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Research paper

Impact of thermal maturation on nano-scale elastic properties of organic matter in shales

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ABSTRACT

The properties of organic matter change during diagenesis and catagenesis, potentially altering the way shales deform and fracture. Although kerogen in mudrocks is thought to become stiffer during thermal maturation, few studies have been able to confirm this by direct measurement, as standard mechanical testing techniques cannot easily be used to measure the micrometer sized organic components in shales. Here, we use a new non-destructive atomic force microscopy technique to map the elastic modulus of organic and inorganic components at the nanometer scale in shales containing Type II kerogen from three different levels of thermal maturation. We found that when vitrinite reflectance increases from 0.40 to 0.82, the average Young modulus of kerogen increases from 6.1 GPa to 16.0 GPa. However, as %Ro increases further from 0.82 to 1.25, the modulus values for kerogen do not change significantly. A high degree of variance is registered in the elastic moduli, particularly at higher levels of thermal maturation, probably reflecting the inherent heterogeneity in the depositional organic matter present in the shales. The mean modulus for bitumen in the same samples – identified as void filling organic matter that was present only at intermediate and higher levels of maturation - was relatively constant with mean values of 7.5 GPa and 8.5 GPa, respectively. In the samples that experienced catagenesis, the modulus maps reveal that individual kerogen macerals possess soft regions - interpreted as exuded bitumen - which act to soften the overall structure of the kerogen. As well as providing high resolution mechanical data, this technique could be used to track the way bitumen and other compounds are generated from kerogen during catagenesis.

1. Introduction

In both conventional and unconventional reservoirs, the mechanical behavior of shales is often poorly understood. As the elastic properties of both the organic and inorganic components that make up shales strongly influence their mechanical behavior, a comprehensive characterization of the constituent components in shales could improve the accuracy of rock mechanics models. However, although the mechanical properties of many of the mineral phases present in shales are reasonably well known, the characteristics of the more compliant (softer) organic components remain enigmatic. During thermal maturation new hydrocarbon phases - such as bitumen - form from kerogen. In addition to altering the kerogen's chemical composition, the cracking process also changes the physical and mechanical properties of the organic matter (e.g., Ujiie, 1978; Okiongbo et al., 2005). However, directly measuring changes to the organic matter within shales has proved challenging because much of the organic matter comprises micrometer-scale kerogen grains, or is present as bitumen occupying nano-scale voids between grains (Fig. 1). Standard techniques, such as nanoindentation, have helped to shed critical light on the problem (e.g., Zeszotarski et al., 2004; Ulm and Abousleiman, 2006; Bobko and Ulm, 2008; Ahmadov et al., 2009; Ahmadov, 2011; Kumar et al., 2012; Shukla, 2013; Zargari et al., 2013), but lack the necessary high resolution to fully characterize the organic components which often have dimensions in the micrometer and even nanometer range. Recently, however, new analytical advances have provided an opportunity to probe directly the elastic

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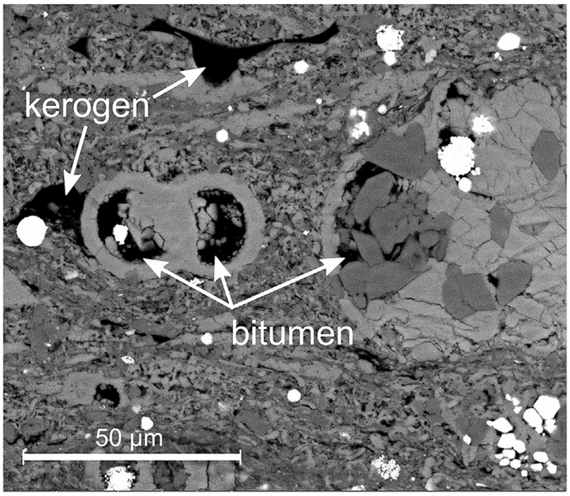

Fig. 1. Scanning electron micrograph (backscattered electron mode) showing organic matter in shale. In the image, bitumen occupies voids within fossil foraminifera tests that have been partially occluded by mineral precipitation. By contrast, kerogen is surrounded by tightly packed small grains.

properties of shales at the nanometer scale (e.g., Wilkinson et al., 2015; Eliyahu et al., 2015).

In this study, we use a new non-destructive technique, based on atomic force microscopy (AFM), to map the elastic moduli of the organic and inorganic components in shale samples that have experienced different levels of natural thermal maturation. Using the method we are able to obtain high resolution maps of mechanical properties for both kerogen and bitumen, and track the evolution of elastic modulus during catagenesis.

2. Methodology

2.1. Sample preparation and characterization

In this study we selected six organic-rich shale samples from three different levels of thermal maturation (increasing burial depth of the same formation). The samples are from a carbonate-rich Cretaceous source rock in the southern United States. At low thermal maturities, organic petrology point count data show that the organic component in the samples is dominated by Type II marine (alginite macerals) with a minor Type III (vitrinite and

Table 1
Summary of sample compositions.

Sample ID	%Ro	[a]TOC [%]	[b]Quartz [%]	[b]Calcite [%]	[b]Dolomite [%]	[b]Pyrite [%]	[b]Marcasite [%]	[b]Kaolinite [%]	[b]Illite + is* [%]	[b]Plagioclase [%]	[b]Apatite [%]	[b]Anatase [%]	[b]K-feldspar [%]
A1	0.40	3.26	33.6	37.9	2.7	3.6	1.5	17	2.3	0.6	0.1	0.1	0.7
A2	0.40	6.62	34.6	34.9	1.9	4.4	0.4	14.8	7.5	0.5	0.1	0.1	0.7
B1	0.82	6.42	18.5	58.4	0.8	2.4	0.7	2.8	11.3	3.9	0.6	0.1	0.6
B2	0.82	11.21	8	60.7	0.9	2.7	0.6	10.5	10.4	4.8	0.7	0.1	0.6
C1	1.25	3.23	14.2	61.1	0.1	2.7	0.8	0.8	15.2	4	0.2	0.1	0.7
C2	1.25	0.76	4.3	82.8	0.3	1.4	0.7	0	8.9	0.3	0.8	0	0.3

[a] Total organic content, (% of total mass).
[b] Values expressed as weight percentage of mineral phases only.

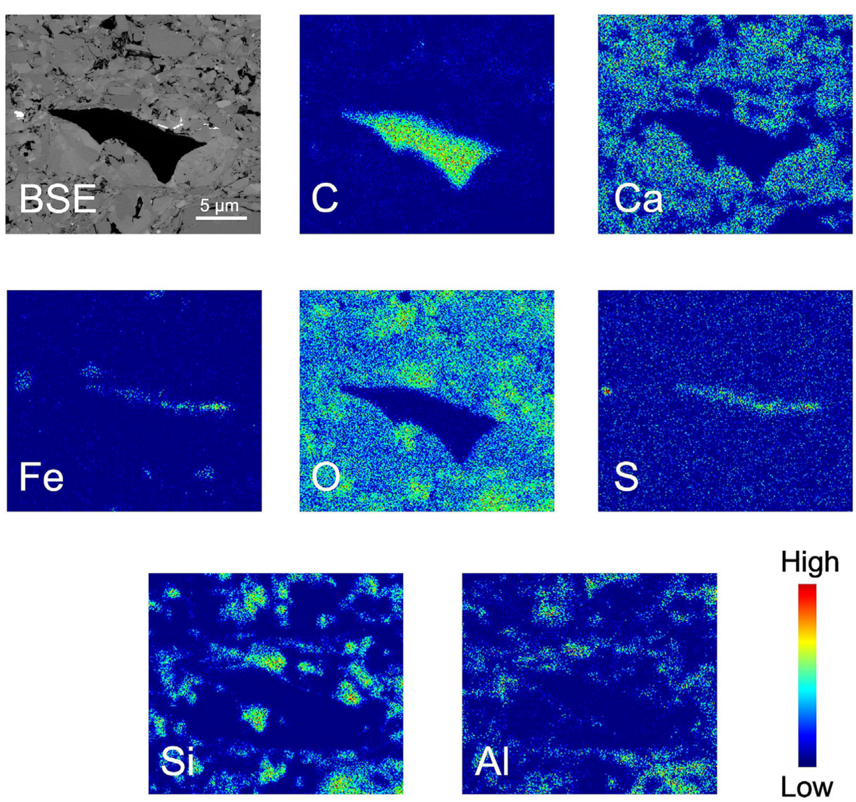

Fig. 2. Elemental maps – obtained using energy dispersive spectroscopy (EDS) – of a region of interest in one of the shale samples. The carbon map confirms that the dark region in the center of the BSE map is in fact organic matter. The primary mineral phases present are calcite, quartz, clays, and iron sulfide.