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Advanced Methods in Petroleum Geochemistry

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Preface

Petroleum geochemistry is a vital domain in the exploration of oil and gas resources, as it involves in-depth analyses of source rocks and the fluids they produce. By applying general chemistry principles, petroleum geochemistry delves into the intricate processes of origin, generation, migration, accumulation, and alteration of petroleum found in organic-rich fine-grain sedimentary rocks. Traditionally, geochemistry methods have relied on bulk samples to provide insights at a macro or basin scale. However, the surge in unconventional shale plays has exposed the limitations of these conventional methods, especially in meeting our needs for nano to micron scale information. The heterogeneity of these resources leads to significant variations in chemistry and formation attributes, occurring at an exceptionally fine scale from source to reservoir rocks, given their close proximity. While conventional methods are adequate for understanding hydrocarbon generation, migration, and accumulation in a broader context, they fall short when it comes to examining finer-scale characteristics.

Addressing these challenges is paramount for advancing our understanding of petroleum systems. To overcome these limitations, researchers must embrace advanced analytical instrumentation, including cutting-edge techniques like Raman spectroscopy, atomic force microscopy-infrared (AFM-IR), nuclear magnetic resonance (NMR), and mass spectroscopy. These innovative approaches open new possibilities for unveiling intricate details and resolving ambiguities in unconventional resources. By incorporating these advanced methods, petroleum geochemistry can provide robust answers to the remaining questions in the field and enable comprehensive evaluations of these valuable energy resources.

In this context, the presented monograph proposes novel methods that have recently emerged in the realm of petroleum geochemistry, with a primary focus on the evaluation of source rocks. As a crucial aspect of organic geochemistry, source rock analysis involves examining organic-rich fine-grain sediments for their thermal maturity, production potential, chemical structure evolution during burial history, and migration patterns. Traditionally, this type of analysis has mainly relied on bulk rock samples, neglecting finer-scale studies at the nano or micro levels. However, with the rise of unconventional resources like shale oil and gas, where organic-rich fine-grain sediments act as both reservoir and source rocks, and hydrocarbons migrate over short distances, conventional methods like programmed pyrolysis prove insufficient to meet the evolving needs of petroleum geochemists and geologists.

In response to these evolving demands, the monograph unveils cutting-edge techniques that go beyond traditional petroleum geochemistry procedures, offering a more comprehensive understanding of petroleum systems. These innovative methods, such as Raman spectroscopy, NMR, AFM-IR, and XPS spectroscopy, are based on advanced and recently developed instrumentation, enabling a multi-scale approach to studying petroleum systems. The monograph seamlessly integrates these unconventional analytical techniques with traditional methods, demonstrating how they can be correlated to reveal a wealth of information at different scales, from the nano to the macro level. Throughout the book, the authors generously provide data, images, and detailed explanations of the methods, data collection, interpretation of results, and intercorrelated characteristics of the study specimens.

By embracing this amalgamation of advanced and traditional techniques, petroleum geochemists can unlock new insights into the mechanisms of petroleum generation, expulsion, migration, and accumulation in reservoirs from the source rock. The integration of these innovative analytical tools paves the way for a more profound and comprehensive understanding of petroleum systems and their inherent complexities, ultimately shaping the future of energy exploration and exploitation.

Kiel, Germany Mehdi Ostadhassan, Ph.D.

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Chapter 1
Molecular Heterogeneity of Organic Matter in Geomaterials by AFM Based IR Spectroscopy

Abstract Several samples were selected at the early and peak thermal maturity stages of organic matter, based on bulk geochemical screening, organic petrology and fluorescence emission of the liptinite group maceral and solid bitumen reflectance. Identified particular organic material in the samples were examined by AFM-IR spectroscopy to evaluate organic matter heterogeneity at the nanoscale, based on chemical variations. A significant chemical heterogeneity was observed within unaltered telalginite and bacterial degraded *Tasmanites*, and also between two separate solid bitumens that are next to one another and at the same stage of thermal progression. Furthermore, considering their separate pathways of generation, these solid bitumen particles were compared in terms of their chemical content. While thermal maturity progression was found to reduce molecular chemical heterogeneity in the organic matter particles during the maturation pathway, on the contrary, during the bacterial degradation, the *Tasmanites* has lost its fluorescence emission and the relative chemical heterogeneity was increased compared to the unaltered telalginite, a phenomenon that was observed for the first time.

Keywords Bakken shale · Thermal maturity · Organic matter heterogeneity · AFM based nano-IR spectroscopy · Organic petrology

1.1 Introduction

Considering shale as a source rock, the organic matter (OM) plays a critical role in increasing the degree of heterogeneity of the rock. For instance, where the organic matter is mostly solid bitumen (SB), overall reservoir quality can get affected [25, 32] leading to a considerable decrease in the permeability and pore throat sizes [21]. Also, the submicron length scale heterogeneity of OM in shale has been demonstrated by SEM observations, where it has occasionally been found that adjacent OM grains have significantly different porosities. This heterogenous nature of the OM may result from inherent variability in the OM caused due to factors like the depositional environment as well as potential regional differences in the degree of thermal

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alteration brought about by catalysis from mineral grains present in close proximity [33]. Assessing shale in multiscale and OM with respect to physio-chemical heterogeneities helps gaining better insight into reservoir performance and mechanisms that would lead to generation of petroleum from the OM [8]. While SEM offers thorough, high-resolution details on OM pores, it offers no details on their type or chemical makeup. Reflected light optical microscopy is employed to distinguish between various OM types, but it does not offer molecular data. Rock–Eval and infrared spectroscopy are two methods that have been used to assess changes in the average chemical composition of OM at various thermal maturities, but they are unable to detect geochemical heterogeneity in shales at low spatial resolution. Although Fourier transform infrared microscopy (micro-FTIR) is used to study this heterogeneity, the diffraction limit prevents it from reliably resolving chemical characteristics at the sub-micron length scale pertinent to shale [7, 33]. The extent of organisation of OM at the micron length scale can also be determined structurally using Raman imaging, but this method is limited by the strong fluorescence background from immature shale samples. In addition to topographic imaging by AFM, AFM-IR, a rapidly developing technique in the materials and life sciences, offers chemical and modulus mapping at the nanoscale that is not affected by the diffraction limit. Yang et al. [33] for the first-time applied AFM-IR to determine the heterogeneity in shales in terms of their chemical and mechanical properties at nanometre scale spatial resolution. They quantified nano chemo-mechanical characteristics of different types of OM (solid bitumen, inertinite, and *Tasmanites* telalginite) on artificially matured (hydrous pyrolysis) samples from the New Albany Shale. They noted that while each maceral type's average composition varies significantly, there is little variation in the composition between different locations that belong to the same maceral type. AFM based nanoIR technique, as was employed by Yang et al. [33] can map chemical variations at the nanoscale without getting affected by the diffraction limit.

1.2 Principle of Atomic Force Microscopy (AFM)

Different methods for characterising rocks are chosen at various resolutions [18]: (i) seismic imaging at resolutions of tens of metres, (ii) well logging and drilling measurements at resolutions of less than 1 m, and (iii) mechanical and petrophysical properties of rocks (permeability, porosity, and capillarity), which can be measured at a resolution of centimetres in core tests. Properties of rocks can be highly heterogenous even at the nanoscale resolution [15]. Thus, nano scale characterization can be a useful tool to improve rock characterization. Atomic force microscopy (AFM) and nanoindentation, generally called as force spectroscopy, are commonly used for micro/nano scale measurement on a wide range of materials to assess chemical, electrical and mechanical properties of various types of biological system, nanoscale materials as well as geomaterials. Although scanning electron microscopy (SEM) can be used to characterise rocks at the nanoscale, it does so by emitting and collecting photons and electrons in a manner similar to our sense of light, whereas AFM uses a stylus tip to scan a sample in a manner similar to our sense of touch [18]. The AFM measures interactive forces between surfaces directly and can be used for:

(a) surface topography measurement
(b) simultaneous determination of the surface materials
(c) determining the local bulk modulus of elasticity of the rock material for use in geomechanical models for hydraulic-fracture design.

Binnig et al. [5] introduced the first AFM model as a scanning-tunneling microscope (STM). A tunnelling current that is inversely proportional to the gap width is produced in STM by bringing a voltage-biased metal tip close to the surface. By moving the tip vertically while scanning the surface, the STM feedback system maintains a constant tunnelling current. The piezoelectric scanner determines the exact x, y, and z positions of the tip. The vertical position provides surface topography because a constant current guarantees a constant gap width. However, specific STM principles only allow imaging of conducting or semiconducting surfaces. Subsequently, Binnig et al. [6] suggested the tip to be mounted on the cantilever spring and observing the deflection of the cantilever relative to surface/tip forces, thereby creating the AFM. Since the force between the surface and the tip is dependent on the width of the gap, feedback system of the AFM can keep an even tip/surface gap by compensating for cantilever deflection with a vertical tip displacement. Imaging the topography of any material, whether conducting or nonconducting, is possible with this method.

Figure 1.1 shows schematic of a typical AFM setup consisting of a cantilever with a tip attached to its end (tip nose radius is 30 nm), a laser source, a chip holder, quadrant photodiode, controlling system, and mirror. The cantilever moves at the prescribed speed vertically with the help of piezoelectric movement. The deflection of cantilever in the z-direction as the tip nears the surface and retracts from it is recorded by the AFM so that it can directly measure the interactive forces between the surfaces (i.e., tip nose and substrate). The cantilever can be modelled as a spring because one end is held, and the other is free. The force between the tip surface and the cantilever can then be calculated using Hooke's law:

$$F = K_c Z_c, \tag{1.1}$$

where "Z_c" denotes cantilever deflection at its free end, "k_c" denotes cantilever stiffness or spring constant, and "F" denotes the force acting between the tip and the surface. In Fig. 1.2a, a tip-cantilever is shown approaching and touching a surface before retracting from the surface in a schematic representation of the approach and the retract movements. In the stages of approach and retract, force responses related to tip/surface interactions are shown in Fig. 1.2b as a function of distance. During the initial phase of the approach, the cantilever simply shows no deflection and detects no interactive force. When the tip gets close to the surface, van der Waals (vdW) forces of attraction start to work and b end the cantilever in the direction of the surface. The tip rises to the surface as soon as the cantilever-spring constant is exceeded by the