

## ON THE PROBLEMS OF TOTAL SPECIFIC SURFACE AREA AND CATION EXCHANGE CAPACITY MEASUREMENTS IN ORGANIC-RICH SEDIMENTARY ROCKS

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**Abstract**—The increasing exploration and exploitation of hydrocarbon resources hosted by oil and gas shales demands the correct measurement of certain properties of sedimentary rocks rich in organic matter (OM). Two essential properties of OM-rich shales, the total specific surface area (TSSA) and cation exchange capacity (CEC), are primarily controlled by the rock's clay mineral content (*i.e.* the type and quantity). This paper presents the limitations of two commonly used methods of measuring bulk-rock TSSA and CEC, ethylene glycol monoethyl ether (EGME) retention and visible light spectrometry of Co(III)-hexamine, in OM-rich rocks. The limitations were investigated using a suite of OM-rich shales and mudstones that vary in origin, age, clay mineral content, and thermal maturity.

Ethylene glycol monoethyl ether reacted strongly with and was retained by natural OM, producing excess TSSA if calculated using commonly applied adsorption coefficients. Although the intensity of the reaction seems to depend on thermal maturity, OM in all the samples analyzed reacted with EGME to an extent that made TSSA values unreliable; therefore, EGME is not recommended for TSSA measurements on samples containing >3% OM.

Some evidence indicated that drying at  $\geq 200^\circ\text{C}$  may influence bulk-rock CEC values by altering OM in early mature rocks. In light of this evidence, drying at  $110^\circ\text{C}$  is recommended as a more suitable pretreatment for CEC measurements in OM-rich shales. When using visible light spectrometry for CEC determination, leachable sample components contributed to the absorbance of the measured wavelength (470 nm), decreasing the calculated bulk rock CEC value. A test of sample-derived excess absorbance with zero-absorbance solutions (*i.e.* NaCl) and the introduction of corrections to the CEC calculation are recommended.

**Key Words**—Bitumen, CEC, EGME, Kerogen, Organic Matter, Shale, Specific Surface Area.

### INTRODUCTION

#### *Clay mineral control on TSSA and CEC*

Apart from exotic lithologies rich in Fe-, Mn-, and Al-(oxyhydr)oxides and zeolites (*e.g.* Derkowski *et al.*, 2007), the bulk-rock TSSA and CEC are both interrelated and controlled almost exclusively by the quantity and type of clay minerals in the vast majority of sedimentary rocks (Środoń, 2009; Środoń *et al.*, 2009; Woodruff and Revil, 2011). To the oil and gas industry and in geotechnical applications, TSSA and CEC are among the most important physicochemical properties of clay-bearing sedimentary rocks and, thus, accurate measurement of these parameters is critical.

The TSSA of clays and clay-bearing rocks is measured by adsorption of polar liquids, the molecules of which cover external surfaces of crystallites and enter interlayer spaces of expandable clay minerals. The TSSA should not to be confused with specific surface area, SSA, which is usually measured using gas ( $\text{N}_2$ , Ar)

adsorption in a vacuum at low temperature (*e.g.* 77 K) and calculated from the BET or Langmuir equations. Under vacuum, expandable clay minerals are completely dehydrated with their interlayers collapsed; therefore, gas adsorption is mainly restricted to external clay surfaces (*e.g.* Dyal and Hendricks, 1950; Chiou *et al.*, 1993; Quirk and Murray, 1999; Derkowski *et al.*, 2012).

Among several polar liquids typically employed for TSSA determination (ethylene glycol, water, polyvinylpyrrolidone), adsorption of ethylene glycol monoethyl ether (EGME) offers the fewest methodological limitations and technical requirements and, therefore, is commonly used by geologists and in the oil and gas industry (Eltantawy and Arnold, 1974; Cihacek and Bremner, 1979; Tiller and Smith, 1990; Chiou and Rutherford, 1997; Quirk and Murray, 1999; Blum and Eberl, 2004; Środoń and McCarty, 2008; Kaufhold *et al.*, 2010a). In this method, the mass of EGME retained by a dried sample after stabilization in EGME vapor is used to calculate the TSSA, referred to hereafter as  $\text{TSSA}_{\text{EGME}}$ , using an assumed or experimentally derived factor of mass of EGME adsorbed per unit surface area (*e.g.*  $2.80 \text{ m}^2 \text{ TSSA/mg EGME}$ ; Tiller and Smith, 1990). By definition, the surfaces available for adsorption of polar liquids in layer silicates are the same as involved

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in cation exchange (Środoń and McCarty, 2008; Środoń *et al.*, 2009; Kaufhold *et al.*, 2010a, 2010b). This has led to debate regarding the mechanism of retention of polar liquids on clay minerals, with some researchers favoring the idea of cation solvation over the monolayer coverage of surfaces. Following several lines of independent evidence (Chiou and Rutherford, 1997; Ferrage *et al.*, 2007; Środoń and McCarty, 2008; Szczerba *et al.*, 2010), however, the present study assumed that EGME retention at medium partial pressure values reflects the physical availability of mineral surfaces, while the solvation of exchangeable cations is a minor factor.

Although a range of methods, based on the chemical analysis of exchangeable cations, is commonly applied in CEC measurements (Chapman, 1965; Czimerová *et al.*, 2006 and references therein), CEC determination *via* exchange with colorizing complex cations is the most widely used technique because the method is simple, accurate, and fast. In this approach, CEC is calculated from the degree of exchange of complex cations by a sample. Reducing the complex cation concentration in the supernatant solution causes a linear decrease in absorbance (color intensity) at a given wavelength, with respect to the initial absorbance of solution (Orsini and Remy, 1976; Bardon *et al.*, 1993; Dohrmann, 2006 and references therein).

To avoid underestimation of CEC and TSSA caused by the additional mass of adsorbed water on air-dried samples, an accurate dry sample mass must be obtained. In analytical chemistry and the oil and gas industry, extensive drying at 105–110°C is standard protocol for removing pore and surface-adsorbed water, after which a sample is considered anhydrous. This paradigm is, however, about to shift, at least in the case of clay-bearing rocks: Środoń and McCarty (2008) found that 200°C is the optimum drying temperature providing the most complete dehydration without inducing dehydroxylation of clay minerals while 105°C is an arbitrary temperature that results in mass loss of water of indeterminate origin. Incomplete removal of the clay-bound water (abundant in shales) decreases the measured values of the sample total porosity – a key factor for evaluation of an unconventional reservoir. Although drying at 105–110°C may cause underestimation of CEC and TSSA values, as a result of the inaccuracy of the measured reference dry mass, the error does not exceed several relative %, which is usually acceptable (Środoń and McCarty, 2008).

#### *EGME retention and CEC measurement in organic-rich rocks*

Recent shifts in hydrocarbon exploration targets, with a focus on shale gas, oil shale, and residual heavy bitumen have made the measurement of TSSA and CEC of samples rich in OM an essential requirement. Studies from soil science, however, reveal OM properties that may interfere with TSSA and CEC measurements. For

example, Chiou *et al.* (1988, 1990, 1993) and De Jonge and Mittelmeijer-Hazeleger (1996) showed that EGME and other polar organic liquids react with soil OM through partitioning in macromolecular compounds, giving artificially high TSSA values when computed using the EGME mass-surface area retention factor. Moreover, OM from both recent pedogenic and marine deposits (referred to hereafter as ‘soil OM’ and defined as recent marine or terrigenous precursors of OM in sedimentary rocks) contains a variety of functional groups that develop a surface negative charge compensated by exchangeable cations, at pH values above the point of zero charge. In particular, terrigenous and marine humic compounds have CEC values that are equivalent to or greater than pure smectite because of weakly bonded hydrogen on carboxyl and phenolic hydroxyl groups (Helling *et al.*, 1964; Rashid, 1969; Rengasamy and Churchman, 1999 and references therein).

A critical question that has remained unresolved is whether ancient sedimentary OM (in the geological sense, to be distinguished from the recent ‘soil OM’), subjected to compaction and diagenesis, exhibits similar properties to those of soil OM that can adversely affect TSSA and CEC measurements? Available evidence regarding the affinity of EGME toward OM in shales and other marine sedimentary rocks is conflicting. Similar values for retention of EGME before and after OM removal from sedimentary samples were observed by Tiller and Smith (1990) and Kennedy *et al.* (2002), and so suggested that OM does not react with EGME. In contrast, Larsen and Li (1997) and Larsen *et al.* (2002) presented evidence that Type I and Type II kerogens of different degrees of maturation react chemically with organic molecules and swell in polar organic liquids, although those liquids seem to react differently depending on the various major constituents of OM (Cornelissen *et al.*, 2005 and references therein). The similarity of kerogen (Larsen and Li, 1997; Larsen *et al.*, 2002) and soil humic acid (Chiou *et al.*, 1988) reactions with various organic liquids suggests that sedimentary OM may retain EGME *via* the mechanism demonstrated by Chiou *et al.* (1993) for soil OM.

Sedimentary OM, which consists largely of kerogen, is generally thought to lack the CEC that characterizes soil OM because all exchangeable sites in functional groups are considered to have been polymerized during burial (Vandenbroucke and Largeau, 2007). However, kerogen is known to undergo certain structural transformations and dehydration reactions upon heating to ~200°C, which has been recommended for obtaining the dry-mass of samples (compare the studies of LeBoeuf and Weber (2000) and of Larsen *et al.* (2005) with those of Środoń and McCarty (2008)). Nevertheless, the effect of drying on the CEC of sedimentary OM is unexplored. In addition, soluble and low-density organic components that cannot be

separated completely from the supernatant solution have the potential to increase absorbance when using visible light (VIS) spectrometry-based CEC determination methods, potentially leading to underestimation of CEC in OM-rich samples.

The examples above raise questions about the reliability of the analytical techniques used for measuring TSSA and CEC in OM-rich rocks. The goal of the present study was to present the limitations and side effects of bulk-rock TSSA and CEC measurements on OM-rich shales, using EGME adsorption and VIS-spectrometry of Co(III)-hexamine, respectively.

## MATERIALS

Natural OM-rich samples from five locations with highly variable degrees of diagenetic maturation, from shallow burial (which have not entered the oil-generation window) to overmature, were used in the present study. Samples from the Miocene Monterey Formation (southern California) represent a conventional reservoir of heavy bitumen and are rich in biogenic opal, immature kerogen, and smectite-rich mixed-layer illite-smectite (I-S) (Isaacs, 1984; Compton, 1991). Black shale from the overmature Doushantuo Formation in Yangtze Gorges, southern China, of Ediacaran age, is composed of saponite- and corrensite-rich, dolomitic Member 2 and illite-dominated, OM-rich Member 4 (Peters *et al.*, 1996; Bristow *et al.*, 2009, 2011). Illite is also a major clay mineral in the early mature Upper Devonian Woodford Formation in Texas (Lewan, 1983; Morton, 1985). Late Cretaceous rocks collected from ODP site 959, section D, drilled in the margin of Ghana, west Africa, have been buried to ~1000 m only, and contain immature kerogen and smectite (Wagner and Pletsch, 1999; Kennedy and Wagner, 2011). Lastly, the sample set also included several thermally early mature samples from the Red Bird section of the I-S-rich Upper Cretaceous Pierre Shale in Wyoming (Schultz, 1978; Jones and Blatt, 1984; Kennedy *et al.*, 2002).

Selected samples with large total organic carbon (TOC) contents were treated with 6% NaOCl solution adjusted to pH 8 to remove organic compounds, following the procedures of Mikutta *et al.* (2005). Although this technique may not have completely removed all the sedimentary OM, the TOC content was reduced significantly, usually to <0.5%, occasionally remaining at 1–2% (unpublished results from other samples). The NaOCl-treated samples are referred to hereafter as ‘bleached.’

Kerogen was separated from samples of the Monterey Fm. and the Pierre Shale using mixed concentrated HF and HCl solutions, following the methodology of Lewan (1986). Ashing the separated kerogen by complete oxidization at 1200°C in air resulted in ≤7 wt.% of mineral residuum, which confirmed the efficiency of kerogen separation.

Prior to all analyses and treatments, natural samples were crushed and hand ground to pass through a 60 mesh (0.25 mm) sieve (W.S. Tyler, Mentor, Ohio, USA). Representative splits of the powder were taken for processing in CEC analyses and EGME adsorption.

## METHODS

The TOC was calculated by subtracting carbonate carbon from total carbon. The total carbon contents of powdered samples, dried for 12 h at 80°C, were measured using a Thermo-Finnegan Flash EA1112 analyzer (CE Elantech, Inc., Lakewood, New Jersey, USA). Repeated measurements of an aspartic acid standard indicated reproducibility of results of within 5%. Total carbonate carbon was determined by measuring the pressure change after acidification of samples with 20% HCl inside sealed-glass tubes.

The clay mineralogy was determined from <0.5 μm grain-size aggregates, separated from selected samples and from clays of the Source Clays Repository of The Clay Minerals Society, following common chemical purification and centrifugation techniques that involved carbonate removal, OM oxidization, and removal of Fe (oxyhydr)oxides (Jackson, 1969). The clay fractions separated from source clays SAz-1, SWy-2, and STx-1 consisted of pure smectite. The fractions were exchanged with Ca, Na, or K cations, depending on the actual measurement (Jackson, 1969). Clay fractions from selected shale samples were analyzed qualitatively and following the method by Moore and Reynolds (1997). The Rietveld-refinement based *Autoquan*® program (Bergmann *et al.*, 1998) and *Quanta* software (Chevron ETC propriety), which uses the mineral intensity factor method in conjunction with a collection of pure standards (Reynolds, 1989), were used for quantitative mineral analysis of bulk samples based on X-ray diffraction (XRD) patterns of samples prepared using the procedure described by Środoń *et al.* (2001).

### *CEC measurement of sedimentary rocks*

The overall contribution of clay minerals to CEC (and TSSA) can be expressed conveniently as the smectite equivalent content (Środoń, 2009; Środoń *et al.*, 2009), which is the theoretical weight fraction of pure smectite in the bulk rock that would give an equivalent TSSA or CEC. The smectite equivalent represents the sum of all mineral surfaces available for adsorption and cation exchange and is dominated by the external surfaces of clay minerals and interlayer space of expandable clays. Clay minerals, including smectite, mixed-layer I-S, and mixed-layer expandable varieties of other common clay minerals (*i.e.* chlorite-smectite and kaolinite-smectite), contribute to the smectite equivalent proportionally to their expandability (%S). Discrete illite is a minor contributor, while other micas and non-expandable clays like chlorite and kaolinite have

negligible impact on the smectite equivalent. In general, the %S and quantity of I-S are the main factors determining bulk-rock CEC and TSSA in the majority of rocks, while chlorite-smectite and kaolinite-smectite contents are minor and uncommon (Środoń *et al.*, 2009; Woodruff and Revil, 2011). Because pure smectite has, on average, CEC values of ~100 meq/100 g (Środoń and McCarty, 2008), measured bulk-rock CEC should roughly equal bulk-rock smectite equivalent.

The CEC was determined using VIS spectrometry (Shimadzu UVmini-1240) and Co(III)-hexamine chloride solution at pH ≈ 7, following the method of Orsini and Remy (1976) and Bardon *et al.* (1993). Co(III)-hexamine stock solutions at absolute concentrations of 14.95 mM, 7.48 mM, 3.74 mM, and 1.5 mM were prepared and used to measure samples with different ranges of CEC values (Bardon *et al.*, 1993). A pre-dried sample (0.5–1 g) was mixed with 25 mL of the stock solution, shaken, and treated with ultrasound for 2 min, then centrifuged for 10 min at 5000 rpm (≈4000 × g). The absorbance of the supernatant solution, analyzed at a wavelength of 470 nm, depended linearly on the amount of [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> cation sorbed by the tested material.

The fundamental CEC calculation from spectroscopic measurement was as follows:

$$CEC = 100v \frac{C_{st} V_{st}}{M_{CoH}} \left( 1 - \frac{Abs_{CoH}}{Abs_{st}} \right) \quad (1)$$

where  $C_{st}$ ,  $V_{st}$ , and  $Abs_{st}$  represent concentration, volume, and absorbance of the stock solution, respectively, while  $v$  is the valence of the exchangeable cation (3 for Co(III)-hexamine).  $Abs_{CoH}$  is the absorbance of the Co(III)-hexamine solution after mixing with a sample of mass  $M_{CoH}$ . The standard deviation of CEC measurements ( $1\sigma$ ) was determined as 1.4 meq/100 g, based on repeated measurements of a source clay sample, which is in accordance with the value of 4.6 meq/100 g ( $3\sigma$ ) reported by Dohrmann and Kaufhold (2009) for bentonites. The CEC detection limit is assumed to be 0.5 meq/100 g.

The effect of heating on CEC values was determined by comparing values of bleached and unbleached samples dried overnight at 110°C (CEC<sub>110</sub>) and 210°C (CEC<sub>210</sub>). In addition, one sample was analyzed in an air-dried state (no pre-drying). The validity of the CEC values measured was assessed independently based on the clay mineralogy and abundance of clays in the samples studied.

To test the degree to which soluble and low-density organic components derived from samples increase absorbance at 470 nm, samples were mixed with 45 mM or 15 mM NaCl solution instead of Co(III)-hexamine chloride and their absorbance measured as above. These NaCl solutions contained the same anion molar concentration and equivalent exchangeable cation

content as the 15 mM and 5 mM Co(III)-hexamine solution, respectively.

#### *Determining the affinity of EGME for sedimentary OM*

Pure smectite has CEC values that range from 80 to 120 meq/100 g and TSSA ranging from 700 to 770 m<sup>2</sup>/g (Laird, 1999; Środoń and McCarty, 2008). In smectite, the actual value of CEC depends on its layer-charge density and molecular weight, while the value of TSSA depends only on molecular weight; in general, the greater the Fe content, the lower the CEC and TSSA due to increased molecular weight (Blum and Eberl, 2004; Środoń and McCarty, 2008). In common diagenetic environments, such as sand-shale hydrocarbon reservoirs, the ranges of typical TSSA and CEC values of the smectitic end-member in I-S are limited because of a narrow range of surface-charge density ( $Q_s = 0.42 \pm 0.03$ , for data with bulk-rock CEC >5 meq/100 g, figure 7 in Środoń, 2009) and a general lack of Fe-rich I-S (Środoń and Eberl, 1984; Środoń *et al.*, 1992). The TSSA/CEC ratios, therefore, fall within a narrow range of values. As a result, TSSA can be predicted from bulk-rock CEC and *vice versa* for the majority of clay-bearing rocks, using a TSSA/CEC ratio of ~7.5 ± 0.5 (Środoń and McCarty, 2008; Środoń, 2009). Therefore, in the present study,  $TSSA_{CEC} = CEC_{110} \times 7.5$ .

Although the difference between  $TSSA_{CEC}$  and  $TSSA$  calculated from EGME retention ( $TSSA_{EGME}$ ) of a sample should ideally be zero, some discrepancy is expected because of minor deviations in TSSA/CEC ratios related to fluctuations in  $Q_s$  values of natural samples. Furthermore, errors in  $TSSA_{EGME}$  measurements may arise because of capillary condensation effects and non-ideal EGME molecular coverage on surfaces with variable crystallochemical features (Quirk and Murray, 1999). Generally, however, the  $TSSA_{CEC} - TSSA_{EGME}$  difference should not exceed 20% (relative) or tens of m<sup>2</sup>/g (Laird, 1999; Środoń and McCarty, 2008; Środoń *et al.*, 2009; see also Table 1). When the value of  $TSSA_{EGME} - TSSA_{CEC}$  is significantly greater than these expected discrepancies, the sample must contain a component that contributes to  $TSSA_{EGME}$  much more than to  $TSSA_{CEC}$ .

The EGME adsorption was performed using the procedure of Cihacek and Bremner (1979). Inert cups containing sample powder were first dried at 105°C overnight then filled completely with EGME liquid and loaded into a large sealed chamber with dry CaCl<sub>2</sub> and connected to a centralized low-vacuum system (~100s torr). After ~3 weeks the samples were weighed every couple of days until they reached a stable mass, a point at which all excess EGME was assumed to have evaporated. Each set of natural samples analyzed was accompanied by SAZ-1 smectite powder, which had a TSSA of 760 m<sup>2</sup>/g (Środoń and McCarty, 2008). The experimental TSSA values of bulk samples were calibrated based on the EGME retention of accompanying Ca-

Table 1. Mass of EGME retained and TSSA calculated for Source Clays and separated organic matter.

Sample	CEC <sub>110</sub> (meq/100 g)	EGME retention (mg/g)	TSSA <sub>EGME</sub> * (m <sup>2</sup> /g)
Smectite SAz-1 <sup>a,b</sup> < 0.5 μm Ca <sup>2+</sup>	124.4, 122.0	277±9 (n = 11)	750±26
Smectite SAz-1 <sup>a</sup> < 0.5 μm Na <sup>+</sup>	118.1, 120.3	242	656
Smectite SAz-1 <sup>a</sup> < 0.5 μm K <sup>+</sup>	111.3	148	400
Smectite SWy-2 <sup>a</sup> < 0.5 μm Na <sup>+</sup>	93.3	251, 244	680, 659
Smectite STx-1 <sup>a</sup> < 0.5 μm Na <sup>+</sup>	76.1	222, 211	601, 571
Kaolinite KGa-1 <sup>a</sup> < 2.0 μm	0.9±0.6 (n = 4)	23±6 (n = 4)	62±17
Milled quartz	1.1±0.5 (n = 4)	8±4 (n = 3)	20±12
Red Bird separated kerogen #55		262	709
Red Bird separated kerogen #70		273	739
Monterey separated kerogen 22406-45	<0.5	318	860
Monterey separated kerogen 22406-46 <sup>c</sup>	<0.5	340±52 (n = 4)	921±140

\* Using the experimental factor 1000 mg/g EGME = 2708 m<sup>2</sup>/g

<sup>a</sup> Source Clay of The Clay Minerals Society

<sup>b</sup> CEC<sub>210</sub> = 122.5 meq/100 g

<sup>c</sup> TOC = 67%

and Na-saturated SAz-1. The average EGME retention value on the Ca-exchanged SAz-1 smectite measured over 11 experiments was 277±9 mg/g, close to the value reported by Środoń and McCarty (2008) (Table 1).

## RESULTS

### Validity of CEC values

The measured CEC<sub>110</sub> values followed the smectite equivalent predicted based on the mineral composition of the bulk rock and the clay fraction (Table 2). ODP samples contain 20–50 wt.% of I-S of high expandability, which in some cases is close to smectite (Kennedy and Wagner, 2011); therefore, the bulk-rock CEC values were expected to remain below 50 meq/100 g, while TSSA should not exceed 380 m<sup>2</sup>/g. Highly expandable I-S R0 is common in the Monterey Fm. samples, where the total clay content does not exceed 35%, resulting in expected CEC <30 meq/100 g and TSSA <250 m<sup>2</sup>/g (Compton, 1991). Total saponite and corrensite content below 30% in Member 2 of the Doushantuo Fm. gives a theoretical maximum CEC of ~30 meq/100 g and TSSA values <250 m<sup>2</sup>/g in the saponite-rich zones, and about half of these values in the corrensite-rich zones (Bristow *et al.*, 2009, 2011). Pure illite or I-S with low %S have CEC values of ~20 meq/100 g and TSSA ≤100 m<sup>2</sup>/g (Blum and Eberl, 2004; Środoń *et al.*, 2009). Bulk CEC and TSSA values of the samples from Member 4 of the Doushantuo Fm. containing <30% illite (Bristow *et al.*, 2009) and the shales from the Woodford Fm. that contain up to 50% illite (Morton, 1985) should, therefore, show proportionally lower values than those of pure illite (Table 2).

Regardless of the clay type, clay content, TOC content, diagenetic maturation, and geological origin,

the CEC<sub>110</sub> values measured on all the samples studied followed trends predicted by mineralogical constraints. Organic matter did not appear to contribute to TSSA<sub>CEC</sub>, even in the most OM-rich samples. The fact that CEC<sub>110</sub> values measured on kerogen separated from the Monterey Fm. samples (Table 1) were below the detection limit of 0.5 meq/100 g, supports the previous assertion that no TSSA<sub>CEC</sub> contribution from OM is expected, except under certain conditions (see paragraphs below). The CEC<sub>110</sub> data were concluded to reliably reflect the smectite equivalent content of samples. This conclusion permits the examination of (1) the affinity of sedimentary OM for EGME through comparison of TSSA<sub>EGME</sub> values with TSSA<sub>CEC</sub>, and (2) influence of pre-drying temperature on measured CEC values.

### Excess CEC and excess absorbance

The drying temperature affected bulk-rock CEC values to a much greater extent than can be accounted for by differential removal of adsorbed water (Figure 1, Table 2). CEC values of the samples from ODP site 959 increased from an average of 34 meq/100 g when pre-dried at 110°C to an average of 56 meq/100 g after drying at 210°C, with some samples tripling their CEC<sub>110</sub> values when preheated overnight at 210°C. The average CEC<sub>110</sub> value of Monterey Fm. samples was 21 meq/100 g while their average CEC<sub>210</sub> was 31 meq/100 g, a ~50% increase in CEC upon heating at 210°C. Regardless of the origin and composition of the samples from the Doushantuo Fm., including saponite-rich samples from Member 2 and illitic shale from Member 4, no consistent increase in the CEC values was observed. Repeated measurements of CEC<sub>110</sub> for natural ODP and Monterey samples gave results within the expected measurement error, while CEC

Table 2. CEC measurements after dehydration at 110°C (CEC<sub>110</sub>) and 210°C (CEC<sub>210</sub>). TSSA calculated from EGME adsorption (TSSA<sub>EGME</sub>) and CEC<sub>110</sub> measurement (TSSA<sub>CEC</sub>) for the samples studied.

Sample	TOC (%)	CEC <sub>110</sub> (meq/100 g)	CEC <sub>210</sub> (meq/100 g)	TSSA <sub>EGME</sub> (m <sup>2</sup> /g)	TSSA <sub>CEC</sub> (m <sup>2</sup> /g)	Excess TSSA (m <sup>2</sup> /g)	Excess CEC (meq/100 g)
<b>ODP site 959D – thermally very immature</b>							
Predicted values							
		— ≤50 <sup>a</sup> —		— ≤380 <sup>a</sup> —			
65R-6W 52-53	4.9	37.0		509	278	232	
65R-6W 57-58	4.7	39.0		446	293	153	
65R-6W 66-67	4.0	40.2	50.5	399	302	97	10.3
65R-6W 70-71	3.1	36.7		389	275	114	
65R-6W 78-79	2.0	32.3	29.2	375	242	133	-3.1
65R-6W 82-83	2.2	32.0		420	240	180	
65R-6W 90-91	3.3	33.6		472	252	220	
65R-6W 96-97	9.8	31.5		438	236	202	
65R-6W 98-99	11.4	33.0		541	248	293	
65R-6W 100-101	11.0	32.5	67.4	558	244	314	34.9
65R-6W 102-103	11.1	33.0	68.5				35.5
65R-6W 106-107	8.4	39.6	44.7	472	297	175	5.1
65R-6W 112-113	4.7	45.0	54.0				9.0
65R-6W 114-115	4.6	43.8		419	329	91	
65R-6W 120-121	4.0	41.0		413	308	106	
65R-6W 134-135	3.8	26.0	51.0	403	195	208	25.0
65R-6W 142-143	2.9	37.7	45.0				7.3
65R-7W 4-5	3.4	30.9, 30.7	37.3	417	232	185	6.4
65R-7W 10-11	4.3	28.2		628	212	417	
65R-7W 16-17	9.2	25.8	57.4				31.6
65R-7W 18-19	8.8	26.3		430	197	233	
65R-7W 21-22	9.1	20.4	60.2				39.8
65R-7W 22-23	9.6	23.5		390	176	213	
65R-7W 24-25	10.2	24.1		395	181	214	
65R-7W 26-27	10.2	26.0, 27.9	64.5	630	195	435	38.5
65R-7W 30-31	10.5e	32.2, 28.7, 29.6*	69.3				37.1
65R-7W 32-33	13.5	31.5	81.6	453	236	216	50.1
65R-7W 35-36	10.8	25.7	64.5	390	193	197	38.8
65R-7W 37-38	6.2	48.2	59.5	505	362	143	11.3
65R-7W 39-40	4.9	42.6	53.8				11.2
65R-7W 42-43	4.6	35.5	47.0				11.5
65R-7W 46-47	4.8	36.1		406	271	135	
65R 6W 106-107 (bleached)		44.2 <sup>†</sup>	45.6				1.4
65R 6W 134-135 (bleached)		27.3 <sup>†</sup>	41.7				14.4
65R 6W 142-143 (bleached)		39.1 <sup>†</sup>	42.5				3.4
65R 7W 4-5 (bleached)		32.3 <sup>†</sup>	36.6				4.3
65R-7W 6-7 (bleached)		33.0		307	248	59	
65R 7W 16-17 (bleached)		29.1 <sup>†</sup>	36.6				7.4
65R-7W 18-19 (bleached)		30.2		362	227	135	
65R-7W 22-23 (bleached)		32.0		370	240	130	
65R-7W 26-27 (bleached)		32.3		318	242	75	
65R-7W 28-29 (bleached)		30.5		327	229	99	
65R 7W 30-31 (bleached)		37.0 <sup>†</sup>	38.2				1.2
65R-7W 32-33 (bleached)		43.4	38.7	374	326	48	-4.8
65R-7W 33-34 (bleached)		40.2		331	302	29	
65R 7W 42-43 (bleached)		37.7 <sup>†</sup>	42.1				4.5
65R-7W 46-47 (bleached)		43.4		359	326	34	
<b>Woodford Fm. – thermally early mature</b>							
Predicted values							
		— ≤10 <sup>b</sup> —		— ≤50 <sup>b</sup> —			
3/23/00-04	11.2	5.9		165	44	121	
3/23/00-05	15.9	7.2		233	54	179	
3/23/00-06	13.2	1.9		206	14	192	
3/23/00-07	4.1	5.8		95	43	52	
3/23/00-08	5.8	1.9		82	14	68	
3/23/00-09	6.5	3.2		149	24	125	
3/23/00-10B	7.8	1.3		147	10	138	

Table 2 (contd.)

Sample	TOC (%)	CEC <sub>110</sub> (meq/100 g)	CEC <sub>210</sub> (meq/100 g)	TSSA <sub>EGME</sub> (m <sup>2</sup> /g)	TSSA <sub>CEC</sub> (m <sup>2</sup> /g)	Excess TSSA (m <sup>2</sup> /g)	Excess CEC (meq/100 g)
3/23/00-11	3.8	< 0.5		50	< 4	50	
3/23/00-12	0.3	10.8		60	81	-21	
3/23/00-13	0.5	10.3		69	77	-8	
3/23/00-14	4.8	3.1		77	23	54	
3/23/00-17	10.1	1.8		127	13	113	
3/23/00-18	3.5	<0.5		75	< 4	75	
3/23/00-19	3.5	2.6		115	19	96	
3/23/00-20	6.7	1.0		131	8	123	
3/23/00-21	11.3	2.8		145	21	125	
3/23/00-22	13.7	1.8		133	13	120	
3/23/00-24	0.6	1.6		60	12	48	
3/23/00-25	3.9	1.8		70	14	57	
3/23/00-26	8.6	3.1		116	23	93	
3/23/00-28	0.6	6.5		78	49	29	
3/23/00-29	1.6	7.6		85	57	29	
3/23/00-30	0.2	< 0.5		41	< 4	39	
<b>Doushantuo Fm., Member 4 – thermally overmature</b>							
Predicted values — ≤6° — — ≤30° —							
61705 2	2.3	4.6		62	35	27	
61705 3a	1.7	<0.5		38	<4	38	
61705 4	2.9	4.0		78	30	48	
61705 6a	1.0	<0.5		39	<4	39	
61705 7	3.2	3.0		74	23	51	
61705 8a	2.3	3.5		75	26	49	
61905 1	1.9	4.2	7.1	45	31	14	2.9
61905 3a	4.0	4.2		63	31	32	
61905 3b	0.9	1.0		45	7	38	
61905 4		4.6	1.4	53	35	18	-3.2
61905 5	5.0	4.5		86	34	52	
61905 7	5.5	4.4		110	33	77	
61905 8a	6.1	4.5		104	34	70	
61905 9	5.9	4.7	5.7	91	35	56	1.0
61905 12	7.4	3.4	2.9	107	26	81	-0.5
61905 13	10.1	5.1	10.1	135	38	97	5.0
<b>Doushantuo Fm., Member 2 – thermally overmature</b>							
Predicted values — ≤30° — — ≤250° —							
61104 15	1.2	13.0		105	98	8	
61104 17	0.6	14.0		94	105	-11	
61104 18	1.2	16.5		105	124	-19	
61104 27	1.2	28.0		198	210	-12	
61104 28	1.4	6.8		51	51	0	
61805 1a	1.9	6.3		54	47	7	
61805 1b	1.2	2.3		29	18	11	
61805 2	1.0	9.8	13.1	81	74	7	3.3
61805 3	1.1	6.0		40	45	-5	
61805-4A		11.2	13.1				1.9
61805 5	2.5	8.8	7.9	65	66	-1	-0.9
61805 6	2.2	6.1		60	45	15	
61805 7	2.4	6.0		69	45	24	
61805 8	1.9	10.7	13.2	68	80	-12	2.5
61805 9	1.6	13.1		117	98	19	
61805 11	1.7	13.0	12.2	87	97	-10	-0.7
61805 12	2.5	17.2	20.6	141	129	12	3.4
61805 13b	1.8	11.6		75	87	-12	
61805 14	2.9	18.5		127	138	-11	
61805-15	1.8	22.5	22.5				0
61805 18	1.7	10.1		54	76	-22	
61805 20	2.2	17.1	18.7	108	128	-20	1.6
61805-21		18.3	17.4				-0.9

Table 2 (contd.)

Sample	TOC (%)	CEC <sub>110</sub> (meq/100 g)	CEC <sub>210</sub> (meq/100 g)	TSSA <sub>EGME</sub> (m <sup>2</sup> /g)	TSSA <sub>CEC</sub> (m <sup>2</sup> /g)	Excess TSSA (m <sup>2</sup> /g)	Excess CEC (meq/100 g)
<b>Monterey Fm. – thermally immature</b>							
Predicted values		— ≤30 <sup>d</sup> —		— ≤250 <sup>d</sup> —			
60105-4	5.0	8.7		126	65	60	
60105-4a	2.3	9.1		126	68	58	
60105-7	4.6	7.1	28.4	137	53	83	21.3
60105-9	6.3	15.8		202	118	84	
60105-10	6.7	20.1		194	151	43	
60105-12	4.2	11.0		175	83	93	
60105-14	2.7	13.1	18.8	226	98	128	5.7
60105-15	0.9	<0.5		92	<4	90	
60105-41	0.7	10.2		165	76	89	
60105-42	1.7	8.6	14.0	206	65	142	5.5
60105-45	4.3	12.1		269	91	178	
60105-46	1.4	5.7		51	43	9	
60105-53	2.2	7.7		100	58	42	
60105-54	3.7	15.8	27.2	147	119	29	11.4
60105-55	5.3	21.6		154	162	-8	
60105-56	4.4	8.2		182	62	120	
22406-36	11.6	25.0	47.5	298	188	110	22.5
22406-39	12.3	38.7	54.9				16.2
22406-44	14.4	15.2	17.4	353	114	239	2.2
22406-50B	9.9	23.9	39.4				15.5
22406-50C	10.5	27.3	43.2				15.9
22406-42	13.7	33.8	47.2				13.4
22406-46	19.3	37.3	48.9				11.6
22406-40	11.0	26.4	33.4				7.0
22406-52	14.9	10.0	14.2				4.2
22406-45	18.0	10.3	15.7				5.4
22406-44 (bleached)		21.3	19.7				-1.6
22406-52 (bleached)	0.2	25.1	25.2				0.1

‘bleached’: samples treated with NaOCl solution to remove organic matter.

Excess TSSA = TSSA<sub>EGME</sub> - TSSA<sub>CEC</sub>.

Excess CEC = CEC<sub>210</sub> - CEC<sub>110</sub>.

Predicted CEC and TSSA values based on mineralogical constraints determined in this study and by <sup>a</sup> Kennedy and Wagner (2011), <sup>b</sup> Morton (1985), <sup>c</sup> Bristow *et al.* (2009, 2011), and <sup>d</sup> Compton (1991); \* measured without pre-drying (air dry);

† calculated as an OM-free sample based on the CEC<sub>110</sub> and TOC of an untreated sample analyzed after complete removal of virtual kerogen, where C<sub>OM</sub> is the concentration in average sedimentary OM (80%, Okiongbo *et al.*, 2005; Tissot and Welte, 1984).

$$CEC_{110(\text{noOM})\text{calc}} = \frac{CEC_{110}}{1 - \frac{TOC}{C_{OM}}}$$

measured on air-dried samples (*i.e.* no pre-drying), also gave equivalent values after the mass of adsorbed water was accounted for (Table 2). Furthermore, the difference between the CEC<sub>210</sub> and CEC<sub>110</sub> values measured on the same sample, termed hereafter ‘excess CEC,’ were negligible for bleached ODP and Monterey samples (Figure 1).

When plotted against TOC, excess CEC values from ODP samples showed a statistically significant linear correlation, R<sup>2</sup> = 0.77 (*n* = 18; Figure 2). A weak tendency to increase with TOC was observed for excess CEC values of Monterey samples, while no trend was observed for Doushantuo samples, regardless of their origin and mineral composition.

All the measured samples showed detectable absorbance at 470 nm wavelength when mixed with NaCl solutions (Table 3), which is termed ‘excess absorbance.’ The lowest absorbance (0.005), the same in the case of both NaCl solutions, was observed in a sample that contained 4.4% TOC, while much larger values (up to 0.019) were observed for samples with much more TOC. When absorbance (measured in relative units) was normalized to sample mass, the measurements showed a weak positive correlation between absorbance and TOC (Figure 3). In general, greater excess absorbance was observed when mixing the samples with the 15 mM NaCl solution than with the 45 mM NaCl solution.

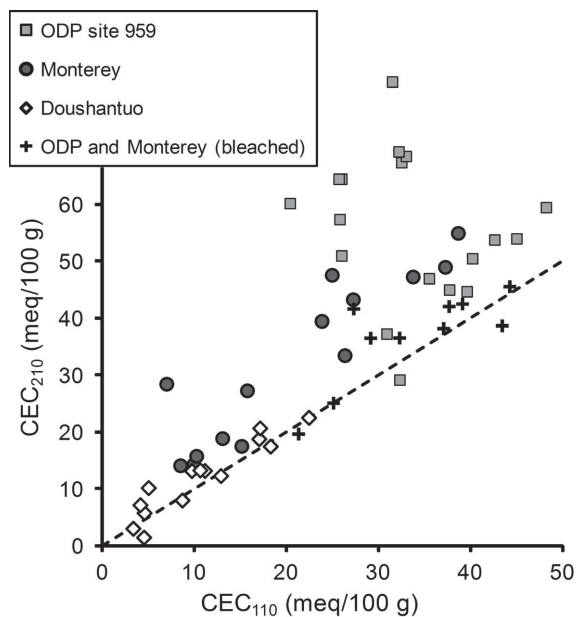


Figure 1. CEC values measured after dehydration at 210°C ( $CEC_{210}$ ) plotted vs. CEC values measured after dehydration at 110°C ( $CEC_{110}$ ) for the samples studied. The broken line shows the 1:1 ratio expected between the measured and calculated values.

#### EGME retention

For almost all the samples tested, the  $TSSA_{EGME}$  values greatly exceeded the  $TSSA_{CEC}$  (Figure 4,

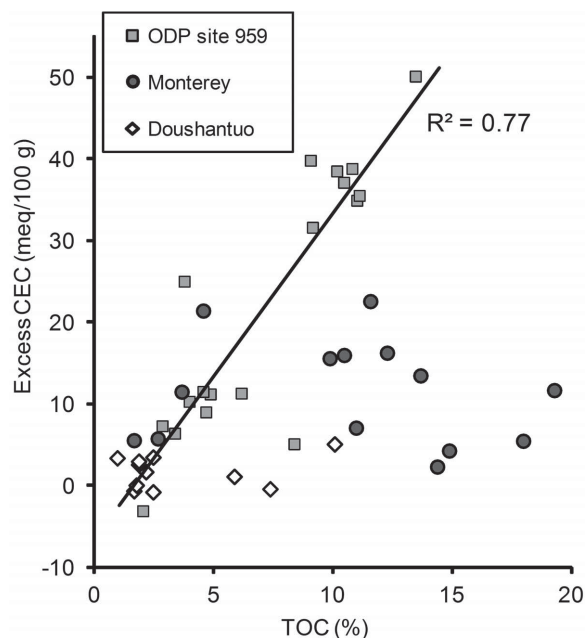


Figure 2. Excess CEC plotted vs. TOC. Excess CEC is the difference between CEC values measured on a sample pre-dried at 210°C and 110°C, respectively. The trend line and  $R^2$  value applies to 18 samples from ODP site 959.

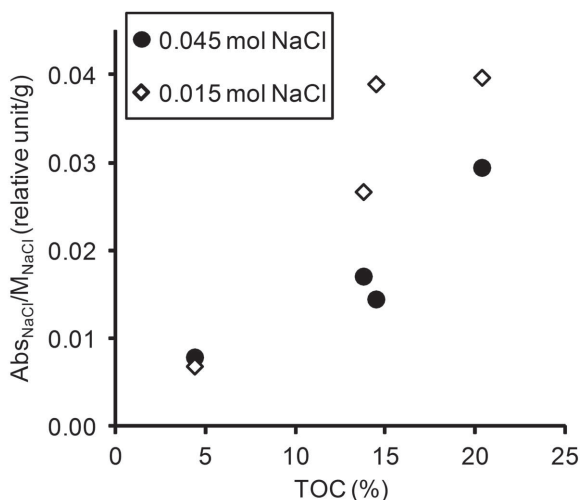


Figure 3. Absorbance of the supernatant NaCl solutions (excess absorbance) after mixing with OM-rich samples from the Doushantuo and Monterey Formations, normalized to the sample mass used (Table 3), plotted vs. TOC values. For abbreviations see equation 2.

Table 2). Only the OM-poor, smectite- and corrensite-rich samples from Member 2 of the Doushantuo Fm. showed a good correspondence between  $TSSA_{EGME}$  and  $TSSA_{CEC}$ . In contrast, the illitic OM-rich shales from Member 4 of the same formation showed a great excess of  $TSSA_{EGME}$ . The largest excess was observed in the illitic samples from Woodford Fm. that reached  $TSSA_{EGME}$  values several times greater than the  $TSSA_{CEC}$  values. The majority of Monterey samples had much greater values for  $TSSA_{EGME}$  than  $TSSA_{CEC}$ . All ODP samples did also. However, after application of the OM-removal procedure,  $TSSA_{CEC}$  and re-measured  $TSSA_{EGME}$  values became significantly closer (Figure 4, Table 2).

When the absolute difference between the  $TSSA_{EGME}$  and  $TSSA_{CEC}$  for a given sample, referred to below as 'excess TSSA,' was plotted against TOC, only data from Member 2 of the Doushantuo Fm. and a few other OM-poor samples showed excess TSSA close to or below zero. Both illitic OM-rich sections from the Woodford Fm. and Member 4 of the Doushantuo Fm. showed a clear correlation between the excess TSSA and TOC, while the ODP samples showed only a weak positive trend (Figure 5). The EGME retention values of ~270 mg/g and >300 mg/g were obtained for kerogen separated from Pierre Shale and Monterey Fm., respectively (Table 1).

## DISCUSSION

#### Effect of dehydration temperature on bulk-rock CEC measurement

While  $CEC_{110}$  values correspond closely to the expected values, based on the smectite equivalent

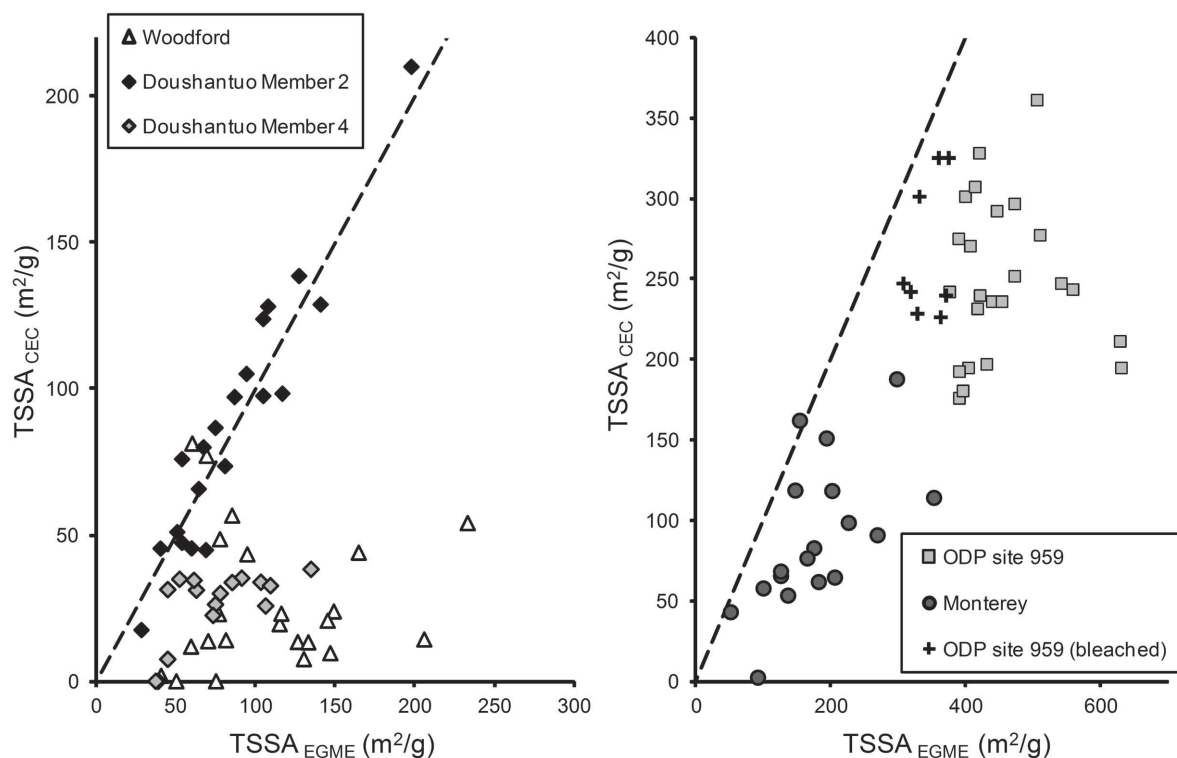


Figure 4. TSSA values calculated based on EGME retention ( $TSSA_{EGME}$ ) plotted vs. TSSA calculated from CEC ( $TSSA_{CEC}$ ). CEC was measured on samples pre-dried overnight at 110°C. The broken line shows the 1:1 ratio expected between  $TSSA_{CEC}$  and  $TSSA_{EGME}$  values.

estimated from mineralogical compositions of samples,  $CEC_{210}$  values, particularly non-bleached ODP and some Monterey samples, were well above reasonable limits imposed by the mineralogical composition. The results strongly suggest that drying at 210°C affected the CEC

of samples, and that this effect was probably linked to the presence of OM. Certain OM-rich samples gained CEC when heated to 210°C not observed after heating at 110°C. Unfortunately, the influence of the pre-drying temperature was not tested on separated kerogen.

Table 3. Sample supernatant absorbance at 470 nm after mixing with NaCl solutions, and the influence of the excess absorbance on CEC values determined using Co(III)-hexamine solution (for abbreviations see equations 1 and 2).

Sample	TOC (%)	$M_{CoH}$ (g)	$C_{st}$ (mM)	$Abs_{st}$ ( $I/I_0$ )	$Abs_{CoH}$ ( $I/I_0$ )	CEC (meq/100 g)	$M_{NaCl}$ (g)	$C_{NaCl}$ (mM)	$Abs_{NaCl}$ ( $I/I_0$ )	$Abs_{NaCl}/M_{NaCl}$	$CEC_{corr}$ (meq/100 g)	diff CEC (meq/100 g)
<b>Doushantuo Fm., Member 4</b>												
61905-15	13.8	0.726	14.95	0.835(1)	0.807	5.2	0.645	45	0.011	0.017	7.5	2.3
61905-15	13.8	0.753	7.48	0.418(1)	0.393	4.5	0.713	15	0.019	0.027	8.0	3.6
<b>Doushantuo Fm., Member 2</b>												
61104-20	4.4	0.712	14.95	0.835(1)	0.698	25.8	0.637	45	0.005	0.008	26.9	1.1
61104-20	4.4	0.720	7.48	0.418(1)	0.280	25.7	0.734	15	0.005	0.007	26.6	0.9
<b>Monterey Fm.</b>												
22406-44	14.5	0.718	14.95	0.835(1)	0.744	17.0	0.415	45	0.006	0.014	19.0	1.9
22406-44	14.5	0.637	7.48	0.418(1)	0.346	15.2	0.334	15	0.013	0.039	20.4	5.2
22406-45	20.4	0.722	14.95	0.835(1)	0.780	10.2	0.408	45	0.012	0.029	14.2	3.9
22406-45	20.4	0.617	7.48	0.418(1)	0.371	10.2	0.353	15	0.014	0.040	15.5	5.3

diff CEC: absolute difference between  $CEC_{corr}$  and CEC (equations 1 and 2).

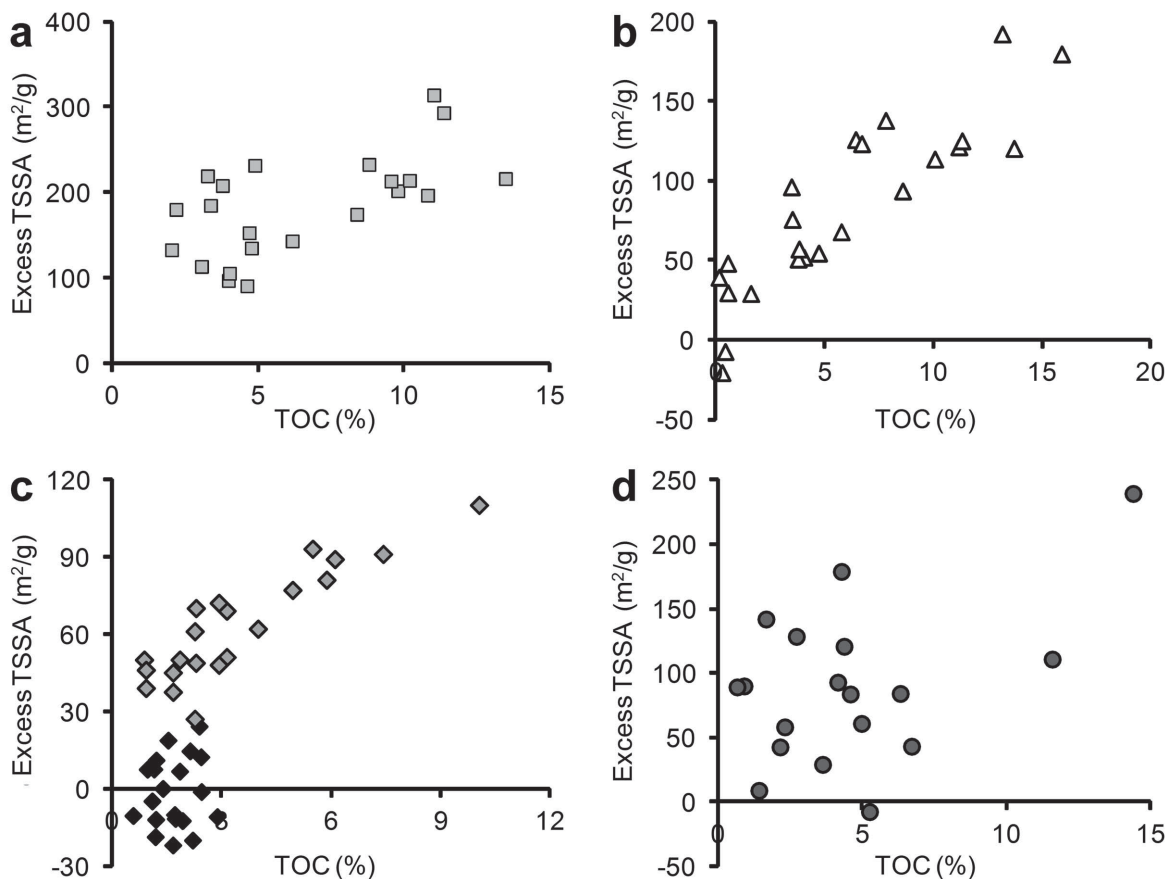


Figure 5. Excess TSSA plotted vs. TOC for samples from (a) ODP site 959, (b) the Woodford Fm., (c) the Doushantuo Fm., Member 2 – gray diamonds, and Member 4 – black diamonds, and (d) the Monterey Fm. As discussed in the text, excess TSSA is the TSSA measured by EGME retention and TSSA calculated based on  $CEC_{210}$  values.

The extent of the pre-drying temperature effect varied according to sample origin. In the case of highly mature Doushantuo Fm. samples (Peters *et al.*, 1996), the influence of OM on  $CEC_{210}$  values was negligible. The immature kerogen from ODP site 959, however, contributed to the bulk-rock  $CEC_{210}$  more than expandable clay minerals in these samples. Extrapolating the trend line in Figure 2, the  $CEC_{210}$  of pure OM contributed to bulk CEC as much as ~300 meq/100 g. A CEC contribution of similar magnitude has been reported for soil humus (Rashid, 1969; Asadu *et al.*, 1997; Rengasamy and Churchman, 1999 and references therein). Monterey samples showed no correlation between the excess CEC and TOC (Figure 2). The irregularity was probably a result of the mixed nature of OM; because of hydrocarbon migration, the variance in the proportions of kerogen and bitumen in the Monterey samples is large, probably leading to variable OM contributions to excess CEC.

The cation exchange properties recognized in soil OM probably do not disappear instantaneously when post-sedimentary burial starts and soil OM is trans-

formed into sedimentary OM. Thus, thermally immature sedimentary OM may be expected to contribute to bulk-rock CEC in the same way as soil OM. Regardless of the degree of thermal maturation, however, the contribution of sedimentary OM to the bulk-rock  $CEC_{110}$  was negligible or remained below detection limits. In contrast, heating to >200°C apparently caused physicochemical activation of the sedimentary OM surfaces.

Heating at temperatures lower than required for hydrocarbon generation and expulsion from kerogen probably triggers a reaction that forms negatively charged sites. These negatively charged sites then require charge-compensating cations and can undergo cation exchange. One possible reaction is analogous to glass-transition phenomena where amorphous domains of OM reorganize their structure upon heating. The glass transition occurs at various temperatures for different types of natural OM, from tens of °C in soil OM to >300°C in coal. Adsorbed water decreases the transformation temperature (LeBoeuf and Weber, 2000). The glass transition for kerogen and/or bitumen in the samples studied is, therefore, expected to lie within the

range of soil OM and coal. Such a transition may potentially create negatively charged sites available for exchangeable cations.

The low-temperature formation of carboxylic acid anhydrides seems to be another good candidate for a mechanism responsible for thermally activated CEC. Studying kerogen and kerogen-rich rocks, Larsen *et al.* (2005) observed the formation of anhydrous carboxylic acids accompanied by release of water molecules during heating between 50 and 180°C. Deprotonation causing a broken hydroxyl bond forms a carboxylate anion. If two carboxyl groups are adjacent to one another, they can form a carboxylic acid anhydride composed of two carboxyl groups sharing a common oxygen atom (Larsen *et al.*, 2005). However, because carboxyl groups cannot easily migrate in kerogen to find a partner for anhydride formation, most carboxyl groups in kerogen are likely to form carboxylate anions (Larsen *et al.*, 2005). The next step recognized in the thermal evolution of carboxylic acid anhydrides is decarboxylation resulting in a chain reaction that forms alkyl radicals and esters (Ashida *et al.*, 2005). This reaction has been found to occur in shales when heated to 200–250°C (Ashida *et al.*, 2005), similar to the experimental conditions in this study. Thus, negatively charged sites produced by thermal alteration of kerogen may be responsible for attracting additional cations from the solution.

The observed dependence of excess CEC on the degree of organic maturity of samples supports the suggested mechanism. The amount of carboxyl groups decreases with increasing kerogen maturity (Tissot and Welte, 1984), and so fewer carboxyl groups are available for deprotonation during the heating of a thermally mature kerogen. Experimental evidence also confirms that carboxylic acid anhydride formation decreases with increased thermal maturity (Larsen *et al.* 2005). The mechanisms of CEC activation presented here are highly speculative, however, and require further study to determine what degree of maturation and what types of organic matter are prone to thermal activation of CEC.

#### *Prevention of CEC measurement artifacts (excess absorbance)*

The excess absorbance can be taken into account in CEC calculations ( $CEC_{corr}$ ) as follows:

$$CEC_{corr} = 100v \frac{C_{st} V_{st}}{M_{CoH}} \left( 1 - \frac{Abs_{CoH} - \frac{Abs_{NaCl} M_{CoH}}{M_{NaCl}}}{Abs_{st}} \right) \quad (2)$$

where the term  $\frac{Abs_{NaCl} M_{CoH}}{M_{NaCl}}$  accounts for the excess absorbance determined with NaCl solution ( $Abs_{NaCl}$ ) normalized to the mass of sample used in both the NaCl ( $M_{NaCl}$ ) and Co(III)-hexamine ( $M_{CoH}$ ) experiments. This is justified because, while the sample mass used in the CEC measurement experiment varies a little, the solution volume,  $V_{st}$ , is kept constant in both experi-

ments. Within such a narrow range of solid/liquid ratios the excess absorbance can be assumed to vary linearly with sample mass. The difference between  $CEC_{110}$  and  $CEC_{corr}$  values are shown in Table 3.

The results from the TOC-rich Monterey Fm. samples, containing a mixture of immature kerogen and bitumen, probably represent a worst case scenario in terms of impact of excess absorbance on CEC measurements. In both analyzed Monterey Fm. samples, excess absorbance produced a bulk-rock CEC decrease of ~5.3 meq/100 g when using a 15 mM NaCl solution. Another TOC-rich sample (13.8% TOC) from the Doushantuo Fm. (sample 61905-15, TOC 13.8%), however, had 3.6 meq/100 g of CEC equivalent in the most dilute NaCl solution, which is less significant when compared to the CEC measurement error ( $\pm 1.4$  meq/100 g). In contrast, the low-TOC Doushantuo sample analyzed (TOC 4.4%) had CEC produced by an excess absorbance within the measurement error.

Based on these findings, the excess absorbance seems negligible for samples with TOC <10%, while this effect is probably detectable but not overwhelming in the samples with TOC >10%. Greater excess absorbance observed in 15 mM NaCl solutions compared with the 45 mM NaCl solutions can be explained as the result of lower solubility of absorbing compounds or better flocculation of fine particles in the more concentrated solution (Figure 3). Besides being influenced by OM, other sample components may also potentially contribute to excess absorbance.

#### *EGME retention on kerogen*

$TSSA_{EGME}$  values in OM-rich samples were much greater than those predicted by mineralogy (Figures 4 and 5, Table 2), thus confirming that  $TSSA_{CEC}$  values are more realistic than  $TSSA_{EGME}$ .

Theoretically, EGME retention in any micro- and mesoporous material may result not only from the adsorption on mineral surfaces but also from capillary condensation in the mineral matrix, although low EGME surface tension makes it less prone to mesopore filling. The capillary condensation, however, if significant, would occur as excess TSSA related to a mesoporous pore network in the mineral matrix, probably corresponding most to the clay mineral content. No such relationship was observed. Instead, data plotted in Figures 4 and 5 leave no doubt that OM is the most probable component that caused excess EGME retention in the studied samples. Extrapolating the relationships of excess TSSA and TOC (Figure 5b,c), the EGME retention on OM was estimated as being equivalent to ~1000 m<sup>2</sup>/g, which is greater than the TSSA of pure smectite. This estimation was verified independently by measuring EGME retention of separated kerogen; combining an experimentally derived EGME retention coefficient from pure SAZ-1 smectite of 2708 mg/g

(EGME/Clay) with the known TSSA of SAZ-1 of  $\sim 760 \text{ m}^2/\text{g}$  revealed that the apparent  $\text{TSSA}_{\text{EGME}}$  calculated for the separated kerogen reaches  $\sim 700\text{--}1000 \text{ m}^2/\text{g}$  (Table 1). The HF/HCl separation procedure does not create either greater porosity or increase the reactivity of the kerogen (Lewan, 1986; Vandenbroucke and Largeau, 2007); therefore, the measured values corresponded to the properties of natural kerogen in sedimentary rocks.

The most significant correlation between excess TSSA and TOC was predicted for low-smectite equivalent samples with large TOC, *i.e.* in OM-rich lithologies with either small total clay content and/or small overall clay-mineral expandability. Such a high correlation was indeed observed in illitic Member 4 of the Doushantuo Fm. and Woodford Fm. (Figure 5). Following the same logic, smectite-rich, TOC-poor samples were predicted to have small excess TSSA, as was observed in Member 2 of the Doushantuo Fm. In intermediate cases such as the ODP and Monterey Fm., when apparent TSSA is attributed in roughly equal proportions to smectitic minerals and OM, significant excess TSSA was expected, but the correlation with TOC was poor because of the combination of CEC,  $\text{TSSA}_{\text{EGME}}$ , and TOC measurement errors. As neither Soxhlet extraction nor the Dean-Stark procedure for bitumen removal was applied prior to analysis, additional scatter in excess TSSA vs. TOC was expected in Monterey samples which probably contain both heavy bitumen and kerogen that may have reacted with EGME to differing degrees (see discussion of OM components and their reactivity with organic compounds in Cornelissen *et al.*, 2005).

The results presented here from immature to over-mature sedimentary OM ranging in age from Ediacaran to Miocene all showed the same strong interactions with EGME as soil OM discussed by Chiou *et al.* (1990, 1993) and De Jonge and Mittelmeijer-Hazeleger (1996). Those authors found that the macromolecular portion of soil OM dissolves in organic liquids (such as EGME and EG) producing an extremely large “apparent surface area” if calculated using regular adsorption factors, while the surface area of soil OM measured by gas adsorption is in fact much lower. The intensity of interaction of sedimentary OM with EGME appears to have been variable in the samples studied. Less mature kerogen exhibited a stronger dissolution effect than more mature kerogen (compare Figure 5a with 5b and 5c). Despite the kerogen maturity, the interaction observed between OM and EGME was so strong that EGME is recommended only to measure TSSA of sedimentary rocks bearing  $<\sim 3\%$  OM (Figure 5c; Środoń, 2009 and unpublished data), or even less OM if a rock has a small smectite equivalent content. Above the  $\sim 3\%$  threshold, OM should be removed before the  $\text{TSSA}_{\text{EGME}}$  measurement (for details and methodology see Mikuta *et al.*, 2005), otherwise any geological or petrophysical interpretation based on the TSSA measured by means of EGME or EG adsorption may be meaningless.

In the OM- and I-S-poor samples from Member 2 of the Doushantuo Fm., a diagenetic saponite-corrensite-chlorite transition occurs within tens of m of the base of the succession as a result of localized hydrothermal activity (Bristow *et al.*, 2011). The good correspondence between  $\text{TSSA}_{\text{EGME}}$  and  $\text{TSSA}_{\text{CEC}}$  in these rocks suggests that the evolution of  $Q_s$  during chloritization of smectite may follow a similar mechanism as the illitization (Środoń *et al.*, 2009).

## CONCLUSIONS

(1) Heating at  $>200^\circ\text{C}$  can activate certain structural components of OM, contributing to bulk-rock CEC. A proposed explanation for this observation involves deprotonation of carboxylic acids, resulting in the formation of additional negatively charged sites which attract cations. The less mature the kerogen, the greater the amount of carboxylic groups, and consequently the greater the susceptibility to thermal activation and increased CEC. Pre-drying at temperatures of  $\sim 100^\circ\text{C}$  did not seem to trigger thermal activation, even in samples containing immature kerogen. Pre-drying at  $\sim 100^\circ\text{C}$  removes  $\geq 90\%$  of free and adsorbed water (Środoń and McCarty, 2008) and gives a reference dry mass that is sufficiently close to give reliable CEC data. When the initial texture of a shale sample needs to be preserved, gentle drying at  $60^\circ\text{C}$  under dry gas may be the most appropriate compromise to keep the fragile texture unaltered and remove the majority of adsorbed water for a ‘dry-mass’ reference. The mechanism of OM heat-induced reactivity and the potential contribution of sedimentary OM to bulk-rock CEC needs to be investigated carefully in the future.

(2) Natural samples may contain leachable components, gels, or particles that remain in suspension, causing absorption of visible light. When using VIS spectrometry for CEC determination, the leachable components of OM-rich sedimentary rock samples contributed to the absorbance at 470 nm, decreasing the calculated bulk-rock CEC values under certain conditions. A test of sample ‘excess absorbance’ with zero-absorbance solutions was applied successfully and is recommended by the present authors. If excess absorbance is significant, pre-washing a sample with water or taking the effect into account during CEC calculations is necessary. Alternatively, elemental analysis of the supernatant solution can be used to calculate the CEC, avoiding errors during VIS analysis.

(3) The EGME was found to react with natural sedimentary organic matter. Retention of EGME by OM-rich rocks produced excess TSSA values which were well beyond the limits imposed by sample mineralogy. An apparent TSSA of pure kerogen,  $\sim 1000 \text{ m}^2/\text{g}$ , was determined using common EGME-adsorption coefficients. Immature kerogen reacted with EGME more than mature kerogen, but the OM in all the

samples analyzed, including overmature shales, reacted with EGME to such an extent as to make TSSA<sub>EGME</sub> values unreliable; therefore, EGME is not recommended for TSSA measurement on TOC-rich rocks. OM <3 wt.% or even lower for samples with low smectite equivalent content is required for reliable TSSA measurement with EGME. Other polar liquids used for TSSA measurements may face similar difficulties.

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