RAPID MINERAL ANALYSIS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

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ABSTRACT

Knowledge of the mineral composition of rocks is critical to many phases in the exploration and exploitation of hydrocarbon reservoirs. Some examples are geological studies, log interpretation, drilling and completion engineering and formation damage prediction.

Techniques such as thin section modal analysis, X-ray diffraction and chemical analyses, or a combination of these, are normally employed when quantitative mineral data are required. Unfortunately, these methods are time consuming and expensive. Consequently, many important decisions turn out to be costly mistakes because good mineral data are lacking.

Energies in the infrared region of the electromagnetic spectrum correspond to the vibrations of molecular bonds. So infrared analysis has long been recognized as a useful method of qualitative analysis of the minerals in rocks. However, recent advances in: i) the instrumentation for Fourier Transform Infrared (FTIR) Spectrometry; ii) microcomputer power, iii) data processing techniques; and iv) sample preparation, have all combined to transform infrared spectroscopy into a reliable tool for rapid, inexpensive and quantitative mineral analysis.

Data acquired on a large number of synthetic and natural samples indicate that FTIR spectroscopy can quantify minerals with an accuracy of 5% or better in a timeframe which allows the data to impact well completion decisions.

INTRODUCTION

The quantitative mineralogy of the sedimentary section from a single well or group of wells is basic to most exploration and production activities. This information can aid in performing log calibration, evaluating reservoir quality, screening samples to identify intervals with problem minerals such as swelling clays, designing a drilling program that will minimize formation damage and interpreting depositional environments. The past decade has seen a great increase in the application of sedimentology and petrology studies to solving exploration and development problems. [1,2] Indeed the concept of the integrated study, combining the expertise of geologists, geophysicists, petrophysicists, petroleum engineers and log analysts has come of age.[3]

When measuring mineralogy quantitatively, there has always been an inverse relationship between analytical speed and data quality. An example is scan speed versus peak resolution when performing an X-ray diffraction (XRD) analysis. A slower scan speed improves peak resolution resulting in greater accuracy. But a slower scan speed also requires greater analytical time. So the petroleum scientist is asked to sacrifice rapid turnaround time in exchange for improved accuracy and precision. Clearly this is not an ideal situation. This inverse relationship holds true in all the widely accepted mineral identification techniques (Table 1). XRD analysis (including overnight glycolation) generally takes from 24 to 48 hours, while thin section preparation (with epoxy impregnation) can take up to 36 hours. XRD results can vary depending on the instrumentation, sample preparation procedures and data reduction software. Thin section modal analysis depends on the skill and experience of the petrologist. There is, therefore, a need for an analytical method that can provide accurate mineral information when time is not available for these sophisticated analyses. A technique, using Fourier Transform Infrared Spectrometry(FTIR), has recently been developed that provides rapid, quantitative and cost effective identification of common rock forming minerals. The data are available in a well completion time frame and both sidewall cores and drill cuttings are suitable for the analysis. Excellent accuracy and precision have been established. In laboratory tests comparing FTIR results with known mineral mixtures, accuracy of 5 weight percent or better has been maintained. This technique has been trademarked MINERALOG.TM

FTIR spectrometry is an ideal sample screening tool and is a natural complement to the more traditional petrographic methods. It can be used to identify zones of potential formation damage and can improve wireline log calibration. The rapid and cost effective nature of this technique make it useful as a routine analysis and the ability to measure small samples is a significant advantage.

INFRARED SPECTROSCOPY OF MINERALS

The Mineralog technique of mineral analysis is based on infrared (IR) spectroscopy. It works because most minerals contain covalent bonds which absorb infrared radiation. The infrared region of the electromagnetic spectrum extends from the red end of the visible spectrum out to the microwave region. The spectral range of greatest use in mineral analysis is the mid-infrared region which covers the frequency range of 400 to 4000 cm^{-1} (25 to 2.5 um).[4] Infrared spectrometry measures the stretching and bending vibrations of atoms within a molecular structure. When infrared light is passed through a mineral sample, some of the frequencies are absorbed and converted into vibrational energy. Other frequencies, not associated with any of the natural vibrations of the mineral components, are transmitted through the sample without being absorbed. When the percent absorbance is plotted against frequency, the result is an infrared absorption spectrum. Figure 1 shows infrared absorption spectra for quartz, feldspar, calcite and kaolinite.

Infrared spectroscopy is basically vibrational spectroscopy. The principal value of the technique lies in the fact that different molecular bonds have different vibrational frequencies. The infrared spectrum of a mineral sample therefore contains features, or peaks, that are characteristic of the molecular structure of the mineral. The positions of these features in the mineral's IR spectrum depend primarily on the size and mass of the atoms which make up the mineral structure and on the covalent bonds between these atoms.

Generally speaking, the heavier the masses involved the lower the vibrational (and hence absorption) frequency. The stronger the bond, the higher the frequency of vibration (cf. the tension in a spring). For example, two typical mineral bonds are the Si-O bond in silicates and the C-O bond in carbonates (Figure 2). Si is heavier than C with the result that the main Si-O absorption occurs at a lower frequency (energy) than that of the main C-O absorption.

Infrared absorption is also influenced by the degree of crystalline order and by the size and type of cations associated with the mineral structure. Figure 3 shows the effect of cation substitution on the position of the secondary carbonate absorption between 675 and 750 cm^{-1}. This provides a basis for differentiating carbonates.

The infrared spectrum of a mineral is therefore sensitive mainly to chemical composition but also to a lesser extent to isomorphous substitution and crystallinity. This makes IR one of the most flexible determinative methods in mineralogy. By comparison, X-ray diffraction responds primarily to variations in interlattice spacing and can provide only limited information on amorphous specimens. IR gives valuable information on such materials. Conversely, elemental analyses like XRF and gamma spectrometry supply chemical composition but no information on mineral structure. Mineral presence has to be inferred from stoichiometric calculations.[5]

It is important to note that only covalent bonds which experience a change in dipole moment when vibrating can interact with electromagnetic radiation. Ionic bonds (e.g. NaCl) and homopolar covalent bonds (e.g. C-C) are transparent to infrared.

QUANTITATIVE MINERAL ANALYSIS BY INFRARED

IR spectroscopy has been in use as a qualitative mineral identification tool for at least 35 years.[6,7] It is only by virtue of some recent developments that reliable quantification of minerals in rock samples is possible. Quantitative IR analysis is based on Beer's Law:

$$I = I_0 \exp(-\mu x)$$

where I_0 is the incident radiation intensity, I is the transmitted or reflected intensity, μ is the absorption coefficient and x is absorber concentration. I_0, I and μ are all functions of wavenumber.

Beer's law states that a sample's absorbance of IR at a given wavenumber is directly proportional to the concentration, in the sample, of those minerals which absorb IR at that wavenumber. By first measuring the absorbance as a function of wavenumber - the absorption spectrum - for known amounts of pure minerals, we can use Beer's law to deduce the presence and concentration of minerals in an unknown sample from its absorption spectrum.

Several criteria relating to three aspects of the IR measurement procedure must be met for this approach to work.[8]

Sample preparation: a variety of methods can be used for investigating rocks with infrared. The best quantitative results are achieved with the simple geometry of a transmission measurement. This requires that the mineral sample be ground and dispersed in an IR transparent matrix material. This mixture is then formed into a pellet, and placed into the beam of the IR spectrometer. Potassium bromide (KBr) is a good choice for the matrix because its refractive index matches well with those of most minerals. This minimizes the Christiansen effect,[9] which distorts absorption features in the spectrum.

The particle size of mineral components in the ground sample must be uniformly less than 2um, to minimize scattering by the sample and produce sufficiently sharp absorption peaks to allow reliable differentiation between minerals.[10] This can be difficult to achieve without altering minerals.[11] For example, some of the effects of excessive grinding are: conversion of calcite to high pressure aragonite[12]; distortion of the structure and order of kaolinite and micas; dehydration of gypsum with subsequent conversion to anhydrite.

It is critical to pay close attention to all aspects of sample preparation. The ground mineral sample must be evenly dispersed within the matrix material and the handling and weighing of the sample must be carefully controlled at all stages. Because water is a strong IR absorber, moisture control is also important. A sample preparation protocol which allows these criteria to be met in a reliable and reproducible fashion is a key component of the Mineralog system.

Infrared Spectrometer: there are three main requirements which an IR spectrometer must meet if it is to be routinely used for quantitative mineral analysis.[13] Firstly, a high signal-to-noise ratio minimizes measurement time. Secondly, good wavenumber resolution maximises the number of spectral features measured. And thirdly, high wavenumber accuracy and reproducibility is critical for comparing unknown spectra with calibration spectra.

These requirements can be met by using a modern Fourier Transform Infrared (FTIR) spectrometer as opposed to a conventional dispersive instrument. The essential difference between the two instruments is in the way they scan through different wavenumbers to build a spectrum. In a dispersive instrument this is done mechanically using a complex system of slits, gratings and filters. In an FTIR this scanning is done mathematically. A Michelson interferometer measures a complex response called an interferogram. A mathematical process called Fourier Transformation - hence the FT in FTIR - is then applied to the interferogram to reveal an infrared spectrum.

The FTIR technique has some major advantages. It measures at all wavenumbers at the same time and can therefore achieve the same signal-to-noise ratio as a dispersive instrument in a fraction of the time. The absence of energy wasting slits, gratings and filters creates a much larger energy flux through an FTIR. This enhances the signal-to-noise advantage. In addition, because an FTIR has only one moving part, a mirror, spectrometer alignment and maintenance are much easier. Finally, a He-Ne laser is used to measure the mirror position resulting in wavenumber accuracy better than 0.01 cm^{-1}.

The measurements discussed here were made on a Perkin-Elmer 1720 FTIR with a signal to noise ratio of 8000:1 on 16 averaged scans acquired in about 3 minutes. Data is acquired at 2 cm^{-1} resolution. A high speed, high capacity personal computer is interfaced with the spectrometer for rapid data collection, storage and interpretation.

Data analysis and calibration: to determine the presence and abundance of minerals in an unknown sample, the IR spectrum of the unknown is compared with the previously measured spectra of pure minerals. This is done numerically using a combination of statistical and peak-fitting procedures. Obviously, it is crucial to have representative mineral standards to build good calibration spectra. Calibration spectra for minerals in one geographical region may not be appropriate to another. Therefore, the list of calibrated minerals is expanded as necessary and as availability of standards allow. Pure mineral standards for more exotic minerals can be difficult to obtain.

The Mineralog system is a unique combination of the requirements outlined above. It is an automated system capable of performing bulk mineral analysis of a sample in a matter of minutes. More than 300 synthetic mineral mixtures, made by combining purified mineral standards, were analyzed to test the system's accuracy. These ranged from binary mixtures to samples containing 12 minerals. Figure 4 compares mineral concentrations measured by Mineralog with the true weighed values for four common minerals which were included in the synthetic samples. Statistical analysis of data like this indicates that Mineralog can measure calibrated minerals to better than 5% by weight with a confidence of 95% (Table 2).

In a typical routine analysis the initial calibration set contains about 10 minerals. This set is divided into a bulk group and a clay group (Table 3). The calibration set is flexible and can be adjusted to reflect different lithologies. It can also be 'regionalized' to include minerals specific to a given geographical area. The Mineralog technique determines the weights of the component minerals in a sample. Therefore, the presence, in significant quantities (>10%), of minerals not included in the calibration set is indicated by comparing the total weight of measured minerals with the weight of sample weighed into the KBr pellet. The presence of well resolved spectral peaks not belonging to any selected minerals also indicates the need to include additional minerals in the calibration set.

Data are presented as a graphical, variable area depth plot (Figure 5). The plot is divided into two tracks with the left track giving the bulk mineral data and the right track giving the relative amounts of clay minerals. Also included, is a matrix density index which is calculated from the fractional weight percent and densities of component minerals. The depth scale is flexible and can be changed for correlation with wireline logs. Mineral percent increases from left to right and total clay is plotted on the extreme left. The percentage of total clay can then be read directly off the scale.

Certain minerals are difficult to differentiate using FTIR, particularly when present in small quantities. Some minerals with similar chemical composition have similar IR spectra making individual quantification difficult. This explains why illite and smectite cannot be independently quantified although their summed percentage can be determined. For the same reason, the Mineralog system cannot easily separate muscovite from illite.

When measuring carbonate minerals, the FTIR method detects shifts in the frequency of the C-O bond resonance (in the carbonate ion) caused by the presence of cations of varying mass and radius. When a nonstoichiometric carbonate (such as ankerite) occurs with a ferroan calcite, in amounts of less than 10 percent for example, it is difficult to make a quantitative measurement within the reported accuracy limits. In most cases, accurate and precise measurements of calcite, dolomite and siderite have been accomplished, over a broad range of carbonate rock types.

APPLICATIONS OF MINERALOG DATA

The ready availability of inexpensive but accurate mineral data should have a significant impact on the understanding and exploitation of oil reservoirs. The most obvious applications are log calibration and reservoir characterization.

Log Calibration: Wireline logs are the most widely used tools in subsurface evaluation. Integration of directly measured mineral data with log data will significantly improve formation evaluation. For example, work over the last twenty years on shaly sand conductivity makes it clear that regardless of which model one chooses to apply, knowledge of the amount and type of clay minerals is important for proper log evaluation.[14] The rapid nature of FTIR analysis makes it possible to have mineralogy data available when logs are being analysed. This will be useful in complex reservoirs where porosity and permeability vary with subtle changes in lithology.

The clay volume index (Vcl) used in shaly sand log analysis, can be derived by calculating the relative gamma ray log index (Igr) and using charts which relate Igr to percent shaliness as a function of formation age. The equation for calculating Igr is

$$Igr = \frac{GR - GRmin}{GR_{max} - GR_{min}}$$

where GR = gamma log response in the interval of interest.

GR_{max} = gamma log response in shale beds.
GR_{min} = gamma log response in clean beds.

or $$I_{gr} = \frac{A - Amin}{Amax - Amin}$$

where A = potassium or thorium response on spectral gamma log.

One limitation of this technique is that nonclay, radioactive minerals such as feldspars, and uranium and thorium bearing minerals, can make sandstones appear "shaly" on a gamma ray log when in fact they are "clean".[15] Documented examples include feldspathic sandstone in California and Canada. Integration of Mineralog data will improve the interpretation of these log responses. The value for total clay as measured by Mineralog, can be used to calibrate the scaling factor used when clay volume is predicted from gamma ray logs. An advantage of the Mineralog total clay value is that it includes kaolinite and chlorite, important clay minerals that do not have a distinctive log signature.

Determination of true resistivity in fresh water, shaly formations or in formations where conductive minerals are present is also a difficult formation evaluation problem. Work on low resistivity sands in the Texas Gulf coast and pyrite bearing sands on the North Slope of Alaska has illustrated this problem.[16,17] Clay minerals with high surface area often form micropores that hold immobile water, making intervalsappear "wet" when they are actually productive.[18] In all of these cases the use of apparently low true resistivity values in water saturation calculations can result in erroneously high Sw. Timely integration of mineral data, combined with scanning election microscopy (SEM) to document the morphology of these conductive minerals and their location in the pore system improves calibration of resistivity logs. FTIR measurements can provide large databases for relatively low cost on specific formations with low apparent Rt.

Density logs are an important tool in evaluating formation porosity. The density log measures electron density which is used to calculate bulk density. This value is used with matrix density and fluid density to calculate porosity:

$$\phi = \frac{\rho ma - \rho b}{\rho ma - \rho f}$$

where ϕ = porosity, ρma = matrix density, ρb = bulk density and ρf = fluid density.

Values for fluid density are estimated based on the type of fluid in the well bore. Lithology is usually predicted from historical data or a density-neutron crossplot. The matrix density of sandstone is often assumed to be the specific gravity of quartz, 2.65 grams/cc. In a similar way, limestone and dolomite are usually assigned matrix densities of 2.71 and 2.87 grams/cc, respectively. In diagenetically altered lithologies these assumptions are often incorrect. Indiscriminate use of a 2.65 gm/cc matrix density can result in serious errors in porosity calculations for some Gulf Coast formations.[19] Using Mineralog data, it is possible to calculate a matrix density index, ρ_{mi}, where

$$1/\rho_{mi} = \sum(k_i/\rho_i)$$

k_i and ρ_i are the fractional weight percent and density of the ith mineral component. In intervals where measured grain density values are not easily obtained use of the calculated matrix density index improves porosity calculations from density logs by reducing the uncertainty of the assumed matrix density term.

Reservoir Characterisation: During the past decade, there has been a growing realisation that efforts to improve the recovery of oil from reservoirs often achieve the opposite result. There are many physical and chemical processes that can have a negative impact on oil production. These processes can be lumped together under the term "formation damage". Two examples of formation damage are mobile fines and fluid sensitivity.[20]

In zones with abundant potassium feldspar, sodium chloride or calcium chloride completion fluids can interact with the feldspar, causing the edges of the feldspar to fray. With subsequent production, fluid forces continue to work on the frayed grain. It eventually becomes dislodged and moves through the formation until it sticks in a pore throat.[21,22] Multiplied many times, this process leads to reduced permeability and therefore reduced production.

Most fluids injected into oil reservoirs react with formation minerals to a certain degree. Swelling clays, like smectite, are sensitive to water. Acids, like hydrochloric and hydrofluoric acid, used to enhance production, can cause significant damage to formations containing calcite or dolomite. Many mineral/fluid combinations will give rise to scale production at the right temperature and pressure.[22] Mineralog data provide a cost effective way of screening reservoirs to identify zones with the potential for formation damage. Once these zones have been identified, the integration of mineral data and SEM data can be used to help design laboratory test programs to investigate the potential problems in more detail - and develop production strategies to minimise these problems.

The same screening principles can also be applied to core samples in the petrophysical analysis laboratory. Cored intervals containing sensitive minerals (such as clays) can be identified and sampling and cleaning methods altered accordingly. Knowledge of mineral composition also helps in the interpretation of apparently anomalous data from petrophysical or engineering core tests.

CONCLUSIONS

There are five main benefits to mineral analysis by FTIR:
1) It is rapid. Data are available in a well completion time frame, enabling rapid formation evaluation.
2) It is quantitative. Most minerals can be measured with an accuracy of 5% by weight.
3) The required sample size is small. Samples as small as 0.5g can be analysed.
4) It is cost effective.
5) It is a direct measurement method. FTIR spectroscopy measures the presence of covalent bonds within a mineral structure. Data from FTIR analyses is therefore much less ambiguous than data from elemental analyses such as x-ray fluoroscopy or gamma-ray spectroscopy.

In the past, infrared measurements of the solid phase have been mostly qualitative. However, improvements in sample preparation techniques, combined with the advent of faster computers and the FTIR spectrometer have led to significant reductions in the time taken to collect and analyse infrared data, while at the same time improving data quality. Modern infrared spectroscopy therefore possesses unique credentials for routine, rapid and quantitative mineral analysis. When integrated with other analytical tools it has valuable applications in log calibration, reservoir characterisation, petrophysics and geological studies.

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Method	**Advantages**	**Limitations**
X-Ray Diffraction	o Semi Quantitative o Detailed Clay Mineralogy is Measured o Most Inorganic Compounds can be Identified	o Time Consuming o Expensive o Unable to Quantify Amorphous Minerals
Thin Section	o Semi Quantitative o Gives Textural Data o Characterize Porosity	o Sample Preparation is consuming o Expensive o Operator Dependent
Chemical Analysis (XRF, Gamma)	o Quantitative o Can Derive Molecular Proportions o Can Differentiate Atomic Valences	o Time Consuming o Must Have Element to Mineral Transforms

Table 1: Summary of Common Mineral Identification Techniques

MINERAL	OBSERVATIONS	r^2	σ
Quartz	260	0.986	2.902
Calcite	170	0.986	2.460
Anhydrite	64	0.993	2.034
Total Clay	258	0.968	2.977

Table 2: Summary of Statistical Results of Analyses on Synthetic Mixture

- Quartz
- Plagioclase Feldspar
- Potassium Feldspar
- Calcite
- Dolomite
- Siderite
- Opal
- Pyrite
- Anhydrite
- Barite
- Celestite
- Kaolinite
- Chlorite
- (Illite + Smectite)

Table 3: Basic Mineral Calibration Set

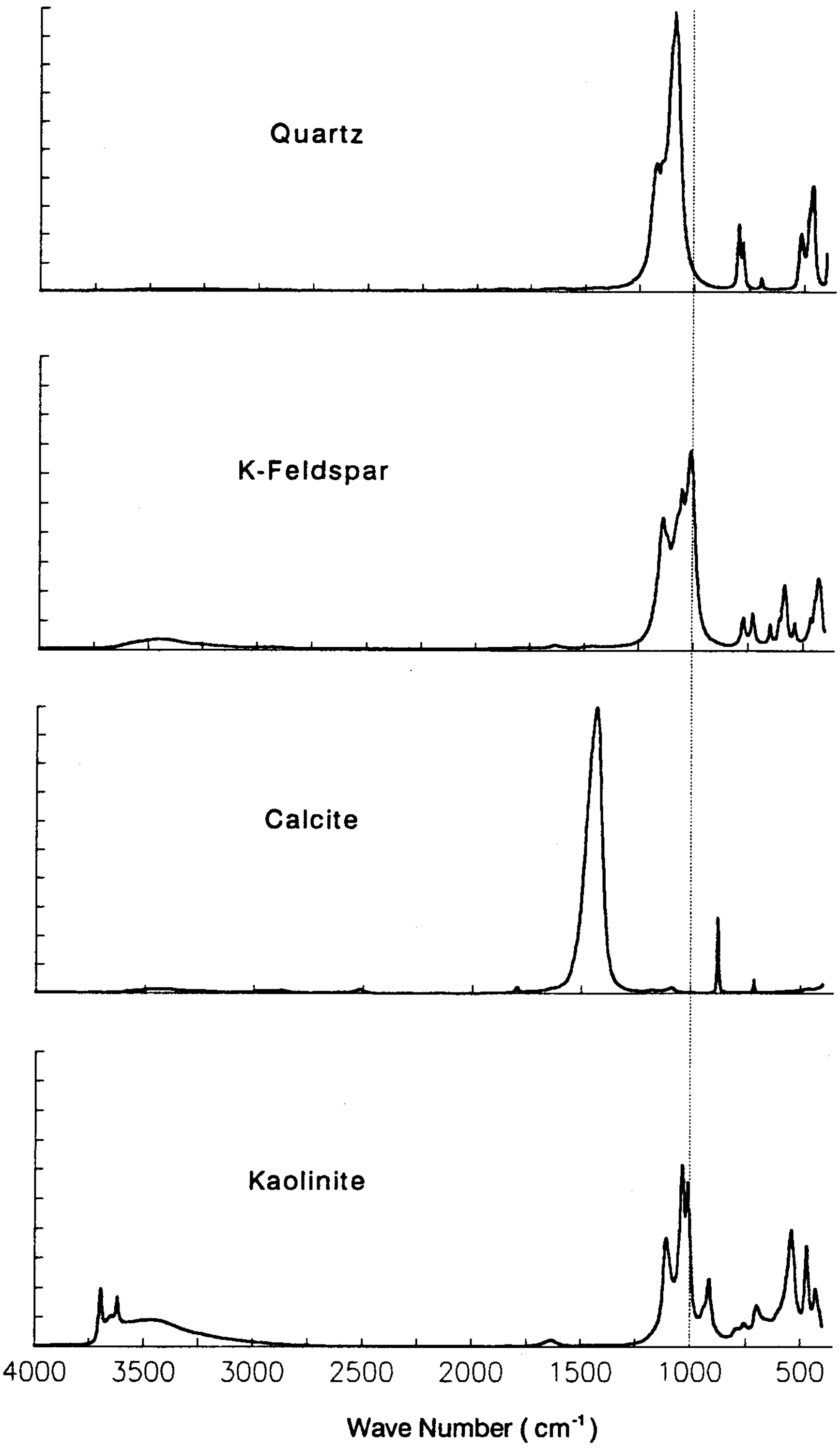

Figure 1: Infrared Absorption Spectra of Four Common Minerals

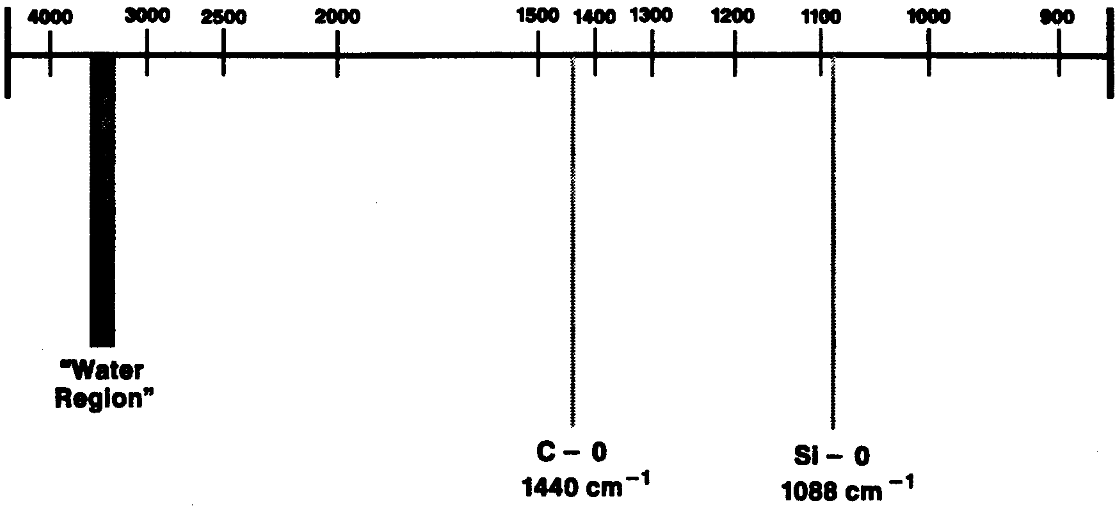

Figure 2: Fundamental IR Absorptions For O-H, C-O and SiO Stretching Vibrations

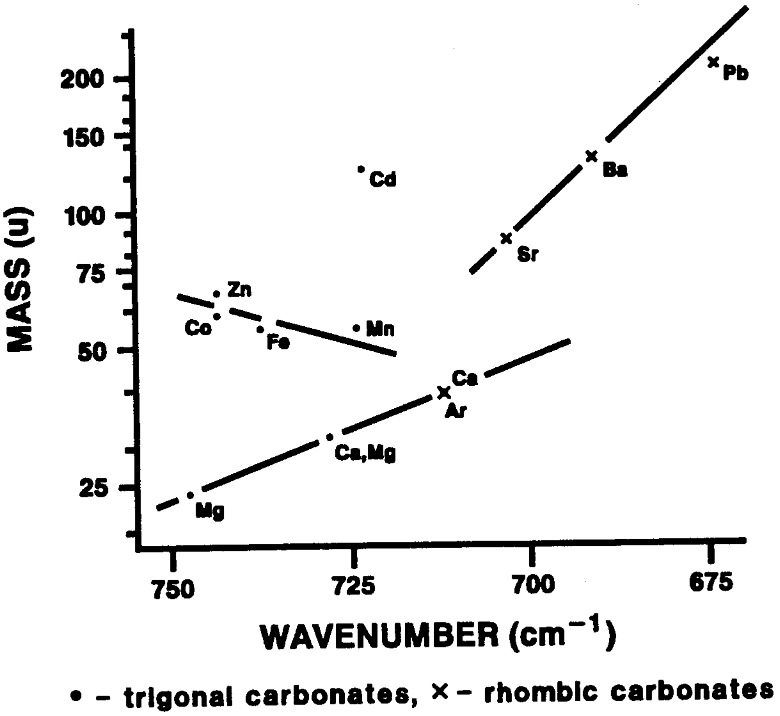

Figure 3: Effects of Cation Substitution on the secondary C-O Absorption at 720 cm^{-1}

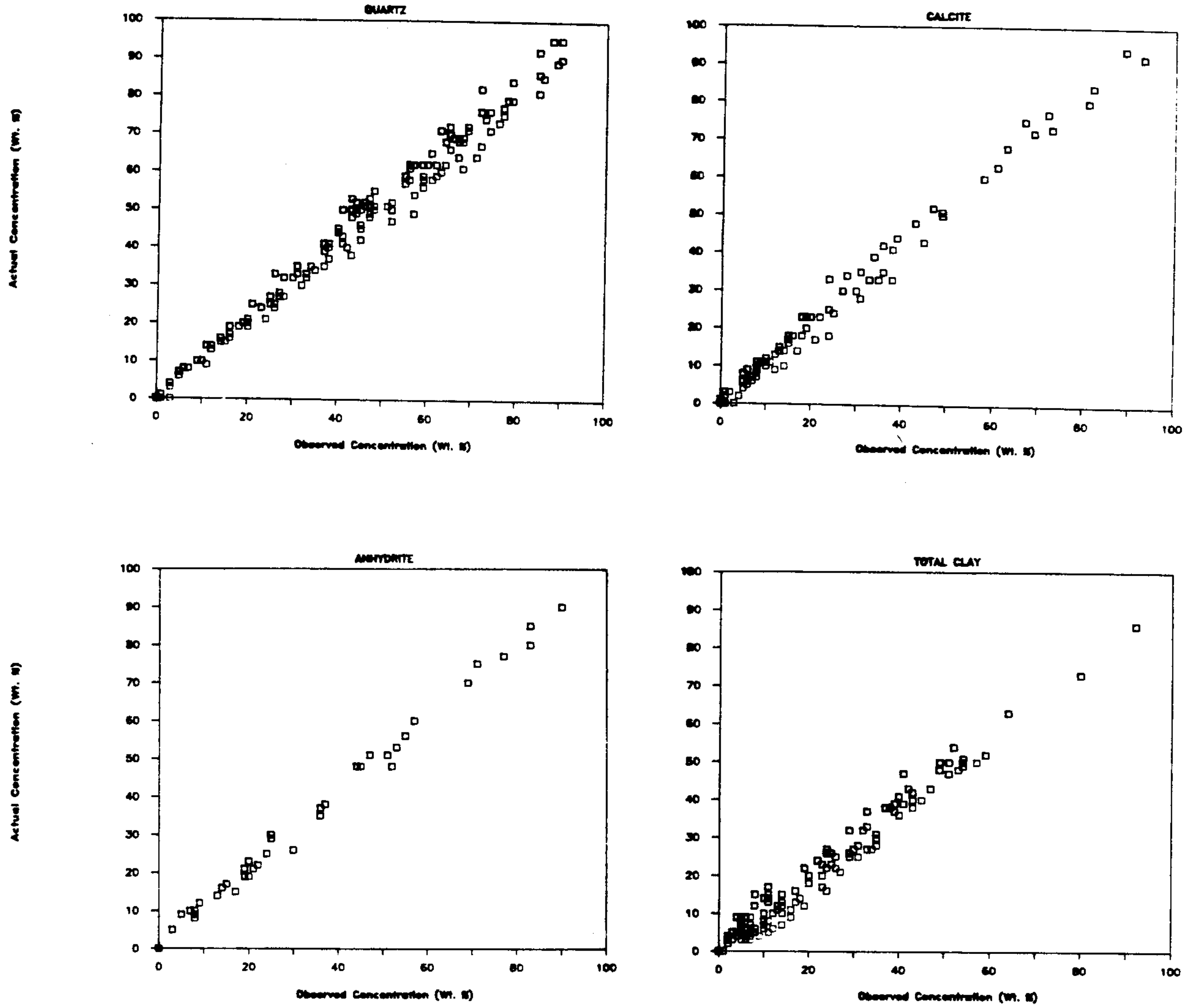

Figure 4: Comparison of Mineral Concentrations Measured by FTIR with Actual Weighed Values for Four Common Bulk Minerals in Synthetic Samples

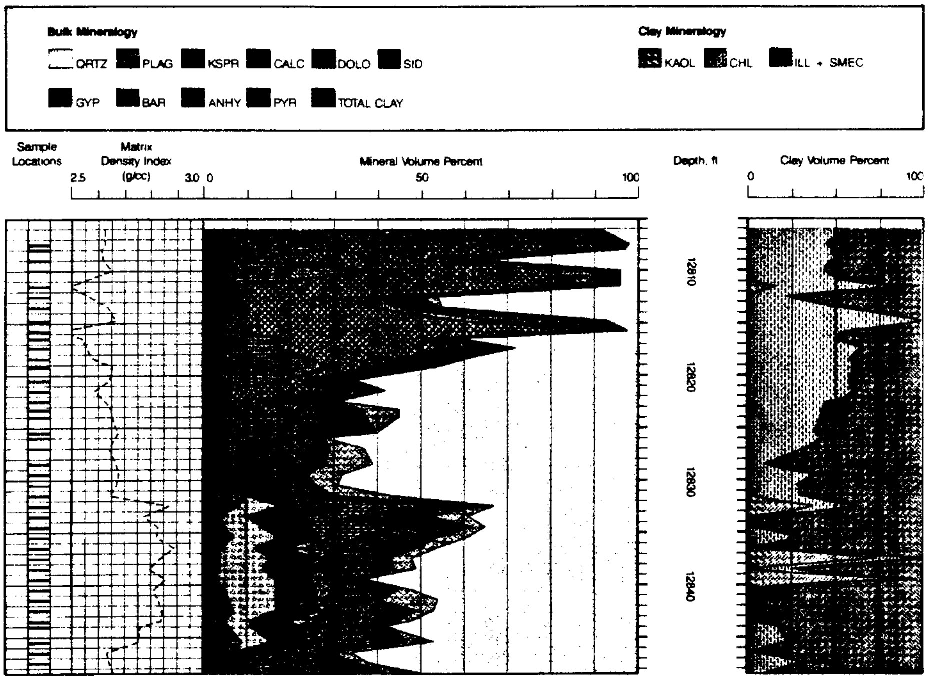

Figure 5: Typical Mineralog™