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Bulk Mineralogical Characterisation of Oilfield Reservoir Rocks and Sandstones using Diffuse Reflectance Infrared Fourier Transform Spectroscopy and Partial Least Squares Analysis

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Abstract

The feasibility of applying Partial Least Squares (PLS) to the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra of mineral mixtures, quarry sandstones and oilfield reservoir rocks has been investigated and shown considerable potential for accurate and precise mineralogical analysis. Rapid spectrum acquisition and data processing together with small sample size requirements are key advantages of the PLS-DRIFTS method.

A PLS model was created from the DRIFTS spectra of mixtures of seven mineral standards chosen to represent the most frequently encountered minerals in sandstone-type rocks; quartz, dolomite, montmorillonite, illite, kaolinite, chlorite and albite. The PLS-DRIFTS model was able to quantify the mineral components of independent mixtures with an absolute error of 1 wt% for all the minerals (concentration range 0-30 wt%) with the exception of quartz which exhibited an absolute error of 3 wt% (concentration range 50-90 wt%). The results provided by applying this PLS-DRIFTS model to several

sandstone-type quarry rocks and a suite of oilfield reservoir rocks were considerably better than anticipated even though the model did not describe all the mineral components present in the samples nor the entire variance of constituent mineral components (e.g. crystallinity). The model was not able to differentiate between montmorillonite and illite probably due to the similarity of the DRIFTS spectra of these minerals, but it was able to quantify the combined (montmorillonite + illite) concentrations to within 1 wt%. The model over-predicted the concentration of albite in the quarry rocks due to the presence of K-feldspar, which has a similar DRIFTS spectrum and was not included in the model. However, the model accurately predicted the total (albite and K-feldspar) concentration to within 4 wt%. A separate PLS-DRIFTS model constructed using the DRIFTS spectra of the oilfield reservoir rocks showed that the carbonate components, calcite and dolomite could be differentiated and quantified to within 5.0 and 3.6 wt%, respectively. This feasibility study confirmed the strong potential of combining DRIFTS with a multivariate statistical approach such as PLS and it is clear that more sophisticated models, that incorporates and describes a higher percentage of the variance in unknowns, would further improve the predictions.

Keywords: 1) Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), 2) Partial Least Squares Analysis, 3) Mineralogical Characterisation, 4) Oilfield Reservoir Rocks, 5) Sandstones.

Introduction

Knowledge of the mineralogical composition of oilfield reservoir rocks is important in optimising oil recovery. Such mineralogical data is useful in i) the initial exploration phase, ii) the construction of geological models and ensuing plans for development and production, and iii) the planning and execution of improved/enhanced oil recovery treatments. For the latter, this is especially important when complex, multi-component treatment fluids are utilised to enhance production (Borling, 1994). Many other industrial sectors are also interested in mineralogical analysis of sandstone rocks and include; construction, water, geophysics and ceramics. Currently, bulk mineralogical analysis relies heavily on X-ray diffraction (XRD) which tends to be supported by data from infrared spectroscopy, chemical analysis and electron microscopy (Środoń, 2002). Indeed, the top three finalists in the Reynolds Cup, a contest which provides the contestants with a valuable opportunity to validate and improve their analytical techniques placed considerable emphasis on XRD for identification and quantification of the major minerals. In contrast, cation exchange capacity measurements and thermogravimetric analysis were used only in a supplementary context (Osomoto et al., 2006). In addition the contest reinforced the view that successful quantification was more dependent on a particular analyst's experience than on the analytical technique or software used. Combining these techniques is time consuming and expensive with typical absolute errors of 3-5 wt%. The relative errors involved with XRD have been expressed as a function of concentration by Hillier (2003) who showed that the relative error varied as a function of $X^{0.35}$, where X = mineral concentration in wt% (i.e. the error at 30 wt% would be +/- 3.3% at 95% confidence). For certain applications, only a few

milligrams of sample are available, e.g. for river suspended sediments, and so infrared spectroscopic techniques are attractive since XRD typically requires 1 g or more for analysis. Of course, representative sampling also needs to be considered in any analysis. Herein, the feasibility of applying multivariate statistical models based on Partial Least Squares (PLS) analysis to infrared spectra obtained via Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is investigated in order to provide a rapid, more convenient and accurate quantification of the bulk mineralogy.

DRIFTS is an increasingly popular and reliable infrared technique that has been used to characterise a variety of powdered samples including cements, soils, coals and minerals (for references see reviews by Mitchell, 1993 and Kelvy and Britt, 1996). A comprehensive study, which highlights the principles and advantages involved in the technique whilst focussing on the distinction between bulk and surface mineralogy of sandstone-type rocks, has been detailed elsewhere (Clegg, 1998). PLS is a multivariate statistical technique (Beebe and Kowalski, 1987; Geladi and Kowalski, 1986) that can be used to quantify analyte components in infrared spectra, whether they are expressed using the Beer-Lambert Law for absorbance or its Kubelka-Munk equivalent for diffuse reflectance. This technique is particularly appropriate when analysing complex multiple-component spectra, which contain many broad and overlapping bands. In essence the PLS algorithm examines regions of the spectra to determine which areas vary as a function of component concentration (vide infra).

Hughes et al. (1991) and Hughes and Jones (1992) initially applied several multivariate calibration techniques to infrared spectra of drilled cuttings/solids, obtained whilst drilling a borehole, to make mineralogical quantitative analysis. Later Hughes et al.

(1995) applied PLS and DRIFTS to Portland cement and were able to describe up to 14 components with adequate accuracy. Janik et al. (1995) applied the techniques to characterise soils and were able to predict not only the major element compositions (SiO_2, Al_2O_3 and Fe_2O_3) but also soil properties such as pH, sum of cations present, and clay content as well as the carboxylic and amide species present (Janik and Skjemstand, 1995). In an earlier report, Janik and Keeling (1993) also combined PLS and DRIFTS for the successful analysis of tubular halloysite in kaolin samples, whilst Peussa et al. (2000) were able to rapidly determine, with sufficient accuracy, the hydroxyl group content in calcined silica thus removing the dependence on time consuming thermogravimetric analysis.

A least square fitting technique was developed by Matteson and Herron (1993) and Herron et al. (1997) using FTIR transmission spectroscopy (herein defined as LS-Trans), which was reported to be accurate to 1 wt% for complicated artificial mineral mixtures. The latter method, which uses wavelet transform calculations to separate useful information from noise, was applied to an extensive collection of mineral standards that included feldspars with Ca, Na and K end members. Another multivariate statistical technique, principal component analysis, has been able to correlate the fractal dimension of kaolinite with brightness, morphology and structural order enabling the calculation of technical properties for use in the paper industry (Aparicio et al., 2004). Mineral analysis of multicomponent mineral mixtures not using least squares fitting methods, but relying on Beers Law, includes the work of Bertaux et al. (1998) who studied the quantification of amorphous and crystallized phases in synthetic and natural sediments. An attempt to determine the composition of river suspended sediment using least squares analysis

(Hillier et al., 2000) provided accurate results when infrared spectroscopy or XRD was applied to simple 2-3 component mixtures. However, XRD results were found to be superior to infrared spectroscopy when the mixtures were more complex. Moreover the total carbonate concentration was accurately determined by XRD when mixtures of carbonate were present but the method was unable to accurately quantify individual carbonates. Other infrared work by Środoń et al. (2002) encountered problems with the reproducibility of experimental conditions and concluded that i) there was not enough information to distinguish reliably between individual minerals in groups such as feldspars and carbonates; ii) it was not sensitive enough to quantify all of the mineral components with acceptable accuracy.

The aim of this feasibility study is to develop a PLS model based on the DRIFTS spectra of mixtures of mineral standards (PLS-DRIFTS MM) and then use the model to determine the bulk mineralogy of several quarried sandstone rocks and a suite of oilfield reservoir rocks. An independent analysis of the quarried sandstone rocks was obtained by XRD, whilst the least-squares analysis FTIR transmission method (LS-Trans), developed by Matteson and Herron, (1993) and Herron et al. (1993), was used as a comparison for data obtained using other FTIR techniques. Independent analysis of the oilfield reservoir rocks was given by XRF elemental analysis (Chevron-Texaco, 1990). Another aim of the study was to develop a PLS model based on a selection of the DRIFTS spectra of the oil field reservoir rocks (PLS-DRIFTS-ORR). This was applied to other DRIFTS spectra of oil field reservoir rocks in order to investigate the use of naturally occurring mineral mixtures. Whereas both models concentrated on distinguishing the classes of minerals (e.g. smectites, carbonates, etc) found in oilfield

reservoir sandstones the PLS-DRIFTS-ORR model also investigated its ability to distinguish between dolomites and calcite.

Experimental

The seven mineral standards used to represent the major mineral components found in sandstones were used as received without further purification and are listed alongside their indicative structural formula and source in Table 1. Twenty one mineral mixtures each containing selected amounts of the seven mineral components were used to create the PLS-DRIFTS MM model. Twelve of the twenty-one mixtures were used in the calibration set, six in the validation set and the remaining three in the independent set. The weight percent ranges of the mineral components in the model are also given in Table 1. Surface quarried sandstones, except Berea and Castlegate, were selected from 'The Building Sandstones of the British Isles Handbook' (Leary, 1986) and are listed in Table 2. Castlegate comes from the Southern Wasatch plateau, Utah, whereas Berea comes from the Amherst quarry, Ohio. The suite of oilfield reservoir rocks were provided by Chevron-Texaco from twenty selected depths in the Lacy 12Y well of the Weber Sand Reservoir, Rangely Field, Colorado (Larson, 1974).

Spectra were recorded on a Nicolet 5DX system FTIR spectrometer using a Collector™ DRIFTS accessory (SpectraTech) which had been modified so that the sample cup could be rotated during spectral collection. Spectra collected from a rotating sample provides data with better reproducibility because it minimises sample-to-sample orientation differences (Christy et al., 1987). All samples, including mineral mixtures and sandstones, were ball milled for 20 minutes prior to dispersing at 10 wt% in oven dried,

ball milled FTIR grade KBr (Aldrich). The mixture was then packed into the sample cup using a small press (20 kg load for 1 minute), enabling highly reproducible spectra, which are critical to the successful quantification, to be collected. Generally, the smaller the particle size the greater the reflectance and hence another reason for milling the samples. It has been shown that micro-absorption affects are related to particle size by Fuller and Griffiths (1978). They showed that a drop in reflectance was observed below 1000 cm^{-1} when the particle size was < 10 μm and was attributed to the wavelength of radiation being approximately equal to the diameter of the particles. This has been debated in the literature, but no such observations were noted in the spectra collected for this paper. Sample spectra were ratioed against a background of KBr that had also been ball milled and oven dried. The authors were alert to the potential amorphisation/destruction of the mineral components during milling (Illes, 2000, Breen et al., 2007). Kaolin is a particularly good marker for such a phenomena (Breen et al., 2007) and none was detected. Even if some restructuring had taken place the effects should be similar in all samples which were treated in an identical manner. Some groups heat mineral samples in an attempt to distinguish between illite and smectite. None of the samples studied here were heated prior to analysis i.e. the clays were in a hydrated state during the DRIFTS analysis. The PLS-DRIFTS MM model incorporated data from the entire mid-infrared region (3900-450 cm^{-1}) and spectra were analysed in absorbance more using 'Turboquant Analyst™' PLS software, which is part of the OMNIC™ software package (Version 1).

Independent quantitative mineralogical analysis of the quarried sandstones was performed using the well documented quantitative X-ray powder diffraction technique as practised by Hillier, (2003 and 2000) and acknowledged by Osomoto et al., (2006). XRD

was performed on both oriented clay fractions and whole rock random powders. The minerals present were quantified using whole rock data. The clay fraction analysis was performed to confirm and refine the identity of the clay minerals and to provide complementary quantitative information (Table 3). Independent quantitative mineralogical analysis of the oilfield reservoir rocks was performed by X-ray fluorescence (XRF) (Chevron-Texaco (1990). XRF data were obtained using both powdered and fused lithium borate flux samples and were interpreted in correlation with coulometric (CO_2 and organic carbon content remaining after extraction with toluene), gravimetric (loss on ignition) and colorimetric (ferrous iron (FeO) in carbonates and silicates) analyses. The elemental analyses were converted into mineral concentrations using equations based on the elemental ratios of pure minerals that are likely to be present. The major assumption in these calculations is that none of the minerals contain any elemental impurities, which is not usually the case for natural minerals.

Partial Least Squares Analysis

In PLS analysis (Brereton, 2003, Beebe and Kowalski, 1987, Geladi and Kowalski, 1986) a regression model is established between a matrix A, containing absorbances at p wavenumbers for m samples and a matrix C, containing the concentration of each of the n components in the same m samples. Prior to modelling, the matrices are divided into calibration, validation and independent sets. A PLS model is created using the calibration set and then the matrices in the validation set are used to determine the optimum number of factors required to accurately predict the concentration of each analyte component. A factor is defined as any linear combination of the original

variables, and factors can be defined using eigenvectors. Eigenvectors are directions in space that describe the maximum amount of variation or spread in the samples. The factors of matrix A are re-expressed in a matrix U, which is termed the score matrix. This matrix results from projecting A onto the eigenvector V, as RV=U. The score matrix U is composed of the original data points in a new co-ordinate system described by the eigenvectors.

The method of PLS is a modelling procedure that simultaneously estimates underlying factors in both A and C (a modelling procedure that only determines the factors in A is called principal component regression). This is accomplished by using the columns of the C matrix to estimate the factors for the A matrix and at the same time the columns of matrix A are used to estimate the factors for matrix C. The resulting models are:-

$$A = TP + E$$

$$C = UQ + F$$

where the T and U are termed the score matrix of A and C, respectively, and P and Q are called the loadings. The loadings are chosen to maximise the correlation between the scores and the analyte. High laodings correspond to a high correlation whereas small loadings correspond to a low correlation. The advantage of this approach is that if a column in the A matrix poorly describes the concentration of a component it can be given a low wighting. The matrices E and F are the residual errors associated with modelling A and C using the PLS model.

In the ideal situation, the sources of variation in A are exactly equal to the sources of variation in C and the factors for A and C are identical. However, this is never the case and the factors for the A and C matrices have the following relationship

$$U = bt + \varepsilon$$

where b is termed the inner relationship between u and t and is used to calculate subsequent factors if more than one factor is necessary to describe the variation, ε is the residue.

In order to determine the optimum number of factors, the predicted error sum of squares (PRESS) is calculated. PRESS is a cross validation technique used to determine the number of statistically significant factors. It begins by determining the predictive ability of using only one factor on a set of validation samples. The next step is to determine the predictive ability of the first and second factors. As the optimum number of significant factors is approached, the prediction should improve and thus the PRESS should decrease. However, when the optimum number of factors is exceeded the model begins to include noise, which results in a poor prediction of independent samples; effectively, the model becomes 'over fitted'. If the number of spectral factors is too low then all the variance in the data may not be represented, leading to poor prediction of independent samples. Validation correlation coefficients are used to indicate the ability of the model to predict the concentration of the components. An excellent value is 0.990 and the ability to predict is considered poor if the value is less than 0.975. Independent samples that are accurately quantified give ultimate confirmation of the predictive ability of a given model.

It should be noted that, occasionally, when unknown samples are analysed by the PLS-DRIFTS MM model, negative mineral predictions can be obtained when the concentrations are low. This is a problem encountered in all PLS models, and can either

be ignored or assigned as containing none of the specified component. Herein, the negative concentrations are not modified in order to indicate when such a situation arises.

Results and Discussion

PLS-DRIFTS Model of Mineral Mixtures (PLS-DRIFTS MM)

The ability of the model to successfully predict the concentration of each mineral standard in the validation and independent samples is represented in Figure 1 as plots of actual against predicted concentrations. The figure reports the correlation coefficients for the validation samples and includes the number of factors used in parentheses. Note that a correlation coefficient of unity represents a plot of the PLS-DRIFTS predicted versus actual concentrations on a straight line at 45º to the axes (dotted line; Figure 1). The figure also contains the maximum and minimum weight percent differences for the independent (I) and validation (V) samples for each mineral mixture. Thus taking the data for quartz as an example; four factors were used to obtain a correlation coefficient of 0.986. The filled diamonds represent the validation set and the maximum and minimum wt% deviations were -1.59 and +1.26. Note that the open circles, which represent the independent set, show a greater scatter around the 45º line and this is reflected in the larger differences i.e. $-2.07 < I > 2.99$. A plot of the combined montmorillonite and illite concentrations is presented because the method produced relatively poor predictions for the individual components. This was anticipated as the DRIFTS spectra of montmorillonite and illite are very similar (Figure 2), which in turn, is a result of their similar elemental compositions, structure and properties. Ideally, the spectral information in each mineral spectrum should be unique. Consequently, if the spectra of two or more components are similar then correlations between spectral and concentration information will be difficult to distinguish and quantitative results will not be accurate.

The least successful predictions were for albite as reflected in the scatter of data and lower correlation coefficient (0.986). This result was anticipated as the DRIFTS spectrum for the feldspar, albite, contained fewer characteristic bands in spectral regions where bands arising from other minerals were absent (vide infra).

The region of the DRIFTS spectrum that is given a higher weighting in the model (i.e. the region of the spectrum used to quantify the component) can be recognised by comparing the DRIFTS spectra of the mineral standards with their reconstructed spectra (Figures 2 and 3). Each reconstructed spectrum is composed of spectral information that correlates with the concentration information for a given component in all of the standards. It is used to evaluate the spectral information that will be used to measure each component in a quantitative method. The regions where good spectral similarities are observed are often the regions given higher weighting. In an ideal situation the variance in the spectral data will be exactly equal to the variation in the concentration data and thus the reconstructed spectra will be identical to that collected experimentally. However, this is never the case and discrepancies do arise. These can be due to poorly characteristic spectral regions (i.e. overlapping bands) and the irreproducible errors within the DRIFTS technique itself that emerge as mismatches in the spectra. The DRIFTS spectrum and the reconstructed spectrum of quartz were very similar (Figure 3), particularly in the overtone/combination region (2000-1500 cm^{-1}). The positions and ratios of all the bands in the reconstructed and DRIFTS spectra of dolomite were also very similar, which is a reflection of the excellent predictive ability of the model in determining the concentration of dolomite. It is considered that the overtone bands between 3000-2500 cm^{-1}, which are in an area of the spectrum free of bands due to other minerals are important contributors

to the excellent prediction of dolomite. This emphasises a key advantage of DRIFTS compared to transmission FTIR spectroscopy because these overtone bands are very weak, if not absent, in transmission FTIR spectra. Similarities between the DRIFTS and reconstructed spectra of albite occurred mainly below 1400 cm^{-1}. Even though the predictive ability of the model to determine albite was relatively low it was still possible to correlate the four highly characteristic bands of albite, which are highlighted in the expanded portions of Figure 3. This is of particular interest because it demonstrates the powerful capability of PLS, and other least square analysis techniques, as identification tools. The DRIFTS spectra of montmorillonite and illite and their combined reconstructed spectrum (Figure 2) displayed similarities, particularly the O-H stretching bands at 3620 and 3380 cm^{-1}. The similarities observed between the actual and reconstructed spectra of kaolinite were good, although it had been anticipated that the ratio of the four diagnostic OH-stretching bands between 3620 and 3695 cm^{-1} would be more comparable. However, there were observed differences that could be due to the contribution of bands from other clay minerals in the same region. It was also suspected that the ball milling used during the sample preparation may result in the distortion of these bands. Indeed, this can be the case as shown when ball milling pure kaolinite (Illes, 2000. Breen et al., 2007) yet the bands in the spectra of the samples containing kaolinite do not show evidence of distortion. This is probably due to the fact the kaolinite is ball milled in the presence of other minerals, hence reducing the severity of the impact it experiences. The bands at 3695 and 917 cm^{-1} are therefore the most likely features to be used in the prediction of kaolinite. Absorption bands at 3534 and 3420 cm^{-1} were observed in both the DRIFTS spectrum of chlorite and its reconstructed spectrum. The presence of the band at 1450

cm^{-1} in the reconstructed spectra of illite and kaolinite suggests there is a correlation between the spectral information and their concentration. However, this is not the case as no bands are present in this particular region of their spectra. The fact that the band is in the same position as the most intense peak of the carbonate suggests contamination, but strict cleaning procedures were employed between the milling of different samples. In addition, no correlation was evident between carbonate and kaolinite or illite concentrations. A possible reason for this band could be due to a deconvolution problem within the algorithm at this particular wavelength, but this has not been confirmed.

Application of PLS-DRIFTS MM model to quarried sandstone rocks.

To test the predictive capability of the PLS-DRIFTS MM model it was applied to a suite of quarried sandstone rocks even though the variance in their spectra due to the presence of additional minerals and varying crystallinity within mineral types were not accounted for in the model. The PLS-DRIFTS predictions were then compared with results obtained using XRD and the least-squares analysis FTIR transmission method (LS-Trans). It is essential that independent analytical techniques are used to compare PLS results and this requirement is achieved by the inclusion of XRD results. The analysis from LS-Trans, which the authors recognise does not qualify as an independent analytical technique is included to illustrate the range of predicted concentrations that are present in the literature. It should be noted that the distribution of minerals within the quarry rock samples is not uniform and thus sampling issues may account for variations in predictions between each technique. Samples used for the XRD and PLS-DRIFTS MM analyses were collected from different areas within the same core, but different cores had been

used for LS-Trans analysis because they were analysed some time ago. The mineral distribution in Hollington Red is particularly non-uniform because it is a banded rock, i.e. there are clay rich strata present. Difficulties in obtaining samples specifically from the clay band (CB) and from between clay bands (BB) resulted in the samples analysed by PLS-DRIFTS being biased towards the different regions. The mineral predictions for Hollington Red using XRD are from a single, amalgamated sample made of portions from the clay band and between bands, which explains why the results are identical in Figure 4. The quarry rocks Castlegate, Clashach and Berea were not analysed using the LS-Trans method, but the bulk mineralogy of Berea has been determined using XRD by Azari and Leimkuhler (1990). The differences between the XRD results of Azari and Leimkuhler (1990) and those from the current study are likely to arise from variances in the mineral components within each sample analysed, although the different sample preparation techniques used in each XRD method may also contribute. For example, a preferred orientation method was used in this contribution, but this cannot be confirmed in the analysis by Azari and Leimkuhler (1990). Note that XRD traces of Hollington Red, Yorkstone and Stancliffe show the most variability when samples from different areas within the core are analysed (Geddes, 2006).

Moreover, the XRD analysis herein does not detect the presence of montmorillonite in the quarry rocks, but rather only mixtures of illite and mixed-layer clays. This contrasts with that determined by the LS-Trans technique, which does identify the presence of montmorillonite. For simplicity, the PLS-DRIFTS MM model has therefore been used to quantify the presence of dioctahedral 2:1 clays, which includes montmorillonite, illite and mixed-layer clays.

Overall, the results shown in Figure 4 demonstrate that the application of PLS to the DRIFTS spectra of sandstones is a viable technique for mineral analysis. Figure 4 presents the predicted mineral concentrations obtained using the different techniques.

The prediction of quartz concentrations for Berea, Birchover, Yorkstone and Castlegate using the PLS-DRIFTS MM model were close to those obtained using XRD (i.e. the actual differences were; -1.5, +2.0, -0.2 and -0.6 wt%, respectively), although they were slightly higher for Stancliffe and Clashach (+7.0 and +6.8 wt%, respectively). The predictions for Hollington Red were similar, despite the marked heterogeneity of the mineral distribution. With the exception of Berea, the concentrations of albite were clearly over-predicted by the PLS-DRIFTS MM model when compared with the values from XRD and LS-Trans. However, a comparison of the results for the total feldspar concentrations, which is the sum of albite and K-feldspar, clearly demonstrated that the latter was contributing to the prediction and that the PLS-DRIFTS MM model was actually quantifying the total feldspar concentration. This was not entirely unexpected given that the PLS-DRIFTS MM model did not include a calibration for K-feldspar, which exhibits a very similar DRIFTS spectrum to albite. It was noticed that XRD predicted a higher concentration of K-feldspar than LS-Trans, whereas LS-Trans predicted a higher concentration of albite than XRD; however, the total feldspar predictions are the same by both techniques. The reason for this is currently uncertain, and requires further scrutiny.

Due to the scale of the graph, the predictions of dolomite by the PLS-DRIFTS MM model appear to be erratic but are in fact accurate to within 1.8 wt%. The LS-trans technique detected carbonate and the authors stated that the amount of dolomite in

Birchover and Stancliffe was less than 1 wt%, which is represented in Figure 4 by the vertical dashed arrows. The concentrations of dolomite predicted by the PLS-DRIFTS MM model were generally higher than those obtained by XRD and LS-Trans, which may be because Berea, York Stone and Hollington Red contain small amounts of other carbonates. The carbonates were identified, by LS-trans, as 1 wt% calcite and 1 wt% siderite in Berea and less than 1 wt% calcite and magnesite in York Stone and Hollington Red, respectively. Calcite, siderite and magnesite exhibit infrared bands in similar spectral regions to those of dolomite and even though they were not included in the model, they may have contributed to the results. Thermogravimetry-mass spectroscopy (TG-MS) has shown that carbon dioxide evolved from the quarry rocks on heating. This probably suggests that carbonates are present at low levels, given that the absence of C-H stretching bands in the DRIFTS spectra negates the possibility of contamination with organic carbon. These qualitative TG-MS results suggest that Stancliffe, Berea and Castlegate produce the largest amounts of carbon dioxide; a result which is in agreement with the PLS-DRIFTS results. The XRD technique did not detect any carbonates in any of the samples suggesting that infrared spectroscopy may be a useful technique for the analysis of trace carbonates. XRD may have failed to detect the presence of any carbonate if it was poorly crystalline.

The concentrations of kaolinite predicted by the three techniques did show some variation and those obtained from the PLS-DRIFTS MM model were generally lower except for the clay band in Hollington Red. This may reflect the variation in clay mineral distributions within the quarry rocks. The prediction of dioctahedral 2:1 clay concentrations from the three techniques also varied, but a pattern was evident in that the

amount predicted was generally less using XRD than DRIFTS-PLS. The predicted concentrations of chlorite from the three techniques were generally in good agreement, although the PLS-DRIFTS MM model presented higher values for York Stone and Stancliffe.

Interestingly, if the sum of the individual clay concentrations (kaolinite + dioctahedral 2:1 clay + chlorite) of each sandstone for all the techniques are plotted (Figure 5), the results are very comparable, with the exception of Berea and Hollington Red. This is particularly notable for Stancliffe, which showed relatively higher deviations in the individual clay mineral predictions and thus supports the contention that PLS-DRIFTS could be a practical and robust approach for predicting total clay concentrations.

The precision of the PLS-DRIFTS MM model (Table 4) was derived by quantifying each mineral component from 3 or 4 spectra of Birchover, Berea and Castlegate. The spectra were collected from different aliquots of the same ball milled sample. Each aliquot was prepared individually as pressed KBr mixtures. Most of the results spread over a small range near 1 wt%, with the exception of the albite concentrations in Birchover and Castlegate, which spread over 3.9 and 3.7 wt%, respectively. The spread of the results is very narrow, and reflects the excellent ability of the DRIFTS technique to generate spectra that are highly reproducible. The reproducibility of the infrared bands at 3695 and 1033 cm^{-1} in duplicate DRIFTS spectra of kaolinite varied by 0.04 and 0.033 absorbance units, which represents a relative difference of 3.9 and 2.4%, respectively. These values are typical of most infrared bands in the DRIFTS spectra but occasionally higher relative differences were observed; for example, the infrared band at 3695 cm^{-1}, in duplicate DRIFTS spectra of Berea sandstone varied by 6.3%.

PLS-DRIFTS MM model applied to oilfield reservoir rocks

Before examining these predictions it is important to note that the mineral types used to describe the suite of oilfield reservoir rocks, as determined by the independent technique, XRF analysis, did not exactly match those used in the PLS-DRIFTS model of the mixtures of mineral standards (Table 5). In essence the clay minerals were quantified as one component (i.e. total clay concentration) within the XRF analysis, whereas they were predicted individually in the PLS-DRIFTS model of mineral standards. In addition, two types of carbonates (dolomite and calcite) and two types of feldspars (albite and K-feldspar) were quantified as individual components within the XRF analysis, whereas only one carbonate (dolomite) and one feldspar (albite) were used in the PLS-DRIFTS model of mineral standards. These differences, in theory, do not allow the PLS-DRIFTS MM model to quantify calcite or K-feldspar since they were not included in the calibration model. However, the clay content in the oilfield reservoir rocks can be determined by addition of the predictions for the individual components.

Accepting that there are likely to be differences in crystallinity between the minerals in the standards and the oilfield reservoir rocks, the PLS-DRIFTS predictions (Figure 6) of quartz, clay, dolomite and albite in the various oilfield reservoir rocks generally compare well with the XRF predictions. Moreover, the transformation of the XRF elemental analyses to mineral concentrations relies on major assumptions and is likely to be less accurate than direct methods. Consequently, although the PLS-DRIFTS model occasionally under or over predicts the mineral quantities the patterns are similar to those predicted by XRF and most importantly reports the same trends.

Figure 6 shows a comparison of the mineral concentrations in a suite of rock samples ,from an oil well, obtained by PLS-DRIFTS and XRF. As expected from the PLS-DRIFTS MM model, the predictions of quartz and dolomite are very good. The trend between the quartz concentrations predicted by PLS-DRIFTS MM and those derived from elemental analysis is clearly evident demonstrating that the model is robust to samples from different environments, i.e. from quarries and oilfield reservoirs.

The ability of the PLS-DRIFTS MM model to predict the dolomite concentration was very good at depths above 6350 ft clearly defining the thin carbonate layer at 6081 ft and the thin carbonate streak at 6149 ft. However, it tended to over-predict at greater depths and this was attributed to the presence of calcite in the reservoir rocks at these depths. Calcite has a similar DRIFTS spectrum to that of dolomite, in that analogous bands for dolomite are shifted to slightly higher wavenumbers (Figure 8). Therefore, as the PLS-DRIFTS MM model did not contain calcite in the calibration set it was unable to differentiate between calcite and dolomite. This led to an erroneous increase in the predicted concentration of dolomite and hence highlights the sensitivity of the technique when all the variables in the model are not described. It is expected that a PLS-DRIFTS model containing both calcite and dolomite concentration data would be able to provide improved predictions, which was strongly supported in the PLS-DRIFTS model derived directly from the oilfield reservoir rocks (vide infra).

Occasionally the clay content, which was obtained by adding the predictions of kaolinite, chlorite, montmorillonite and illite, was over predicted but a comparable trend was observed between the actual and predicted concentrations. Interestingly, the main contribution to the predicted clay content was from montmorillonite and illite, whereas

little, if any, was from kaolinite and chlorite. Indeed the DRIFTS spectra of the oilfield reservoir rocks do contain bands indicative of illite and montmorillonite, but not of kaolinite or chlorite.

The extent to which the PLS-DRIFTS MM model over predicts the albite concentration paralleled the observation from the quarry rocks and demonstrated that it was actually predicting the combined albite and K-feldspar concentration. This was expected as their DRIFTS spectra are very similar and the variance had not been accounted for in the model. Given that the DRIFTS spectra of feldspars do not contain many bands in unique positions of the spectrum where bands from other minerals are not present the predictions are much better than anticipated.

It is very important to realise that although there are some differences between the XRF and PLS-DRIFTS results, the same geological information can be gleaned from the data. Such data include i) the presence of a shale bed at the lowest depth, ii) carbonate streaks at 6081 and 6149 ft, iii) clay rich sandstone beds between 5956 and 6027 ft, and iv) thick sandstone formation below 6158 ft. Combined with the speed at which the DRIFTS data can be collected the reality of using such a technique for not only oilfield, but also other geological applications and general mineralogical characterisation is easily envisaged. Once again it should be stressed that a more detailed calibration can be developed and would increase the predictive ability of the model.

PLS-DRIFTS model of oilfield reservoir rocks (PLS-DRIFTS ORR)

A PLS model from the DRIFTS spectra recorded from the oilfield reservoir rocks (PLS-DRIFTS ORR) was primarily constructed in order to determine whether a data set containing naturally varying mineral crystallinity within a mineral group (e.g. quartz, dolomite) would affect its ability to predict the concentration of samples of a similar nature. It should be noted that because natural rocks were used i) the spread of mineral concentrations within the calibration set did not cover the optimum ranges, ii) many of the samples used as calibration standards did not contain any of the mineral components to be quantified, which may result in a poorly predicting model, iii) there was a weak inverse relationship between calcite and dolomite content and iv) a strong co-linearity was present between the quartz and total carbonate concentrations. Despite these potential limitations the results presented in Figure 7, which display the data in the same format as Figure 1), are very promising and highlight issues that require further development. Twenty oilfield reservoir rock samples used to create the PLS-DRIFTS ORR model. Twelve of these samples were used in the calibration set, another five for the validation set and the remaining three for the independent set. The justification for building this model was that in a scenario where a large range of samples needed to be assessed, a rapid assessment could be readily obtained which could be validated by full mineralogical analysis performed on a selection of samples by XRD or XRF.

The results show that the model is able to distinguish between calcite and dolomite even though their DRIFTS spectra are very similar. This is apparent in their reconstructed spectra (Figure 8), which show the subtle band position and intensity differences, that

enable the unique characterisation of these carbonates, match those of the mineral standards. This is particularly notable for the fundamental bands at 886 and 879 cm^{-1} and the overtone bands at 2534 and 2512 cm^{-1} for dolomite and calcite, respectively. The PLS-DRIFTS ORR model was able to predict the total carbonate concentrations of the validation and independent samples relatively accurately when calcite and dolomite were combined to represent one component (i.e. total carbonate in Figure 7).

The ability of the model to predict the clay mineral concentration was reasonable despite the low validation correlation coefficients. Moreover, the model was able to distinguish that the dominant clay species in the oilfield reservoir rocks was either illite and/or montmorillonite. A comparison of the spectra of the mineral standards with that of the reconstructed spectrum of clay (Figure 8) shows that a good correlation was obtained for the O-H stretching band at 3630 cm^{-1} and the Si-O stretching bands at 1024 cm^{-1}. This latter result was somewhat unexpected because of the proximity of the Si-O bands in the clays with those of quartz.

The ability of the PLS-DRIFTS ORR model to predict quartz was poorer than anticipated and was possibly due to the co-linearity in concentration between quartz and total carbonate concentration. Support for this was shown by the reconstructed spectrum of quartz, which exhibits negative bands in the same position as those from the carbonate minerals (not illustrated). The ability of the PLS-DRIFTS ORR model to predict albite or K-Feldspar concentration was relatively poor, but the model did show evidence that it could distinguish between the two minerals in that the concentrations of albite were not over-predicted due to the higher concentrations of K-Feldspar and vice versa. Finally, it

was still possible to reasonably predict the total Feldspar content when combining albite and K-Feldspar to represent one component.

The uncertainty in the compositions derived from XRF analysis may explain why the clay and feldspar predictions from the PLS-DRIFTS ORR model are poor. It is possible that the XRF results are not accurate and therefore the PLS-DRIFTS ORR model, which is dependant on precise calibration, is subsequently flawed. Moreover, the predictions for clay and feldspars in the oilfield reservoir rocks using XRF analysis could be less accurate than the PLS-DRIFTS MM method because in part the former relies on indirect analysis based on assumptions, whilst the latter relies on a direct analysis. Evidence to support this includes the fact the predictions of clay and albite in the oilfield reservoir rocks from the PLS-DRIFTS MM, relative to the XRF measurements, were poor yet were good in the quarry sandstones. This may suggest that there is more clay in the oilfield reservoir rocks than is predicted by the XRF analysis.

Conclusions

This study demonstrates the high potential of successfully quantifying the mineral components in a sandstone-type rock by applying PLS analysis to their DRIFTS spectra. Moreover, the speed of spectral acquisition and data processing together with the small sample size requirements makes for a desirable analytical technique. Quantification of the mineral components albite, calcite, kaolinite, chlorite, montmorillonite and illite in mineral mixtures was achievable within 1 wt% accuracy, whereas quartz was within 3 wt%. Application of a PLS model constructed from the DRIFTS spectra of mixtures of mineral standards to quarry rocks and oilfield reservoir rocks generated accurate

predictive models, although the full mineral content and crystallinity variance in the rocks was not described. In addition a basic PLS-DRIFTS model constructed from oilfield reservoir rocks showed that calcite and dolomite could be distinguished with adequate accuracy even though their DRIFTS spectra are only subtly different. Moreover, as with all analyses the potential to improve quantification could be achieved by extending the model to include larger numbers of standards and real samples with data that covers all the expected variance in the rocks.

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Captions for Tables

Table 1: Mineral Standards used to describe the typical mineral components found in sandstone-type rocks.

Table 2: Sandstone-type quarry rocks

Table 3: XRD results of quarry sandstones.

Table 4: Precision of PLS-DRIFTS model of mineral mixtures.

Table 5: Mineral types used to describe the components in oilfield reservoir rocks and the PLS-DRIFTS model of mineral standards.

Table 1:

Mineral and Source	Typical Structural Formula	Weight % ranges for PLS-DRIFTS MM Model
Quartz (Chelford Sand)	SiO_2	50-90
Na-Feldspar – Albite (BCS No. 375)	$NaAlSi_3O_8$	0-17
Montmorillonite (SWy-2)*	$[Al,Mg,Fe)_2(OH)_2Si_4O_{10}$ $(Ca,Mg,Na,K)]nH_2O$	0-10
Kaolinite (KGa-2)*	$Al_4Si_4O_{10}(OH)_8$	0-10
Silver Hills Illite *	$Al_4Si_4O_{10}(OH)_2.K,Al$	0-10
Chlorite (CCa-2)*	$(Mg, Fe, Al)_6$ $(Al,Si)_4O_{10}(OH)_8$	0-10
Carbonate – Dolomite (BCS No. 368)	$CaCO_3.MgCO_3$	0-30
BCS = British Chemical Standards, *Clay Minerals Society – Source Clay Repository		

Table 2:

Quarry Rock	Source	Colour	Grain Size
Birchover	Matlock, Derbyshire	Pink to Buff	Medium to Course
Clashach	Hopeman, Moray Firth Coast	Buff to Fawn	Fine
Hollington Red	Hollington, Staffordshire	Dull Red	Fine to Medium
Stancliffe	Chesterfield, Derbyshire	Buff	Fine
York Stone	West Yorkshire	Buff	Fine
Castlegate	Southern Wasatch plateau, Utah	Buff	Fine to Medium
Berea	Amherst, Ohio	Buff to Fawn	Fine to Medium

Table 3:

Quarry Rock	Mineral Concentration (wt%)								
	Quartz	Albite	K-Feldspar	Kaolin	Dioctahedral 2:1 clay	Chlorite	Carbonate	Hematite	Total
Birchover	76.3	5.1	10.4	4.7	2.6				99.1
Berea	88.5	0.8	6.7	3.9	1	Trace			100.9
Stancliffe	72.4	7.3	11.5	4.4	2.9				98.5
Hollington Red	76.4		14.2	2.1	5.4			1.1	99.2
York Stone	72.2	10.2	6	4.3	4.3	3.4	0.2 (calcite)		100.6
Castlegate	91.2		4.6	2.4	3.4				101.6
Clashach	88.3		11.4	trace	1.6				101.3

Table 4:

Mineral Concentration - wt% (Figures in parenthesises denote the highest and lowest difference from the average)					
Quartz	**M & I**	**Kaolinite**	**Chlorite**	**Dolomite**	**Albite**
Birchover - average of 4					
78.69 (+0.57/-0.4)	**7.07** (+0.71/-0.31)	**2.63** (+0.43/-0.38)	**0.62** (+1.88/-0.59)	**-0.12** (+0.59/-0.4)	**20.39** (+1.87/-2.06)
Castlegate - average of 3					
91.06 (+1.18/-0.72)	**5.91** (+0.57/-0.67)	**0.55** (+1.48/-1.49)	**-0.49** (+0.22/-0.27)	**1.74** (+0.47/-0.5)	**3.12** (+1.61/-2.07)
Berea - average of 3					
88.10 (+1.13/-1.11)	**5.57** (+0.47/-0.35)	**2.73** (+0.71/-0.77)	**-0.98** (+0.41/-0.58)	**2.74** (+0.52/-0.57)	**3.54** (+0.39/-0.66)

Table 5:

PLS MM	Oilfield rocks
Quartz	Quartz
Montmorillonite and Illite, Kaolinite, Chlorite.	Total Clay (including montmorillonite and illite, kaolinite, chlorite).
Albite	K-Feldspar, Albite
Dolomite	Dolomite, Calcite

Captions for Figures

Figure 1: Plot of actual against PLS-predicted concentrations (wt%) for the validation (♦) and independent (○) samples using the PLS-DRIFTS model of mineral standards. Calibration correlation coefficients and optimum number of factors used (in parentheses) are displayed together with the maximum and minimum weight differences for validation (V) and independent (I) samples. Thus, for quartz four factors were used to give a correlation coefficient of 0.986 and the weight differences for the validation set varied from -1.59 wt% and 1.26 wt%. A dashed line is shown at 45° to aid visualisation of accuracy.

Figure 2: DRIFTS and reconstructed (PC) spectra of clay minerals derived from the PLS-DRIFTS model of mineral mixtures.

Figure 3: DRIFTS and reconstructed (PC) spectra of quartz, dolomite and feldspar derived from the PLS-DRIFTS model of mineral mixtures.

Figure 4: Comparison of PLS-DRIFTS predicted mineralogy in quarry rocks, with those measured by XRD, LS-Trans and XRD by Hillier (co-author) or Azari and Leimkuhler (1990).

Figure 5: Sum of individual clay concentrations predicted using PLS-DRIFTS MM for each sandstone compared with XRD and Least Squares - FTIR transmission data.

Figure 6: Comparison of predicted PLS-DRIFTS MM model versus predicted XRF mineral concentrations of oilfield reservoir rocks

Figure **7**: Plot of XRF results against predicted concentrations for the validation (♦) and independent (○) samples using the PLS-DRIFTS model of oilfield reservoir rocks. Calibration correlation coefficients and optimum number of factors (in parentheses) used

are displayed and also maximum and minimum weight differences for validation (V) and independent (I) samples.

Figure 8: DRIFTS and reconstructed (PC) spectra of calcite, dolomite, montmorillonite and illite derived from the PLS-DRIFTS model of oilfield reservoir rocks.

Figure 1

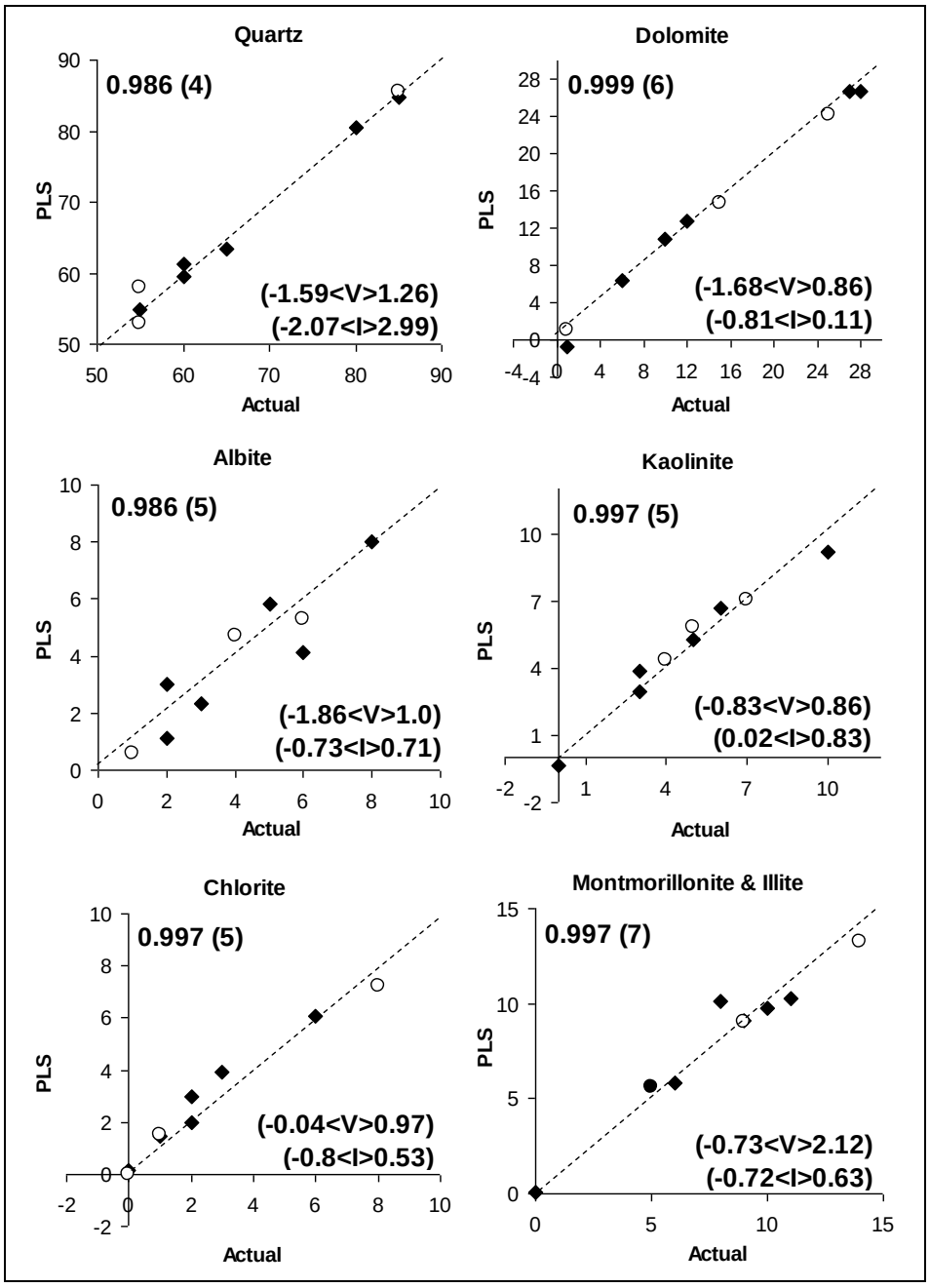

Quartz
0.986 (4)
(-1.59<V>1.26)
(-2.07<I>2.99)
Dolomite
0.999 (6)
(-1.68<V>0.86)
(-0.81<I>0.11)
Albite
0.986 (5)
(-1.86<V>1.0)
(-0.73<I>0.71)
Kaolinite
0.997 (5)
(-0.83<V>0.86)
(0.02<I>0.83)
Chlorite
0.997 (5)
(-0.04<V>0.97)
(-0.8<I>0.53)
Montmorillonite & Illite
0.997 (7)
(-0.73<V>2.12)
(-0.72<I>0.63)
PLS
Actual

Figure 2:

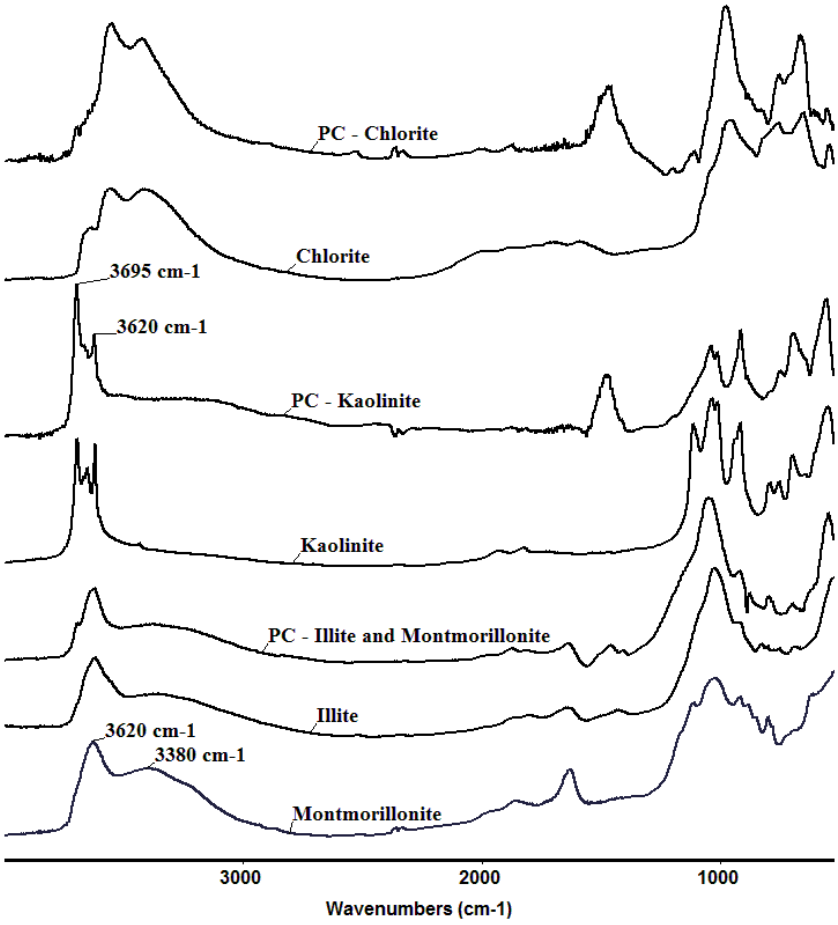

PC - Chlorite
Chlorite
3695 cm-1
3620 cm-1
PC - Kaolinite
Kaolinite
PC - Illite and Montmorillonite
Illite
3620 cm-1
3380 cm-1
Montmorillonite
3000
2000
1000
Wavenumbers (cm-1)

Figure 3:

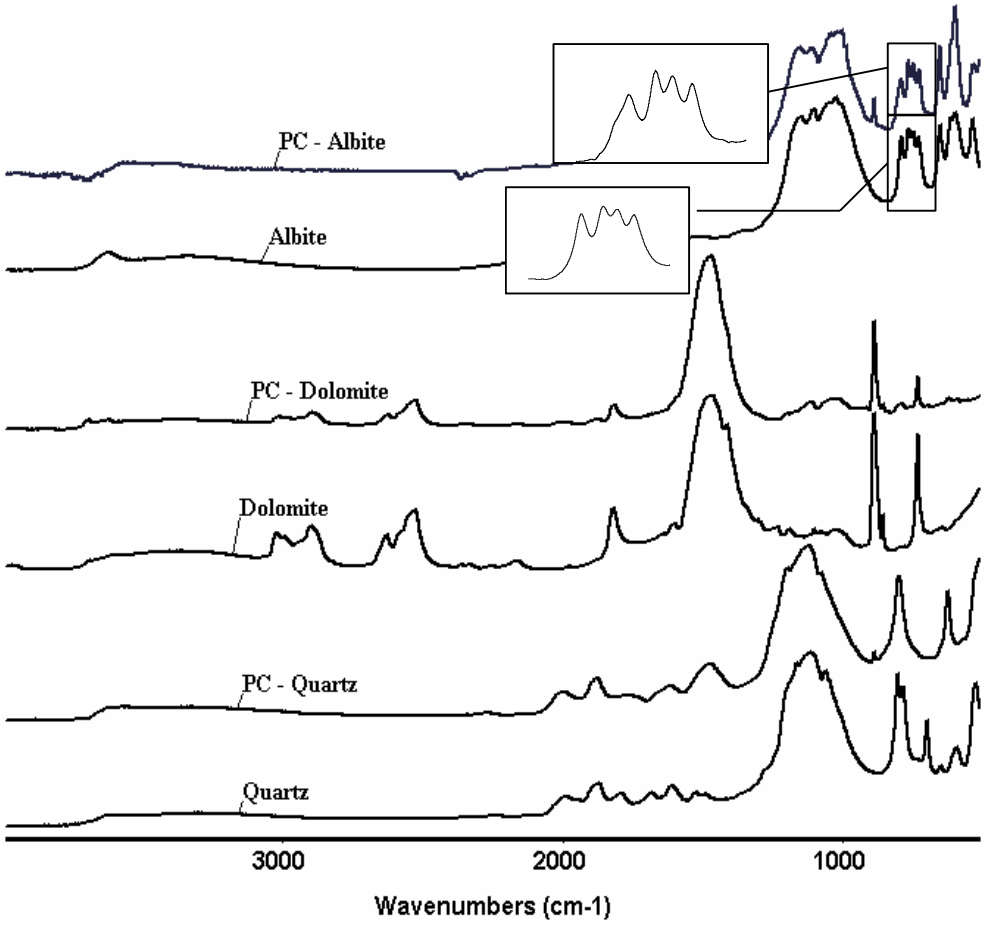

PC - Albite
Albite
PC - Dolomite
Dolomite
PC - Quartz
Quartz
3000
2000
1000
Wavenumbers (cm-1)

Figure 4:

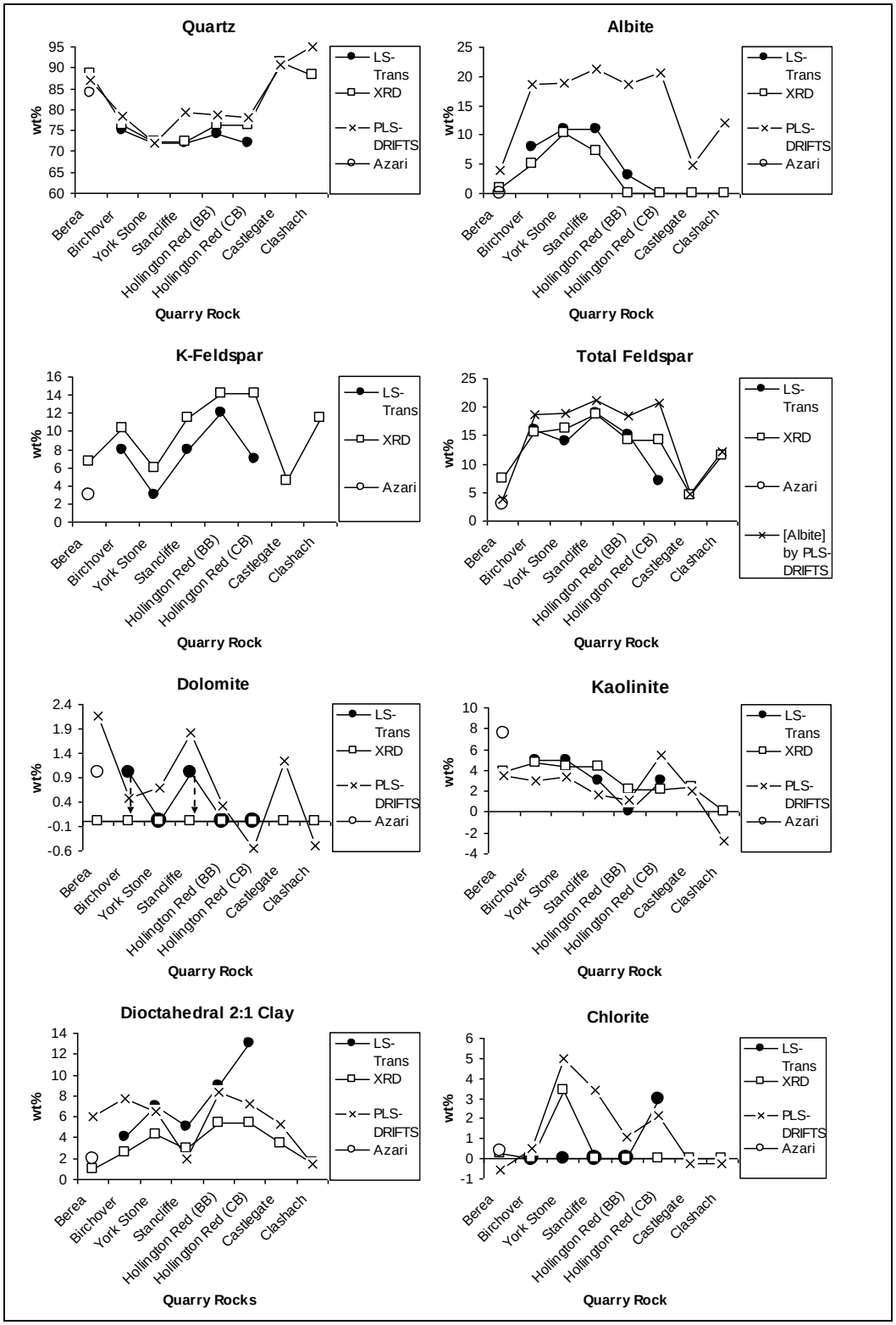

Quartz
wt%
95
90
85
80
75
70
65
60
Berea
Birchover
York Stone
Stancliffe
Hollington Red (BB)
Hollington Red (CB)
Castlegate
Clashach
Quarry Rock
LS-Trans
XRD
PLS-DRIFTS
Azari
Albite
wt%
25
20
15
10
5
0
Quarry Rock
LS-Trans
XRD
PLS-DRIFTS
Azari
K-Feldspar
wt%
16
14
12
10
8
6
4
2
0
Quarry Rock
LS-Trans
XRD
Azari
Total Feldspar
wt%
25
20
15
10
5
0
Quarry Rock
LS-Trans
XRD
Azari
[Albite] by PLS-DRIFTS
Dolomite
wt%
2.4
1.9
1.4
0.9
0.4
-0.1
-0.6
Quarry Rock
LS-Trans
XRD
PLS-DRIFTS
Azari
Kaolinite
wt%
10
8
6
4
2
0
-2
-4
Quarry Rock
LS-Trans
XRD
PLS-DRIFTS
Azari
Dioctahedral 2:1 Clay
wt%
14
12
10
8
6
4
2
0
Quarry Rocks
LS-Trans
XRD
PLS-DRIFTS
Azari
Chlorite
wt%
6
5
4
3
2
1
0
-1
Quarry Rock
LS-Trans
XRD
PLS-DRIFTS
Azari

Figure 5:.

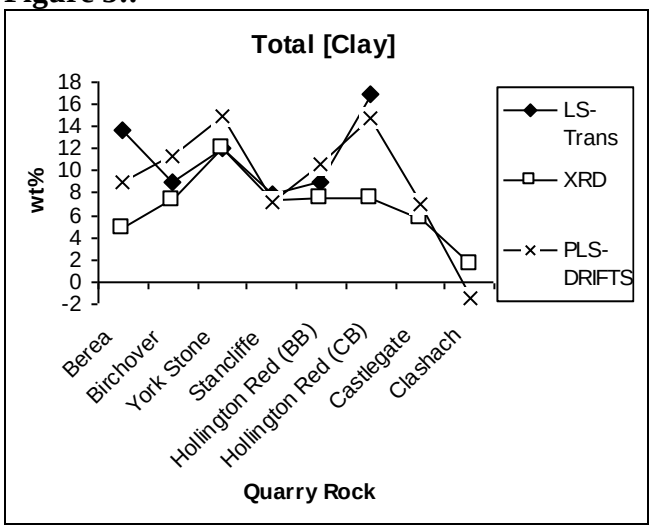

Total [Clay]
wt%
18
16
14
12
10
8
6
4
2
0
-2
Berea
Birchover
York Stone
Stancliffe
Hollington Red (BB)
Hollington Red (CB)
Castlegate
Clashach
Quarry Rock
LS-Trans
XRD
PLS-DRIFTS

Figure 6:

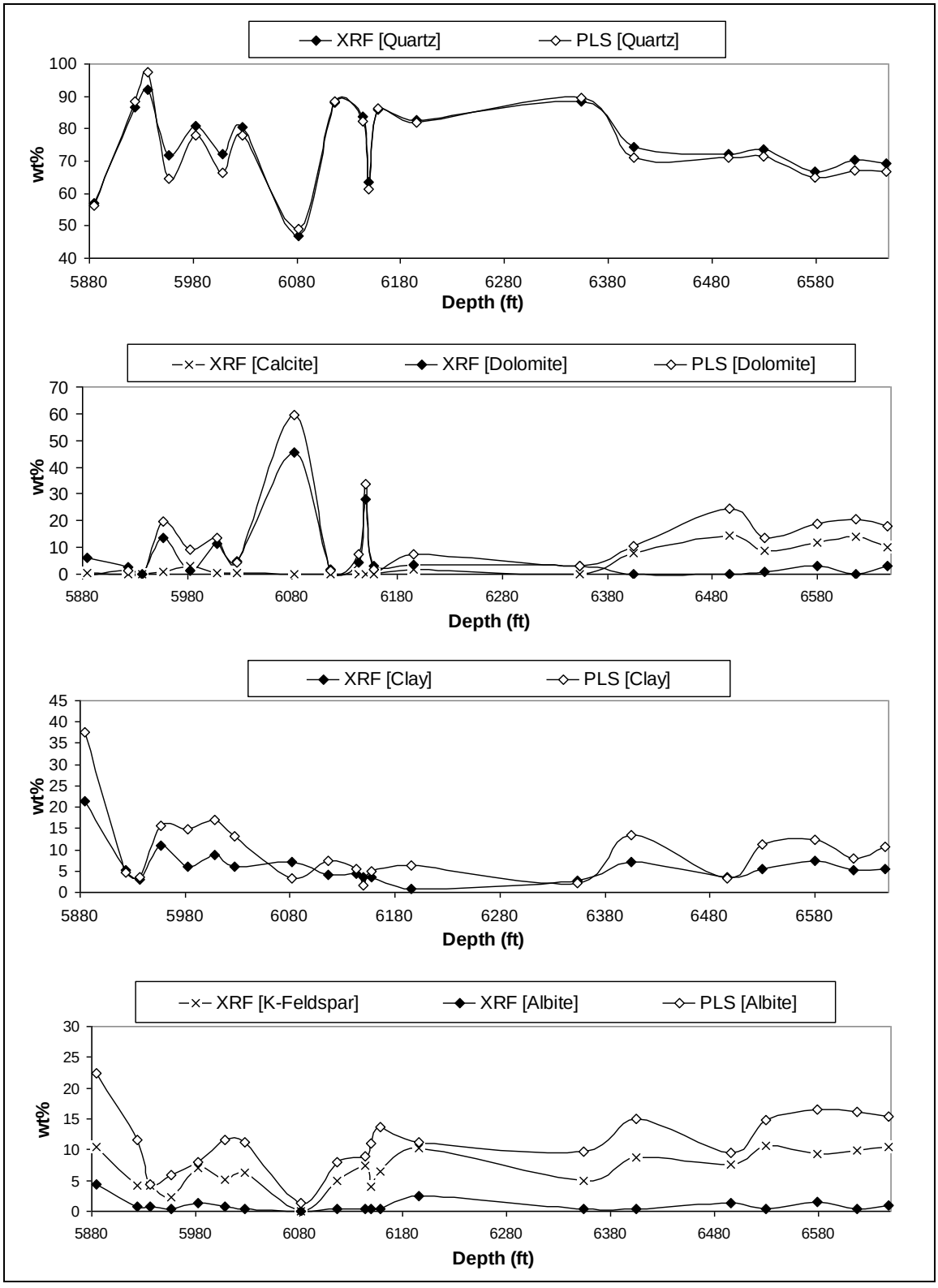

XRF [Quartz]
PLS [Quartz]
wt%
Depth (ft)
XRF [Calcite]
XRF [Dolomite]
PLS [Dolomite]
wt%
Depth (ft)
XRF [Clay]
PLS [Clay]
wt%
Depth (ft)
XRF [K-Feldspar]
XRF [Albite]
PLS [Albite]
wt%
Depth (ft)

Figure 7:

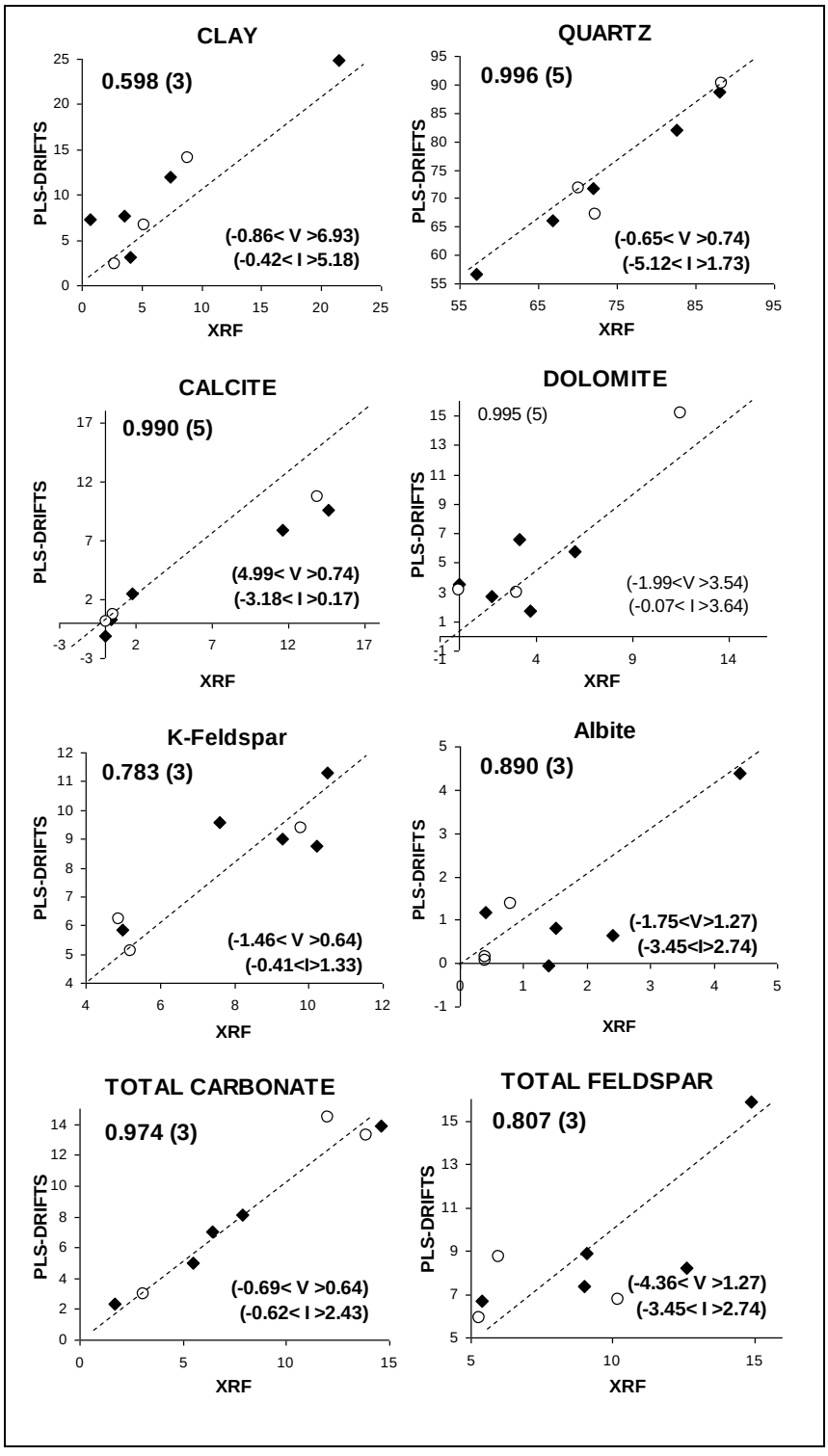
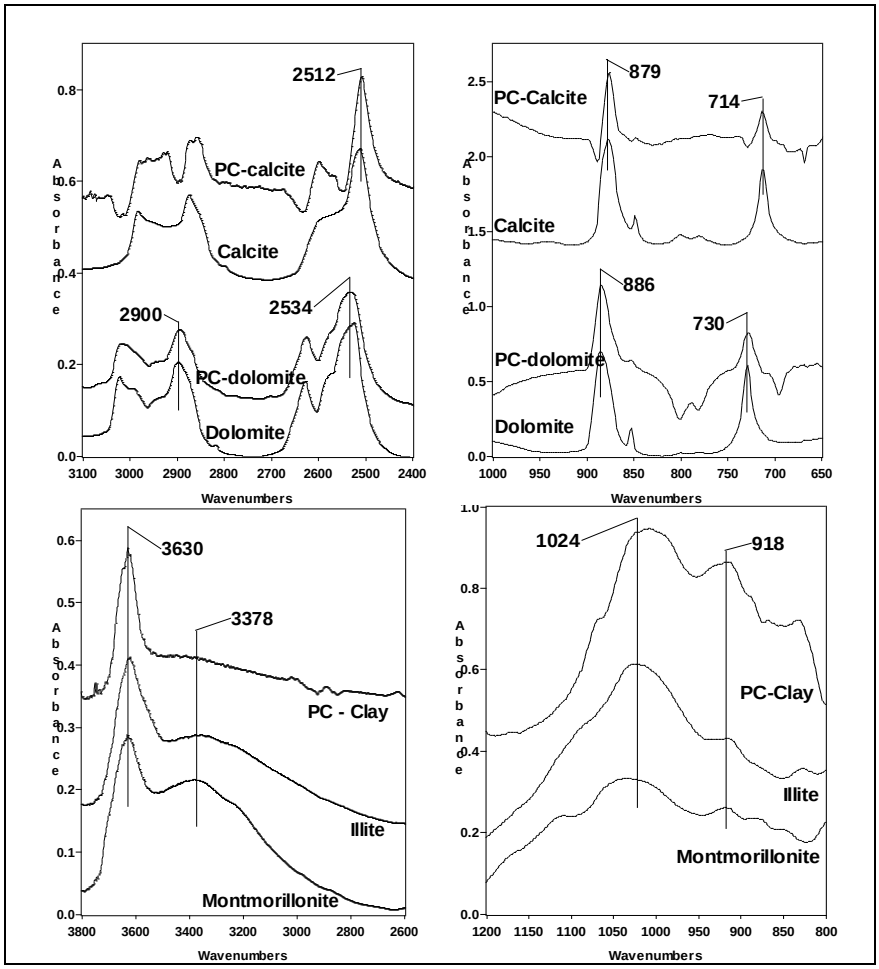

CLAY
0.598 (3)
(-0.86< V >6.93)
(-0.42< I >5.18)
QUARTZ
0.996 (5)
(-0.65< V >0.74)
(-5.12< I >1.73)
CALCITE
0.990 (5)
(4.99< V >0.74)
(-3.18< I >0.17)
DOLOMITE
0.995 (5)
(-1.99<V >3.54)
(-0.07< I >3.64)
K-Feldspar
0.783 (3)
(-1.46< V >0.64)
(-0.41<I>1.33)
Albite
0.890 (3)
(-1.75<V>1.27)
(-3.45<I>2.74)
TOTAL CARBONATE
0.974 (3)
(-0.69< V >0.64)
(-0.62< I >2.43)
TOTAL FELDSPAR
0.807 (3)
(-4.36< V >1.27)
(-3.45< I >2.74)
PLS-DRIFTS
XRF

Figure 8:


2512
PC-calcite
Calcite
2900
2534
PC-dolomite
Dolomite
Absorbance
Wavenumbers
879
PC-Calcite
714
Calcite
886
730
PC-dolomite
Dolomite
3630
3378
PC - Clay
Illite
Montmorillonite
1024
918
PC-Clay
Illite
Montmorillonite