Portable X-ray diffraction for unconventional and conventional petroleum exploration

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SUMMARY

X-ray diffraction (XRD) is a well-established technique in the earth sciences as it can be used to identify and quantify minerals and is particularly useful for fine-grained sedimentary rocks. Due to the capital cost, environmental requirements and significant sample preparation, XRD instruments are generally confined to laboratories. Recent advances in XRD sample holders and X-ray sources have allowed for the development of portable XRD (pXRD) devices where the sample preparation is simpler and does not require regular calibrations by a technical expert. This technology was initially developed by NASA for the Mars Science Laboratory rover Curiosity, to perform mineralogical analysis of the Martian surface.

Due to its portability, minimal sample preparation, fast collection times, and excellent correlation with laboratory-based XRD devices, pXRD has been shown to be of great use to petroleum geologists and engineers by providing rapid, quantitative mineralogical data. For mudlogging quantitative mineralogy is being used to guide directional drilling towards the target formations and to ensure lateral drilling stays within the target formations. Quantitative mineralogy from the target formation and overburden rock also provides important information regarding the engineering properties of these rocks (e.g. fracturability), and can help determine the most appropriate acid for acid-fracturing stimulation. For conventional petroleum exploration quantitative mineralogy onsite, can be used to understand geophysical responses, and as a screening tool for selecting samples for more detailed analysis.

Key words: pXRD, XRD, quantitative mineralogy, scaling

INTRODUCTION

X-ray diffraction (XRD) is a well-established tool in the earth sciences as it can identify and quantify minerals. XRD is particularly useful in the mineralogical assessment of fine-grained sedimentary rocks. However, due to the capital cost, environmental requirements and significant sample preparation, XRD instruments are rarely deployed to site. Recent advances in XRD sample holders and X-ray sources have allowed for the development of portable XRD (pXRD) devices where the sample preparation is simpler and does not require regular calibrations by a technical expert. This technology was initially developed by NASA for the Mars Science Laboratory rover Curiosity, to perform mineralogical analysis of the Martian surface (Blake, 2010).

Mudlogging traditionally utilized qualitative data, but it recent years has benefited from quantitative mineralogy, onsite which is provided by pXRD (Loermans *et al.*, 2011). Conventional petroleum exploration typically utilizes a range of quantitative measurements, but quantitative mineralogy onsite is rarely available. Asides from the geological applications of pXRD to conventional and unconventional petroleum exploration pXRD is also used to characterise corrosion and scaling products onsite to help determine the most effective corrosion management strategy.

CHEMIN AND PORTABLE X-RAY DIFFRACTION

pXRD was initially conceived to perform mineralogical analysis of Mars, as part of NASA's Mars Space Laboratory (MSL) mission (Blake, 2010). The XRD onboard Curiosity Rover was termed CheMin, for chemistry and mineralogy as it conducts X-ray fluorescence (XRF) and XRD, simultaneously. To do so CheMin utilizes a miniature microfocus X-ray source, a transmission sample cell and a direct excitation charge coupled detector (CCD) "camera" (Bish *et al*., 2013; Figure 1). The sample cell has a piezoelectric vibration system that vibrates the sample without macroscopic movement of the sample holder. The collimated X-ray beam (50 µm) is directed at the vibrating, powdered sample and the energy-discriminating CCD detects X-rays that have diffracted and fluoresced (Fig. 1), thus producing a 2D diffraction pattern (circumferentially summed in a 1D diffractogram). The X-rays fluoresced are also summed into a histogram illustrating energy vs. number of counts. By vibrating the powdered sample the crystallites are exposed to the X-ray beam at random orientations helping to reduce orientation effects and produce superior particle statistics (Sarrazin *et al*., 2005).

The Olympus Terra portable XRD was developed using the same principles as CheMin (Sarrazin *et al*., 2005). It weighs 15 kg and is housed in a field ruggedized, portable case (Figure 2) with Li-ion batteries capable of 4 hours autonomous operation. The Terra's CDD can measure an energy range of 3 to 25 keV at a resolution of 250 eV at 5.9 keV, making it capable of qualitative elemental analysis of elements Cl through to U. The angular range measured by the CCD is 5 to 55° 2θ, with resolution of 0.25-0.30° 2θ FWHM. The instrument only requires 15 mg of powdered sample at a grain-size of < 150 µm. Like CheMin, the Terra also utilises a piezo-harmonic sample holder to reduce orientation effects (Figure 2).

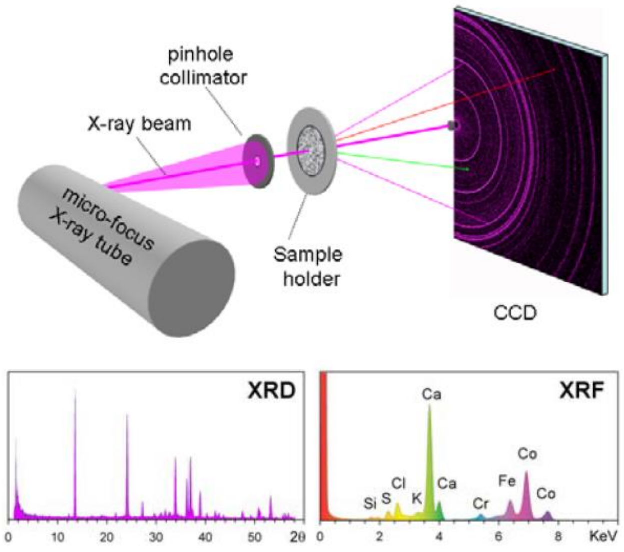

Figure 1: Schematic illustration of the CheMin instrument as well as the data output. The instruments CCD simultaneous collects XRD and qualitative XRF data [Sarrazin *et al.*, 2005].

Figure 2: The Olympus Terra portable XRD instrument (left image) and the vibrating sample (right image).

RESULTS

Numerous studies have been conducted to ensure that pXRD is a viable method for qualitative and quantitative mineralogical assessment of geological materials (Loermans, 2011; Uvarova *et al.*, 2014; Burkett *et al.*, 2015; Turvey *et al.* 2017). Preliminary studies on the qualitative and quantitative capabilities of pXRD for mudlogging and mineral exploration were undertaken by Loermans *et al.* (2011) and Uvarova *et al.* (2014), respectively.

Burkett *et al.* (2015) explored the quantitative capabilities more fully through the analysis of a larger suite of synthetic mixtures of natural minerals, and a variety of field sourced samples with pXRD, laboratory XRD and verification with laboratory XRF. For this study quantification of mineral phase abundances from diffractograms was made using the Rietveld-based SIROQUANT™ technique of Taylor (1991). A comparison of the results obtained from pXRD compared to those from a laboratory based, PANalytical Empyrean II X-ray diffractometer are presented in Figure 3, and illustrate excellent correlation between the results obtained on the two instruments.

This study also investigated the performance for pXRD at varying runtimes through comparisons with the laboratory XRD (Figure 4). The results from this analysis revealed R^2 values of 0.97 to 0.99 for runtimes of 5 and 40 minutes, respectively. In saying this the accuracy reduces with shorter runtimes (i.e. R^2 values for 5, 10, 20, and 40 minutes were 0.80, 0.87, 0.92, and 0.88, respectively; Burkett *et al.*, 2015).

In light of these results the collection times set by the user for petroleum exploration are determined on the basis of the required accuracy, and detection limits. For broad rock type classification in petroleum exploration runtimes between 30 seconds to 3 minutes are adequate for the geologist or engineer

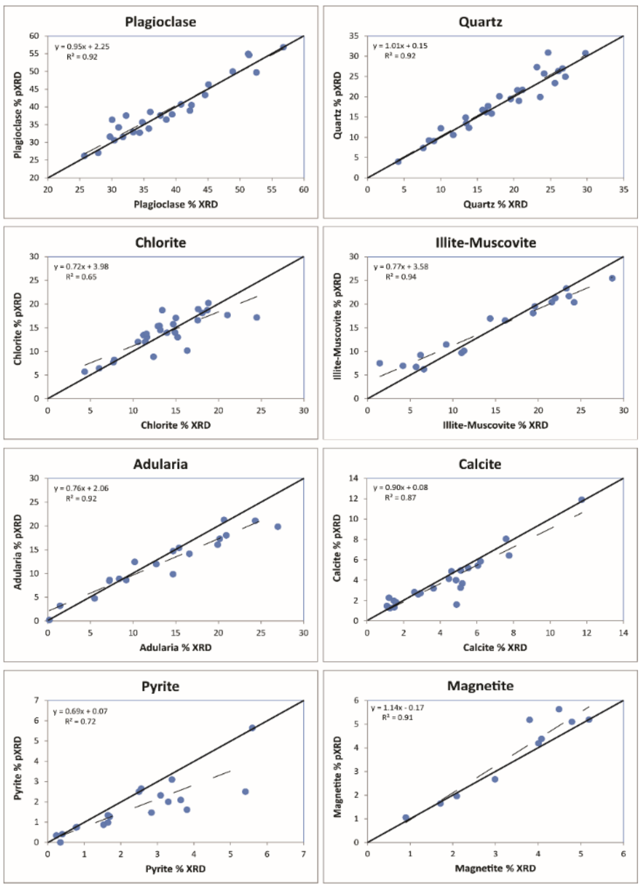

Figure 3. Comparison between mineral percentages deduced from SIROQUANT™ for the Empyrean II XRD (x-axis) and the Terra pXRD (y-axis; Burkett *et al.*, 2015).

to identify significant stratigraphic horizons and determine whether they have intersected the basement. For more detailed mineralogical analysis (e.g. results used to understand geophysical responses) runtimes in excess of 5 minutes are typically adopted.

PXRD FOR UNCONVENTIONAL AND CONVENTIONAL PETROLEUM EXPLORATION

pXRD has numerous benefits for both unconventional and conventional petroleum exploration. In unconventional exploration pXRD analysis of drill cuttings allows the geologist to identify formation tops and correlate between drill holes. By having an understanding of where the drill-bit is in the geological sequence the drilling teams can "geosteer" towards favourable stratigraphic horizons or allow them to drill horizontally once target formations are intesected.

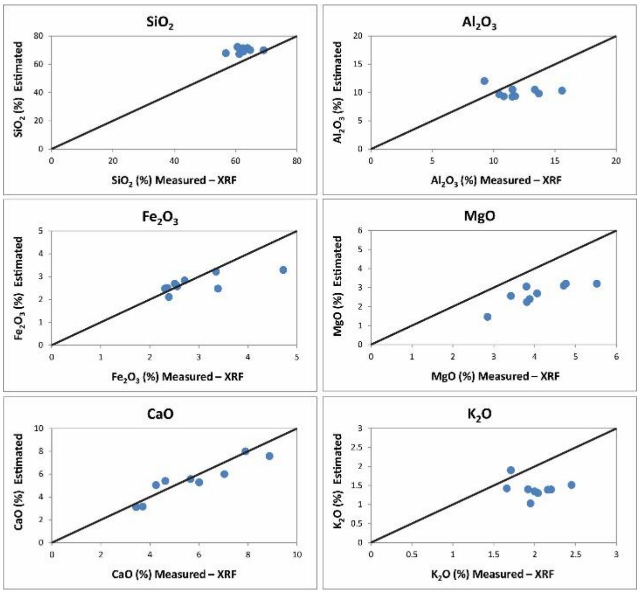

Figure 5: Comparison between percentages of major elements inferred from quantitative XRD data and percentages from XRF analysis.

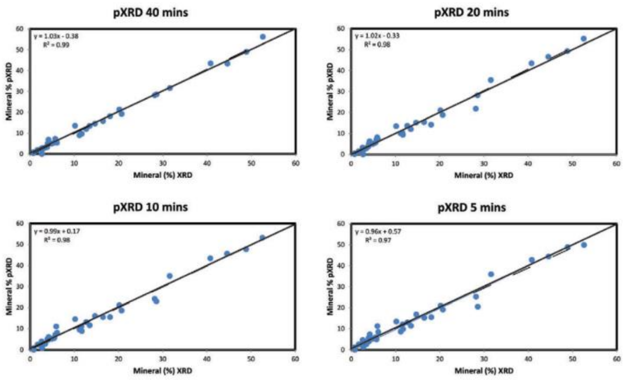

Figure 4: Comparison between mineral percentages deduced from SIROQUANT^{TM} for the Empyrean II XRD (x-axis) and the Terra pXRD (y-axis) at varying runtimes (Burkett *et al.*, 2015).

Analysis of drill cuttings with pXRD also provides a more objective method to lithological logging; a procedure which has historically been highly subjective. To verify the qualitative mineralogical results from the pXRD analysis the geologist can use the qualitative XRF data obtained from the instrument (e.g. presence of K in samples containing illite). To verify the quantitative mineralogical results the user can calculate an estimate of the chemical composition of their samples from pXRD and compare these results to hand-held or laboratory XRF data. An example of this approach for a mudlogging project is presented in Figure 5. The high degree of correlation between the chemical estimates from pXRD and results from XRF verify the quantitative pXRD results for these samples. It is worth noting that the deficiencies in MgO may be attributed to chlorites in the samples being more Mg-rich than is reflected in the idealized chlorite compositions.

For unconventional petroleum exploration quantitative mineralogy is utilised by engineers to determine the engineering properties of the rocks, such as the fracturability. It can also be used to assess whether a formation is likely to reheal after fracturing and in the case of the acid-fracturing stimulation, mineralogy can help determine which acid is most appropriate to stimulate the well.

In conventional petroleum exploration an understanding of the mineralogical composition of the overburden rock can be used to understand and predict its engineering properties. It can also be used to understand downhole geophysical responses. For example, pXRD can help determine whether K is responsible for contributing to gamma ray signals and whether the K is related to illite or potassium feldspar. Another example where pXRD can be applied is in helping the geologist interpret conductivity readings. High conductivity could represent water held in clays or the presence of pyrite in sedimentary rocks.

For conventional petroleum exploration many samples are often sent off site for detailed analysis by other laboratory-based techniques. Although detailed analysis may be warranted it can be important for the geologist to have some mineralogical data in near real-time (rather than weeks or months later). Further to this it can be hard for a geologist to determine which samples are the most appropriate to send off site for more detailed analysis. By stacking diffractograms quickly onsite, the geologist can verify whether a single geophysical response represents a single rock type and can also use this information when determining which samples to send offsite for more detailed analysis.

Corrosion and scaling products are common in petroleum exploration and production, and can result in significant downtime. If corrosion engineers can identify corrosion and scaling products onsite, they can quickly develop the most appropriate corrosion maintenance strategy. An example of this includes calcium scaling. Calcium scaling typically comprises calcite or anhydrite. Calcite can be treated using HCl, but cannot be dissolved using chelate solutions. Anhydrite on the other hand can be removed using chelate solutions but cannot be dissolved using HCl. If the corrosion engineer can identify the composition of the scaling onsite, they can quickly remediate the problem, resulting in reduced downtimes, rather than having to experiment with different treatment strategies or waiting an appreciable time for samples to be sent offsite and analysed at a laboratory.

CONCLUSIONS

The pXRD technique based on the CheMin XRD instrument developed for the Mars Rover has been shown by numerous authors to provide accurate, quantitative mineralogical data for a range of geological and maintenance applications. These results are being utilised by both geologists and engineers to optimise drilling projects, eliminate the subjectivity around logging of geological samples, helping to understand the engineering properties of rocks, interpreting geophysical responses and selecting samples for analysis by other laboratory techniques. It also helps maintenance teams devise the most appropriate corrosion management strategy, the first time.

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