

Short communication

Nanoscale mineralogy and organic structure characterization of shales: Insights via AFM-IR spectroscopy

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Abstract:

Atomic force microscopy coupled with infrared spectroscopy (AFM-IR) is one of the most effective and widely employed mixed techniques capable of providing direct access to infrared spectroscopic imaging and chemical analysis at the nanoscale spatial resolution. In this communication, AFM-IR was applied to evaluate the *in-situ* nanoscale mineralogy and to characterize the organic structure of shale. Significant chemical and microstructural heterogeneity could be observed on the mirror-like surface of naturally deformed shale. It was also apparent that slickensides formed on the mirror-like surface potentially influence the spatial distribution of organic matter. This technique provides an effective combination for direct and *in-situ* studies of the morphology and physicochemical properties of geological rocks at the nanoscale, opening a new avenue for investigations to help reveal some complex geological phenomena, such as organic carbon graphitization and mineral transformation during fault deformation. Furthermore, this technique makes it possible to determine the chemical composition, molecular structure and functional group information of shale organic matter, which is crucial information for investigating the hydrocarbon generation potential, maturity evaluation, and oil and gas migration mechanisms in shale.

1. Introduction

The diversity of organic and inorganic compounds in shale causes an interplay of ingredients at the micro- to nanoscale (Wang et al., 2020; Zhu et al., 2021; Gou et al., 2022). This necessitates the use of analytical methods with good spatial resolution at the nanoscale to separate their components and understand their distribution connection. Some microscopic techniques such as atomic force microscopy (AFM), scanning electron microscopy, and transmission electron microscopy can perform the type, size, shape, and morphology characterization of shale composition at the nanoscale spatial resolution (Zhu et al., 2018, 2021; Gao et al., 2024), but they are unable to chemically identify organic and mineral particles in

geological materials. In contrast, conventional spectroscopic techniques such as infrared spectroscopy (IR) are excellent tools for exploring vibrations at the molecular and atomic scales of organic and inorganic compounds (Zhou et al., 2020; Wang et al., 2022). Nevertheless, these methods have shortcomings when utilized for the semiquantitative evaluation of organic and mineral functional groups at the nanoscale (Phan et al., 2022, 2023).

Atomic force microscopy coupled with infrared spectroscopy (AFM-IR) is an emerging infrared microscopy technique that can provide direct access to IR spectroscopic imaging and chemical analysis on the surface of some geological materials at the nanoscale spatial resolution (Dazzi and Prater, 2017; Abarghani, 2020; Schwartz et al., 2022;

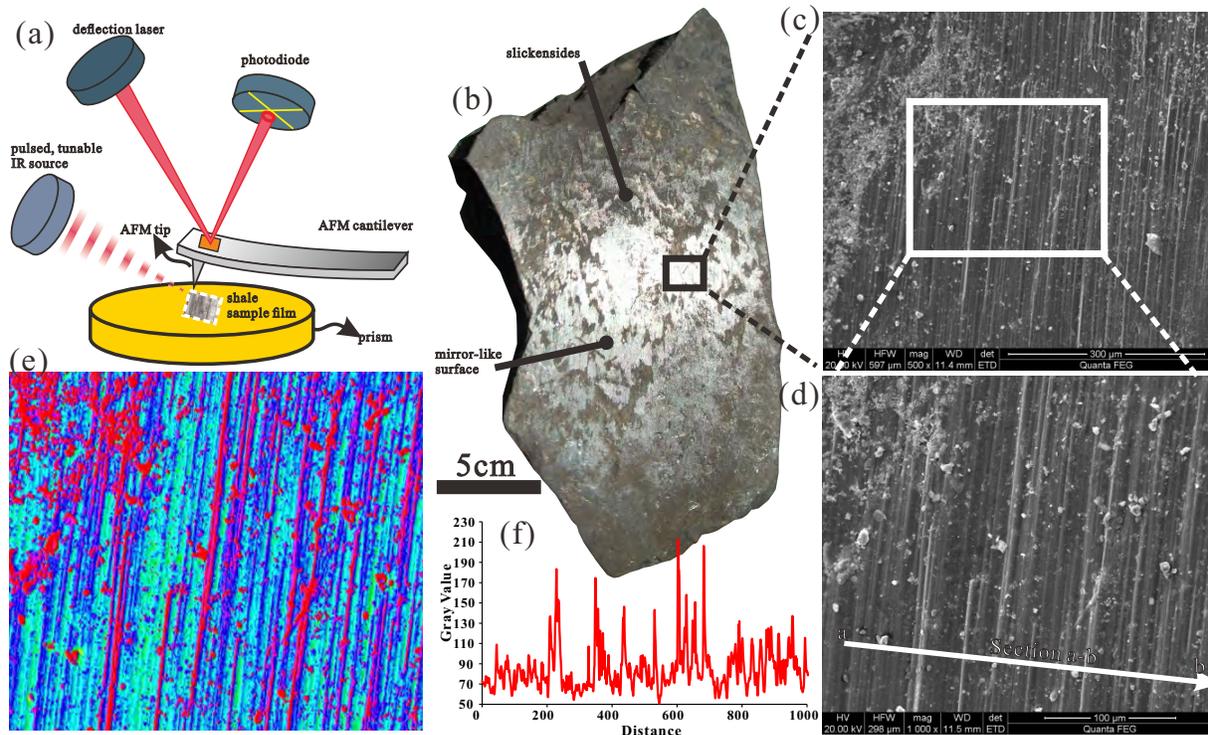


Fig. 1. (a) Schematic model showing the AFM-IR equipment, (b) Photograph of Qiongzhusi shale sample revealing significant mirror-like surface and slickensides, (c) Low- and (d) high-magnification SEM image illustrating microstructures on the mirror-like surface, (e) 3D topography obtained by Image J revealing lineations on the mirror-like surface of (d), (f) 2D profile (e.g., section a-b in fig. 1(d)) of the lineation topography obtained by Image J.

Phan et al., 2023). An illustration of the AFM-IR equipment is exhibited in Fig. 1(a). However, the challenge in conducting this experiment on geological materials is twofold. First, rock sample preparations do not create artefacts and preserve the complex intrinsic fabrics and structure of organic or inorganic particles, which are difficult to process. Second, obtaining quantitative data is necessary *in-situ* from visual 2D and 3D images. The surface of the tested sample must be extremely smooth (Zhou et al., 2020). Typically, the sample must be manually profiled by techniques such as argon ion profiling and focused ion beam (FIB) technology. It should be noted that the fault has a naturally occurring structural deformation product, namely the fault mirror, whose surface has minimal roughness and is very smooth (Fig. 1(b)). Using high-resolution electron imaging, it was discovered that the shale-hosted fault mirror is made up of many nanofibers (Figs. 1(c) and 1(d)). The 3D topographies revealed a ridge-in-groove texture populating the mirror-like surface with a peak-to-peak distance of 5 μm or less (Fig. 1(e)). From Fig. 1(e), it is evident that such surface is composed of about $<3 \mu\text{m}$ wide bright-colored lineations aligned subparallel to the slip deformation direction. Fig. 1(f) reveals the 2D profile of these bright-colored lineations. The convex ridges and grooves appear as peaks and gaps in the 2D planes, respectively. Thus, secondary treatments become unnecessary if AFM-IR tests are conducted directly on this natural mirror-like surface.

This work presents the results obtained using AFM-IR on a Lower Cambrian Qiongzhusi shale sample. The objectives were to: (1) assess the performance of the AFM-IR for shale samples, (2) provide insights into the variability of mineralogy and organic structure on shale-hosted fault mirror-like surface with AFM-IR, and (3) discuss the impact of fault deformation on the nature of organic components and structure.

2. Sample and methods

A sample from the Lower Cambrian Qiongzhusi Shale was taken from the fresh outcrop of the Guizhou Qiandongnan in South China. The sample was structurally deformed as it was taken from an intensively faulted zone. Slickensides and a fault mirror can be observed on the rock surface (Fig. 1(b)). SEM was conducted on both selected chip samples with mirror-like surface and argon ion-milled samples and used for the characterization of shale microstructural deformation. In the SEM images, the typical deformed microstructures can be identified in 3D using image-processing techniques. The equipment model of SEM used in this study was FEI Quanta 200F, Zeiss Gemini 450. Energy dispersive spectroscopy (EDS) analysis was conducted on the sample to identify the predominant compositions. AFM-IR measurements were performed using nanoIR3, Ansys Instruments (now Bruker Nano GmbH). A scanning range of $5 \mu\text{m} \times 5 \mu\text{m}$ was selected. The IR spectra

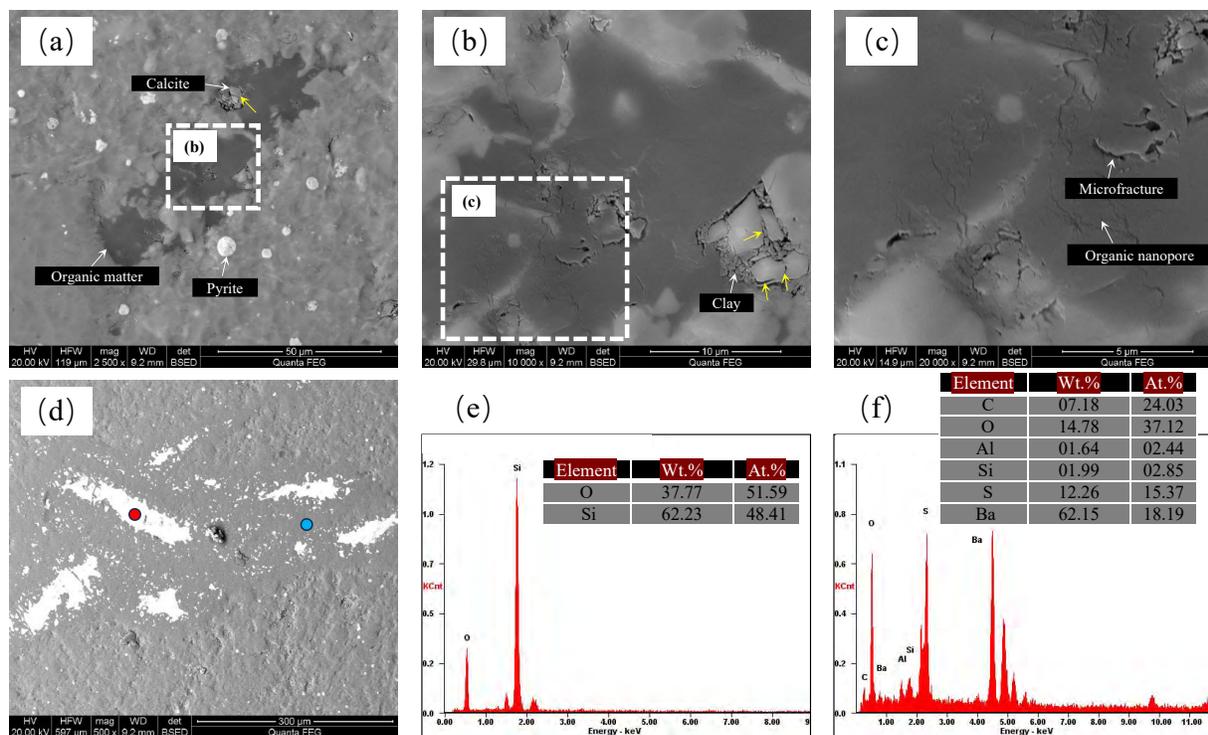


Fig. 2. Microstructures and mineral components of shale sample determined by SEM (a-d) and EDS analysis (e-f).

were collected between 1000 and 1900 cm^{-1} . AFM-IR images through each region of interest were collected from each section at IR frequencies of 1036, 1182, 1450, 1600, and 1720 cm^{-1} corresponding to C-O-C, R-O-C, methylene (CH_2) bending, sp² aromatic (C=C), and carbonyl (C=O) stretching, respectively. Analysis Studio software was used to process the AFM topographical images. A detailed description of the AFM-IR can be found in the work of Liu et al. (2021).

3. Results and discussion

Fig. 2 presents the predominant constituents in the shale sample identified by SEM and EDS analysis, which include organic matter, quartz, calcite, clays, pyrite, and barite. The mirror-like surface of the shale sample exhibits distinct structural characteristics on both the macro- and the micro-scale. Macroscopically, the mirror-like surface has a relatively smooth plane (Fig. 1(b)), which is the result of the friction surface being continuously polished and ground while the fault moves. SEM observation reveals irregular asperities, such as tiny scratches and grooves on the mirror-like surface (Figs. 1(c) and 1(d)), which could result from the local stress differential created by friction as well as the unequal distribution of mineral particles.

Furthermore, the sample exhibits typical particle deformation characteristics. The fault slip clearly breaks rigid minerals like calcite and quartz (Figs. 2(a) and 2(b), indicated by yellow arrows). Microcracks may form within mineral particles. The distribution and orientation of these cracks indicate the stress transfer path during fault slip. The friction mechanism causes

clay particles to rearrange and form a directional microstructure (Fig. 2(b)). In addition to affecting the physical characteristics of clay minerals, this microstructure deformation may also alter the fluid adsorption and transport capacity. Extrusion or shear stress on organic particles alters the pore shape and molecular structure (Fig. 2(c)). These microstructural changes clearly underscore the effects of fault slip on the physical structure of shale.

The 2D IR maps of the sample were recorded with the IR source tuned to 1036, 1182, 1450, 1600, and 1720 cm^{-1} corresponding to C-O-C, R-O-C, CH_2 bending, C=C, and C=O, respectively (Figs. 3(a)-3(f)). The relevant 3D views are shown in Figs. 3(g)-3(l). Most of these five types of chemical functional groups are linearly distributed in space, which may be restricted by mirror scratches. The comparison to the AFM topographic maps (Figs. 3(a) and 3(g)) reveals that some of the trends are related to surface height. The area with micro-protrusion or the topographic high height shows an overall higher AFM-IR intensity (Figs. 3(b) and 3(h)). Generally, these maps reveal the presence of correlated organic matter absorption at 1450 (Figs. 3(d) and 3(j)), 1600 (Figs. 3(e) and 3(k)), and 1720 cm^{-1} (Figs. 3(f) and 3(l)), as well as significant signatures of silicate minerals that would generate absorptions around 1000 cm^{-1} (Figs. 3(b) and 3(h)). Notably, these IR maps suggest that the shale has strong heterogeneity in terms of both component and structure and they also emphasize the general need to work with smooth and flat surfaces for AFM-IR measurements (Phan et al., 2022, 2023).

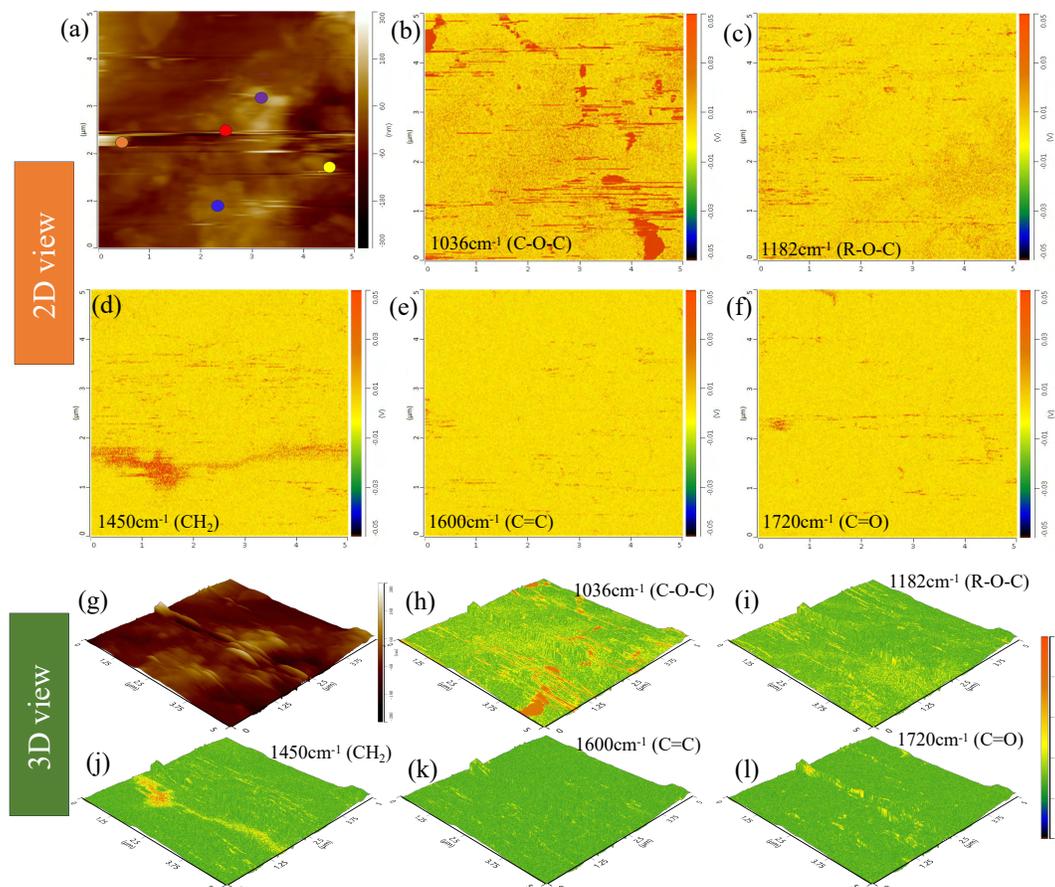


Fig. 3. (a) 2D AFM image showing the microstructural characteristics of mirror-like surface of the sample. 2D IR mapping images at different wavelengths: (b) 1036 cm^{-1} , (c) 1182 cm^{-1} , (d) 1450 cm^{-1} , (e) 1600 cm^{-1} , and (f) 1720 cm^{-1} . (g) 3D AFM image showing the microstructural characteristics of mirror-like sample surface. 3D IR mapping images at different wavelengths: (h) 1036 cm^{-1} , (i) 1182 cm^{-1} , (j) 1450 cm^{-1} , (k) 1600 cm^{-1} , and (l) 1720 cm^{-1} .

In the areas of interest, five areas distributed at various locations of the sample mirror-like surface (Fig. 3(a)) were selected to acquire IR spectra from the 900 ~ 1900 cm^{-1} frequency range (Fig. 4(a)). The AFM-IR spectra of selected areas reveal abundant C=C stretch vibration, lower C-O-C and R-O-C, and fewer CH₂ and C=O signals (Fig. 4(a)), indicating compositional homogeneity. Importantly, a very high silicate Si-O stretching can be observed in the region 1000 ~ 1200 cm^{-1} wavenumber (Fig. 4(a)), indicating abundant quartz and clay mineral components (Phan et al., 2022).

Some semi-quantitative tracers produced from AFM-IR spectra can be estimated to determine the chemical properties of the organic matter of shale (Phan et al., 2023). These include factors *A* and *C*, which can be calculated by:

$$A = \frac{I_{1450}}{I_{1450} + I_{1600}} \quad (1)$$

$$C = \frac{I_{1720}}{I_{1720} + I_{1600}} \quad (2)$$

where I_{1450} represents height intensity of the absorption band at 1450 cm^{-1} , I_{1600} represents height intensity of the absorp-

tion band at 1600 cm^{-1} , and I_{1720} represents height intensity of the absorption band at 1720 cm^{-1} .

Factor *A* is estimated from the CH₂ bending at 1450 cm^{-1} and the C=C stretch at 1600 cm^{-1} and can specifically assess the hydrocarbons potential of source rocks. Factor *C* is a quantization parameter used to measure the degree of organic matter maturation, which represents differences in the ratio of the C=O to C=C groups. The results shown in Figs. 4(b) and 4(c) reveal that some of the trends are related to mirror scratches. The areas with slickensides or the topographic high height show an overall higher factors *A* and *C*, indicating a high hydrocarbon generation potential and organic matter maturation.

The application of AFM-IR technology to directly evaluate geological materials with fault mirror-like surface provides some distinct advantages and possible drawbacks. The benefits include the following: (1) High-resolution chemical imaging. The ability of AFM-IR technology to produce high-resolution nanoscale chemical images of geological materials is crucial for studying the distribution of organics and minerals, microstructure features, and micro-chemical changes in the fault

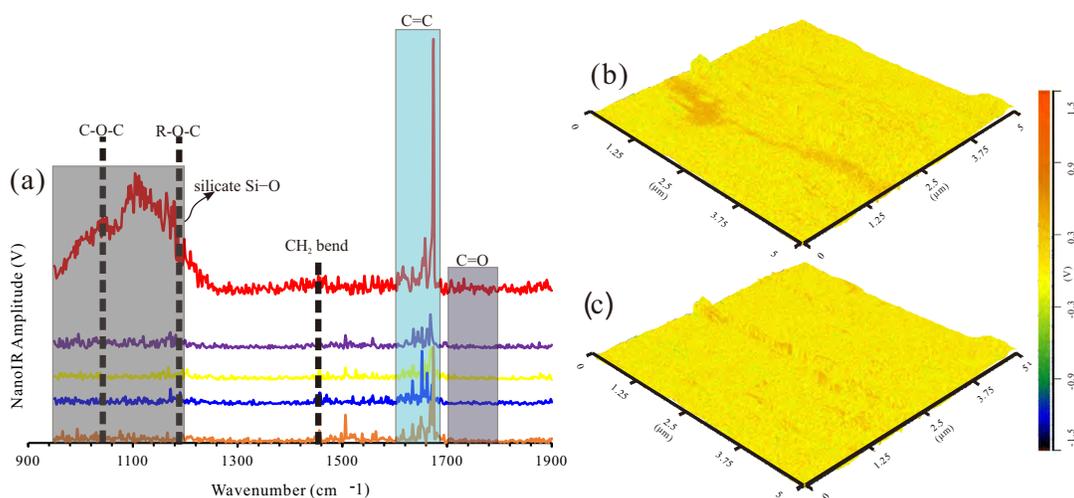


Fig. 4. (a) IR single-point spectra in the $1900 \sim 900 \text{ cm}^{-1}$ range were acquired in selected five locations shown on the AFM image in Fig. 3(a). Distribution of nanoscale factor A (b) and factor C (c) on the shale sample surface.

mirror-like surface. (2) Nondestructive testing. AFM-IR causes minimal physical damage to materials when used in non-contact or tapping mode, making it ideal for a non-destructive assessment of priceless geological samples (Phan et al., 2022, 2023; Swiech et al., 2024). This makes it easier to do more research and analysis while still preserving the sample's original qualities and integrity. (3) Multi-environmental adaptability. AFM-IR works under a variety of environmental conditions, including vacuum, air and even liquid environments. As a result, this method may be used to characterize a variety of geological materials, including those that must remain stable in a particular setting. (4) Wide range of applications. In addition to the analysis of geological samples, AFM-IR is extensively utilized in materials science, biology, nanotechnology, and other domains (Liu et al., 2021; Mathurin et al., 2022; Phan et al., 2022, 2023; Swiech et al., 2024). This broad application strongly supports the interdisciplinary study of geology and other fields.

However, this technology also has the following inherent disadvantages: (1) Slow imaging. AFM-IR has a slower imaging speed than other imaging techniques, mostly because of its complicated signal processing and high-resolution imaging needs. As a result, processing a larger area or a lot of samples could be time-consuming. (2) High requirements for the sample surface. AFM-IR technology requires a smooth and flat sample surface (Liu et al., 2021; Phan et al., 2022, 2023). To assure image quality, geological materials with complicated surface topography may need additional surface treatment or preparatory work. (3) Analyzing complex samples poses a significant challenge. As a result, the analytical capability of AFM-IR technology for geological samples with complicated chemical compositions and microstructures may be limited (Liu et al., 2021; Wang et al., 2022). When there are several interacting chemical groups in a sample, it may be essential to integrate different analytical techniques to achieve detailed characterization.

4. Conclusions

Combined AFM-IR is a newly emerging strategy for *in-situ* chemical analysis and compositional imaging at the nanoscale spatial resolution in geological rocks, such as shales and coals. It can obtain 2D and 3D IR maps at selected wavelengths or spectra at the desired positions of interest. In this work, we applied AFM-IR to capture the *in-situ* morphological and chemical structure of mirror-like surface of a naturally deformed shale and mapped the distribution of typical functional groups nondestructively at the nanoscale resolution. The application of this technique to examine the nanoscale chemical and microstructural heterogeneity in shale is of clear relevance for hydrocarbon production and structural geology studies. Our results demonstrate that AFM-IR is a useful qualitative and quantitative analytical technique that is suitable for shale samples and other organic-rich coals and mudstones.

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Conflict of interest

The authors declare no competing interest.

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