

## Lab Report XRD 82

# X-Ray Diffraction in the Petrochemical Industry: Wellsite Mineralogical Analysis of Shale Formations with the D2 PHASER

**X-ray diffraction (XRD) is an essential technique in the analysis of shale rock formations, allowing for qualitative and quantitative mineralogical characterization. This information provides insight into wellsite behavior and enables better steering decisions, tailoring of drilling fluids, calculations of brittleness and hardness, understanding of chemical reactivity, and more.**

In this lab report, we discuss the mineralogical analysis of drill cuttings from shale rock using the D2 PHASER mobile X-ray diffractometer.

### Introduction

The analysis of shale reactivity typically involves a variety of analytical techniques, including but not limited to X-ray diffraction, X-ray fluorescence, gamma logging, optical microscopy, electron microscopy, total organic content, and cation exchange capacity. From a mineralogical perspective, XRD is widely considered to be the favored technique, particularly for discrimination between elementally similar phases. For example, hematite ( $\text{Fe}_2\text{O}_3$ ) and siderite ( $\text{FeCO}_3$ ) give similar elemental signatures but distinct diffraction patterns.

Diffraction data are often obtained for both vertical and horizontal segments of wellbores. Analysis of the vertical section allows for the identification of zones with desirable physical properties. In horizontal segments of unconventional reservoirs, XRD is primarily used in geosteering, to ensure that the wellbore stays within a specific geological bed.



Figure 1: D2 PHASER benchtop diffractometer with LYNXEYE detector.

Phase	Minerals	Chemical Formula
Silica	Quartz Cristobalite	$\text{SiO}_2$ $\text{SiO}_2$
Feldspars	Albite	$\text{NaAlSi}_3\text{O}_8$
	Orthoclase	$\text{KAISi}_3\text{O}_8$
	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
	Plagioclase	$\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$
Carbonates	Calcite	$\text{CaCO}_3$
	Dolomite	$\text{CaMg}(\text{CO}_3)_2$
	Siderite	$\text{FeCO}_3$
	Ankerite	$\text{Ca}(\text{Fe}, \text{Mg})(\text{CO}_3)_2$
Clays	Illite	$\text{K}_x(\text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$
	Montmorillonite	$(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
	Chlorite	$(\text{Mg}, \text{Fe})_5\text{Al}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$
	Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Additional Phases	Pyrite	$\text{FeS}_2$
	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	Apatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$
	Hematite	$\text{Fe}_2\text{O}_3$

Table 1: Some commonly occurring minerals in shale formations. Note that given chemical formulae are representative. Exact compositions - especially for feldspars and clays/phyllosilicates - will vary due to intercalations and ionic substitutions.

Although the exact mineralogical composition changes from site to site, the more frequently observed rocks include clastics, carbonates, and clays. A more detailed list of commonly occurring minerals is given in Table 1.

Wellsite geologists employ a number of different models and equations to calculate rock properties. For example, a higher value for Young's modulus indicates a stiffer rock that is easier to fracture. Similarly, Poisson's ratio can be used to determine rock strength. Quantitative mineralogy, including calculations of total quartz and carbonate content, can be used to provide additional information, such as brittleness indices for determining the brittleness within a specific region of a reservoir.<sup>1-2</sup> Generally speaking, higher quartz and carbonate concentrations are associated with more brittle rocks and higher clay concentrations indicate a more elastic (i.e., more difficult to fracture) region.

Core segments, particularly full diameter cores, are the ideal sample for thorough analysis, but are typically not used for mineralogical analysis due to practical or economic considerations. However, drill cuttings (Figure 2) are readily available at the wellsite and share the same mineralogical properties as the core. This allows XRD analysis of the cuttings to be conducted onsite and, when sampled at regular intervals, provide a useful picture of the mineralogy as a function of measured depth, leaving more of the core segments available for techniques such as fracture development tests.

In this report, we present powder X-ray diffraction results of shale cuttings from a lateral well segment using the D2 PHASER (Figure 1) mobile benchtop diffractometer.

## Experimental

Drill cuttings were collected every 10 m for 170 m along a horizontal well segment. The collected drill cuttings were rinsed with dichloromethane to remove residual oil and organic matter and then dried for several days in an oven. The clean cuttings were then ground to a fine particle size using a micronizing mill.

Diffraction specimens were prepared by using back-loaded sample holders to reduce the effects of preferred orientation. Materials were analyzed using a D2 PHASER with cobalt (Co) radiation and a high speed silicon strip detector (LYNXEYE). Total scan time was approximately fifteen minutes per sample. Diffraction data were analyzed using two software programs: DIFFRAC.EVA for identification of mineralogical phases and DIFFRAC.TOPAS for quantification.



Figure 2: Core segments and drill cuttings.

## Discussion

For qualitative analysis, XRD can be used as a fingerprinting tool to identify crystalline phases based on characteristic peak locations and intensities. Representative data from a shale sample is shown in Figure 3. Major phases include quartz, calcite, dolomite, and several clay species. Reference patterns from the ICDD PDF-4 database are provided along the 2-Theta axis for reference.

It is important to note the exceptional data quality – with respect to peak resolution, signal-to-noise, and instrument background – across the entire scanning range. Narrow peak resolution is important for resolving closely spaced reflections, which are commonly observed in complex mixtures like naturally occurring rocks. Low achievable background, when combined with the reflection geometry of the D2 PHASER, allows for accurate measurement of low angle peaks and speciation of clay minerals.

A waterfall plot of all collected data is shown in Figure 4, highlighting the similarities in diffraction patterns. This indicates comparable mineralogical compositions and – as these samples were obtained from a lateral segment – good geosteering.

Weight percentages of each observed phase were calculated using quantitative Rietveld analysis with DIFFRAC.TOPAS. A standardless quantification model was used for these samples, which eliminates the need for separate calibration curves with pure standards. Rietveld analysis also allows for more robust quantification due to the ability to account for preferred orientation, absorption effects, peak overlap, and varying cationic occupancies (e.g., different compositions within potassium-rich feldspars). Data for a representative sample is shown in Figure 5.

The same refinement model was applied to each data set and quantification is shown in Figure 6. Carbonate minerals and feldspars are combined into two separate groups for clarity and ease of viewing. Clay minerals include both swelling and non-swelling members as well as chlorites, which are occasionally left as a distinct group. Although decisions vary from site to site, optimal shale compositions generally have a combined weight percent of > 50-60% for quartz, feldspars, and carbonates.<sup>3</sup>

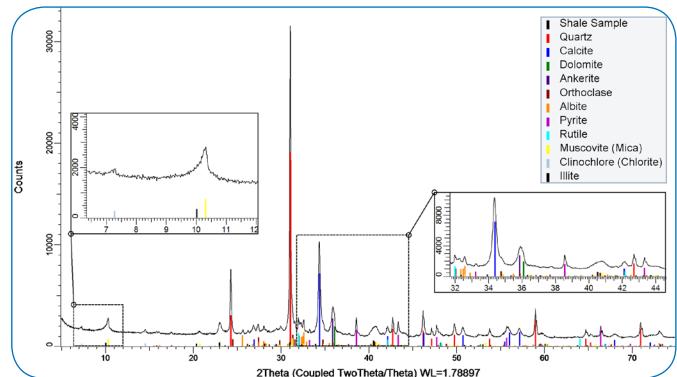


Figure 3: Representative diffraction data from a shale sample. Mineralogical phases were identified with DIFFRAC.EVA. Database patterns for identified phases are provided along the 2-Theta axis for reference.

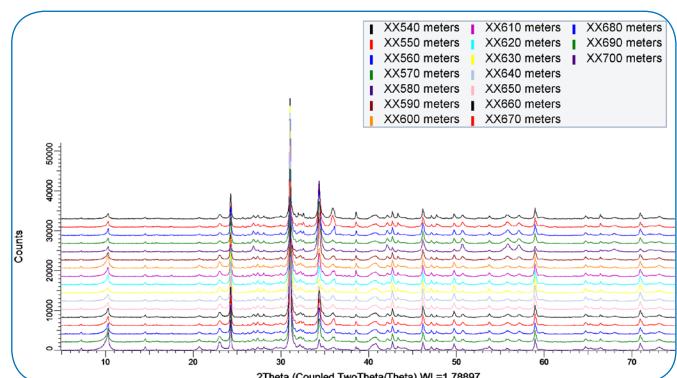


Figure 4: Waterfall plot for all samples. A y-offset was applied for ease of viewing and to illustrate the similarities in diffraction data.

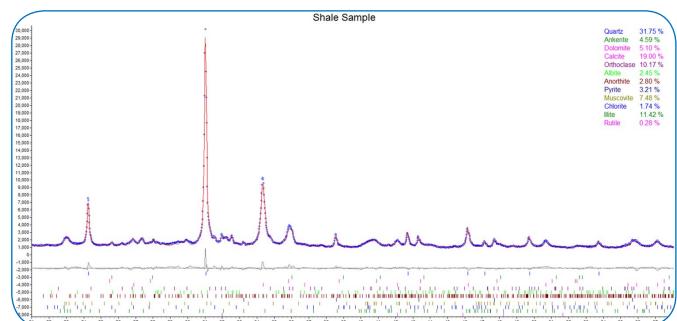


Figure 5: Quantitative Rietveld refinement with DIFFRAC.TOPAS. Collected data is plotted in blue. Refined data is plotted in red. A difference curve between collected and refined data is plotted in grey.

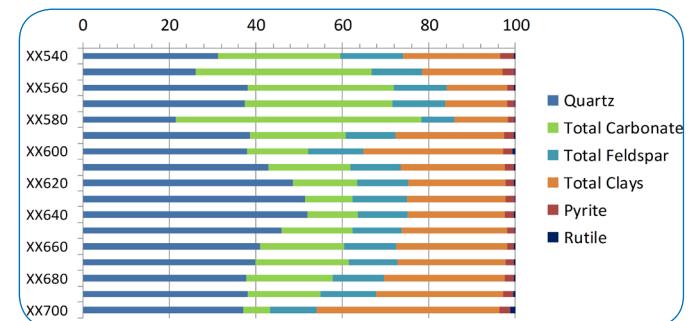


Figure 6: Overall mineralogy plotted as a function of measured depth. Brittle rocks generally contain high concentrations of quartz, carbonates, and feldspars and low concentrations of clay minerals.

## Conclusions

Drill cuttings from a horizontal leg were collected at regular intervals and analyzed using the D2 PHASER mobile benchtop diffractometer. Identified phases include a number of commonly occurring minerals, such as quartz and calcite. Quantification was performed by Rietveld refinement<sup>4</sup>, revealing high concentrations of brittle minerals, such as quartz, feldspars, and carbonates. The results indicate fairly consistent rock compositions, as would be expected in a well-steered section.

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