Minerals matter: A Breakthrough in micron-scale Mapping of Shale Mineral Composition using Mixed Phase X-Ray Spectra

David Haberlah, Owen, M., and R. Jain

FEI Australia, 73 Northbourne Ave, Canberra 2600 ACT, Australia

Presenting author, E-mail: david.haberlah@fei.com

Abstract

In this paper, the theory, potential, and physical limitations of high-resolution x-ray mineral mapping applied to the analysis of unconventional reservoir rocks are explained. Latest research and development in automated SEM-based energy-dispersive X-ray spectroscopy (automated mineralogy) is being applied to mapping the surface of rocks traditionally considered too fine-grained to result in accurate compositional representations, due to a high ratio in mixed mineral spectra. These physical limitations relating to the minimum x-ray excitation volume are computationally resolved into sub-micron mineral assemblages and displayed in the form of colour-coded mineral intensity maps. First results based on a range international shale plays as well as synthetic control samples are presented and evaluated. Finally, applications in both unconventional and conventional reservoir characterisation and production are being discussed.

Introduction

Automated Scanning Electron Microscope (SEM)-based energy-dispersive X-ray spectroscopy (EDS) is commonly referred to as automated mineralogy. Automated mineralogy has been employed for decades to map the mineralogy of sediments and rocks at the micron scale. The rock surface is being systematically scanned by a focused electron beam at a predefined stepping interval defining the pixel spacing. The electrons that strike the sample at each point interact with the mineral constituents and produce signals that can be analysed and imaged (Fig.1). Of principle interest for mapping rocks are:

- Primary beam electrons back-scattered from the sample surface. The resulting grey-scale BSE images are a reflection of the density of the material
- X-rays emitted as a result of interaction of the primary electrons and the sample (shell transitions). These energy-dispersive x-rays (EDX) are characteristic of the chemical composition of the sample and can be classified into phases (i.e. minerals).

The spectral analysis engine (SAE) is an integrated hardware-software component that classifies the EDX spectra at each acquisition point into discrete phases. Classified phases/minerals over the area of acquisition are imaged in form of colour-coded mineral maps (1-3). The currently existing approaches can be grouped into:

- Best spectral match between measured spectra and reference phase EDX spectra (e.g. MLA), and
- Lookup table of pre-defined compositional ranges of elemental matches with measured spectra and additional qualifiers

Both approaches display fundamental limitations when applied to shale, because of the size of the x-ray excitation volume being larger than the mineral constituents of fine-grained rocks in that they report only single dominant phases or pre-defined 'boundary (mixed) phases' per pixel. At the minimum accelerating e-beam voltage required to excite the characteristic energy lines of heavier

elements such as Fe (15 keV), fine-grained samples with significant mineralogical heterogeneity commonly result in mixed x-ray spectra or 'mixels'.
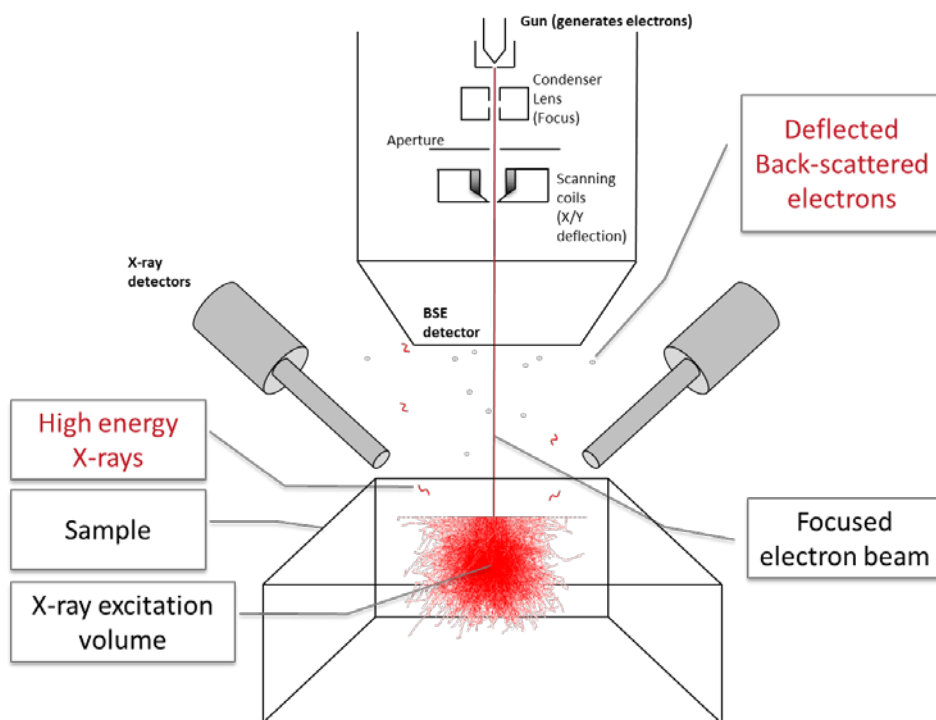

Fig.1. SEM-EDX system with focused electron beam and resulting x-ray excitation volume shown in red, and measured back-scattered electrons (BSE) and energy dispersive electrons (EDX) indicated.

Here, a next generation SAE has been developed with the objective to accurately quantify multiple mineral components within an e-beam interaction volume. The SAE must further work with a low count of x-rays (e.g. 1-5k) commonly used in automated mineralogy to rapidly scan large areas. In the new approach, measured EDX spectra are deconvolved into best matches of multiple minerals, by applying patented algorithms that rapidly produce unique best-match solutions taking into account contextual intelligence.
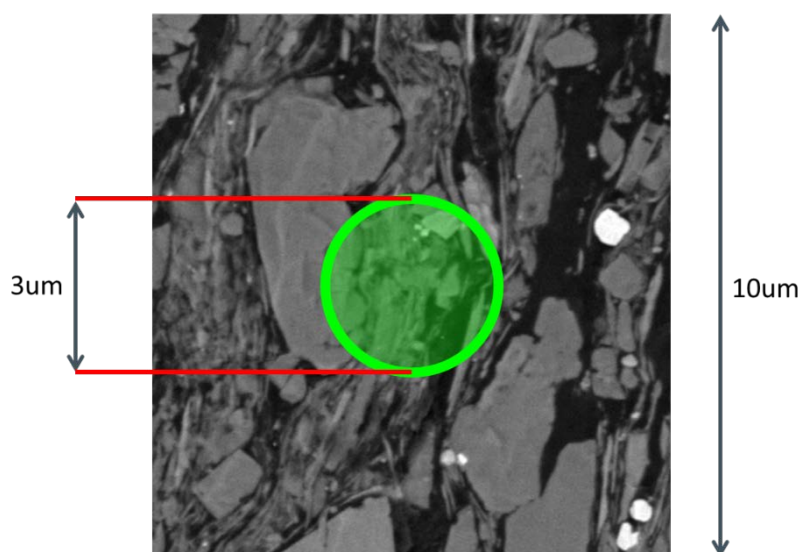

Fig.2. High-res BSE image with a green circle indicating the approximate excitation volume for EDX generation at 15 kV (in 2D).

Methodology

The new SAE is based on >100 mineral and elemental EDX reference spectra, including all O&G relevant mineral standards from The Clay Mineral Society, USGS, and SPI. High-count reference spectra have been collected at multiple common system configurations for measurements (SEM platform, EDS detector configuration, accelerating e-beam voltage). Each reference spectrum is complemented by additional information, such as its chemical composition, common elemental ranges, grain density, and BSE values. This information is used to further improve mineral ID, and to allow for the reporting of modal mineralogy in weight percentages and calculated chemical assays.

Low-count spectra, typically set to 5,000 photon counts per acquisition point, are collected across the sample surface at a user-defined spacing (e-beam stepping interval). Sequentially, each measured EDX spectrum is de-convolved into non-unique best matches of multiple pure phases/minerals. The best match that further passes additional qualifiers and thresholds is then reported as a modal mineralogy percentage for each pixel. For a measured area combined, the output is presented in form of a stack of co-registered colour-coded mineral intensity images (Fig.3), as well as numerical modal mineralogy and chemical assays. Reports can be generated for interactively selected regions of interest (ROI). The patented deconvolution algorithm is optimised to rapidly process the data and quantify the quality of the spectral match. It allows for setting quality thresholds, below which pixels remain unclassified and will be reported as such. Unclassified pixels can be reviewed, and if found to relate to discrete minerals/phases lacking reference spectra, these can be added for reclassification.
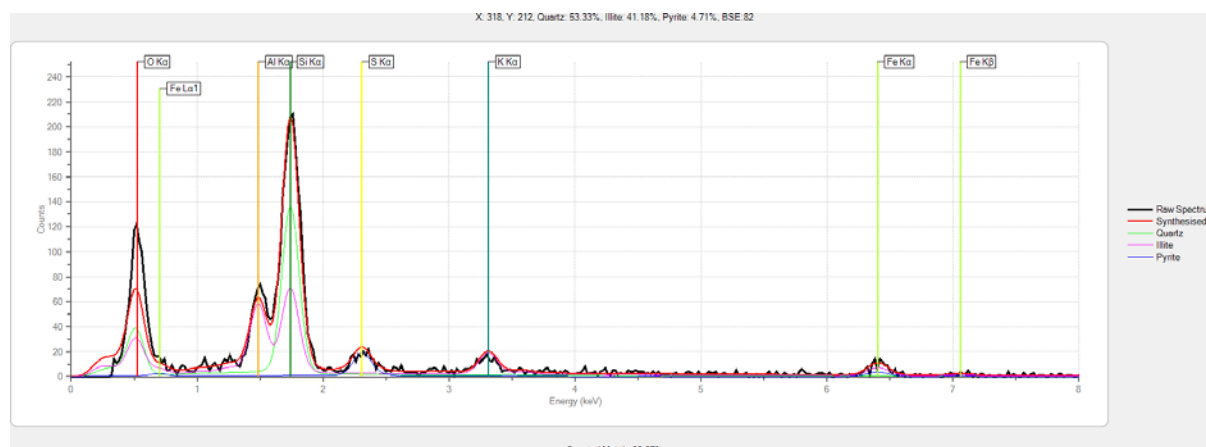

Fig.3. Single-pixel deconvolution of 5,000 photon 15kV measured 'raw spectrum' (black), overlaid by corresponding synthesized 'best match spectrum' (red), and constituent mineral reference spectra.

Results and Discussion

The performance of the new SAE has been tested on a range of O&G samples, including reservoir and seal rocks from international shale plays, and synthetic rocks of know composition (4). The results demonstrate that the new approach can accurately identify and quantify mineral species for which spectra have been added to the reference library.

In this paper, classification results between conventional 'one mineral per pixel' and the new deconvolution 'multiple minerals per pixel' approaches are being evaluated against additional data generated during measurements, i.e.; EDX spectra for selected acquisitions point (Fig.3), and high-resolution BSE images providing mineral shape and contextual information (Fig.4). This approach removes the ambiguity of comparing results between different mineral analytical techniques. Table 1 lists some fundamental differences between XRD, FTIR, and automated mineralogy, explaining why results, while complementary, must not be compared one-on-one. In contrast to the bulk sample numerical results of XRD and XRF, spatial mineralogy images and associated modal mineralogy and chemical assay data provide a good basis for the evaluation of classification results, including information on phase associations, grain texture, and chemical zoning (Figs.4 & 5). Any trace phases will be reported, if intersected in the measured area and included in the spectra reference library.
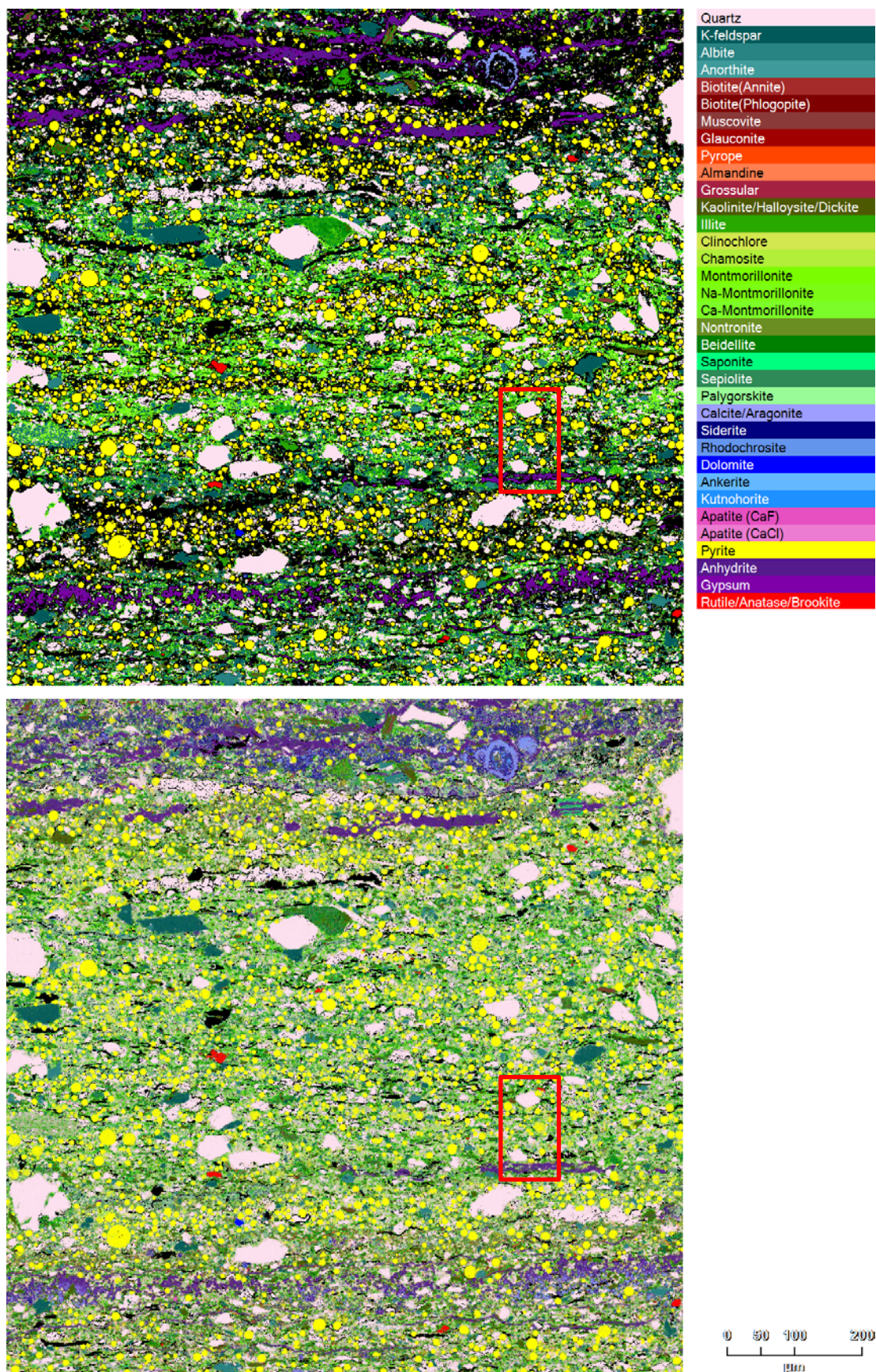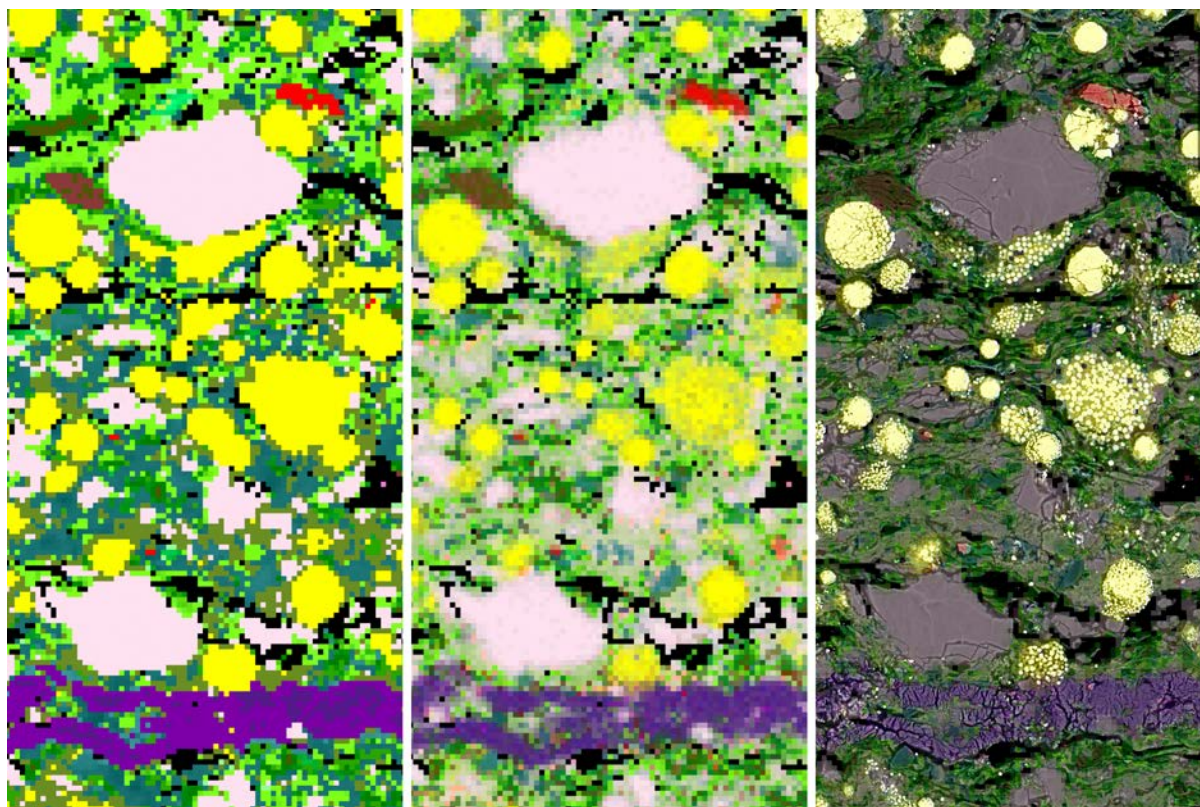
Fig.4. Comparison of spatial mineralogy images of Australian shale sample applying EDX spectra classification using; a) single (dominant) mineral per pixel, and b) multiple minerals per pixel. The red box indicates the enlargement area in Figure 4 (same 1 µm resolution).

Fig.5. Enlargement from Fig.4, highlighting differences in mineral classification between; a) 'single (dominant) mineral' and b) 'multiple minerals per pixel' classifications. Image c) is a BSE overlay.
Sample courtesy of Martin Kennedy & Stefan Löhr, Sprigg Geobiology Centre, University of Adelaide

Figure 4 shows a square mm large measurement of a TOC-rich Australian shale, displaying sub-mm scale banding associated with clays/pyrite versus gypsum/Mn-rich carbonates. In the conventional single/dominant mineral per pixel classification, a large percentage of pixels remain unclassified. Figure 5 shows the same resolution enlargement in more detail, focusing on a ~200 nm thick gypsum band (purple) within a range of feldspar alteration products. While using the same reference spectra, the new 'multiple minerals per pixel' classification approach significantly reduces unclassified 'mixels' in complex bands (Fig. 4). It further resolves a prominent issue of misidentification of illite (green) into chemically similar K-feldspars (dark cyan). The sheets of illite clay minerals can be clearly discriminated from the feldspar grains in the nano-scale BSE image.

Overall, the co-registered mineral map and nano-scale BSE images in Figure 5c suggest a good match capturing the compositional heterogeneity. The black areas which have not been measured relate to organic matter, pores and cracks in the sample. A BSE threshold has been set to prevent x-ray acquisition on material and areas that produce low count rates, in order to speed up measurement acquisition. Discrimination between organic matter, porosity, and unclassified phases is best achieved by multi-modular post-processing including 'image fusion' (5).

Conclusions

A new methodology that can accurately map the mineral composition of fine-grained rocks at sub-micron resolution has been developed and demonstrated on a range of O&G samples. Both acquisition of EDX (compositional) and BSE (textural) data, as well as the mineral classification is fully automated. This method provides accurate, quantitative, and spatially relevant data on the distribution of sub-micron mineral constituents in shale and mudrocks. The new spectral analysis engine can readily be applied to sedimentary rocks other than shale. In conventional sandstone reservoirs, sub-meter thin clay coatings on quartz grains have been mapped and characterised. In carbonates, sub-micron grain coatings of clays can be quantified and thin zones of elemental variation or alteration in

solid solution series can be mapped. Further integration of EDX and BSE modalities has the potential to provide additional nano-scale contextual information, such as quantification of pore-lining mineralogy, or modelling of rock response to EOR or hydraulic fracturing.

Table 1. Comparison of common mineral analysis techniques X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and automated mineralogy (SEM-EDS).

	XRD	FTIR	SEM-EDS
Sample preparation	**pulverization/ physical clay fractionation**	pulverization/ small aliquot	encapsulating, sectioning, conductive coating
Sample presentation	3D fine-grained powder	3D fine-grained powder	**2D surfaces of solid rock or encapsulated particles**
Measurement source	primary x-ray beam	polychromatic light source	focused electron beam
Measured property	**crystallinity**	chemical composition	chemical composition
Raw data output	1 diffractogram for entire sample	1 IR absorption spectrum for entire sample	**1 EDX spectrum at each measurement point**
Mineral identification	peak comparison with large # of standard reference minerals	peak comparison with small # of selected reference minerals	peak comparison with elemental and mineral reference spectra, **additional qualifiers**
Mineral quantification	bulk modal mineralogy	bulk modal mineralogy	**particle-by-particle quantification, mineral maps including ROI**
Discrimination	polymorphs	isomorphs, non-crystalline phases	isomorphs, non-crystalline phases, **trace phases**

References

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