



## Reactivation of cation exchange properties in black shales



Arkadiusz Derkowski<sup>a,\*</sup>, Leszek Marynowski<sup>b</sup>

<sup>a</sup> Institute of Geological Sciences, Polish Academy of Sciences, Research Centre in Krakow, Senacka 1, PL-31-002 Krakow, Poland

<sup>b</sup> Faculty of Earth Sciences, University of Silesia, Będzinska 60, PL-41-200 Sosnowiec, Poland

### ARTICLE INFO

#### Article history:

Received 13 October 2015

Received in revised form 4 March 2016

Accepted 4 March 2016

Available online 5 March 2016

#### Keywords:

Black shale

Cation exchange capacity

Illite–smectite

Kerogen

### ABSTRACT

Cation exchange capacity (CEC) is among most important properties of sedimentary rocks, broadly applied in various means of geosciences research and industry. The organic matter (OM) in ancient black shales is thought to be a negligible source of cation exchange capacity (CEC), due to the loss of polar functional groups from extensive diagenetic transformations that occur during burial. OM in modern soils and sediments contains weakly bound hydrogen on carboxyl and phenolic hydroxyl groups, providing negatively charged functional groups that facilitate CEC on the order of hundreds of  $\text{cmol}_{(+)}/\text{kg}$ . Kerogen in ancient sediments may either retain a portion of polar oxygen groups or these functional groups can be (re)gained upon drying, revealing an overlooked source of charge in black shales.

Analyzing an extensive series of shales from the Baltic Basin (Poland) and Marcellus Shale (USA) with varying OM content and diagenesis we found that CEC, measured using Hexamminecobalt(III), of heated samples ( $\geq 200^\circ\text{C}$ ) is up to ten times greater than CEC measured on air-dry samples. Moreover, CEC measured on the heated samples is greater than theoretical CEC estimated from clay minerals composition. The excess CEC correlates with the content of oxygen-rich groups determined with OM pyrolysis and infrared spectroscopy. Carboxyl groups formed in OM due to thermal oxidation at temperatures ranging from  $200^\circ\text{C}$  to  $310^\circ\text{C}$ , in the presence of oxygen and under vacuum, are responsible for excess CEC. Our results reveal that kerogen in black shales is not chemically inert in the case of cation exchange and the OM can provide a considerable portion of the apparent CEC measured in bulk rock samples.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

The bulk rock cation exchange capacity (CEC) of a typical sedimentary rock is controlled almost exclusively by the type and abundance of clay minerals (Kaufhold, 2006; Śröder, 2009; Śröder et al., 2009; Kaufhold et al., 2010; Derkowski et al., 2015). Expandable clay minerals, including smectite, interstratified illite–smectite (I–S), and less common expandable interstratified clays (i.e. chlorite–smectite and kaolinite–smectite), contribute to the bulk CEC proportionally to their content in the rock, expandability (%S; percent of smectitic surfaces and interlayers), and surface charge density.

In modern sediments and soils, bulk CEC is dominated by clay minerals and organic matter (OM), while other components (opal, Al-, Fe-, and Mn-oxyhydroxides, zeolites) are either less abundant or participate mostly in anion exchange. The soil OM is rich in oxygen-containing polar functional groups (especially carboxyls), providing negatively charged surfaces with elevated CEC. In many modern environments, the CEC of OM exceeds levels measured in expandable clay minerals with high negative charge density, i.e. smectite and vermiculite (Parfitt et al., 1995; Kaiser

et al., 2008; Rengasamy and Churchman, 1999). While in recent soils and sediments bulk sample CEC is commonly partitioned between the clay minerals and OM, oxygen-containing polar groups have not been considered as a significant source of CEC in ancient sedimentary rocks.

Black shales and other OM-rich sedimentary rocks are subject to diagenesis upon burial, resulting in the loss of functional groups (O, N, H) as thermal maturation and hydrocarbon generation occurs. The loss of functional groups and polymerization is thought to eliminate the ionic nature of OM that is observed in modern soils and sediments. (cf. Allen-King et al., 2002; Vandembroucke and Largeau, 2007). Kerogen, however, retains a portion of these oxygen groups during diagenesis and maturation that react to form ester, carbonyl, carboxyl, ether, phenolic, quinone, hydroxyl, or ketone groups (e.g., Petersen et al., 2008). Their content decreases strongly with OM maturation, as expressed by the O/C ratio decrease from  $>0.3$  to  $<0.02$  (Robin and Rouxhet, 1978). Mild oxidation that is insufficient to remove OM completely (e.g., during weathering) leads to a significant increase in O/C ratio and produces a variety of O-rich compounds in kerogen (Landais et al., 1991; Rose et al., 1998; Faure et al., 1999; Petsch et al., 2000; Marynowski et al., 2011). Such oxidation could create OM surface activity and CEC via the formation of carbonyl and carboxyl bonds in a process similar to oxygenated biochar (Lee et al., 2013) or natural soil OM (Liang et al., 2006; Cheng and Lehmann, 2009).

\* Corresponding author.

E-mail address: [ndderkow@cyf-kr.edu.pl](mailto:ndderkow@cyf-kr.edu.pl) (A. Derkowski).

Using a spectrophotometric method of CEC determination of Orsini and Remy (1976); Derkowski and Bristow (2012) found that heating at >200 °C strongly increased CEC in certain OM-rich shales and the extent of CEC increase can correlate with the total organic carbon (TOC) content. They speculatively suggested that heating activates certain structural components of OM, which may involve deprotonation of carboxylic acids, increasing the negative charge density thus attraction of cations to the OM surfaces. The mechanism of OM activation, however, was not explained by Derkowski and Bristow (2012), and the OM susceptibility to thermal activation upon drying seemed not consistent among black shales.

Drying a rock by heating under vacuum or in air is commonly used to remove adsorbed water from rocks and minerals during pretreatment for numerous analytical techniques in geoscience, oil & gas industry, raw materials mining and processing, and mineral technologies (e.g., drying at 200 °C; Środoń and McCarty, 2008; Kuila et al., 2013, 2014). If drying was confirmed to alter OM properties, the validity of CEC analyses of black shales could be questioned. Because in petrophysics, CEC is linked to immobile, adsorbed water of particular properties, excess CEC in black shales may overestimate the quantity of adsorbed water on clay surfaces, leading to effective porosity underestimation when using conventional dual water theory (Clavier et al., 1984; Revil et al., 2013). Moreover, because kerogen can be naturally rich in carboxyl groups, the effect of CEC-bearing OM can potentially occur even without artificial oxidation. For these reasons, the effect found by Derkowski and Bristow (2012) needs to be tested and explained.

CEC determination using the spectrophotometric Hexamminecobalt (III) assay provides a fast and reliable method that avoids numerous problems associated with conventional cation exchange methods (Orsini and Remy, 1976; Aran et al., 2008; cf. Dohrmann and Kaufhold, 2009), despite certain pitfalls identified at reducing conditions (Hadi et al., 2016). Therefore, it is broadly used in hydrocarbon exploration, including oil- and gas-shales (cf. Derkowski et al., 2015). Because Hexamminecobalt(III) adsorption on humic acids (Ghabbour et al., 2006) or a partially oxidized carbon (Tomita and Tamai, 1971) can serve as a model for adsorption on natural OM, CEC methodology with Hexamminecobalt(III) cation can be used to probe changes in kerogen surface activity (Derkowski and Bristow, 2012; cf. Allen-King et al., 2002).

Using the Hexamminecobalt(III) method, we investigated changes in the CEC of black shales from marine and terrigenous environments at various states of maturity. The aims of the present study are to (a) characterize the conditions that lead to the surface activation of ancient kerogen by thermal oxidation, (b) determine what type of functional groups form the surface charge, (c) test the extent of OM activation in a function of OM maturation suggested by Derkowski and Bristow (2012). By characterizing this process, we will provide insights into the OM surface charge in black shales, which has traditionally been overlooked as a source of CEC.

## 2. Materials and methods

### 2.1. Samples

The lowermost Silurian strata of the Baltic Basin (northeast Poland) were deposited on a Paleozoic continental slope that underwent subsequent subsidence, resulting in present-day depths of 1400 to 5700 m in the NW–SE transect. The samples are represented by an OM-rich shale that has recently become a target for shale gas exploration (e.g. Poprawa, 2010). The samples were collected from geochronologically equivalent strata of Llandovery from eleven boreholes spread across several hundred km of the declining slope of the Baltic Basin. The collected set represents a complete sequence of burial diagenesis, from the beginning of the oil window to post-mature stage (Kuila et al., 2014; Topór et al., under review). Another set of samples were collected from a shale gas borehole drilled in the Middle Devonian Marcellus Shale of the Appalachian Basin (Pennsylvania, USA), at a depth of  $\sim 1500 \pm 20$  m. Due the narrow depth range of the section, OM

maturation in the collected samples does not vary, opposite to the Baltic Basin series.

### 2.2. Sample pretreatment

Bulk rock was gently crushed by hand with a mortar and pestle and passed through a <0.4 mm sieve, then homogenized and split into representative portions. Portions of 0.5 to 1 g of powder were dried at  $\leq 60$  °C for 2–12 h in a laboratory dryer with air circulation, only to remove pore water and weakly bound adsorbed water (cf. Kuila et al., 2013). Some samples were not dried at all during laboratory procedures; instead they remained at  $\leq 35$  °C for extended period of time in a core storage. For practical purpose, all these samples are referred hereafter to as in an air-dry state. Thermal treatment was performed by drying 0.5–1 g portions in a low vacuum dryer (5–9 kPa) at 200 °C for 18 h. Selected sample subsets, where specified in text, were heated in a laboratory dryer with air circulation at various temperatures of 200 °C, 250 °C, and 310 °C, for 18 h. Each pretreatment was performed on a fresh portion of powdered rock.

A subset of twelve Baltic Basin samples representing an entire range of maturation and TOC content underwent OM removal using a 6% NaOCl solution adjusted to pH of 8.5 and subsequent dialysis to remove excess salts (Mikutta et al., 2005). The applied protocol, besides OM removal, oxidizes and removes pyrite; the method has been shown to produce little or no removal or alteration of minerals in black shale samples (Kuila et al., 2014).

Another subset of seven Baltic Basin samples (Table 1) was treated using the accelerated solvent extractor Dionex ASE 350 at extraction conditions of 60 °C, under 150 bars, and a solvent mixture of dichloromethane/methanol (5:1 vol.). After the procedure, all extractable OM fractions (bitumen) were removed, and the remaining OM was represented exclusively by kerogen. The samples were then converted into a Ca-form by multiple washing with  $\text{CaCl}_2$  in order to exchange all exchangeable cations into  $\text{Ca}^{2+}$ . Excess salt was removed by dialysis (Jackson, 1969).

Fifteen representative samples from both locations were used for a clay fraction extraction. Clay mineral composition was investigated in <2  $\mu\text{m}$  or <0.2  $\mu\text{m}$  grain size fractions, separated by chemical purification including carbonate removal, OM oxidation, and Fe-(oxy)-hydroxides removal followed by centrifugation (Jackson, 1969).

### 2.3. Analytical procedures

Mineral quantification in bulk samples was performed using X-ray diffractometry (XRD) analysis on a Thermo X'TRA diffractometer using the Chevron ETC proprietary Quanta software (Środoń et al., 2001; Omotoso et al., 2006). In this method the total dioctahedral Al-rich 2:1 layer clays (illite, muscovite, dioctahedral Al-rich smectite, interstratified illite-smectite) are quantified together (Środoń et al., 2001) and are referred to as the illite + smectite group (I + S).

Structural details of the clay minerals were identified and quantified using the XRD patterns collected on oriented specimens of extracted and Ca-exchanged clay fractions, in the air-dry state and after saturation with ethylene glycol (EG). Qualitative and quantitative clay minerals analyses were performed using a full XRD pattern computer simulation method (Sakharov et al., 1999; McCarty et al., 2009) with Sybilla software (Chevron ETC proprietary), employing the formalism described by Drits and Tchoubar (1990).

Fourier transform infrared spectroscopy (FTIR) was performed on bulk samples using a Thermo Scientific Nicolet 6700 instrument equipped with a diffuse reflectance FTIR accessory (DRIFT) Praying Mantis by Harrick company. Bulk powder was gently ground with KBr in 1:10 mass ratio to ensure homogenous mixing and analyzed as 100-scan averages with  $4 \text{ cm}^{-1}$  resolution ( $\Delta\nu = 2 \text{ cm}^{-1}$  by interferogram zerofill).

Download English Version:

<https://daneshyari.com/en/article/1752793>

Download Persian Version:

<https://daneshyari.com/article/1752793>

[Daneshyari.com](https://daneshyari.com)