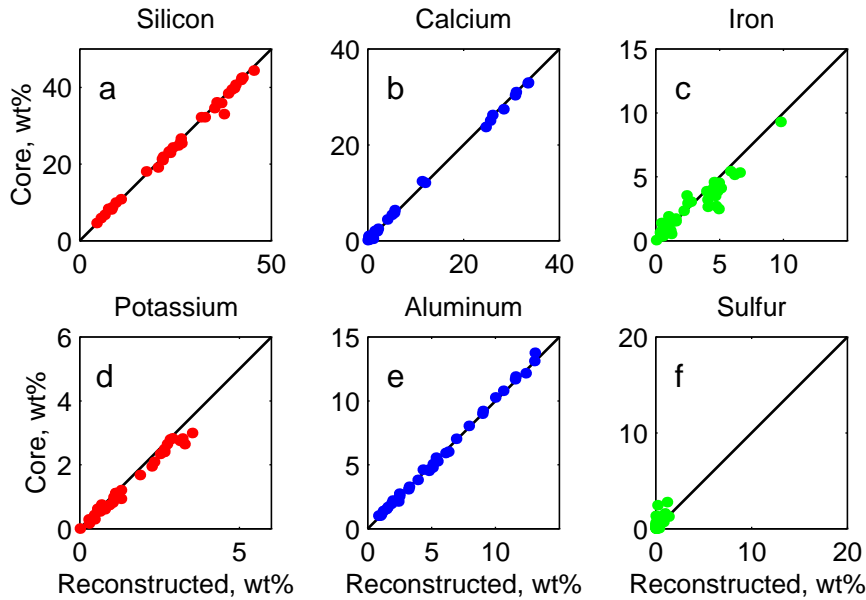


Figure 6. Measured elemental concentrations compared with concentrations reconstructed from the FT-IR mineralogy and the end-member concentrations in Table 2. The solid line is a 1:1 line. The agreement shows the accuracy of the FT-IR mineralogy.

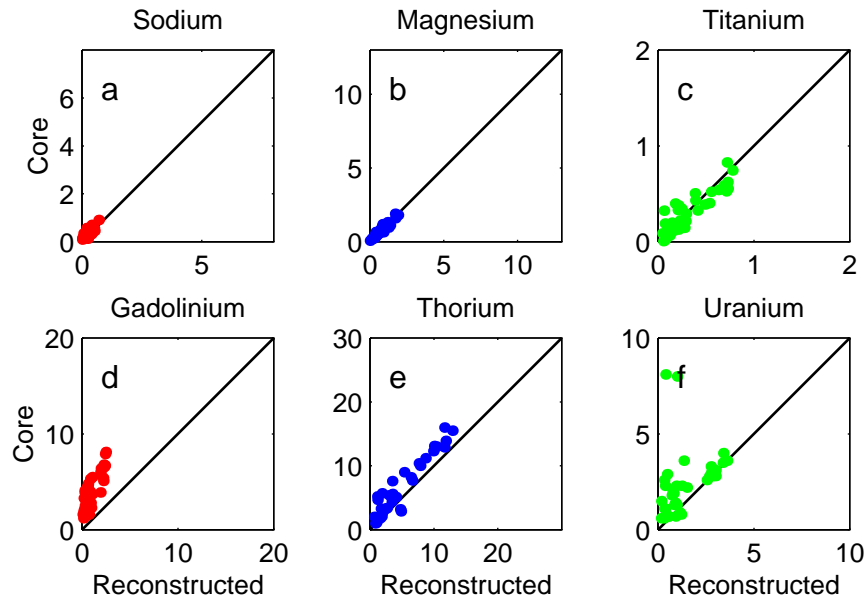


Figure 7. Measured elemental concentrations compared with concentrations reconstructed from the FT-IR mineralogy and the end-member concentrations in Table 2. The solid line is a 1:1 line. Figures a, b and c are in wt %; d, e, and f are in ppm. In siliciclastics it is common to find real concentrations exceeding the reconstructed values of Ti, Gd, Th and U due to organic matter and heavy minerals which contribute chemically but are not detected by the FT-IR methodology.

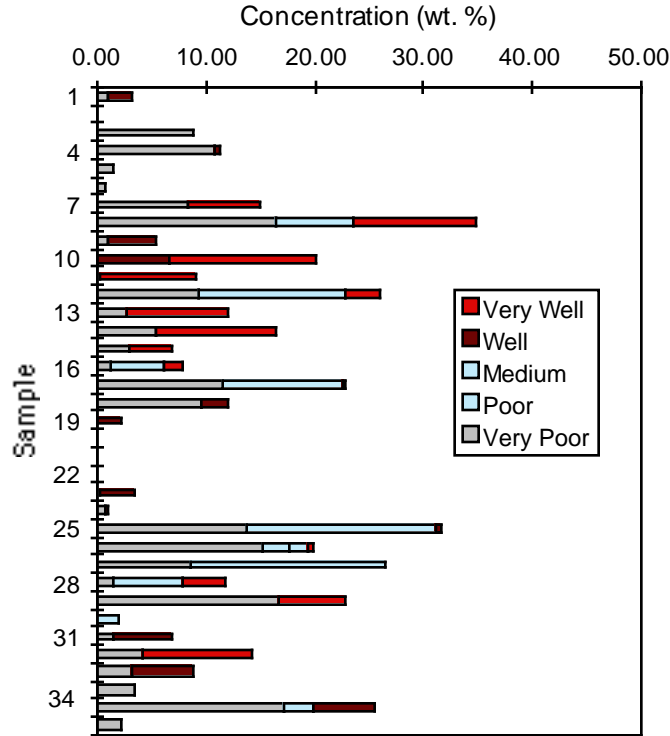


Figure 8. Kaolinite speciation in the Europe well samples. Poorly ordered kaolinites (gray) probably represent detrital kaolinite. Well ordered kaolinite (black) probably represents authigenic kaolinite as evidenced by well defined booklets in scanning electron microscopy images.

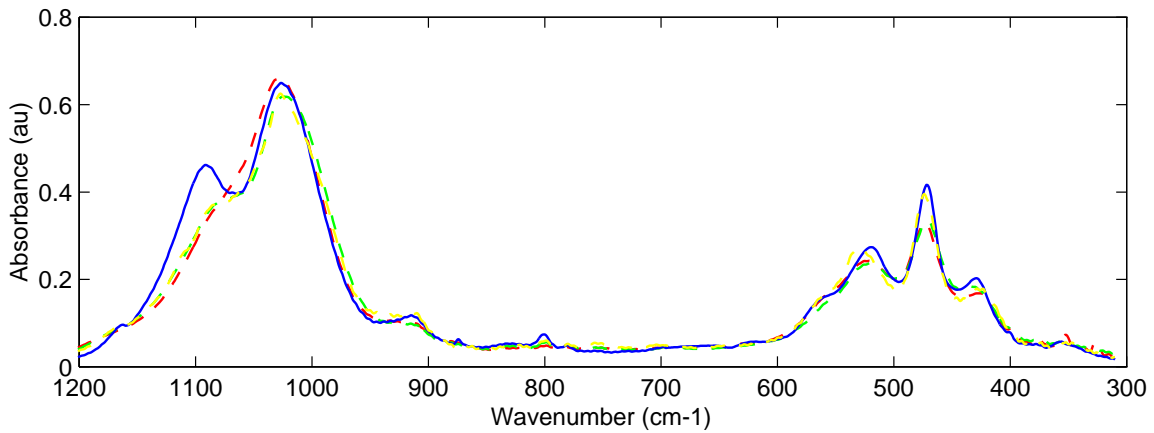


Figure 9. Dual range FT-IR spectra for four illite standards. The dotted spectra represent Fithian, Silver Hill and an Oklahoma illite. The solid line represents the Texas illite spectrum which has a well developed peak at 1092 cm^{-1} that is only a shoulder in the other spectra.