MULTISCALE PROPERTIES OF UNCONVENTIONAL RESERVOIR ROCKS

by

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ABSTRACT

A multidisciplinary study of unconventional reservoir rocks is presented, providing the theory, forward modeling and Bayesian inverse modeling approaches, and laboratory protocols to characterize clay-rich, low porosity and permeability shales and mudstones within an anisotropic framework. Several physical models characterizing oil and gas shales are developed across multiple length scales, ranging from microscale phenomena, e.g. the effect of the cation exchange capacity of reactive clay mineral surfaces on water adsorption isotherms, and the effects of infinitesimal porosity compaction on elastic and electrical properties, to meso-scale phenomena, e.g. the role of mineral foliations, tortuosity of conduction pathways and the effects of organic matter (kerogen and hydrocarbon fractions) on complex conductivity and their connections to intrinsic electrical anisotropy, as well as the macro-scale electrical and elastic properties including formulations for the complex conductivity tensor and undrained stiffness tensor within the context of effective stress and poroelasticity. Detailed laboratory protocols are described for sample preparation and measurement of these properties using spectral induced polarization (SIP) and ultrasonics for the anisotropic characterization of shales for both unjacketed samples under benchtop conditions and jacketed samples under differential loading. An ongoing study of the effects of kerogen maturation through hydrous pyrolysis on the complex conductivity is also provided in review. Experimental results are catalogued and presented for various unconventional formations in North America including the Haynesville, Bakken, and Woodford shales.
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CHAPTER 1
INTRODUCTION

Shale oil and shale gas are of central interest as North American unconventional hydrocarbon reserves, representing an energy resource of equivalent size to the known conventional reserves worldwide. The prevalence of shale plays in the U.S. represents a significant factor in progress toward reducing American dependence on foreign oil. According to the 2012 U.S. Geological Survey National Assessment of Oil and Gas Project, the United States has over 36 billions of barrels of oil and 1,106 trillions of cubic feet of gas, representing 97% of the total discovered and undiscovered hydrocarbon resources in the U.S.: unconventional reservoirs account for more than half of the estimated resource. The majority of contemporary hydrocarbon resources of interest in North America are relegated to formations characterized by low porosity and low permeability. They are commonly referred to as unconventional resource plays (e.g., Bartis, 2005). This rather broad categorization encompasses many rock types with varied mineralogies ranging from clay- and carbonate-rich shales to marls, siltstone, and tight sandstone formations. Due to the “tight” nature of these rocks, typical permeabilities measure in the microDarcy and milliDarcy range, the production of these resources is only possible through hydraulic fracturing and stimulation techniques. Hence, detailed knowledge of the intrinsic material properties ranging from mechanical properties, strength and stress sensitivity, to the textural, mineralogical and transport properties, is of utmost importance to the successful stimulation and production of these reservoirs.

Shales are also some of the most diverse, complex materials found in nature, posing some unique and challenging problems in the exploration and development of these resources. SIP is a compelling approach to the study and characterization of shale rocks. It is a non-intrusive
measurement, sensitive to the surface conductance of the mineral grains, the frequency-dependent polarization of the electrical double layer, and the bulk conductance of the pore water. Therefore, the electrical response is dependent upon many parameters of principal importance in unconventional shale formation evaluation (e.g., the distribution of pore throat sizes, formation factor, \( m \) and \( n \), permeability, fluid saturation and wettability). Due to the intricate microstructure, characteristic directional dependence of the mineral fabric, and diverse interfacial properties, shales are also an ideal material for the scientific study of multiscale phenomena, electrochemistry, electrical and seismic anisotropy, physical and electrochemical properties of porous media. Measuring and quantitatively characterizing reservoir rock properties is integral to improving our knowledge of unconventional reservoirs.

This work is an integrated approach to 1) characterize the surface properties of clay minerals and their role in the fluid-surface interactions in shales 2) describe the effect of anisotropy on the complex conductivity of tight oil shales, and the related textural, physical and chemical properties, which govern the anisotropy, 3) provide a theoretical basis for the physics of SIP in shales and implement the theory in numerical analysis and inversion, 4) develop experimental protocols to study and characterize anisotropic, clay rich formations, 5) study the role of the effective stress on complex conductivity, and the implications of the stress-dependence of the electrochemical properties, 5) and relevant applications to the joint analysis of complex conductivity and ultrasonic data in rock physics and petrophysical analyses.

Background

The bulk electrical properties of shales are strongly dependent on the microscopic interaction of the pore fluids with mineral surfaces (Miller et al., 2007; Woodruff and Revil, 2011), as well as the nature of the rock fabric (Revil et al., 1998; Revil, 1999). The preferential
orientation of these properties produces a directional dependence in the SIP response, governed by the intrinsic (microscopic) properties of the medium. The induced polarization method (IP, both in the time domain TDIP, and frequency, or spectral, domain induced polarization SIP) has been used, historically, to measure the physicochemical nature of porous materials, proving to be a powerful tool in geophysics due to the sensitivity of the method to the textural, petrophysical and electrochemical properties. Recent models have been introduced to describe the nature of SIP in shales (e.g., Revil, 2012, Revil, 2013). The multiscale structure found in the organization of clays in sedimentary rocks also has known effects on their velocity dispersion, amplitude attenuation, and seismic wave speeds (Vernik and Liu, 1997; Vernik and Nur, 1992; Castagnede et al., 1998; Yang and Zhang, 2002), evidencing important connections between the macroscopic behavior of a material to the stress-dependent nature of its meso- and microscopic structure. Further, the effective stress coefficient (i.e., a modulating parameter which accounts for the stress-sensitivity of a material; it is often denoted $\alpha$ or $n$ (see Biot, 1956a,b, 1973; Todd and Simmons, 1972) has been shown to impact laboratory seismic measurements as a function of the relative change in porosity at a given stress state (e.g., Hofmann et al., 2005, and references therein). Compaction of the pore space, and corresponding changes in the mineralogical structure and orientation will also affect SIP measurements, due to the sensitivity of the electrical properties to changes in porosity. These physically distinct methods provide complementary information; the integration of rock physics measurements of the elastic parameters (elastic moduli, Poisson’s ratio, and rock strength) with electrical measurements dependent on the electrochemical, textural and petrophysical parameters governing transport and electromigration in porous media (e.g., porosity, permeability, fluid composition and saturation, as well as TOC, the maturation, specific surface area and distribution of kerogen, and wettability) will prove to be
of central importance in the characterization of the complex nature of shales and other unconventional reservoir rocks.

**Unconventional shale formations**

The term unconventional reservoir broadly refers to shale gas, coal bed methane, tight gas, heavy oil, and shale oil resource plays. The common thread among these vastly different types of hydrocarbon accumulations is that they are complex systems, with unique challenges associated with drilling, completion and production. As such, detailed knowledge and characterization of the material and transport properties is required to provide solutions for the successful development of unconventional resources plays. This study aims to answer some fundamental questions about the nature of shale formations, which comprise a large part of the unconventional resources under development today. Several formations will be studied, including the Haynesville, Bakken, and Woodford shales. A general overview of each of these formations is provided, below.

**Haynesville formation**

The Haynesville shale is a smectitic mudstone characterized by heterogeneous mineralogy located in the Texas-Louisiana Salt Basin. The formation varies compositionally, depending on the position in the stratigraphic column. *In situ* sampling in the field has revealed clay content of 30% (± 10%), 15% (± 10%) calcite, and 4% (± 3%) TOC, by mass (Spain and Anderson, 2010). These rocks are generally characterized by silty, argillaceous mudstones, silty, calcareous mudstones, and dolomitic mudstones and dolostones. Organic matter comprises Type II kerogen distributed in the argillite. The textural characteristics, and corresponding physical properties, are closely correlated with the calcite content; exhibiting laminated fabrics ranging on both the scale of the mineral foliations, as well as that of the depositional bedding planes. Recovered samples are fissile and exhibit decompressional stress fractures. Petrophysical
properties (as evidenced from both borehole and laboratory measurements) show a strong correlation to porosity, indicating that the rock-physics (including electrical properties) may be intrinsically tied to the mechanical characteristics of the Haynesville. Due to the relatively ubiquitous volume fraction of clay and homogeneous water saturations, both the porosity and the density are also tied closely to the calcite distribution (Skelt, 2011).

**Upper and Lower Bakken formations**

The Bakken formations in the Williston basin comprise a widespread oil shale accumulation of central interest in North America. It is one of the largest producing unconventional reservoirs, with an estimate of over 3.5 billions of barrels of oil in place. The interval is characterized stratigraphically by three formations named the Upper, Middle and Lower Bakken formations. The Upper and Lower Bakken units are shales, whereas the middle unit is mixed siliciclastic and carbonate lithology (due to characteristically low TOC, the Middle Bakken is not of interest in this study).

The upper Bakken shale is a poorly sorted, laminated formation composed of silt-sized grains. The extent of the laminations can vary across the basin. The upper shale is organic rich with TOC ranging from 5% to 25%, and consists of minor amounts of clay, silt, and dolomitic grains. The poorly-crystalline carbonaceous fraction can range from 5% to 25% (generally, in inverse proportion to TOC). Sedimentary structures from thinly laminated beds to massive, poorly sorted beds of silt-sized material (LeFever, 2008a). The maturity of the kerogen is 432° C on average, and the hydrogen index HI (a measure of the hydrogen content of the formation, normalized by that of water) is generally above 700 mg/g, with isolated zones below 200 mg/g.

The Lower Bakken shale is a fissile, non-calcareous, organic-rich shale, dark brown to black in color. The shale is characterized by extensive natural fracture networks, which are
subparallel to bedding and are generally oil wet. It is generally less organic than the upper shale; however, this relationship varies regionally throughout the basin. The organic matter appears to be distributed throughout the member; however, TOC can vary from 1% to 20%, on average. Quartz is the dominant mineral with minor amounts of muscovite, illite and other clays. Pyrite is present in lenses, laminations, or is finely disseminated throughout (LeFever, 2008b). Kerogen maturity and HI are equivalent to the upper member, averaging 432º C, with an HI generally above 700 mg/g.

**Woodford formation**

The Woodford shale is a widespread unconventional source rock in the Anadarko and Arkoma basins. Hydrocarbon plays in the Woodford are generally rich in silica (typically greater than 50% to 80% quartz and less than 15% total clay content by volume); they range in classification from carbonaceous to siliciclastic cherts and siltstones. The kerogen content of the gas shales is immature to marginally mature, with TOC ranging from 0.5% to 8%. Due to the relatively immature kerogen content, thermal effects on hydrocarbon production are of particular interest. Also, the intermediate maturity of much of the Woodford results in mixed wettability conditions due to the generation of bitumen in the early stages of kerogen maturation.

**Anisotropy**

The relevance of anisotropy in transport and material properties of interest in unconventional plays is well known. In shales, and more specifically clay-rich laminated rocks, the orientation of bedding planes and fractures (e.g., Dewhurst and Siggins, 2006), foliation of the mineralogical fabric (Bird, 1984; Katsube and Williamson, 1994; Sintubin, 1994; Ho et al., 1999), including the plate-like surface morphology of clay minerals and the layered structure of the crystalline lattice itself (e.g., Eseme et al., 2012), can all contribute to the nature and governing symmetry of the physical properties of the material (see Huang et al., 2009).
Furthermore, many kerogen-bearing shale formations are considered to be self-sourcing (i.e., the hydrocarbons are generated in place through geochemical maturation of the organic matter), lending to the central importance of understanding kerogen properties and derivative compounds, including oil, gas, bitumen, asphaltenes and resins.

The directional dependence of the physical properties of a medium are described using vector- or n-dimensional-valued functionals, or tensors. Tensors describe and account for the correlation of the anisotropic response of the medium to the directional components of external forces acting on that medium, and are generally described by a governing symmetry. In acoustics, we study the infinitesimal deformation of the medium resulting from an applied stress (refer to Fuck and Tsvankin, 2009, and included references for example elastic tensors and symmetries), whereas electrical methods study the potentials resulting from an applied electromotive force (e.g., Yi et al., 2011, for electrical anisotropy). Both phenomenologies include the frequency-dependent dispersion of the energy in the system.

Summary

The goal of this work is to understand the roles of anisotropy, mechanical properties and kerogen content on the electrical conductivity and physicochemical polarization mechanisms in shales and clay rocks. I developed methodologies to measure the directional dependence of electrical and acoustical properties in anisotropic shale samples, and relate these dependencies to the textural, mechanical, physical and chemical properties of unconventional reservoir rocks. With the support of my academic committee, research team including students from Geophysics and Petroleum Engineering at Mines, and in conjunction with academic, government and industry partners (the United States Geological Survey, USGS, North Dakota Geological Survey, NDGS, Chevron, and the University of Texas at Austin Formation Evaluation Consortium
members), I have studied the nature anisotropic induced polarization of shales. This interdisciplinary effort is centered on the SIP response in these rocks, but also employs ultrasonic rock physics, hydraulic loading experiments, BET sorption, and rudimentary thermogravimetric analyses. I have characterized the electrical anisotropy in shales, intrinsic connections to physical and chemical rock properties such as the surface conductivity, cation exchange capacity (CEC), formation factor and tortuosity, and a quantified connection between the mechanical stress-state and the electrical response. This work is a compilation of several research papers providing both the theoretical framework and laboratory protocols to measure and study unconventional reservoir rocks, advancing the state of the art in the fields of rock physics, geophysics, geomechanics and petrophysics.

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CHAPTER 2
CEC-NORMALIZED CLAY-WATER SORPTION ISOTHERM

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Abstract

A normalized clay-water isotherm model based on BET theory and describing the sorption and desorption of the bound water in clays, sand-clay mixtures, and shales is presented. Clay-water sorption isotherms (sorption and desorption) of clayey materials are normalized by their Cation Exchange Capacity (CEC) accounting for a correction factor depending on the type of counterion sorbed on the mineral surface in the so-called Stern layer. With such normalizations, all the data collapse into two master curves, one for sorption and one for desorption, independent of the clay mineralogy, crystallographic considerations, and bound cation type; therefore, neglecting the true heterogeneity of water sorption/desorption in smectite. The two master curves show the general hysteretic behavior of the capillary pressure curve at low relative humidity (below 70%). The model is validated against several data sets obtained from the literature comprising a broad range of clay types and clay mineralogies. The CEC values, derived by inverting the sorption/adsorption curves using a Markov Chain Monte Carlo approach, are consistent with the CEC associated with the clay mineralogy.

Introduction

The development of a unified model for coupled flow in unsaturated clayey materials is needed to model the transport of contaminants in clayey soils and through clay liners, to study the storage of nuclear wastes in argillaceous formations and to understand transport properties in gas shales (Mitchell, 1992; Sammartino et al., 2003; Delay and Distinguin, 2004; Rousseau-
We have recently developed a unified set of constitutive equations for the transport of ionic species in clay materials (Revil et al., 2011). The extension of this theory to the unsaturated case requires a precise analysis of the water retention curves in these materials, especially the clay-water sorption isotherms at low relative humidity (below 70%).

According to Saarenketo (1998), Aochi and Farmer (2010), and Conin et al. (2011), the pore water in clay materials can be divided into two important categories (i) hygroscopic water and (ii) capillary and free waters. In the present paper, we are especially interested in the sorption and desorption of the hygroscopic water. The hygroscopic (sorbed) water on the surface of a clay mineral is classically seen as consisting of (1) a monomolecular layer mainly located around the negatively charged mineral surface sites (with an approximate thickness of 2 nm) and (2) additional water molecules loosely bound to the mineral surface with a thickness on the order of 4 nm (Saarenketo, 1998). This kind of multi-layer model is the basis for several empirical relationships used in modeling sorption isotherms (see Cancela et al., 1997; Furmaniak et al., 2005; Limousin et al., 2007) in addition to physically-based sorption models (e.g., Tuller and Or, 2005). In the case of smectite, the hydration sequence is often described by the intercalation of 1, 2 and less commonly 3 water layers leading to the individualization of hydration steps on water sorption curves corresponding to 0, 1, and 2 water sheets in the interlayer. Deviation from this representation is usually associated with (i) hydration heterogeneity, i.e., the interstratification of layers with different hydration states that smoothen the sorption curve and (ii) capillary sorption in pore network at high relative humidity (Cases et al., 1997; Bérend et al., 1995; Ferrage et al., 2005; Michot et al., 2005; Ferrage et al., 2010; Malikova, et al., 2007).
This uniform layer model is challenged, however, by other researchers. For instance Laird (1999) suggested that instead of a uniform film, the water molecules are clustered around cation/charge sites. This implies that the cation exchange capacity, rather than the specific surface area, should be used to normalize clay-water sorption isotherms.

Clay-water sorption and desorption isotherms define the relationship between the water content and the relative humidity at a prescribed temperature and effective pressure. For clay minerals, the water content is given as the mass of water per gram of dry clay plotted as a function of the water activity (relative humidity). This water activity is defined as the ratio of the partial pressure of water to the saturation vapor pressure of the water phase. Sorption isotherms are observed to be hysteretic (Cancela et al., 1997; Likos and Lu, 2002; Shang et al., 1995). The amount of sorbed water in a given clay is known to be influenced by the texture of the clay material and therefore by its mineralogy (Stepkowska et al., 2004; Newman, 1983; Rinnert et al., 2005) and by the specific metal ion sorbed in the Stern layer, the inner layer of the electrical double layer (Salles et al., 2009; Dontsova et al., 2004; Montes-Hernandez et al., 2003; and Cancela et al., 1997).

The classical BET theory recognizes the strong correlation between the specific surface area and monolayer sorption of water (see the de-Boer t-curve approach and its application, Kowalczyk et al., 2005). In the present paper, we develop a normalized clay-water sorption isotherm by using the CEC of the clay material as a normalizing parameter. Saarenketo (1998) showed, for instance, that the dielectric constant of a clayey material is both correlated to the amount of water sorbed per unit weight of dry clay and to the CEC. The CEC is observed to be linearly related to the specific surface area of clay minerals (Newman, 1983; Revil et al., 1998, Srodon and McCarty, 2008; Salles et al., 2009; Conin et al., 2011) (see Figure 2.1). In addition,
Figure 2.1 Specific surface area of clay minerals (in m$^2$ g$^{-1}$) as a function of the (absolute) (in meq g$^{-1}$ with 1 meq g$^{-1}$=96,320 C kg$^{-1}$ in SI units) for various clay minerals. The ratio between the CEC and the specific surface area gives the equivalent total surface charge density of the mineral surface. Generalized regions corresponding to kaolinite, illite, and smectite are represented by shaded circles. Figure adapted from Revil and Leroy [2004]. The two lines corresponds to 1 to 3 elementary charges per unit surface area. Data from: Patchett [1975], Lipsicas [1984], Zundel and Siffert [1985], Lockhart [1980], Sinitsyn et al. [2000], Avena and De Pauli [1998], Shainberg et al. [1988], Su et al. [2000], and Ma and Eggleton [1999].

because of the clustering of the water molecules around the cations/charge sites, we suggest that the CEC of the mineral can be used as a better surrogate for the specific surface area in a normalized model, enabling the prediction of the clay-water sorption isotherm (including the hysteresis loop) from a single pair of master curves in the low relative humidity range (more precisely at low thicknesses of surface-sorbed water corresponding to one or two monolayers). The significant linear correlation between CEC, specific surface area, and hygroscopic water content has been shown earlier for soils (e.g., Banin and Amiel, 1970; Smith et al., 1985;
Yukselen-Askoy and Kaya, 2010). Therefore, it is evident that a similar model based on specific surface area normalized sorption may yield a similar master "water-retention curve". We will discuss the advantages of using the CEC instead of the specific surface area as the normalizing parameter later in this paper.

**Background**

In the present section, we discuss the relationships between the Cation Exchange Capacity (CEC), the specific surface area, and the density of sorbed water molecules in clay materials.

**The cation exchange capacity (CEC)**

The CEC represents the capacity of a porous material (generally a soil) to exchange cations (generally Ca, Mg, K, and Na) between the mineral surface and the pore water solution. It is generally measured at pH 7 (Carroll, 1959). The pH dependence of the CEC can only be understood in terms of the electrical double layer attached to the mineral surface. In SI units, the CEC is expressed in C kg$^{-1}$, but is classically expressed in meq g$^{-1}$ (with 1 meq = 1 mmol equivalent charge, e.g., $1 \times 10^{-3} eN$, where $e=1.6\times10^{-19}$ C and $N$ is the Avogadro constant, $6.022\times10^{23}$ mol$^{-1}$). For clay mixtures, the average CEC is determined from the respective exchange capacities of the constituent clay types. For example, the cation exchange capacity of a mixture of kaolinite, illite and smectite is given by (Rabaute et al., 2003),

$$CEC = \chi_K \text{CEC}_K + \chi_I \text{CEC}_I + \chi_S \text{CEC}_S,$$

(2.1)

where $\chi_i$ represents the mass fraction of mineral $i$, and K, I, and S stand for kaolinite, illite, and smectite, respectively. Equation 2.1 is scaled by the mass fraction of the clay minerals $\phi_i$, which can be obtained by XRD analysis. Equation 2.1 can be adapted to clayey sands and sandstones by neglecting the CEC associated with the silica grains (Rabaute et al., 2003).
Active surface sites at the edge of a. 1:1 clays (e.g., kaolinite) and b. 2:1 clays (e.g.,
smectite or illite). In the case of kaolinite, the surface sites are located primarily on the edge of
the mineral grain (\{110\} and \{010\} planes). In the case of smectite and illite (in the pH range
near neutrality, 5 to 9) the surface sites are predominantly located on the basal plane (\{001\}
plane) and they are due to isomorphic substitutions inside the crystalline framework. Note the
difference in the morphology of the clay particles and the variety of crystallographic planes. The
letters T and O represent tetrahedral and octahedral sheets, respectively. Adapted from Leroy and
Revil [2009].

The CEC is also linearly correlated to the specific surface area $S_{Sp}$ (in m$^2$ g$^{-1}$) of the
mineral grains (Patchett, 1975; Revil et al., 1998; Revil and Leroy, 2004; Yukselen and Kaya,
$CEC = Q_S S_{Sp}$, \hspace{1cm} (2.2)
where $Q_S$ (C m$^{-2}$) is the surface charge density of the clay fraction, which is related to the total
excess of electrical charge per unit pore volume $Q_V$ (expressed in C m$^{-3}$) as $Q_S = Q_V (S/V_p)^{-1}$,
where $S$ is the surface area of the mineral grain and $V_p$ represents the pore volume (see Figure
2.1). Figure 2.1 shows the linear data trend for the specific surface area, $S_{Sp}$ (in m$^2$ kg$^{-1}$), as a
function of the CEC. Revil et al. (1998) and Revil and Leroy (2004) obtained an equivalent
charge density comprised between 1 to 3 charges per nm$^2$ at pH 7 with an average surface charge
density of 2 elementary charges per nm$^2$ (Figure 2.1).

The type of crystalline planes at the mineral water interface varies considerably among
clay types. A sketch of two representative end-members, kaolinite and smectite, is provided in
Figure 2.2. Despite the complex crystalline structure of clay minerals, the properties of clays and
shales (like the surface electrical conductivity) depend mainly on macroscopic parameters like
the specific surface area and the CEC. In the water sorption case, this indicates that the sorption
Figure 2.2  Active surface sites at the edge of a. 1:1 clays (e.g., kaolinite) and b. 2:1 clays (e.g., smectite or illite). In the case of kaolinite, the surface sites are located primarily on the edge of the mineral grain (\{110\} and \{010\} planes). In the case of smectite and illite (in the pH range near neutrality, 5 to 9) the surface sites are predominantly located on the basal plane (\{001\} plane) and they are due to isomorphic substitutions inside the crystalline framework. Note the difference in the morphology of the clay particles and the variety of crystallographic planes. The letters T and O represent tetrahedral and octahedral sheets, respectively. Adapted from Leroy and Revil [2009].

Heats are generally independent of the type of crystalline planes and can be therefore similar for clays of different mineralogy.

The specific surface area can be obtained from water sorption isotherms by estimating the cross-sectional area of a water molecule $\epsilon$ (typically $\epsilon = 10$ Å² per molecule see Middleton,
Salles et al. (2009) use the following relationship to determine the specific surface area of a clay material from water sorption isotherms,

\[ S_{sp} = \epsilon n_m M_w , \]  

(2.3)

where \( n_m \) denotes the number of water molecules sorbed in a monolayer (in mol) and \( M_w \) is the molar mass of water (kg Mol\(^{-1}\)). It follows that the specific surface area can be obtained from the mass fraction of water in the sample during the first stage of sorption assuming, like the BET theory, that water sorbs by first filling a monolayer (no local condensation of packs of water molecules). However, this is a vast simplification, because capillary condensation on rough particle surfaces and clustering of water molecules around charge sites can be important. In addition, water sorption is also correlated to the ionic potential of the exchangeable cation sorbed on the active mineral surface sites present on different crystalline planes (see Figure 2.2) (Dontsova et al., 2004; Salles et al., 2009).

As discussed above, the CEC is an average parameter describing the sorption of counterions on the surface of the clay grains. The reality is, however, more complex: different crystalline planes, with different electrochemical characteristics, contribute to complex sorption behavior. For instance, a bivalent ion like Cu\(^{2+}\) can form both monodentate and bidentate complexes with the clay surface. For silica, the former occurs as an inner sphere ligand, and the latter occurs as an outer sphere ligand (Vaudelet et al., 2011a, b). To account for this complexity, we introduce an empirical scaling parameter \( \delta_i \) that depends only on the exchangeable cation \( i \) and is independent of the clay type. This parameter is used to scale the measured cation exchange capacity with a given cation \( i \) as,

\[ \text{CEC}_i = \delta_i \text{CEC} , \]  

(2.4)

where \( \text{CEC}_i \) is a value of the cation exchange capacity for ionic species \( i \), while CEC is the
absolute cation exchange capacity. The absolute cation exchange capacity is measured using a cation that has a very strong affinity with the mineral surface (like ammonium or cobalt); it corresponds to the cation exchange capacity reported in Figure 2.1. Other cations always have affinities smaller than the cations used to measure the absolute cation exchange capacity; therefore, $\delta_i \leq 1$ and $\text{CEC}_i \leq \text{CEC}$. A description of the empirical analysis performed to constrain the scaling parameter $\delta_i$ is provided below. The following set of values will be discussed: $\delta$(Li)=0.4, $\delta$(Na)=0.5, $\delta$(Mg)=0.6, and $\delta$(Ca)=0.8. The scaling parameter $\delta_i$ reflects the affinity of the cations for the mineral surface (i.e., the parameter is equal to one for cobalt and ammonium).

Relative humidity and water content

For the non-hydroscopic water and at thermodynamic equilibrium, the capillary pressure $p_c$ (in Pa) is classically defined as the pressure differential between the fluid and vapor pressures across an interface by the Young-Laplace equation,

$$p_c = \frac{2\gamma \cos\theta}{r},$$  \hspace{1cm} (2.5)

where $\gamma$ denotes the surface tension (N m$^{-1}$), $\theta$ the wetting angle (in rad), and $r$ the effective radius of the meniscus between the two phases (in m). Capillary pressure depends on the saturation of the wetting phase and the saturation/desaturation history in the porous material, and is defined as the difference of the pressures of the wetting (index $w$) and non-wetting (index $n$) phases,

$$p_c = p_n - p_w.$$  \hspace{1cm} (2.6)

The change in vapor pressure due to the shape of the meniscus with radius $r$ is given by the Kelvin equation
\[ RT \ln \left( \frac{p_v}{p_v^0} \right) = -\frac{2\gamma M_v}{r}, \]  

where \( M_v \) (m\(^3\) mol\(^{-1}\)) is the molar volume of water, \( p_v^0 \) is the vapor pressure of the reference state (saturated vapor pressure), \( R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \) is the universal gas constant, and \( T \) is the absolute temperature (in Kelvin). The saturation vapor pressure is given by (Likos and Lu 2002; Jougnot et al., 2010),

\[ p_v^0 = p_v^{sat}(T) = 10^{f(T)}, \]  

\[ f(T) = a + (T - T_0) \left[ b + c (T - T_0) \right]^{-1}, \]

where the superscript “0” indicates the saturated reference state (\( p_c = 0, \ p_w = p_v^0 = p_{am} \)), \( T_0 = 273.5 \text{ K}, \ a = 2.7858 \) (dimensionless), \( b = 31.559 \text{ K}, \ c = 0.1354 \) (dimensionless).

The relative humidity \( h_r \) (given usually in %) (alternatively, the water activity \( p_v / p_v^0 \)) can be related to the pressure of the water phase by (Shang et al., 1995),

\[ h_r \equiv \frac{p_v}{p_v^0} = \exp \left[ \frac{M_v}{RT} \left( p_w - p_w^0 \right) \right]. \]  

The connection between the volumetric or gravimetric water content associated with the adsorption of water molecules onto a charged mineral surface and the water saturation \( S_w \) is easily established. The volumetric water content \( \theta \) is defined as the ratio of the volume of water \( V_w \) to the total volume of the medium \( V_T \); porosity \( \phi \) is defined as the ratio of the void volume \( V_v \) to the total volume \( V_T \); water saturation, \( V_w / V_T \), can be written as,

\[ S_w = \frac{\theta}{\phi}. \]  

Water saturation can also be obtained from the gravimetric water content \( v \) (dimensionless). The gravimetric water content represents the mass of water divided by the mass of mineral grains. It is normally measured by taking the weight of a moist sample and the weight of a dried sample of
the same material, which yields $\theta = \nu \rho_{\text{dry}} / \rho_w$, where $\rho_{\text{dry}} = (1 - \phi) \rho_g$ represents the mass density of the dry porous material, $\rho_g$ the mass density of the grains (typically 2600 to 2800 kg m$^{-3}$), and $\rho_w$ the density of the pore water (all in kg m$^{-3}$). Using this relationship together with Equation 2.11 yields,

$$S_w = \frac{1 - \phi}{\phi} \frac{\rho_g}{\rho_w} \nu .$$  (2.12)

**Modeling water sorption isotherms**

Sorption isotherms represent the retention and/or release of liquid compounds on a solid interface (Limousin et al., 2007). Numerous empirical and mechanistic models have been developed to characterize sorption phenomena, resulting in several general isotherm types (Brunauer et al., 1938; Broekhoff and Boer, 1967a; Gauden, 2005; Limousin et al., 2007), which have been empirically validated in the literature for macroscopic phenomenology and simplified micro-scale geometries (see Broekhoff and Boer, 1967b; Cancela et al., 1997; Neimark and Ravikovitch, 2001; Ravikovitch and Neimark, 2002; Furmaniak et al., 2005). Water sorption isotherms in clayey materials are generally characterized by sigmoidal curves, marked by a point of inflection between the minimum and maximum values. We will show later that this point of inflection corresponds to the saturation of the first layer of sorbed water on the mineral surface.

A classical model describing the sorption of a gas (like nitrogen) on a reactive mineral surface is the Brunauer, Emmett, and Teller (BET) model (Brunauer et al., 1938). This theory has been extended to the case of water vapor sorption in clays (Mooney et al., 1952; Chemkhi et al., 2004; Mihoubi and Bellagi, 2006). The BET theory is an extension of the Langmuir theory for a monolayer molecular adsorption. Assuming the formation of several layers for molecular sorption with no interaction between the layers, the BET equation is written as (e.g., Cancela et al., 1997),
\[ \frac{1}{\nu \left[ \frac{1}{h_r} - 1 \right]} = \frac{C - 1}{\nu_mC} h_r + \frac{1}{\nu_mC}, \]  

(2.13)

where \( \nu \) represents gravimetric water content discussed above and \( \nu_m = n_m M_w / M_g \) (dimensionless) represents the gravimetric water content when the first monolayer is fully saturated, i.e., the monolayer adsorbed water mass \( n_m M_w \) per mass of the grains \( m_g \), where \( M_w \) is the molar mass of water in kg Mol\(^{-1}\) \((18.02 \times 10^{-3} \text{ kg Mol}^{-1})\) and \( n_m \) denotes the number of water molecules sorbed in a monolayer (expressed in mol). The so-called BET constant \( C \) is an energetic term representing the balance of adsorption energies at constant temperature,

\[ C = \exp \left( \frac{E_a - E_l}{RT} \right), \]

(2.14)

where \( E_a \) is the heat of adsorption of the first layer of water molecules covering the clay surface, \( E_l \) is the heat of adsorption for the second and third layer of water molecules covering the mineral surface and is equal to heat of water liquefaction, \( R \) is the molar gas constant \((8.31 \text{ J mol}^{-1} \text{K}^{-1})\), and \( T \) is temperature (in Kelvin, K). Using Eqs. (10) and (13) the BET equation can be rewritten as,

\[ \frac{h_r}{\nu \left[ \frac{1}{h_r} - 1 \right]} = \frac{C - 1}{\nu_mC} h_r + \frac{1}{\nu_mC}. \]

(2.15)

The term of this equation can be arranged as follows,

\[ \nu = \nu_m \left( \frac{h_r}{1 - h_r} \right) \left( \frac{C}{(C - 1)h_r + 1} \right). \]

(2.16)

We will normalize this curve by the cation exchange capacity to produce new master curves in the next section.

**Normalized sorption curve model**

For the purposes of this derivation, the two quantities \( \nu \) and \( \nu_m \) will be expressed in gram of
water per gram of dry solid rather than in m$^3$. The mechanisms governing water sorption in a clay matrix change as a function of water content. At both low and high water activities, sorption isotherms exhibit highly variable and nonlinear character. At low water activity, non-linear effects may be due to local condensation of the water molecules due to the roughness of the mineral/water interface. At high water activity (above 0.61, discussed below), capillary effects start to dominate. However, for a wide range of water activities (e.g., $h_r \equiv p_r / p_r^0 \in [0.05, 0.70]$), the isotherms exhibit a reproducible character that is consistent across a diverse set of clay types (Salles et al., 2009; Cancela et al., 1997; Likos and Lu, 2002). This is a consequence of the fact that vapor sorption in this regime is driven by the interaction of water molecules with the surface of the negatively charged clay particles (at pH 7).

The CEC is a measure of the amount of exchangeable charge per unit mass of the solid. It is directly related to the specific surface area $S_{Sp}$ of the clay (Figure 2.1). As such, the CEC can be used to scale the sorption isotherms measured for different clays, effectively collapsing the various, respective isotherms into a single master curve corresponding to the water sorption equivalent $\nu / \text{CEC}$ (expressed in g meq$^{-1}$, gram of water per milliequivalent) as a function of the activity of the fluid phase (relative humidity). By simply normalizing Equation 2.15 by the CEC, we obtain an equivalent sorption isotherm that is valid for individual subsets of clays,

$$\frac{\nu}{\text{CEC}} = \frac{\nu_m}{\text{CEC}} \left( \frac{h_r}{1 - h_r} \right) \left( \frac{C}{(C - 1)h_r + 1} \right).$$

(2.17)

According to Equation 2.15, the relationship between the BET parameter $h_r / [\nu(1 - h_r)]$ and the relative humidity $h_r$ is a line with a slope $(C - 1)/(C\nu_m)$. Recognizing that the slope for the normalized isotherm must be the same for all clay types, we redefine the CEC-normalized BET monolayer sorption constant as $\nu_m^{\text{CEC}} = \nu_m / \text{CEC}$ and the slope parameter from Equation 2.15 as
\[ \xi = \frac{(C-1)}{(C_{\text{CEC}})} \]. Hence, the BET constant can be written in terms of the slope parameter as 
\[ C = \left(1 - \xi \nu_{\text{CEC}}\right)^{-1} \]. From these considerations, we obtain a master equation for the CEC-normalized sorption model,

\[ \frac{\text{CEC}}{\nu} \left( \frac{h_r}{1-h_r} \right) = \frac{1}{\nu_{m}} + \xi (h_r - 1). \quad (2.18) \]

To account for different types of cations sorbed on the mineral surface, we introduced a scaled CEC parameter \( \text{CEC}_i \), defined by Equation 2.4 above. For the sake of clarity, this parameter effectively replaces the CEC in Equations 2.17 and 2.18 and has been determined empirically from the data analysis presented below. The effect of this parameter is illustrated in Figures 2.3 and 2.4 where we show that adopting the normalization by the scaling parameter \( \delta_i \) collapses all the sorption curves into a master curve. This yields the following normalized sorption isotherm,

\[ \frac{1}{\bar{\nu}} \left( \frac{h_r}{1-h_r} \right) = \frac{1}{\bar{\nu}_{m}} + \bar{\xi} (h_r - 1), \quad (2.19) \]

where the two normalized parameters are defined as,

\[ \bar{\nu} = \nu / \text{CEC}_i, \quad (2.20) \]

\[ \bar{\nu}_m = \nu_m / \text{CEC}_i, \quad (2.21) \]

\[ \bar{\xi} \equiv \frac{(C-1)}{(C\bar{\nu}_m)}. \quad (2.22) \]

To constrain the value of the scaling parameter \( \delta_i \) for a selection of ions \( i \), mont-morillonite and bentonite pairs were selected from the works of Cancela et al. (1997) and Montes-Hernandez et al. (2003). Separate inversions of CEC values were performed for the respective Ca, Li, and Mg-exchanged members of these two data sets. As the model predicts, each subset collapses to a unique CEC-normalized trend. The resulting CEC values were compared with the output of the
Figure 2.3  The effect of the mineralogical parameter $\delta$ on CEC-normalized isotherms comprising clays of different subsets. a. Sorbed water content. b. BET-normalized linear trends. For clays of similar mineralogy with the same surface hydration energy, i.e., exchanged counterion, CEC-normalized isotherms correspond to several characteristic equivalent curves shown as black lines. Scaling the respective CEC values by $\delta_i$ (counterion dependent) collapses these curves into a single normalized model.

Water sorption in porous media almost ubiquitously exhibits hysteresis. This behavior may arise from any of the following effect: (a) capillary condensation, (b) changes in clay morphology, (c) effects of pore topology in which filling and emptying pathways differ (Dontsova et al., 2004), and (d) Contact angle dynamics on chemically heterogeneous and rough surfaces (Tuller and Or, 2005). The general character of hysteresis in the wetting/drying loop is such that the desorption isotherm exhibits higher water content than its adsorption counterpart at the same relative humidity. Indeed, there is some variability observed in the hysteresis, which
Figure 2.4  CEC values were inverted independently for three clay subsets comprising the Ca, Li, and Mg members of separate montmorillonite and bentonite data sets. The CEC-normalized data define three unique curves, which collapse to a normalized curve when scaled by the normalized cation exchange capacity \( \overline{\text{CEC}} \). a. Water content. b. Equivalent BET-parameter straight lines. In both cases, the dashed line corresponds to the normalized isotherm. Data from both Cancela et al. [1997] and Montes-Hernandes et al. [2003].

may indicate the cumulative influence of the aforementioned affects in sequential experiments (see Aochi and Farmer, 2010). The present model accounts for hysteresis by considering all mechanisms contributing to the retention of additional water in the drying loop as “bound water” \( \text{bw} \) represented by an empirical constant \( \Gamma = \text{bw} / \overline{\text{CEC}} \) of the same dimensionality as the water content (i.e., g g\(^{-1}\) or mmol g\(^{-1}\)). This term is added to the normalized monolayer parameter \( \overline{\nu}_m \) in our present formulation. Hence, we reparameterize Equation 2.18 to arrive at a formulation of master curves for the normalized sorption/desorption model,

\[
\frac{1}{\overline{\nu}} \left( \frac{h_r}{1 - h_r} \right) = \frac{1}{\overline{\nu}_m + \Gamma} + \overline{\nu} (h_r - 1). \tag{2.23}
\]

Although Equation 2.19 has been derived from BET theory, similar relationships can be obtained by the same reasoning for other models of clay-water sorption isotherms. Equation 2.23 is the
The main equation derived in our paper. It will be tested in the next section using a variety of literature data.

**Validation of the model**

The model, Equation 2.23, was applied to data taken from the literature. We first apply the model to desorption data obtained for Na-exchanged kaolinite-smectite mixtures. The data set is then expanded to include additional water sorption measurements in a variety of clays including kaolinite, smectite, montmorillonite, and bentonite, comprising a diverse array of exchangeable cations for these clays (see Tables 1 and 2 for the appropriate references). To mitigate the effect of temperature on the present analysis, data were selected only from data sets collected at temperatures ranging from 20-30 °C. The influence of temperature will be evaluated further, and we will see that this assumption is well justified. Thermodynamic analysis indicates that temperature variation on the order of 10 °C produces comparable water retention characteristics in clays (Schneider and Goss, 2011).

**Sorption isotherms in Na-exchanged kaolinite-smectite mixtures**

Likos and Lu (2002) conducted experiments to measure water adsorption as a function of the clay fraction of respective kaolinite-smectite mixtures. Pure kaolinite and smectite end-members were slurry-mixed to achieve mass-controlled clay ratios of 20%, 50%, 70%, 80%, 90% smectite. Vapor desorption isotherms were then determined for each composite clay type for $h_r$ ranging from 0% to 95%. The theory is applied to the data as a first-order verification of the proposed model. The sorption isotherms were normalized by estimated CEC values for the end member specimens, as well as for all of the clay mixtures, showing promising results (see Figures 2.5 and 2.6).

CEC values were inverted using a stochastic inversion algorithm based on an McMC approach called the Adaptative Metropolis Algorithm (AMA, see Haario et al., 2000; Woodruff
Figure 2.5 Preliminary inversion. **a.** Raw adsorption isotherms. **b.** CEC-normalized sorption isotherms for the kaolinite and smectite end-members. The shaded grey region represents the saturation regime in which capillary effects begin to dominate vapor sorption in the clays, causing a departure from the normalized model. CEC values for used for the normalization are also shown.

et al. (2010), and references therein, see discussion in Appendix A). The resulting CEC values and the normalized sorption isotherm for these clays are provided in Figure 2.7. In Figure 2.7b, we plot the inverted CEC (determined from the peak of the posterior probability densities) as a function of the clay content. We see that the CEC of the two end-members (kaolinite and smectite) are consistent with the range of CEC values for these two clays (see Figure 2.1). Also the inverted CEC of a given mixture is consistent with a linear mixture model (see Equation 2.1, $\text{CEC(mixture)} = \chi_K \text{CEC}_K + (1 - \chi_K)\text{CEC}_S$ where $\chi_K$ is the relative mass fraction of kaolinite and $\text{CEC}_K$ and $\text{CEC}_S$ represent the CEC of the two end-members, kaolinite and smectite, respectively).
Figure 2.6 Comparison of raw (open) and CEC-normalized (filled) data using estimated values for the CEC. The shaded region represents the saturation regime in which vapor desorption is dominated by capillarity, causing a departure from the proposed model. Data from Likos and Lu [2002].

**Application of the normalized model**

The procedure outlined above was repeated for the expanded data set. However, the data were inverted for the scaled exchange parameter $\overline{CEC}_i$ instead of the CEC. A comparison of the raw data to the inverted data (scaled by $\overline{CEC}_i$) is presented in Figure 2.8. This $\overline{CEC}_i$-normalized data set was then used to invert the normalized monolayer water content $\overline{\nu}_m$, the normalized BET energy constant $\overline{\xi}$ and the bound water parameter $\Gamma$, which define the normalized sorption curve. Normalized data and the corresponding model fit are shown in Figures 2.9 and 2.10 (see Appendix A for the explanations regarding the optimization scheme used in this analysis).
Inversion results. a. Normalized desorption isotherm computed from the mean CEC value of the posterior distributions obtained from the inversion. The normalized water content in all clay mixtures is shown collectively as filled circles, and the raw values are shown collectively as crosses. The inverted CEC values are also shown. b. A linear relationship between the CEC and the clay content (in weight) was observed from the inverted CEC. This is consistent with Eq. (1) of the main text. Data from Likos and Lu [2002].

The normalized isotherm accurately fits the data fairly well. It captures the wetting/drying hysteresis exhibited by the data (Figure 2.11). It also provides a model applicable to clays, sand-clay mixtures, and sandstones. The results of the inversion are reported in Tables 2.3 and 2.4.

For this analysis, the energy constant was allowed to differ for adsorption and desorption, implying that the difference in sorption heats \( \Delta E = E_a - E_i \) (see Equation 2.14) is dependent on the position in the wetting/drying loop. The respective \( \tilde{\xi} \) values were comprised between 11.9 and 6.9 (dimensionless) for adsorption and desorption data, respectively. This corresponds to a difference in sorption heats \( \Delta E = RT \ln C \) on the order of 1 to 5 kJ mol\(^{-1}\), which is consistent with values reported in the literature (refer to the data sources in Tables 2.1 and 2.2; inverted values are provided in Tables 2.3 and 2.4). Note that this narrow range of sorption energies comprises a diverse set of clay mineralogies; hence, at first order, water sorption is generally

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Figure 2.7 Inversion results. a. Normalized desorption isotherm computed from the mean CEC value of the posterior distributions obtained from the inversion. The normalized water content in all clay mixtures is shown collectively as filled circles, and the raw values are shown collectively as crosses. The inverted CEC values are also shown. b. A linear relationship between the CEC and the clay content (in weight) was observed from the inverted CEC. This is consistent with Eq. (1) of the main text. Data from Likos and Lu [2002].
Figure 2.8 Plots of all data points used to invert the normalized cation exchange capacity $\text{CEC}_i$. The raw data (triangles, upper figures) show significantly more scatter than the $\text{CEC}_i$-normalized data plots (circles, bottom circles). Both adsorption (right side) and desorption data (left side) sets are used here. See Table 1 for data sources.

independent of the crystalline plane (sorption heats are the same for all surface sites including external and interlayer sites for 2:1 clays).

In the present formulation, the bound water parameter is closely related to the monolayer water content for desorption data, and cannot be accurately constrained without determining $\nu_m$ from the adsorption data as input in the desorption analysis. In the absence of adsorption data, the sum $\nu_m + bw$ can be used as a proxy for $\nu_m$, as long as it is recognized that some component of irreducible water is accounted for in this measure. Values for clay bound water $bw$ are provided in Table 2.4. The optimal $\text{CEC}_i$-normalized monolayer water content determined from this analysis is on the order of $bw \approx 100$ mg of water per gram of clay.
Figure 2.9 Resulting fit of the $\text{CEC}_i$-scaled BET parameter space. a. Adsorption trend. b. Desorption trend. See Table 1 for data sources. The departure from the linear trends at high values of the relative humidity represents the transition from the hydroscopic and capillary waters. Correlation values of 0.79 and 0.93 for adsorption and desorption, respectively, for $h_r [0.1 \ 0.61]$.

Figure 2.10 Resulting fit of the normalized sorption model to the normalized data set, see Equation (2.20), using $\text{CEC}_i$ in place of the CEC. a. Adsorption master curve isotherms. The point at which the first monolayer (corresponding to $\nu_m = 0.08 \ \text{g meq}^{-1}$) is filled is also shown. b. Desorption master curve isotherms. See Table 1 for data sources. Correlation values of 0.94 and 0.92 were calculated for adsorption and desorption, respectively, for $h_r [0.1 \ 0.61]$. 
Figure 2.11 Measured versus predicted water sorption on four samples of vermiculite. Our model clearly underpredicts the sorption of water at low relative humidities.

From Equation 2.16, we can determine the critical relative humidity at which the first equivalent monolayer is filled ($\nu_m - \nu$). We obtain a second-order polynomial and the positive root of this polynomial yields,

$$h_r(\nu = \nu_m) = \frac{\sqrt{C} - 1}{C - 1},$$

with $C = (1 - \xi \bar{\nu}_m)^{-1}$. Taking $\xi = 6.9$ meq g$^{-1}$ and $\bar{\nu}_m = 0.08$ g meq$^{-1}$, we obtain a critical relative humidity of approximately 0.40 correlated to the inflection point of the sigmoidal adsorption isotherm (Figures 2.10 and 2.11). This is in fair agreement with Newman (1983) who found that a complete monolayer of water is obtained at a mean relative humidity of 0.47 for 58 British soils. In the case of Na-montmorillonite, Cases et al. (1997) showed that at room relative humidity (around 40%), their sample still contained 50% dehydrated layers, which indeed
Table 2.1 Data sets used in the analysis and corresponding citations for the adsorption data.

<table>
<thead>
<tr>
<th>Clay type</th>
<th>Citation</th>
</tr>
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<tbody>
<tr>
<td>Ca-Montmorillonite</td>
<td>Cancela et al. [1997]</td>
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<tr>
<td>Cu-Montmorillonite</td>
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<tr>
<td>Fe-Montmorillonite</td>
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<td>Shale-A (Na)</td>
<td>Krushin [2005]</td>
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<td>Shale-C (Na)</td>
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<td>Shale-D (Na)</td>
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<td>MidwayShale (Na)</td>
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<tr>
<td>Bentonite (Al-Fe-Mg-Na-Ca-K)</td>
<td>Mihoubi and Bellagi [2006]</td>
</tr>
<tr>
<td>Bentonite (Ti-Al-Fe-Mn-Mg-Ca-Na-K-P)</td>
<td>Mokrejš et al. [2005]</td>
</tr>
<tr>
<td>Ca-Bentonite</td>
<td>Montes-Hernandez et al. [2003]</td>
</tr>
<tr>
<td>K-Bentonite</td>
<td></td>
</tr>
<tr>
<td>Li-Bentonite</td>
<td></td>
</tr>
<tr>
<td>Mg-Bentonite</td>
<td></td>
</tr>
<tr>
<td>Na-Bentonite</td>
<td></td>
</tr>
<tr>
<td>Raw-Bentonite (Na/Ca)</td>
<td></td>
</tr>
<tr>
<td>Sapponite (Al-Mg-Na)</td>
<td>Rinnert et al. [2005]</td>
</tr>
</tbody>
</table>

corresponds to 1 fully saturated layer of water in our model. Using the same approach as above, it is easy to find the critical relative humidity at which the second equivalent hydration layer is fully-saturated. This yields,

\[ h_r(\nu = 2\nu_m) = \frac{C - 4 + \sqrt{C^2 + 8C}}{4(C - 1)} \]  \hspace{1cm} (2.25)

Taking \( \bar{\bar{\zeta}} = 6.9 \) meq g\(^{-1}\) and \( \bar{\nu}_m = 0.08 \) g meq\(^{-1}\), we obtain a critical relative humidity of approximately 0.61, which is in excellent agreement with what is shown in Figure 2.5 and Figure
Table 2.2 Data sets used in the analysis and corresponding references for the desorption data.

<table>
<thead>
<tr>
<th>Clay type</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wyoming montmorillonite (Na)</td>
<td>Krushin [2005]</td>
</tr>
<tr>
<td>Wyoming smectite, SWy-1 (Na)</td>
<td></td>
</tr>
<tr>
<td>Wyoming montmorillonite, Clay Spur (Na)</td>
<td></td>
</tr>
<tr>
<td>MX-80 Bentonite, Wyoming (Na)</td>
<td></td>
</tr>
<tr>
<td>Natural Volclay, Wyoming bentonite (Ca-Mg-Na)</td>
<td></td>
</tr>
<tr>
<td>Natural Volclay, Wyoming bentonite (Na)</td>
<td></td>
</tr>
<tr>
<td>Shale-A (Na)</td>
<td></td>
</tr>
<tr>
<td>Shale-C (Na)</td>
<td></td>
</tr>
<tr>
<td>Shale-D (Na)</td>
<td></td>
</tr>
<tr>
<td>100% Smectite (Na)</td>
<td>Likos and Lu [2002]</td>
</tr>
<tr>
<td>100% Kaolinite (Na)</td>
<td></td>
</tr>
<tr>
<td>10/90 Kaolinite-Smectite (Na)</td>
<td></td>
</tr>
<tr>
<td>20/80 Kaolinite-Smectite (Na)</td>
<td></td>
</tr>
<tr>
<td>30/70 Kaolinite-Smectite (Na)</td>
<td></td>
</tr>
<tr>
<td>50/50 Kaolinite-Smectite (Na)</td>
<td></td>
</tr>
<tr>
<td>80/20 Kaolinite-Smectite (Na)</td>
<td></td>
</tr>
<tr>
<td>Bentonite (Al-Fe-Mg-Na-Ca-K)</td>
<td>Mihoubi and Bellagi [2006]</td>
</tr>
<tr>
<td>Bentonite (Ti-Al-Fe-Mn-Mg-Ca-Na-K-P)</td>
<td>Mokrejš et al. [2005]</td>
</tr>
<tr>
<td>Ca-Bentonite</td>
<td>Montes-Hernandez et al. [2003]</td>
</tr>
<tr>
<td>K-Bentonite</td>
<td></td>
</tr>
<tr>
<td>Li-Bentonite</td>
<td></td>
</tr>
<tr>
<td>Mg-Bentonite</td>
<td></td>
</tr>
<tr>
<td>Na-Bentonite</td>
<td></td>
</tr>
<tr>
<td>Raw-Bentonite (Na/Ca)</td>
<td></td>
</tr>
<tr>
<td>Sapponite (Al-Mg-Na)</td>
<td>Rinnert et al. [2005]</td>
</tr>
<tr>
<td>Soil-716</td>
<td>Schneider and Goss [2011]</td>
</tr>
</tbody>
</table>
2.9b. Note that the concept of having one or two homogeneous hydration layers is fictitious if we believe that, in reality, the water molecules are mainly located around the cation surface sites. We will discuss the number of water molecules per cation surface site later in this work.

**Model limitation**

It is always interesting and instructive to find a dataset for which our model does not work, because it does not correctly account for the discrimination between a monolayer hydration state, bilayer hydration state, and pore water sorption. Michot et al. (2005) reported sorption / desorption isotherms for 4 samples of synthetic Na-vermiculite, which belongs to the smectite group. The cation exchange capacity of the samples are not reported by Michot et al. (2005), but Lipsicas (1984) gave a CEC for vermiculite of 1.8 meq/g. Taking $\delta$(Na)=0.5. We obtain $\overline{\text{CEC}}$(Na) = 0.8 meq g$^{-1}$ and can now predict the amount of sorbed water on the surface of vermiculite as a function of the relative humidity, using the BET equation scaled with $\overline{\text{CEC}}$(Na) = 0.8 meq g$^{-1}$. The measured versus predicted amounts of water sorbed on the mineral surface are shown in Figure 2.11. Clearly, the BET equation is unable to reproduce the clay-water sorption isotherm for these samples, especially at low relative humidities. The scaling proposed in the present paper could be applied to a more sophisticated sorption/desorption model accounting for discrimination between monolayer and bilayer hydration state and interlayer versus external sorption (Laird, 1999; Michot et al., 2005; Ferrage et al., 2010).

**Influence of Temperature**

Here, we briefly discuss the effect of temperature at standard conditions (10-30°C).

Using the scaled BET equation, the influence of temperature is explicitly described as

$$
\frac{1}{\overline{V}} \left( \frac{h_r}{1-h_r} \right) = \frac{1}{\overline{V}_m} + \overline{\xi}(T)(h_r - 1),
$$

(2.26)
Table 2.3 Inversion results for adsorption isotherms: CEC estimates obtained by inversion of Ca, Li, Mg, and Na-clay subsets with a standard deviation $\sigma$ of the posterior probability distribution for the CEC. The scaling parameter $\delta_i^{-1}$ is determined from independently inverted $\overline{\text{CEC}}$, and CEC values. The monolayer concentrations $\nu_m$ are calculated using the optimized $\overline{\text{CEC}}$-scaled concentration $\overline{\nu}_m = 0.08 \text{ g meq}^{-1}$ and the following value of the slope parameter $\zeta = 11.9 \text{ meq g}^{-1}$. The difference in desorption energies $\Delta E$ is calculated from the scaled BET slope parameter at 25°C.

<table>
<thead>
<tr>
<th>Clay type</th>
<th>CEC [meq g$^{-1}$]</th>
<th>$\overline{\text{CEC}}_i$ [meq g$^{-1}$]</th>
<th>$\sigma$ [-]</th>
<th>$\delta_i^{-1}$ [-]</th>
<th>$\nu_m$ [g g$^{-1}$]</th>
<th>$\Delta E$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-Montmorillonite$^b$</td>
<td>1.053</td>
<td>0.790</td>
<td>0.021</td>
<td>1.33</td>
<td>0.063</td>
<td>3.5</td>
</tr>
<tr>
<td>Cu-Montmorillonite</td>
<td>--</td>
<td>0.475</td>
<td>0.022</td>
<td>--</td>
<td>0.038</td>
<td>1.5</td>
</tr>
<tr>
<td>Fe-Montmorillonite</td>
<td>--</td>
<td>0.664</td>
<td>0.009</td>
<td>--</td>
<td>0.053</td>
<td>2.5</td>
</tr>
<tr>
<td>Li-Montmorillonite$^b$</td>
<td>2.017</td>
<td>0.847</td>
<td>0.014</td>
<td>2.38</td>
<td>0.068</td>
<td>4.1</td>
</tr>
<tr>
<td>Mg-Montmorillonite$^b$</td>
<td>1.636</td>
<td>0.900</td>
<td>0.025</td>
<td>1.82</td>
<td>0.072</td>
<td>4.8</td>
</tr>
<tr>
<td>Na-Montmorillonite</td>
<td>--</td>
<td>0.465</td>
<td>0.015</td>
<td>--</td>
<td>0.037</td>
<td>1.4</td>
</tr>
<tr>
<td>Shale-A (Na)$^a$</td>
<td>0.095</td>
<td>0.065</td>
<td>0.016</td>
<td>1.5</td>
<td>0.005</td>
<td>0.2</td>
</tr>
<tr>
<td>Shale-C (Na)$^a$</td>
<td>0.500</td>
<td>0.299</td>
<td>0.024</td>
<td>1.7</td>
<td>0.024</td>
<td>0.8</td>
</tr>
<tr>
<td>Shale-D (Na)$^a$</td>
<td>0.250</td>
<td>0.177</td>
<td>0.026</td>
<td>1.4</td>
<td>0.014</td>
<td>0.5</td>
</tr>
<tr>
<td>MidwayShale (Na)</td>
<td>--</td>
<td>0.715</td>
<td>0.002</td>
<td>--</td>
<td>0.057</td>
<td>2.8</td>
</tr>
<tr>
<td>Bentonite (Al-Fe-Mg-Na-Ca-K)</td>
<td>--</td>
<td>0.543</td>
<td>0.014</td>
<td>--</td>
<td>0.043</td>
<td>1.8</td>
</tr>
<tr>
<td>Bentonite (Ti-Al-Fe-Mn-Mg-Ca-Na-K-P)</td>
<td>--</td>
<td>0.520</td>
<td>0.008</td>
<td>--</td>
<td>0.042</td>
<td>1.7</td>
</tr>
<tr>
<td>Ca-Bentonite$^b$</td>
<td>0.945</td>
<td>0.737</td>
<td>0.019</td>
<td>1.28</td>
<td>0.059</td>
<td>3.0</td>
</tr>
<tr>
<td>K-Bentonite</td>
<td>--</td>
<td>0.287</td>
<td>0.038</td>
<td>--</td>
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</tr>
<tr>
<td>Li-Bentonite$^b$</td>
<td>0.977</td>
<td>0.381</td>
<td>0.024</td>
<td>2.56</td>
<td>0.030</td>
<td>1.1</td>
</tr>
<tr>
<td>Mg-Bentonite$^b$</td>
<td>1.041</td>
<td>0.635</td>
<td>0.023</td>
<td>1.64</td>
<td>0.051</td>
<td>2.3</td>
</tr>
<tr>
<td>Na-Bentonite</td>
<td>--</td>
<td>0.483</td>
<td>0.039</td>
<td>--</td>
<td>0.039</td>
<td>1.5</td>
</tr>
<tr>
<td>Raw-Bentonite (Na/Ca)</td>
<td>--</td>
<td>0.375</td>
<td>0.038</td>
<td>--</td>
<td>0.030</td>
<td>1.1</td>
</tr>
<tr>
<td>Sapponite (Al-Mg-Na)</td>
<td>--</td>
<td>0.865</td>
<td>0.018</td>
<td>--</td>
<td>0.069</td>
<td>4.3</td>
</tr>
</tbody>
</table>

$^a$Na-exchanged clays used in Section 3.1
$^b$Ca, Mg, Li-exchanged clays used in Section 3.3
Table 2.4 Inversion results for desorption isotherms: CEC estimates obtained from the inversion of Na-clay subsets with a standard deviation $\sigma$ of the posterior PDF for the CEC. The value of the scaling parameter $\delta_i^{-1}$ is determined from independently inverted $\overline{CEC}_i$ and CEC values. The monolayer concentrations $\nu_m$ are calculated using the optimized $\overline{CEC}_i$-scaled concentration $\bar{\nu}_m = 0.08 \text{ g meq}^{-1}$ and the following value of the slope parameter $\gamma = 0.053$. The estimates for clay bound water $bw$ are determined from the optimized value $\Gamma = 0.053$. The difference in desorption energies $\Delta E$ is calculated from the scaled BET slope parameter at 25°C.

<table>
<thead>
<tr>
<th>Clay type</th>
<th>CEC  [meq g$^{-1}$]</th>
<th>$\overline{CEC}_i$ [meq g$^{-1}$]</th>
<th>$\sigma$ [-]</th>
<th>$\delta_i^{-1}$ [-]</th>
<th>$\nu_m$ [g g$^{-1}$]</th>
<th>$bw$ [g g$^{-1}$]</th>
<th>$\Delta E$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wy. mont. (Na)$^a$</td>
<td>0.996</td>
<td>0.540</td>
<td>0.021</td>
<td>1.8</td>
<td>0.043</td>
<td>0.029</td>
<td>1.7</td>
</tr>
<tr>
<td>Wy. smectite, SWy-1 (Na)$^a$</td>
<td>0.820</td>
<td>0.455</td>
<td>0.022</td>
<td>1.8</td>
<td>0.036</td>
<td>0.024</td>
<td>1.3</td>
</tr>
<tr>
<td>Wy. mont., Clay Spur (Na)$^a$</td>
<td>0.950</td>
<td>0.557</td>
<td>0.009</td>
<td>1.7</td>
<td>0.045</td>
<td>0.030</td>
<td>1.8</td>
</tr>
<tr>
<td>MX-80 Bentonite, Wyoming (Na)$^a$</td>
<td>0.760</td>
<td>0.510</td>
<td>0.014</td>
<td>1.5</td>
<td>0.041</td>
<td>0.027</td>
<td>1.6</td>
</tr>
<tr>
<td>Nat. Volclay, Wy. bentonite (Ca-Mg-Na)$^a$</td>
<td>0.900</td>
<td>0.557</td>
<td>0.025</td>
<td>1.6</td>
<td>0.045</td>
<td>0.030</td>
<td>1.8</td>
</tr>
<tr>
<td>Nat. Volclay, Wy. bentonite (Na)$^a$</td>
<td>0.900</td>
<td>0.545</td>
<td>0.015</td>
<td>1.7</td>
<td>0.044</td>
<td>0.029</td>
<td>1.7</td>
</tr>
<tr>
<td>Shale-A (Na)$^a$</td>
<td>0.095</td>
<td>0.065</td>
<td>0.016</td>
<td>1.5</td>
<td>0.005</td>
<td>0.003</td>
<td>0.2</td>
</tr>
<tr>
<td>Shale-C (Na)$^a$</td>
<td>0.500</td>
<td>0.299</td>
<td>0.024</td>
<td>1.7</td>
<td>0.024</td>
<td>0.016</td>
<td>0.8</td>
</tr>
<tr>
<td>Shale-D (Na)$^a$</td>
<td>0.250</td>
<td>0.177</td>
<td>0.026</td>
<td>1.4</td>
<td>0.014</td>
<td>0.009</td>
<td>0.4</td>
</tr>
<tr>
<td>100% Smectite (Na)$^a$</td>
<td>0.900</td>
<td>0.370</td>
<td>0.002</td>
<td>2.4</td>
<td>0.030</td>
<td>0.020</td>
<td>1.0</td>
</tr>
<tr>
<td>100% Kaolinite (Na)$^a$</td>
<td>0.100</td>
<td>0.050</td>
<td>0.014</td>
<td>2.0</td>
<td>0.004</td>
<td>0.003</td>
<td>0.1</td>
</tr>
<tr>
<td>10/90 Kaolinite-Smectite (Na)$^a$</td>
<td>0.622</td>
<td>0.336</td>
<td>0.008</td>
<td>1.9</td>
<td>0.027</td>
<td>0.018</td>
<td>0.9</td>
</tr>
<tr>
<td>20/80 Kaolinite-Smectite (Na)$^a$</td>
<td>0.564</td>
<td>0.286</td>
<td>0.012</td>
<td>2.0</td>
<td>0.023</td>
<td>0.015</td>
<td>0.8</td>
</tr>
<tr>
<td>30/70 Kaolinite-Smectite (Na)$^a$</td>
<td>0.506</td>
<td>0.256</td>
<td>0.012</td>
<td>2.0</td>
<td>0.020</td>
<td>0.014</td>
<td>0.7</td>
</tr>
<tr>
<td>50/50 Kaolinite-Smectite (Na)$^a$</td>
<td>0.390</td>
<td>0.234</td>
<td>0.011</td>
<td>1.7</td>
<td>0.019</td>
<td>0.012</td>
<td>0.6</td>
</tr>
<tr>
<td>80/20 Kaolinite-Smectite (Na)$^a$</td>
<td>0.216</td>
<td>0.121</td>
<td>0.015</td>
<td>1.8</td>
<td>0.010</td>
<td>0.006</td>
<td>0.3</td>
</tr>
<tr>
<td>Clay type</td>
<td>CEC [meq g⁻¹]</td>
<td>CEC_i [meq g⁻¹]</td>
<td>σ [-]</td>
<td>δ⁻¹ [-]</td>
<td>V_m [g g⁻¹]</td>
<td>b_w [g g⁻¹]</td>
<td>ΔE [kJ mol⁻¹]</td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------------</td>
<td>-----------------</td>
<td>-------</td>
<td>--------</td>
<td>-------------</td>
<td>-------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Bentonite (Al-Fe-Mg-Na-Ca-K)</td>
<td>--</td>
<td>0.543</td>
<td>0.015</td>
<td>--</td>
<td>0.043</td>
<td>0.029</td>
<td>1.7</td>
</tr>
<tr>
<td>Bentonite (Ti-Al-Fe-Mn-Mg-Ca-Na-K-P)</td>
<td>--</td>
<td>0.520</td>
<td>0.019</td>
<td>--</td>
<td>0.042</td>
<td>0.028</td>
<td>1.6</td>
</tr>
<tr>
<td>Ca-Bentonite</td>
<td>--</td>
<td>0.737</td>
<td>0.008</td>
<td>--</td>
<td>0.059</td>
<td>0.039</td>
<td>2.8</td>
</tr>
<tr>
<td>K-Bentonite</td>
<td>--</td>
<td>0.287</td>
<td>0.002</td>
<td>--</td>
<td>0.023</td>
<td>0.015</td>
<td>0.8</td>
</tr>
<tr>
<td>Li-Bentonite</td>
<td>--</td>
<td>0.381</td>
<td>0.009</td>
<td>--</td>
<td>0.030</td>
<td>0.020</td>
<td>1.1</td>
</tr>
<tr>
<td>Mg-Bentonite</td>
<td>--</td>
<td>0.635</td>
<td>0.008</td>
<td>--</td>
<td>0.051</td>
<td>0.034</td>
<td>2.2</td>
</tr>
<tr>
<td>Na-Bentonite</td>
<td>--</td>
<td>0.483</td>
<td>0.009</td>
<td>--</td>
<td>0.039</td>
<td>0.026</td>
<td>1.5</td>
</tr>
<tr>
<td>Raw-Bentonite (Na/Ca)</td>
<td>--</td>
<td>0.375</td>
<td>0.005</td>
<td>--</td>
<td>0.030</td>
<td>0.020</td>
<td>1.0</td>
</tr>
<tr>
<td>Sapponite (Al-Mg-Na)</td>
<td>--</td>
<td>0.865</td>
<td>0.003</td>
<td>--</td>
<td>0.069</td>
<td>0.046</td>
<td>3.9</td>
</tr>
<tr>
<td>Soil-716</td>
<td>--</td>
<td>0.080</td>
<td>0.004</td>
<td>--</td>
<td>0.006</td>
<td>0.004</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Na-exchanged clays used in Section 3.1

\[ \bar{\xi}(T)\bar{V}_m = \frac{\exp\left(\frac{\Delta E}{RT}\right) - 1}{\exp\left(\frac{\Delta E}{RT}\right)}. \quad (2.27) \]

For the temperature range 10-30°C, the relative change of \( \bar{\xi}(T)\bar{V}_m \) is very small. For \( \Delta E \) ranging from 1 to 4 kJ, the relative variation of \( \bar{\xi}(T)\bar{V}_m \) is between 2.6% to 5.0% in this temperature range. Therefore, our earlier assumption to neglect the temperature effect for datasets taken in the temperature range 20-30°C is well justified.

**Discussion**

We will first discuss the numbers of molecules of water per site. The number of water molecules is per cation exchange site is given by,

\[ \bar{N}_w = \frac{\bar{V}_e}{\text{CECM}_w} = \frac{\bar{V}_e}{M_w}. \quad (2.28) \]
When the first hydration layer is saturated ($\bar{\nu} = \bar{\nu}_m$), we obtain from Equation 2.28 an amount of 4.4 water molecules per cation site, a result consistent with the work by Michot et al. (2005) (4±1 water molecules per Na\textsuperscript{+} site for four synthetic Na saponites). When the second layer of water molecules is filled, we have $\bar{\nu} = 2\bar{\nu}_m$. From Equation 2.28, we obtain 8.8 water molecules per site using the normalized CEC. For a specific ion $i$, this water has to be divided by $\delta_i$. For Mg\textsuperscript{2+} for instance, we have $\delta(Mg) = 0.6$ and therefore we obtain 15 water molecules per cation sites. This value can be compared with the value obtained by Laird (1999) for some Mg-saturated 2:1 phyllosilicates: 24 water molecules per surface site. From an independent approach, Henry and Bourlange (2004) obtained 12 bound water molecules per cation exchange site for clay-rich sedimentary rocks. A value of 15 bound water molecules per surface site has been proposed for smectite from theoretical considerations by Ransom and Helgenson (1994). This distribution of values also masks the fact that hydration heterogeneity in smectites has been reported systematically in the literature. Laird (1999) showed that all the layers are not similarly hydrated, with smaller hydration numbers for the interlayer sites than for the external cation exchange sites.

We now discuss the advantages of using the CEC rather than the specific surface area to normalize clay-water isotherms. Our first motivation is that the CEC is the key parameter used in the transport equations developed by Revil et al. (2011) in clayey materials. If we want to generalize this transport model to the unsaturated case, it is important to show that very few parameters are needed to characterize transport properties in unsaturated conditions. In the introduction, we briefly discussed that isotherms based on the specific surface area assume a uniform distribution of the water on the mineral surface. Because of the clustering of water molecules around cation surface sites, the CEC seems to be a better surrogate to predict clay-
water sorption isotherms. The third reason is that the CEC can account for the ionic composition of the pore water, which can be sorbed in the Stern layer, enabling the calculation of the effect of these cations upon the clay-water sorption isotherm. Hence, the model developed in this paper is promising as a simple, first-order approach to predict clay-water sorption isotherms in clayey materials.

Lastly, all analyses presented here refer to monoionic clays. In realistic geochemical conditions, clay sediments and shales are heteroionic and the pore water is a multicomponent solution with various concentrations of cations. Leroy et al. (2007) have developed an original approach based on Donnan equilibria and triple layer concepts to compute the sorption of cations on the surface of clay minerals for any pore water composition and mineral types. Their approach could be used to estimate relevant CEC values to properly scale the clay-water isotherms in our model.

**Concluding statements**

A model for clay-water isotherms has been presented. This model is based on the normalization of sorption isotherms by the CEC of the clay fraction accounting for the type of counterions located at the surface of the clay minerals. Only ions with large ionic potentials (Li\(^+\), Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)) have been tested in this work. It will be interesting for future analysis to use clays exchanged with larger ions having small ionic potentials (e.g., K\(^+\)), which do not show significant interlayer hydration. A comparison with the dataset by Michot et al. (2005) shows some limitations of the present approach. However, the key concepts of the present paper (normalization by the CEC and by the type of counterions) could be applied to another isotherm model, which would be more general than the BET model.
We plan to combine this model with a description of the capillary pressure curve to produce generalized capillary pressure curve for clay materials. This model will be coupled with a general model of cross-coupled flows in unsaturated clayey media extending the recent modeling effort made by Revil et al. (2011), which is itself based on unifying the transport properties of clay media using the CEC as a key-parameter.

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CHAPTER 3

COMPLEX CONDUCTIVITY TENSOR OF ANISOTROPIC HYDROCARBON-BEARING SHALES AND MUDROCKS

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Abstract

A model was recently introduced to describe the complex electrical conductivity and high frequency dielectric constant of isotropic clayey porous materials. That approach is generalized here to the case of anisotropic and tight hydrocarbon-bearing shales and mudrocks by introducing tensorial versions of both formation factor and tortuosity. It is shown that in-phase and quadrature conductivity tensors have common eigenvectors, but that the eigenvectors of the dielectric tensor may be different due to influence of the solid phase at high frequencies. In-phase and quadrature contributions to complex electrical conductivity depend on saturation, salinity, porosity, temperature, and cation exchange capacity (alternatively, specific surface area) of the porous material. Kerogen is likely to have a negligible contribution to the cation exchange capacity of the material because all exchangeable sites in the functional groups of organic matter may have been polymerized during diagenesis. An anisotropic experiment is performed to validate some of the properties described by the proposed model, especially to verify that the electrical anisotropy factor is the same for both in-phase and quadrature conductivities. We use two samples from the Bakken formation. Experimental data confirm the validity of the model. It is also found that the range of values for cation exchange capacity determined when implementing the new model with experimental data agree with the known range of cation exchange capacity for the Bakken shale. Measurements indicate that the bulk-space tortuosity in
the direction normal to bedding plane can be higher than 100.

**Introduction**

Shale formations are of increasing interest in hydrocarbon exploration worldwide. They comprise a diverse set of rock types, but are generally characterized as fine-grained, low porosity and low permeability rocks, with a non-negligible clay fraction in terms of bulk petrophysical properties. Due to preferential orientation of mineral foliations and finely laminated bedding planes, shales and mudrocks are almost ubiquitously anisotropic in several of their macroscopic physical properties. The term mudrock is used to describe all fine grained shaly and non-shaly formations. It is of great interest to petrophysicists to develop new models to describe seismic and electromagnetic (EM) measurements in these anisotropic materials.

Oil-shale deposits correspond to immature, organic-rich source rocks resulting in high kerogen mass fractions due to limited burial and thermal maturation histories—effectively, they have not been heated sufficiently to release their hydrocarbons. Hence, oil shales and mudrocks are typically water-wet, single- or dual-phase fluid systems, characterized by a heterogeneous solid phase comprising both siliciclastic, carbonate, and organic components. Mudrock-oil formations involve complex multiphase fluid systems, in which the degradation of kerogen, through geochemical thermal maturation processes (i.e., catagenesis and metagenesis), has both altered the nature of the solid fraction and produced economically significant polar and non-polar, aromatic and hydrocarbon fluid fractions. Oil-shale and shale-oil deposits represent two generalized regimes in the continuum of shale thermal maturation, exhibiting measurable differences in the characteristics of both solid and fluid phases. In what follows, we refer to all these rock formations in a general manner as shales, tacitly implying that their properties are intrinsically related to the maturation history of each formation. Note however, that mudrocks is
a geologically more appropriate term to use since that term denotes does not specify any lithology, rather it denotes a fine-grained rock system.

There is a growing need to better characterize the so-called “sweet spots” of tight oil-mudrock formations using an arsenal of geophysical methods with the objective to optimize hydrocarbon detection and production. Among such methods, galvanic and EM measurements can be used to determine the complex electrical conductivity of formations through borehole and cross-well imaging. What is missing is a general effective complex electrical conductivity model specific for shales and mudrocks, which includes the relative effects of porosity, water saturation, kerogen content and type, clay content and type, and a tortuosity tensor describing the anisotropy of the material (generally expected to be transversely isotropic, TI). As discussed in Revil (2013), such a model should also include the description of the high frequency permittivity of the material and possibly Maxwell-Wagner polarization. Recent developments in logging technology now allow one to resolve the macroscopic effects of anisotropy. Despite progresses on the experimental front (e.g., Weller et al., 2010), robust theoretical models describing the full effective complex conductivity tensor are still lacking (Bittar et al., 2009).

Revil and colleagues (Leroy et al., 2008; Leroy and Revil, 2009; Revil and Florsch, 2010) have recently invoked a strong role of the Stern layer (the inner portion of the electrical double layer coating the surface of mineral grains) to explain the low-frequency polarization of mixed, sandy, and clayey materials. The model of Stern layer polarization appears to be reliable to explain the dependence of complex electrical conductivity on cation exchange capacity (CEC) and specific surface area (Revil, 2012, 2013), salinity (Revil and Skold, 2011; Weller and Slater, 2012), pH (Skold et al., 2011), sorption of cations and organic molecules (Vaudelet et al., 2011a, b; Schwartz and Furman, 2012), influence of grain size (Revil et al., 2012), the relationship
between surface conductivity and quadrature conductivity (Revil and Florsch, 2010; Revil, 2012), temperature (Zisser et al., 2010a), and water saturation (Revil et al., 2012; Revil, 2013). Here, we generalize this model to the case of anisotropic formations with the intent to quantify the role played by kerogen on both surface conductivity and quadrature conductivity. Beside the contribution of the electrical double layer of non-conducting minerals, there is also a strong role played by the presence of pyrite above oil reservoirs (e.g., Veeken et al., 2009) and in the shallow subsurface associated with the biochemistry of contaminant plumes (Flores Orozco et al., 2011). Pyrite plays an active role in spectral induced polarization as long as its surface has not been oxidized. In addition, with the exception of the work by Zisser and Nover (2009) and Zisser et al. (2010b), there are a few open publications documenting and or explaining the polarization and anisotropy of tight (low-permeability) porous rocks.

Ampère's law in isotropic media

Let \( \omega = 2\pi f \) designate angular frequency and \( f = \omega / (2\pi) \) linear frequency (in Hertz). For isotropic materials, Ampère's law is written as (e.g., Vinegar and Waxman, 1984)

\[
\nabla \times \mathbf{H} = \left[ \sigma_{\text{eff}} - i\omega \varepsilon_{\text{eff}} \right] \mathbf{E},
\]

\[
\sigma_{\text{eff}} = \sigma'(\omega) + \omega \varepsilon''(\omega),
\]

and

\[
\varepsilon_{\text{eff}} = \varepsilon'(\omega) - \frac{\sigma''(\omega)}{\omega},
\]

where \( \mathbf{H} \) and \( \mathbf{E} \) denote magnetic and electrical fields, respectively, \( i = \sqrt{-1} \) denotes the pure imaginary number, and \( \sigma' \) and \( \sigma'' \) (expressed in S m\(^{-1}\)) denote the real (in-phase) and imaginary (out-of-phase or quadrature) components of the complex conductivity \( \sigma^* \), respectively, and are given by
\[ \sigma^* = \sigma' + i\sigma'' = |\sigma| \exp(i\varphi), \] (3.4)

with the magnitude of the conductivity written as 
\[ |\sigma^*| = (\sigma'^2 + \sigma''^2)^{\frac{1}{2}} \]
and the phase lag, \( \varphi \), given by 
\[ \tan \varphi = \frac{\sigma''}{\sigma'} . \]

In the frequency range 0.1 - 1000 Hz, in-phase and quadrature conductivities are only slightly frequency dependent because grain polarization occurs over a broad range of scales (Vinegar and Waxman, 1984; Revil, 2012, 2013). Complex conductivity is written as \( \varepsilon^* = \varepsilon' + i\varepsilon'' \). By neglecting the polarization of water molecules (above 1 GHz) and Maxwell Wagner polarization, one can safely neglect the imaginary component of the dielectric constant, whereby \( \varepsilon^* \approx \varepsilon' \), thus giving rise to the approximation \( \sigma_{\text{eff}} \approx \sigma'(\omega) \).

**In-phase conductivity**

Revil (2013) developed a new model to describe the complex conductivity of clayey materials using a volume-average approach. According to Revil (2013) and assuming volumetric averaging to describe effective conductivity, the in-phase conductivity \( \sigma' \) (in S m\(^{-1}\)) of porous materials is given as a function of pore water conductivity \( \sigma_w \) (in S m\(^{-1}\)) by the expression

\[
\sigma' = \frac{1}{F} \left\{ S_w'' \sigma_w + S_w' \left( \frac{F - 1}{F\phi} \right) \rho_s \beta_{\text{a}}^2 (1 - f) + \beta_{\text{a}}^2 (1 - f) \right\} \text{CEC},
\] (3.5)

where \( F \) (dimensionless) denotes the (intrinsic) formation factor for resistivity. It is related to connected porosity \( \phi \) by Archie's equation \( F = \phi^{-m} \) where \( m \) (dimensionless) denotes the porosity exponent. The total connected porosity entering Archie’s law does not distinguish between kerogen and matrix porosities. The parameters \( n \) and \( p \) (both dimensionless) denote the second Archie exponent (saturation exponent) and the saturation exponent for surface conductivity, respectively (with \( p=n-1 \) as introduced by Vinegar and Waxman, 1984 and demonstrated by Revil, 2013, using a volume-averaging approach). \( f \) denotes the fraction of
counterions in the Stern layer (see Leroy et al., 2008 and Revil, 2012, for discussion for sand and clayey materials), \( \rho_s \) denotes mass density of the solid phase (typically 2650±50 kg m\(^{-3}\) for the crystalline framework of clay minerals), \( \beta_{(\text{\text{+}})} \) is the mobility of counterions in the diffuse layer, and \( \beta_{\text{\text{S}}(\text{\text{+}})} \) is the mobility of counterions in the Stern layer (both in m\(^2\)s\(^{-1}\)V\(^{-1}\)). For clay minerals, the mobility of counterions in the diffuse layer is equal to the mobility of the same counterions in bulk pore water (e.g., \( \beta_{(\text{\text{+}})}(\text{Na}^+, 25^\circ\text{C}) = 5.2 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1} \), see Revil, 2012). Mobility of counterions in the Stern layer is substantially smaller and equal to \( \beta_{\text{\text{S}}(25^\circ\text{C}, \text{Na}^+)} = 1.5 \times 10^{-10} \text{ m}^2\text{s}^{-1}\text{V}^{-1} \) for clay minerals (Revil, 2012, 2013). The acronym CEC (expressed in C kg\(^{-1}\)) denotes cation exchange capacity of the material. In Equation 3.5, \( S_w \) denotes saturation of the water phase (\( S_w = 1 \) for a water-saturated material).

Because the formation factor is generally much higher than unity for tight formations (\( F >> 1 \)), Equation 3.5 can be written as

\[
\sigma' = \frac{1}{F} S_w n \sigma_w + S_w^p \left( \frac{1}{F \phi} \right) \rho_s \left[ \beta_{(\text{\text{+}})} (1 - f) + \beta_{\text{\text{S}}(\text{\text{+}})} f \right] \text{CEC} .
\]  (3.6)

The second additive term in this last equation corresponds to the surface conductivity \( \sigma_s \).

Equation 3.6 is also very close to the equation proposed by Revil et al. (1996) (their equation 15) for water-saturated doleritic core samples from the oceanic crust. A simple generalization of the above expression to anisotropic media yields the following expression for the in-phase conductivity tensor:

\[
\sigma' = \sigma'_{ij} x_i \otimes x_j ,
\]  (3.7)

\[
F = F_{ij} x_i \otimes x_j ,
\]  (3.8)

\[
T = T_{ij} x_i \otimes x_j ,
\]  (3.9)
and

\[ \sigma_{ij} = F_{ij} \left( S_w \sigma_w \right) + T_{ij} S_w \rho_s \left[ \beta(1 - f) + \beta_s (1 - f) \right] \text{CEC}, \]  

(3.10)

where \( x_i (i = 1, 2, 3) \) denote the basis vectors of the Cartesian frame of reference (\( x_i \cdot x_j = \delta_{ij} \) where \( \delta_{ij} \) denotes the Kronecker delta), \( a \otimes b \) represents the tensorial product between vectors \( a \) and \( b \), \( F_{ij} \) denotes the components of the (symmetric second-rank) formation factor tensor for the conductivity \( F \), and \( T_{ij} \) denotes the components of the (symmetric second-rank) tortuosity tensor of the pore space \( T \). We designate \( T \) as a connectivity tensor, as its entries vary between 0 and 1 and represent the inverse of the tortuosity defined in the isotropic case (see Bear, 1988; Bear and Bachmat, 1991; Bear and Cheng, 2010). Usually, in clayey materials, one has \( \beta(1 - f) >> \beta_s (1 - f) \) (Revil, 2012, 2013) whereby the last term of Equation 3.10 can be further simplified to \( T_{ij} S_w \rho_s \beta_s (1 - f) \text{CEC} \). Our model also assumes that the saturation exponent remains more or less the same in different directions. We will see later that this assumption agrees well with the experimental data.

The components of the conductivity formation tensor and connectivity tensor are related to each other by

\[ F_{ij} = T_{ij} \phi. \]  

(3.11)

Therefore, both conductivity formation factor and connectivity tensors share the same eigenvectors and, for the case of TI materials, the anisotropy ratio should be the same for bulk and surface conductivities. This important technical point will be experimentally verified in the last section of the present paper. In the isotropic case, one has

\[ F_{ij} = (1/F) \delta_{ij}, \]  

(3.12)

whereby
\[ T_y = (1/F\phi)\delta_y. \] (3.13)

Note that the tortuosity, \( \tau \), of the pore space in the isotropic case (\( \tau \geq 1 \)) is defined as (e.g., Pride, 1994; Zhang and Knackstedt, 1995; Clennell, 1997; Sevostianova et al., 2010; Zhang and Sherer, 2012)

\[ F = \frac{\tau}{\phi}, \] (3.14)

\[ \tau = F\phi = \phi^{1-m}, \] (3.15)

where we have used Archie’s equation (\( F = \phi^{-m} \) with \( m \) designating the porosity exponent, Archie, 1942). The iso-conductivity point designates the point characterized by a macroscopic conductivity equal to the pore water conductivity (e.g., Revil et al., 1998). Above the iso-conductivity point, surface and quadrature conductivity share the same bulk tortuosity, as discussed, for instance, by Revil and Glover (1997); the reason is the following: above the iso-conductivity point, surface conductivity is only a perturbation to the pore water conductivity and the electrical field is controlled by the conductivity of the pore space (see discussion in Bernabé and Revil, 1995, and Revil and Glover, 1997). Such a behavior explains why the same tortuosity is applied to the bulk and surface conductivities in the "high-salinity" regime. When surface conductivity dominates, conductivity is controlled by the distribution of surface conductance, and the tortuosity of electrical current along the surface of the minerals is different (usually higher) from that in pore water (see Bernabé and Revil, 1995, for a pore network modeling of this effect).

**Quadrature conductivity**

The expression for quadrature conductivity obtained by Revil (2013) is

\[ \sigma'' = S_w \rho \frac{1}{F\phi} \rho_{3S} s_i f CEC. \] (3.16)
We emphasize that the explicit dependence of quadrature conductivity on the inverse of the product \((F\phi)\) and on water saturation raised to the power \(p = n - 1\) are consistent with findings by Vinegar and Waxman (1984) and Revil (2013). However, Equation 3.16 is based on a volume averaging procedure while Vinegar and Waxman’s (1984) model is predominantly based on empirical considerations. Equation 3.16 agrees with Vinegar and Waxman’s (1984) observations in the laboratory (see also Revil, 2012 and 2013 for some tests using additional data sets). Field observations also confirm an effect of oil saturation upon quadrature conductivity (e.g., Olhoeft, 1986; Deceuster and Kaufmann, 2012).

The generalization of Equation 3.16 to anisotropic media is straightforward, namely,

\[
\sigma = \sigma_{ij}''x_i \otimes x_j, \quad (3.17)
\]

and

\[
\sigma_{ij}'' = T_{ij}S_{w}^{p}\rho_{3}\beta_{i+},f_{m}CEC, \quad (3.18)
\]

where \(\sigma''\) denotes the complex conductivity tensor and \(\sigma_{ij}''\) identifies the entries of this tensor. Our model also assumes that the \(p\)-exponent remains more or less the same in different directions like for the saturation exponent. We will see later that this assumption agrees well with the experimental data.

The complex conductivity tensor is defined as,

\[
\sigma^* = \sigma_{ij}^*x_i \otimes x_j, \quad (3.19)
\]

and

\[
\sigma_{ij}^* = \sigma_{ij}^{'}, \quad (3.20)
\]

where \(\sigma_{ij}^{'}\) and \(\sigma_{ij}''\) are given by Equations 3.10 and 3.18, respectively.
Dielectric constant

The remaining component of the generalized model is the (true or high-frequency) dielectric constant of porous material. In what follows, the notation $\varepsilon_w$ and $\varepsilon_o$ designates the dielectric constant of the water and oil phases, respectively, while $\varepsilon_S$ designates the dielectric constant of the solid phase. By invoking volume averaging, Revil (2013) obtained

$$\varepsilon' = \frac{1}{F} \left[ S_w^n \varepsilon_w + (1 - S_w^n) \varepsilon_o + (F-1) \varepsilon_S \right],$$

(3.21)

which can be simplified as

$$\varepsilon' = \frac{1}{F} \left[ S_w^n \varepsilon_w + (1 - S_w^n) \varepsilon_o \right] + \varepsilon_S,$$

(3.22)

for tight formations (recalling that $F>>1$). For anisotropic formations, Equation 3.22 can be generalized as

$$\varepsilon = \varepsilon_{ij} x_i \otimes x_j,$$

(3.23)

and

$$\varepsilon_{ij} = F_{ij} \left[ S_w^n \varepsilon_w + (1 - S_w^n) \varepsilon_o \right] + \varepsilon_{ij}^S,$$

(3.24)

where $\varepsilon_{ij}^S$ designates the components of the dielectric tensor of the solid phase $\varepsilon_S = \varepsilon_{ij}^S e_i \otimes e_j$. Note that the eigenvectors of this tensor correspond to the anisotropy of the solid matrix, and may be different from the eigenvectors associated with the tortuosity tensor of the pore space. In tight formations, the entries of $\varepsilon_S$ can be obtained by taking the core sample in vacuo, and measuring the components of the dielectric tensor in different directions. That said, we expect that in most conditions the eigenvectors of the dielectric constant to be aligned with the eigenvectors of the complex conductivity tensor. Josh et al. (2012) observed that the anisotropy ratio can reach a factor 5 for the high frequency dielectric constant (>0.1 GHz).
Ampère's law in anisotropic media

The general form of Ampère's law in tight formations is, therefore, given by

\[ \nabla \times \mathbf{H} = \left[ \sigma_{\text{eff}} - i\omega \varepsilon_{\text{eff}} \right] \cdot \mathbf{E}, \tag{3.25} \]

\[ \varepsilon_{\text{eff}} = \varepsilon_{ij} x_i \otimes x_j, \tag{3.26} \]

\[ \sigma_{\text{eff}} = \sigma_{ij} x_i \otimes x_j, \tag{3.27} \]

\[ \sigma_{ij}^{\text{eff}} \approx \sigma_{ij}' \approx F_{ij} S_w \rho_p S_\beta (1 - f) \text{CEC}, \tag{3.28} \]

and

\[ \varepsilon_{ij}^{\text{eff}} = F_{ij} \left[ S_w n \varepsilon_w + (1 - S_w n) \varepsilon_a \right] + \varepsilon_{ij}' - \frac{1}{\omega} T_{ij} S_w \rho_p S_\beta f_M \text{CEC}. \tag{3.29} \]

The above equations neglect an important polarization mechanism in the intermediate frequency range (0.1 MHz-100 MHz), often referred to as Maxwell-Wagner polarization. This polarization mechanism is related to the discontinuity of displacement currents at interfaces of porous composites. According to Revil (2013), Maxwell-Wagner polarization is not negligible but not as important as often emphasized in the technical literature. We acknowledge that this mechanism should be included in future studies.

In the next section, we discuss the properties of the tortuosity and formation factor tensors and describe their definition for anisotropic porous material.

**Formation factor and tortuosity tensors**

We first invoke the definition of two textural parameters, \( F \) and \( \Lambda \), defined in a number of previous studies (e.g., Johnson et al., 1986; Avellaneda and Torquato 1991; Pride, 1994). The canonical boundary value problem for the normalized potential \( \Gamma \) of a cylindrical representative elementary volume of porous material of length \( L \) can be written as

\[ \nabla^2 \Gamma = 0 \text{ in } V_p, \tag{3.30} \]
Figure 3.1  Description of the Representative Elementary Volume (REV) centered at point O. Vector $\hat{n}_s$ denotes the unit vector locally normal to the grains, $E$ denotes the macroscopic electrical field applied to the REV. The local electric field is written as $e$ in the main text and, in absence of electrical double layer, it is locally tangential to grain surfaces.

$$\hat{n}_s \cdot \nabla \Gamma = 0 \text{ on } S,$$  \hspace{1cm} (3.31)

and

$$\Gamma = \begin{cases} L \text{ at } z = L \\ 0 \text{ at } z = 0 \end{cases} \text{ on } S,$$  \hspace{1cm} (3.32)

where $z$ denotes the distance along the axis of the cylindrical core. In the above equations, $\hat{n}_s$ denotes the unit vector normal to the pore water/mineral interface, $S$ (directed from the pore to the solid phase, Figure 3.1), and $V_p$ designates pore volume. Boundary conditions defining the normalized potential $\Gamma$ are representative for the injection of an electrical current into a rock.
sample in the absence of surface conduction along the pore/water interface (see Johnson et al.,
1986, Avellaneda and Torquato, 1991). The formation factor \( F \) is defined as (Johnson et al.,
1986)

\[
\frac{1}{F} = \frac{1}{V} \int_{V_p} |\nabla \Gamma|^2 \, dV_p ,
\]  

where \( V \) is the total volume of the considered representative elementary volume. Similarly, the
tortuosity of the pore space is defined by Pride (1994) as

\[
\frac{1}{\tau} = 1 + \frac{\hat{z}}{V_p} \int_S \hat{n} \Gamma dS ,
\]  

where the integration is performed over the surface of the grain/pore water interface, \( S \).
Similarly, surface tortuosity could be defined from the surface formation factor introduced by
Revil and Glover (1997). However, such surface tortuosity is required in our model for the
reasons explained above.

In what follows, we designate \( e = -\nabla \Gamma \) the normalized electrical field (local electrical
field divided by the norm of the macroscopic imposed field). The previous set of definitions can
be readily generalized to the anisotropic case in the following manner:

\[
\mathbf{F} = \frac{1}{V} \int_{V_p} e \otimes e \, dV_p ,
\]  

and

\[
\mathbf{T} = \frac{1}{V_p} \int_{V_p} e \otimes e \, dV_p .
\]

Equations 3.35 and 3.36 show that \( \mathbf{F} \) and \( \mathbf{T} \) are symmetric.

Tortuosity and formation factor tensors can also be written in terms of three eigenvalues
\( T' \) (positive and less than one) for \( \mathbf{T} \) and \( (1/F_i^2) \) (\( F_i \) positive and greater than one) for \( \mathbf{F} \) and the
eigenvectors \( t' \) as
\[ T = \sum_{i=1}^{3} T^i t^i \otimes t^i, \quad (3.37) \]

and

\[ F = \sum_{i=1}^{3} \left( \frac{1}{F^i} \right) t^i \otimes t^i. \quad (3.38) \]

For isotropic media, the above formulations simplify to the classical tortuosity and formation factor (see Bear, 1988 for a description of the connectivity tensor),

\[ T^1 = T^2 = T^3 = \frac{1}{\tau}, \quad (3.39) \]

and

\[ F^1 = F^2 = F^3 = \frac{\tau}{\phi}. \quad (3.40) \]

The inverses of connectivity and conductivity formation factor tensors are obtained through the expressions

\[ T^{-1} = T_{ij}^{-1} e_i \otimes e_j = \sum_{i=1}^{3} \frac{1}{T^i} t^i \otimes t^i, \quad (3.41) \]

and

\[ F^{-1} = F_{ij}^{-1} e_i \otimes e_j = \sum_{i=1}^{3} F^i t^i \otimes t^i. \quad (3.42) \]

respectively. Note that for TI media, with (1,2) being the symmetry plane, one has \( F^1 = F^2 \neq F^3 \) and \( T^1 = T^2 \neq T^3 \). The anisotropy ratio is defined as \( \lambda = F^3 / F^1 = T^3 / T^1 \). Mudrock formations are expected to have a petrofabric obeying this type of symmetry. In such a case, our model predicts that the anisotropy ratio for in-phase conductivity should be the same as that of quadrature conductivity. In addition, the anisotropy ratio for formation factor should be the same for both surface and quadrature conductivities. We verify this prediction below.
Figure 3.2 Linear relationship between quadrature conductivity and cation exchange capacity of clayey materials assuming fully saturated conditions (NaCl solution), equal salinity (0.1 M), same temperature, same frequency (approximately 10 Hz), and same pH range (5-7). The solid line was calculated for a tortuosity of 1.5. Higher tortuosities would generate lines parallel to the one shown but would predict smaller quadrature conductivity amplitudes for the same values of CEC and salinity.

Influence of organic matter and kerogen content on complex conductivity

As emphasized above, CEC plays a critical role in controlling not only the surface conductivity of clayey materials (Waxman and Smits, 1968), but also their quadrature conductivity (Vinegar and Waxman, 1984; Revil, 2012), or equivalently the low-frequency dielectric constant (Josh et al., 2012; Revil, 2013). This behavior is illustrated in Figure 3.2 for the quadrature conductivity of porous siliciclastic materials.

In our model, quadrature conductivity can be expressed as a function of CEC as
\[ \sigma'' = -b \text{CEC}_M, \]  
(3.43)

and

\[ b = \beta_{(\tau),j}^S \rho_s T. \]  
(3.44)

For isotropic and kerogen-free materials, Figure 3.2 plots Equation 3.43 with \( b = bI \) (\( I \) denotes the identity \( 3 \times 3 \) matrix) and \( b = 2.38 \times 10^{-7} \text{ S kg C}^{-1} \text{ m}^{-1} \) (\( F\phi \) has been replaced by a tortuosity of \( 3/2 \), roughly the tortuosity of a path around spherical grains) against measurements. For fine-grained shales, tortuosity is expected to be much higher than 1.5. The last section of this paper shows that the tortuosity of bulk pore space of a mudrock can exceed 100. In turn, this behavior implies that for the same CEC, the quadrature conductivity of a mudrock is much smaller than for the case of a porous shaly sand (typically 1.5 to 3, see Vinegar and Waxman, 1984). Such an observation will also be discussed in the last section of the paper.

In Figure 3.3, we also test the fact that, according to our model, the salinity dependence of quadrature conductivity is governed by the salinity dependence of the partition coefficient, \( f \). This salinity dependence is discussed in Appendix B. As \( f \) increases with salinity, we expect the magnitude of the quadrature conductivity to increase with salinity in agreement with what is shown in Figure 3.3 (see also Weller et al., 2011; Revil and Skold, 2012; Weller and Slater, 2012; and Revil et al., 2013).

In mudrocks (or in soils rich in organic matter), one may wonder about the role of kerogen or humic substances on complex conductivity. Kerogens are commonly present in high concentration in mudrocks, which clearly indicates they are potential source rocks for hydrocarbon deposits. However, this also indicates the solid phase comprises an additional component, which is characteristically distinct from the mineral rock matrix and should be accounted for in the analysis of complex conductivity.
Figure 3.3 Influence of the salinity on the magnitude of quadrature conductivity. The increase of salinity is responsible for an increase of the magnitude of quadrature conductivity. In our model, this effect is related to the effect of salinity on the partition coefficient, $f$, of counterions in the Stern layer.

To understand the CEC or specific surface area (SSA or $S_{sp}$) of kerogen-rich rocks, it is important to emphasize the CEC or specific surface area of the kerogen itself. Few published works have considered the CEC / specific surface area measurements in oil or gas mudrocks. In that context, Derkowski and Bristow (2012) addressed the important question of whether sedimentary organic matter (mostly kerogen) in oil and gas mudrocks exhibits similar properties to those of organic matter found in soils. Indeed, during burial, organic matter has been subjected to pressure and temperature changes; these changes can alter the original properties.
Helling et al. (1964) reported a CEC for organic matter in soils, for pH between 6 to 8, in the range 1.6 to 2.1 meq g\(^{-1}\) [1 meq g\(^{-1}\) = 96,320 C kg\(^{-1}\), equating to (1.5-2.0)\(\times\)10\(^5\) C kg\(^{-1}\) in SI units]. Kaiser et al. (2007) reported CEC values for organic matter of soils in the order of (0.3-3.5)\(\times\)10\(^5\) C kg\(^{-3}\) at pH 7. These values are extremely high and similar to the cation exchange capacity of smectite (about 1 meq g\(^{-1}\), 10\(^5\) C kg\(^{-3}\), e.g., Revil, 2012), the clay mineral with the highest cation exchange capacity. Humus is known to have a CEC greater than smectite. This cation exchange capacity is explained by the high reactivity of the surface of organic matter as well as by the existence of isomorphic substitution in the organic macromolecules themselves (such as with smectite). Figure 3.4 shows different reactive sites on the surface of organic matter that are responsible for their high CEC. At near neutral pH values, the number of electrical charges per unit surface area can be determined as the ratio of total charge per unit mass CEC to total surface area per unit mass SSA; for humus: 559 cMol kg\(^{-1}\) (5.6\(\times\)10\(^5\) C kg\(^{-3}\)) by 7.2 \(\times\) 10\(^5\) m\(^2\) kg\(^{-1}\); this yields a surface charge of 0.78 C m\(^{-2}\) (about 5 elementary charge per nm\(^2\)), a value that is approximately twice that of clays (e.g., Woodruff and Revil, 2011).

The CEC and specific surface area of soil or oil mudrocks can therefore be written as

\[
\text{CEC} = \sum_{i=1}^{N} \chi_i \text{CEC}_i, \tag{3.45}
\]

and

\[
S_{sp} = \sum_{i=1}^{N} \chi_i S_{sp,i}, \tag{3.46}
\]

where \(N\) is the number of the mineral phases (including kerogen in oil mudrocks or organic matter in soils) and \(\chi_i\) denotes the mass fraction of the \(i\)–th mineral with respect to the total mass of dry solid. In oil mudrocks, CEC can be expected to be dominated by clay minerals and kerogen, whereby
Figure 3.4 Surface sites of organic substances such as humic acids. \textbf{a.} The surface of organic matter is generally negative at neutral pH values and characterized by high values of specific surface area and cation exchange capacity. Surface charge can be positive below pH 2. A pH-dependent charge on the surface of these macromolecules, there is a permanent electric charge associated with isomorphic substitutions. \textbf{b.} Example of humic acid (Leonardite) showing different types of surface sites. Note that CEC also increases with oxidation of such organic molecules (modified from http://www.phelpstek.com/portfolio/samples/humic_acid.html).
where the subscripts K, I, and S refer to kaolinite, illite, and smectite, respectively, while Ke refers to kerogen. There are five types of kerogen defined in the literature: Type I (sapropelic, formed from protein and lipids of mostly algae), Type II (Planktonic, formed from lipids of plankton deposited under reducing conditions), Type II-S (similar to type II with a high sulfur content), Type III (humic, from terrestrial plants), and Type IV (contains mostly decomposed organics). It is possible the kerogen CEC and SSA depend on the type and maturity of kerogen.

The CEC of humic matter and kerogen can be related to the quantity of carbon in oil mudrocks. For soils that are rich in organic matter, it is known that cation exchange capacity is highly correlated with carbon content (Figure 3.5). Therefore, one could expect a correlation between TOC (total amount of organic carbon content in weight %) of kerogen and cation exchange capacity of the material. That said, experimental results available in the literature are conflicting (see the discussion in Derkowski and Bristow, 2012). The CEC of kerogen is believed to be very small compared to the CEC of organic matter in soils because all the
available exchangeable sites in functional groups shown in Figure 3.4 may have been polymerized during burial (see Vandenbroucke and Largeau, 2007). Derkowski and Bristow (2012) indicate that the thermal treatment used prior to CEC measurements can reanimate some of these functional sites (possibly through the deprotonation of carboxylic acids) and lead to a CEC associated with kerogen which may explain conflicting results found in the literature. Derkowski and Bristow (2012) observed an inverse relationship between kerogen maturity and the amount of carboxylic groups. It then follows that immature kerogen has greater susceptibility to thermal activation. Therefore, the thermal treatment applied to less mature kerogen may substantially increase the CEC of the material, as well as surface conduction and quadrature conductivity (polarization).

In summary, we believe that the CEC of kerogen can be neglected in the evaluation of the quadrature conductivity of hydrocarbon-bearing tight mudrocks (Derkowski and Bristow, 2012) but not the specific surface area, which can be very high. Derkowski and Bristow (2012) reported a specific surface area in the range from 700 to 920 m² g⁻¹ for kerogen extracted from the mature Red Bird and Monterey formations. This represents a range of values very similar to that measured for smectite (e.g., Woodruff and Revil, 2011). For the Woodford formation, Derkowski and Bristow (2012) measured the excess specific surface area not accounted for by clay minerals. As shown in Figure 3.6, such an excess surface area is correlated with total amount of organic carbon content (in weight %). The relationship can be written as

\[
S_{sp}(\text{Kerogen}) = a \text{TOC}(%),
\]

where \( a \approx 10 \). For pure kerogen, the above expression yields \([ \text{TOC}(%)=100]\) a specific surface area of 1000 m² g⁻¹, which is only slightly higher than values given above. Therefore, specific surface area is given by
Figure 3.6 Relationship between excess specific surface area (clay contribution removed) and total organic content (weight %) for kerogen-rich oil shales. Data from Derkowski and Bristow (2012) for the Woodford formation.

\[ S_{sp} = \chi_{Clay} S_{sp,clay} + S_{sp,Ke} \text{TOC}, \quad (3.50) \]

where TOC is expressed in mass fraction (in %). However, it is unclear at this point whether kerogen would impact the quadrature conductivity through its surface area. In principle, if there is no Stern layer associated with kerogen (no reactive sites), presence of kerogen in oil and gas mudrocks should have no impact on quadrature conductivity. Therefore if the specific surface area is used to assess the quadrature conductivity, the former should be corrected for the contribution of kerogen. The TOC content might also change the tortuosity of the porous body and indirectly affect the bulk conductivity. Furthermore, if bitumen is present, the polar components might contribute to the surface conductivity. However, these effects need to be verified by experimental evidence.

Comparison to experimental data

This section analyzes the complex conductivity of two Bakken core samples. The Bakken formation is a Late Devonian Early Mississippian shale (deposited approximately 360
Table 3.1 Properties of the two core samples. Porosity is non-kerogen matrix porosity. The reported density is bulk density (grain density is estimated at 2650 kg m\(^{-3}\)). Reference depth: Kelly bushing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>(\phi)</th>
<th>Density (kg m(^{-3}))</th>
<th>TOC (wt%)</th>
<th>Hydrogen Index</th>
<th>Maturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakken A</td>
<td>2630</td>
<td>0.028</td>
<td>1,990</td>
<td>20.1</td>
<td>584</td>
<td>II</td>
</tr>
<tr>
<td>Bakken B</td>
<td>3098</td>
<td>0.032</td>
<td>2,220</td>
<td>12.1</td>
<td>436</td>
<td>III</td>
</tr>
</tbody>
</table>

millions of years ago) located in the Williston Basin, underlying parts of Montana, North Dakota, and Saskatchewan. Sample A was acquired at a depth of 2630 m while Sample B was acquired at 3098 m. The deeper sample, Sample B, is from the higher-temperature, central portion of the Williston Basin, whereas the second core sample is from the basin’s margin. Table 3.1 summarizes the properties of the two core samples. Porosity was measured by hydrogen adsorption, which does not account for the percentage weight (wt\%) of kerogen; 20wt\% kerogen results in 40-70 vol\% kerogen, depending on the density of kerogen (Prasad et al., 2011). Average non-kerogen porosity in Bakken shale samples is approximately 3%.

**Material and methods**

Spectral induced polarization measurements were performed using an apparatus developed at the Central Laboratory for Electronics, ZEL, at the Forschungszentrum Jülich, in Germany by Zimmermann et al. (2008). Various tests of this impedance meter have been documented by Revil and Skold (2011) and will not be repeated here. Electrodes used were sintered Ag/AgCl\(_2\) 2 mm pellet electrodes for voltage measurements (http://www.science-products.com/Products/CatalogG/IVM-AgAgCl\(_2\)-Pellets/ivm.html), and transcutaneous electrical nerve stimulation (TENS) adhesive electrodes (https://www.djoglobal.com/products/chattanooga/dura-stick-ii-self-adhesive-electrodes) for current injection (see Figure 3.7 for a description of the position of the electrodes).
Figure 3.7 Cell and geometry of measurement acquisition for transverse and in-plane electrical conductivity measurements with respect to bedding plane. a. Sketch of the cell. b. Geometry of the electrodes. A and B denote current electrodes while M and N denote voltage electrodes. The geometric factor was computed as $k = A/L$, where $L$ is the distance between the M and N electrodes (1/3 of the height of the sample) and $A$ is the cross sectional area of the cylindrical core sample. The current electrodes are coupled to the sample with a conductive electrolytic gel-adhesive (designed for use on human skin in nerve stimulation therapy applications), while the potential electrodes are coupled to the sample through a conductive electrolyte gel. The current electrodes can be removed and reused in repeat acquisitions; here depicted as detached from the sample to illustrate the size and shape, corresponding to the end faces of the sample. The sample surface (except at the position of the electrodes) is covered with quick dry nail polish, which prevents desaturation and is a good insulator.

The Bakken samples were saturated with three pore-water solutions of varied salinity derived from an equilibrium solution obtained by saturating (distilled) DI water with a soluble mineral fraction of pulverized core fragments. A low-salinity limit of 0.5 mM was estimated as the equilibrium concentration of NaCl. Solutions were also prepared for 0.05 M and 0.5 M. The samples were initially saturated with equilibrium water under sequential pressurizations up to 10.3 MPa (1500 psi), and re-saturated with the remaining solutions in two stages. Spectral induced polarization acquisitions were made at each of the three stages. Due to the low diffusion
Table 3.2  In phase $\sigma'$ and quadrature conductivity $\sigma''$ at different salinities ("I" stands for in-plane measurements while "T" stands for transverse measurements with respect to bedding plane).

<table>
<thead>
<tr>
<th></th>
<th>0.5 mM</th>
<th></th>
<th>0.05 M</th>
<th></th>
<th>0.5 M</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in-phase</td>
<td>quadrature</td>
<td>in-phase</td>
<td>quadrature</td>
<td>in-phase</td>
<td>quadrature</td>
</tr>
<tr>
<td>Bakken A-I</td>
<td>7.82E-03</td>
<td>2.91E-05</td>
<td>1.01E-02</td>
<td>3.46E-05</td>
<td>1.54E-02</td>
<td>6.59E-05</td>
</tr>
<tr>
<td>Bakken A T</td>
<td>8.87E-04</td>
<td>4.65E-06</td>
<td>1.17E-03</td>
<td>5.52E-06</td>
<td>1.96E-03</td>
<td>4.03E-06</td>
</tr>
<tr>
<td>Bakken B-I</td>
<td>3.33E-04</td>
<td>6.29E-06</td>
<td>1.53E-03</td>
<td>2.06E-05</td>
<td>3.15E-03</td>
<td>3.21E-05</td>
</tr>
<tr>
<td>Bakken A-T</td>
<td>4.73E-05</td>
<td>9.23E-07</td>
<td>1.53E-04</td>
<td>2.72E-06</td>
<td>9.22E-04</td>
<td>4.05E-06</td>
</tr>
</tbody>
</table>

coefficient for the NaCl solution in the samples, approximately $10^{-11}$ m²s⁻¹ (Revil et al., 2005), the equilibration time at each stage is in the order of several weeks (the average radius of the cylindrical samples is 0.010 m, yielding $1 \times 10^{-4} / 2.5 \times 10^{-11} = 4 \times 10^6$ s $\approx$ 46 days). The brine is degassed prior to the saturation. The saturated samples are immersed in the respective equilibrium solution and stored at low pressure close to vacuum conditions.

Complex spectra of the eigenvalues of the electrical impedance tensor were obtained directly by following the single-component polarization protocol with the 4 electrode impedance spectroscopy method developed by Zimmermann et al. (2008). The Bakken B specimens are cylindrical cores with a radius of 12.6 mm and heights 38.3 mm and 30.8 mm for the in-plane and transverse directions, respectively; geometric factors were obtained numerically using a Comsol Multiphysics simulator. We perform the measurements at laboratory temperature and pressure; we coated the samples in quick dry nail polish to prevent both evaporation at the core surface, as well as impose an insulating boundary, constituting a closed electrical system for the measurements. With this approach, no sample holder is required. The coating is easily removed with acetone to maximize surface exposure for subsequent pressurizations. Spectral complex conductivity tensors were determined from the measured directional impedances of the samples. Table 3.2 summarizes the in-phase and quadrature conductivity of the two core samples at 1 Hz.
Figure 3.8 Measured phases for Samples A and B. Note the continuous increase of the magnitude of the phase with the frequency. The high frequency response is likely due to Maxwell Wagner polarization.

We also performed spectral induced polarization at five different stages, referred to below as stages I through V, during the pressurized saturation sequence, capturing unsaturated measurements at different water contents for Sample B. The samples were pressurized at increasing sequential maximum confining (hydrostatic) pressures of 0.69 MPa, 3.45 MPa, 6.89 MPa, and 10.34 MPa. Stages I and II were completed in two successive 24 hour periods, and stages III and IV in successive 48 hour periods. An additional measurement was made after 30 days to represent the final saturation state, stage V (the datasets of stages IV and V are equivalent, evidencing full saturation of the sample; the stage V measurements are used in our analysis). The water content is determined through gravimetric monitoring at each saturation stage.
Results under saturated conditions

Figure 3.8 shows the raw data for the phase. The tangent of the phase angle is defined as the ratio of quadrature conductivity to in-phase conductivity. Figure 3.8 reveals only a fair agreement between the phases measured in the in-plane and transverse directions of the core samples at low frequencies. The magnitude of the phase increases slightly with frequency below 100 Hz and faster above 100 Hz. The polarization of the electrical double layer is expected to dominate the response of the quadrature conductivity below 100 Hz, while above 100 Hz, the response is partly controlled by the true dielectric polarization of the material with some influence from the Maxwell-Wagner polarization (see Revil, 2013) and possibly some electromagnetic coupling effects.

The complex conductivity spectra are plotted as a function of frequency for the three salinities in Figure 3.9 for Sample A, and in Figure 3.10 for Sample B. In-phase conductivity data display only weak dependence with respect to frequency as already observed for other clay-
Figure 3.10 Complex electrical conductivity spectra of Bakken core Sample B. **a.** In-phase electrical conductivity versus frequency at three salinities (0.5, 0.05, and 0.005 M NaCl). **b.** Quadrature electrical conductivity versus frequency at three salinities (0.5, 0.05, and 0.005 M NaCl).

Rich materials (see Vinegar and Waxman, 1984; Slater and Lesmes, 2002; Revil, 2012). Quadrature conductivity spectra exhibit a plateau at low frequencies and an increase in magnitude at high frequencies due to Maxwell-Wagner polarization and true dielectric polarization (Revil, 2013).

We first test our prediction regarding anisotropy ratio for in-phase and quadrature conductivities (see Figure 3.11). The mean anisotropy ratio is 8.1±3.1 (N = 12, N: number of measurements) for in-phase and quadrature conductivity data acquired together for the two core samples (7.6±2.3, N = 6, for the in-phase conductivity and 8.5±3.8, N = 4, for the quadrature conductivity). The anisotropy ratio is approximately the same for both in-phase and quadrature conductivities. This behavior is consistent with the predictions of our model.

We now focus on the relationship between in-phase conductivity and pore water conductivity of NaCl solutions. Electrical conductivity of water can be described using the semi-
Figure 3.11 In-phase and quadrature electrical conductivities for core samples A and B at 1 Hertz.  

- **a.** In-phase electrical conductivity, Sample A. Lines identify the model fit (equation 5 at saturation).
- **b.** In-phase conductivity, Sample B. For the two upper graphs, the lines identify the model fit. Formation factors and surface conductivities are reported in Table 3.
- **c.** Quadrature electrical conductivity, Sample A (the points at the highest salinity are not shown because of their uncertainties). The vertical line serves as guide.
- **d.** Quadrature conductivity, Sample B. For the two lower graphs, the lines serve as guides. Anisotropy ratio is defined as the ratio of the highest to the lowest eigenvalues of the tensor; it exhibits a mean of $8.1 \pm 3.1$ ($N = 12$).
Table 3.3 Formation factor, $F$, surface conductivity, $\sigma_s$, porosity exponent, $m$, and tortuosity, $\tau$ ("I" stands for in-plane measurements while "T" stands for transverse measurements with respect to bedding plane). The tortuosity in a given direction is determined by the product of the formation factor times porosity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F$(I)</th>
<th>$F$(T)</th>
<th>$\sigma_s$(I, $\times 10^{-4}$ S/m)</th>
<th>$\sigma_s$(T, $\times 10^{-4}$ S/m)</th>
<th>$m$(I)</th>
<th>$m$(T)</th>
<th>$\tau$(I)</th>
<th>$\tau$(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakken A</td>
<td>543±100</td>
<td>3770±530</td>
<td>84±7</td>
<td>9.6±0.8</td>
<td>1.76</td>
<td>2.30</td>
<td>15.2</td>
<td>106</td>
</tr>
<tr>
<td>Bakken B</td>
<td>406±130</td>
<td>4350±30</td>
<td>3.2±0.8</td>
<td>0.43±0.03</td>
<td>1.75</td>
<td>2.43</td>
<td>13.0</td>
<td>139</td>
</tr>
</tbody>
</table>

The empirical relation derived by Sen and Goode (1992), i.e.

$$
\sigma_f(C_f;T) = (d_1 + d_2 T + d_3 T^2)C_f - \frac{d_4 + d_5 T}{1 + d_6 C_f} (C_f)^{3/2},
$$

where $d_1 = 5.6$, $d_2 = 0.27$, $d_3 = -1.51 \times 10^{-4}$, $d_4 = 2.36$, $d_5 = 0.099$, $d_6 = 0.214$, $\sigma_f$ is electrical conductivity of water (in S m$^{-1}$), $T$ is temperature (in °C) and $C_f$ is salinity (in M, mol L$^{-1}$). This relation yields pore water conductivities of 3.82 S m$^{-1}$, 0.49 S m$^{-1}$, and 0.0054 S m$^{-1}$. Figure 3.11 shows the corresponding in-phase and quadrature conductivities as a function of conductivity of pore water solution. The relationship between in-phase conductivity and pore water conductivity is used to determine formation factor and surface conductivity in the in-plane and transverse directions with respect to bedding plane. Table 3.3 reports the formation factors and surface conductivities, together with the determination of Archie’s porosity exponent ($m = -\ln F / \ln \phi$ in the two directions) and tortuosity ($\tau = F \phi$). For Samples A and B, the surface conductivity anisotropy ratios are $8.8\pm0.9$ and $7.4\pm0.8$, respectively. These values are comparable to the anisotropy ratios for the quadrature conductivity, $6.3\pm0.7$ and $6.8\pm0.8$, respectively for Samples A and B.

The immature sample A may have higher clay content, which could explain the higher surface conductivity than observed for sample B. Regarding quadrature conductivity, the in-plane (I) and transverse (T) quadrature conductivities are given by
\[ \sigma''(I) = -\frac{\beta_s^+ f \rho_s}{\tau_I} CEC_M, \quad (3.52) \]

and

\[ \sigma''(T) = -\frac{\beta_s^+ f \rho_s}{\tau_T} CEC_M, \quad (3.53) \]

while surface conductivities in the in-plane and transverse directions are given by

\[ \sigma_s(I) = \frac{\rho_s \beta_{(+)}(1-f)}{\tau_I} CEC_M, \quad (3.54) \]

and

\[ \sigma_s(T) = \frac{\rho_s \beta_{(+)}(1-f)}{\tau_T} CEC_M, \quad (3.55) \]

respectively, where \( \beta_{(+)}(\text{Na}^+, 25^\circ\text{C}) = 5.2 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1} \) and \( \beta_{(+)}^s(25^\circ\text{C}, \text{Na}^+) = 1.5 \times 10^{-10} \text{ m}^2\text{s}^{-1}\text{V}^{-1} \) for clay minerals (Revil, 2012, 2013). We first determine the CEC using Equations 3.53 and 3.54, and \( f \) close to 1. Very consistent values are obtained at high salinities with CEC = 2500 ± 300 C kg\(^{-1}\) for sample A and CEC = 1200 ± 300 C kg\(^{-1}\) for sample B. This behavior agrees with the known CEC of the Bakken shale, which is in the order of \( 10^{-2} \) to \( 10^{-1} \) meq g\(^{-1}\) (about 1000 to 10,000 C kg\(^{-1}\); data obtained from the North Dakota Industrial Commission, Department of Mineral Resources, Oil and Gas Division online subscription database, https://www.dmr.nd.gov/oilgas/subscriptionservice.asp). Using Equations 3.54 and 3.55, we obtain \( f = 0.78 \pm 0.03 \) for Sample A and \( f = 0.99 \) for Sample B. The values of CEC and \( f \) obtained by our model are consistent with the expected their respective relationship to clay type, and may imply that sample A is richer in smectite and that Sample B is rich in kaolinite.

Figure 3.12 describes the impact of anisotropy and increase of tortuosity for the Bakken shale by comparison to shaly sands investigated by Vinegar and Waxman (1984) and the
Figure 3.12 Influence of anisotropy and tortuosity upon quadrature conductivity (1 Hertz). The high tortuosities found in Bakken rocks are responsible for a decrease of quadrature conductivity at a given salinity and CEC. For Bakken rock samples, data are consistent with a tortuosity value of 15 in the bedding plane and over 100 in the transverse direction.

Saprolites investigated by Revil et al. (2013). As predicted by our model, at given values of CEC and salinity, the magnitude of quadrature conductivity is expected to decrease with the increase of tortuosity and differ in the in-plane and transverse directions (respective to bedding). Tortuosity in the in-plane direction is also found to be much smaller than in the transverse direction. As shown in Figure 3.13a, differential compaction during burial is responsible for the formation of a bedding plane with the shale, thereby becoming a TI medium. In this case, we expect the tortuosity in the in-plane direction to be substantially smaller than in the transverse direction (Figure 3.13b). Tortuosity in this case can also be related to the aspect ratio of grains,
Figure 3.13 Influence of burial on both petrofabric and tortuosity tensor. **a.** Differential compaction is responsible for the formation of petrofabric in clayey materials (clay particles are shown in black). Depositional facies and burial are typically responsible for the formation of TI (transversely isotropic) media. **b.** In TI media, the in-plane tortuosity is expected to be much smaller than the tortuosity in the direction transverse to bedding plane.

as discussed in Mandelson and Cohen (1982). Other published experimental works have reported very high tortuosities; for instance Revil et al. (1996) reported tortuosities in the range of 2 to 46 for doleritic core samples. Zhang and Scherer (2012, their Table 3.6) have reported electrical tortuosities in the range 2 to 118 for tight shales. Values higher than 100 were obtained for very tight specimens with porosities below 3%.

**Results under unsaturated conditions**

Figure 3.14 shows the in-phase and quadrature conductivities of Sample B at different saturations. It is clear from this figure that saturation does not change the anisotropy ratio of the material. In-phase and quadrature conductivity data are plotted as a function of saturation in Figure 3.15. Measurements are fitted with a power-law relationship to determine the saturation $n$-
Figure 3.14  Influence of saturation upon in phase and quadrature conductivities of Sample B. a. In-plane measurements for in-phase and quadrature conductivities. b. Transverse measurements for in-phase and quadrature conductivities. Note that a change in saturation affects the magnitude of the in-phase and quadrature conductivities, not the anisotropy ratio. This result is consistent with our assumption to consider that $n$ and $p$ do not depend too much on the direction.
Figure 3.15 Influence of the saturation on the in-phase and quadrature conductivity of Sample B at 1 Hz. a. In-phase conductivities (in-plane and transverse measurements). b. Quadrature conductivities (in-plane and transverse measurements).

The first observation is that the $n$ and $p$ exponents do not exhibit significant anisotropy ($n = 2.7\pm0.4$ in the in-plane direction and $n = 2.4\pm0.3$ in the transverse direction and $p = 1.8\pm0.1$ in the in-plane direction and $p = 1.4\pm0.2$ in the transverse direction). Figure 3.16 reports the values of the two exponents together with the $n$ and $p$ exponents of isotropic sedimentary materials (see Revil, 2013). All the data conform fairly well to the general trend $p = n-1$.

Conclusions

We introduced a new petrophysical model to describe the complex electrical conductivity tensor of oil mudrocks. The model accounts for anisotropy, saturation, porosity, and cation exchange capacity/specific surface area of rocks. Verification experiments were performed on two core samples from the Bakken formation. The following conclusions stem from the work presented in this paper:
Figure 3.16 Relationship between the $p$-exponent used to describe the saturation dependence of the quadrature conductivity and the $n$-exponent (saturation exponent) used to describe the saturation dependence of the in-phase conductivity when surface conductivity is negligible. The plain line corresponds to the relationship developed in Revil (2013), which is consistent with the prediction of the model of Vinegar and Waxman (1984).

(1) In-phase electrical conductivity is controlled by a formation factor tensor while quadrature conductivity is controlled by a tortuosity tensor of the bulk pore space. Both tensors are interrelated through the connected porosity.

(2) The CEC of kerogen is believed to be very small in comparison to the CEC of organic matter in soils. Indeed, because of diagenesis, all the exchangeable sites in the functional groups of organic matter may have been polymerized; therefore, the surface of kerogen may not impact both surface and quadrature conductivity of oil and gas mudrocks.

(3) Experimental data confirmed our model prediction that the anisotropy ratio is the same for in-phase and quadrature conductivities. It was also confirmed that the anisotropy ratio is the same for formation factor and surface conductivity. The anisotropy ratio for the complex
conductivity tensor is $8.1 \pm 3.1$ for the two Bakken core samples. Our model predicts an invariant phase angle for both in-plane (I) and transverse (T) measurements for all frequencies. This behavior is only approximately shown by experimental data acquired at low frequencies; additional data will be needed for verification.

(4) Measurements performed on two rock samples from the Bakken formation indicate that our model provides a simple explanation for (a) the dependence of quadrature conductivity on salinity and (b) the effect of increase of tortuosity on the decrease of the magnitude of quadrature conductivity. The bulk tortuosity in the direction transverse to bedding plane is found to be higher than 100. This very high value of tortuosity is likely associated with the aspect ratio of grains.

(5) The decrease of saturation does not significantly change the degree of anisotropy observed for the quadrature and in-phase conductivities under saturated conditions. It follows that the $p$-exponent characterizing the saturation dependence of quadrature conductivity can be related to the saturation exponent $n$ by $p = n-1$.

Acknowledgments

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CHAPTER 4
LABORATORY DETERMINATION OF THE COMPLEX CONDUCTIVITY TENSOR OF UNCONVENTIONAL ANISOTROPIC SHALES

A publication in Geophysics

W. F. Woodruff, A. Revil and C. Torres-Verdin

Abstract.

A four-electrode acquisition system is developed to measure the complex conductivity tensor of tight and anisotropic shale cores using an accurate impedance meter. The complex conductivity tensor was obtained by inverting complex electrical potential data (amplitude and phase) acquired over a distributed electrode array. Inversion of the acquired data is performed with a Markov chain Monte Carlo (McMC) sampler that can explicitly take into account the non-uniqueness of the inverse problem. This approach is validated with direct measurements of impedance tensor eigenvalues with a single-component measurement technique. Consistent results were obtained using these two methods validating those obtained through the McMC sampling strategy. Both the in-phase and quadrature conductivities are anisotropic with the same anisotropic ratio in agreement with a recently developed petrophysical model based on volume averaging. The type of anisotropy of the Bakken and Haynesville core samples is found to be transverse isotropic (TI), with the anisotropic ratio on the order of 10. In-phase conductivity is found to be independent of frequency up to 100 Hertz while the magnitude of the quadrature conductivity increases with frequency in the range 0.1 to 45 kHz. Both components are sensitive to water saturation. Surface conductivity can be reliably predicted from the quadrature conductivity, which is in agreement with the model prediction.
Introduction

The prevalence of shale plays in the U.S. represents a significant factor in progress toward reducing American dependence on foreign oil. According to the 2012 U.S. Geological Survey National Assessment of Oil and Gas Project, the United States has over 36 billions of barrels of oil and 1,106 trillions of cubic feet of gas, representing 97% of the total domestic discovered and undiscovered hydrocarbon resources. Unconventional reservoirs account for more than half of this estimated resource. However, the exploration and development of oil and gas shales pose some unique and challenging problems, which have triggered recent research projects to better understand the petrophysical and geophysical properties of those materials.

Spectral Induced Polarization (SIP) is non-intrusive approach to study and characterize the complex conductivity of shale rocks because of its sensitivity to fluid-phase saturation (Cosenza et al., 2007; Ghorbani et al., 2009; Jougnot et al., 2010). Despite the fact that the understanding of induced polarization presents challenges of its own, there have been significant progresses in the past few years in our mechanistic understanding of induced polarization in clay-rich materials (see for instance the POLARIS model developed by Revil, 2012, and extended by Revil, 2013a, b, Revil et al., 2013a, b, c). Additionally, the complex conductivity of porous rocks is dependent upon parameters of prime importance in unconventional shale formation evaluation including the distribution of pore throat sizes (Revil et al., 2013d), salinity (Weller et al., 2011; Revil and Skold, 2011), formation factor (Vinegar and Waxman, 1984), permeability (Slater and Lesmes, 2002; Revil and Florsch, 2010; Zisser et al., 2010), and saturation and wettability of the fluid phases (Vinegar and Waxman, 1984; Schmutz et al., 2010, 2012).
A number of published studies have focused on the anisotropy of the electrical resistivity of rocks including shales (Clavaud, 2008; Ellis et al., 2010; Kickhofel et al., 2010; Robion et al., 2012) and various methods have been introduced to determine their electrical conductivity/resistivity tensor (Kohn and Vogelius, 1984; Lee and Uhlmann, 1989; Pain et al. 2003). However, as far as we know, the present work is the first one to deal with the stochastic inversion of azimuthal complex conductivity measurements to determine the complex conductivity tensor of shales in the frequency range 0.1 Hz to 45 kHz. Previous works were based on deterministic approaches, which may lead to incorrect results in the presence of non-uniqueness in the inverse solution (e.g., in the presence of strong heterogeneities).

Zisser and Nover (2009) investigated the complex resistivity tensor of tight rocks at frequencies >10 kHz. These frequencies are mostly higher than those investigated in the present work. At these higher frequencies, the polarization of the rock is general dominated by Maxwell-Wagner and true dielectric polarization effects (Revil, 2013a). There are also a number of theoretical works on modeling the conductivity of anisotropic media (Mendelson and Cohen, 1982; Kachanov and Sevostianov, 2005; Dewhurst and Siggins, 2006; Sevonstianova et al., 2010) but they do not discuss surface conductivity and the existence of quadrature conductivity. It follows that the frequency-dependent, complex conductivity tensor, with in-phase and quadrature components, has received no attention so far.

In the present work, we focus on the inversion of the complex conductivity tensor of oil- and gas-bearing shales in the frequency range 0.1 Hz to 45 kHz and we discuss the interpretation of the new experimental data. We performed azimuthal sampling of the complex electrical potentials (magnitude and phase) when the samples were subject to an imposed harmonic electrical current. The raw data are inverted with a Markov chain Monte Carlo (McMC)
sampling strategy solving the complex Laplace equation for the forward model and taking into account the position of the electrodes, their size, and the boundary condition for the current density at the border of the sample. This method will be validated by a direct measurement of the eigenvalues of the complex conductivity tensor using a polarized, single-component stimulus current, for which the principal eigenvectors of the sample are assumed to be known.

The complex conductivity tensor

We summarize here the results of Revil et al. (2013c) in developing a model describing the physics of the low-frequency (<10 kHz) complex conductivity tensor of shale and mudrocks. The complex conductivity tensor accounts for both conduction (corresponding to the real or in-phase components of the tensor) and polarization (corresponding to the imaginary or out-of-phase components). In clay-rich materials, the observed low-frequency polarization is mostly due to the polarization of the electrical double layer (Leroy and Revil, 2009). Unfractured compacted shales are intrinsically anisotropic and exhibit characteristic hexagonal symmetry (transverse isotropy, TI), which usually implies that there is a plane of symmetry in the material (e.g., Cosenza et al., 2006). This plane of symmetry can be either assumed using independent information or inverted from a collection of data at different frequencies with an array of electrodes.

The complex conductivity tensor $\sigma^*$ is related to its complex-valued components $\sigma_{ij}^*$ by,

$$\sigma^* = \sigma_{ij}^* e_i \otimes e_j,$$

where $e_i$ ($i = 1, 2, 3$) denote the basis vectors of the Cartesian frame of reference ($e_i \cdot e_j = \delta_{ij}$ where $\delta_{ij}$ denotes the Kronecker delta), $a \otimes b$ represents the tensorial product between vectors $a$ and $b$, and
\[ \sigma_{ij}^* = \sigma_{ij}' + i\sigma_{ij}'' , \] (4.2)

where \( i^2 = -1 \) (\( i \) is the pure imaginary number) and each component \( \sigma_{ij}^* \) can be written as a complex number. The components \( \sigma_{ij}' \) represent the real (in-phase) components of the complex conductivity tensor while the components \( \sigma_{ij}'' \) denote the imaginary (out of phase or quadrature) components.

Revil (2013a) developed a model based on volume-averaging to determine the complex conductivity of isotropic porous media. Revil et al. (2013c) extended this model and described the real and imaginary components of the complex conductivity tensor using the equations

\[
\sigma_{ij}' = F_{ij} S_w^\sigma \sigma_w + T_{ij} S_w^\rho \rho_s \left[ \beta_{(+)}(1-f) + \beta_{(+)}^S f \right] \text{CEC}, \tag{4.3}
\]

\[
\sigma_{ij}'' = T_{ij} S_w^\rho \rho_s \beta_{(+)}^S f \text{CEC}, \tag{4.4}
\]

respectively. In these equations, \( F_{ij} \) denotes the components of the (symmetric second-rank) formation factor tensor for the conductivity, \( F \), and \( T_{ij} \) denotes the components of the (symmetric second-rank) tortuosity tensor of the pore space, \( T \). In isotropic conditions, we have \( F_{ij} = (1/F) \delta_{ij} \) and \( T_{ij} = (1/\alpha) \delta_{ij} \), where \( F \) and \( \alpha \) denote the (resistivity) formation factor and the bulk tortuosity of the pore space, respectively. In Equations 4.3 and 4.4, the partition coefficient \( f \) denotes the fraction of counterions in the Stern layer, \( \rho_s \) denotes mass density of the solid phase (typically 2650±50 kg m\(^{-3}\) for the crystalline framework of clay minerals), \( \sigma_w \) denotes the conductivity of the pore water (S m\(^{-1}\)), CEC (C kg\(^{-1}\)) corresponds to the cation exchange capacity of the material, \( \beta_{(+)} \) denotes the mobility of counterions in the diffuse layer, and \( \beta_{(+)}^S \) corresponds to the mobility of counterions in the Stern layer (both in m\(^2\)s\(^{-1}\)V\(^{-1}\)). For clay minerals, the mobility of counterions in the diffuse layer is equal to the mobility of the same counterions in bulk pore water (e.g., \( \beta_{(+)}(\text{Na}^+, 25^\circ\text{C}) = 5.2 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1} \), see Revil, 2012).
Counterion mobility in the Stern layer is substantially smaller and equal to $\beta_{(r)}(25^\circ C, Na^+) = 1.5 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \text{V}^{-1}$ for clay minerals (Revil, 2012, 2013a, b; Revil et al., 2013a, b, c).

The components of the conductivity formation factor tensor and connectivity tensor are related to each other by $F_{ij} = T_{ij} \phi$ (we prefer calling $T$ the connectivity tensor and $T^{-1}$ the tortuosity tensor). Therefore, both conductivity formation factor and connectivity tensors share the same eigenvectors and, for the case of TI materials, the anisotropy ratio should be the same for bulk and surface conductivities.

**Forward modeling**

In a laboratory experiment, a harmonic current is injected into a rock sample between electrodes A and B, while the electric field is measured as the potential difference for a set of electrode pairs M and N (see Figure 4.1). Because a broad range of frequencies is typically explored, this method is called “spectral” induced polarization. In the forward modeling of such an experiment, the electric potential can be expressed as the complex number (Kemna, 2000):

$$U^*(\omega) = U'(\omega) + iU''(\omega).$$  \hspace{1cm} (4.5)

The amplitude of the complex voltage $|U^*(\omega)|$ and the phase lag $\phi(\omega)$ are given by,

$$|U^*(\omega)| = \sqrt{[U'(\omega)]^2 + [U''(\omega)]^2},$$  \hspace{1cm} (4.6)
$$\phi(\omega) = \text{atan} \left( \frac{U''(\omega)}{U'(\omega)} \right).$$  \hspace{1cm} (4.7)

The relation between the complex conductivity and the complex potential is given by (Weller et al., 1996)

$$\nabla \cdot [\sigma(x, \omega) \cdot \nabla U^*(x, \omega)] = -I(\omega) \delta(x - x_s),$$  \hspace{1cm} (4.8)

where $x$ is the position vector, $\delta(x)$ denotes the delta function, $\sigma$ denote the conductivity tensor, and $I(\omega)$ is the injected current (in Ampères, A) at angular frequency $\omega$ represented here.
as a point source at position \( x \). Equation 4.8 is a Poisson equation with current sources imposed at the boundary of the domain corresponding to the core sample. In these conditions, the boundary-value problem consists in solving Laplace’s equation (the left-side of Equation 4.8 with no source term) for the complex electrical potentials and using Dirichlet conditions at each of the boundaries where the current is injected/retrieved. The normal component of the gradient of the potential is zero for all other boundaries, which are insulating boundaries. Laplace’s equation can be solved with the finite-element method (Kemna, 2000). In our case, we use the finite element solver Comsol Multiphysics 4.3a (Pryor, 2011) with an optimized tetrahedral mesh to minimize the cost of the forward operator, resulting in a solution time of approximately 6 seconds for up to 10 independent frequencies. The determination of the geometrical factor is discussed in details in Appendix C.

**Inverse modeling**

To our knowledge, there is no published work in inverting the complex conductivity tensor. The works cited in the introduction deal only with the real component of this tensor, using deterministic inversion to perform the task, taking the implicit risk of having the inversion trapped in a secondary minimum of the objective function to minimize. Because of the possible non-uniqueness of the inverse problem (especially in the case of very heterogeneous materials), we decided to estimate the complex conductivity tensor using a stochastic method. The Bayesian solution to our inverse problem will be based on combining the information originating from the complex potential measurements (amplitude and phase) with some prior knowledge regarding the eigenvalues and eigenvectors of the complex conductivity tensor.

The Bayesian analysis considers both the data vector, \( d \), and the model parameter vector, \( m \), as random variables. The objective of inverse modeling is to update the information on \( m \)
Figure 4.1 Sketch of the electrode array and equivalent circuit. a. Circuit diagram of the impedance measurement. A and B denote the current electrodes (Transcutaneous Electrical Nerve Stimulation, TENS, medical electrodes) while the electrodes M and N denote the voltage electrodes (sintered, nonpolarizing Ag/AgCl pellet electrodes). Ze1 to Ze4 correspond to the contact impedance between the electrodes and the sample. The stimulus voltage $U_1$ and current $I_0$ are modulated over at a set of predesigned frequencies ranging from 1 mHz to 45 kHz, grounded across the sample at the locations 1 and 4. The true sample impedance $Z_x$ is calculated from the transfer current $I_x$ in the sample, the potential drop $U_x$ between the potential electrodes, 2 and 3 (also denoted M and N), and the known resistance $R_s$ of the shunt resistor. Electrode contact impedances $Z_e$, and the known input impedance $Z_v$ (~1 GΩ) of the acquisition system are also depicted. Current, impedance and voltage are measured in Ampère (A), Ohm (Ω), and Volts (V), respectively (adapted from Zimmermann et al., 2008a, b). b. In-plane impedance measurements with respect to the bedding plane. c. Transverse impedance measurements with respect to the bedding plane. The bedding planes are indicated with fine parallel lines/curves. The stimulus electrodes generate a uniform surface current density over the end surfaces of the core samples. Axes are labeled in centimeters to indicate approximate size.
a) Equivalent electrical circuit

- Insulated surface (boundary)
- Sample
- Stimulus (TENS/pellet) electrodes
- Ze1, Ze2, Ze3, Ze4
- Ux, Zx
- Ix
- Potential (pellet) electrodes
- Stimulus (TENS/pellet) electrodes
- A(1) B(4)
- M(2) N(3)
- 50 Ohm
- U1, U2, U3, U4
- I0, I1, I2, I3, I4, Is
- Function generator
- Acquisition system

b) In-plane

- TENS electrodes
- Sintered electrodes
- Height, cm
- Width, cm

M N

0 0.5 1.0 1.5 2.0 2.5

0 1.25 0 1.25

0 0.5 1.0 1.5 2.0 2.5

0 1.25 0 1.25

TENS electrodes

99
given the data \( d \) and some prior information regarding \( m \). Prior information can come from independent observations regarding the eigenvectors or the type of anisotropy used to characterize the sample. In a probabilistic sense, the inverse problem corresponds to maximizing the conditional probability of occurring \( m \) of a model \( M \) given the data vector \( d \). The model \( M \) can correspond to a choice of anisotropy and we can consider several \( M \)-models but we are also free to ignore such prior information and to invert the 6 independent components of the tensor. We denote \( P_0(m|M) \) as the a prior probability density or belief of parameters \( m \) of model \( M \) and such a model generates the probability density of likelihood \( P(d|m,M) \) corresponding to the data fit.

In a Bayesian approach, the posterior probability density \( \pi(m|d) \) of the model parameters \( m \) given the data \( d \) is obtained from Bayes formula:

\[
\pi(m|d,M) = \frac{P(d|m,M)P_0(m|M)}{P(d|M)}, \quad (4.9)
\]

where \( P(d|M) \) is called the evidence,

\[
P(d|M) = \int P_0(m|M)P(d|m,M)d\mathbf{m}. \quad (4.10)
\]

This marginal likelihood \( P(d|M) \) is usually ignored because it is not a function of the parameters \( \mathbf{m} \). For any given model \( M \), the evidence will have a constant value.

We will assume below that the model \( M \) is certain (transverse isotropy in this paper) and henceforth we drop the term \( M \) in Equations 4.9 and 4.10. The posterior probability density \( \pi(m|d) \) of the model parameters \( m \) given the data \( d \) is written as (e.g., Mosegaard and Tarantola, 1995):

\[
\pi(m|d) \propto P(d|m)P_0(m). \quad (4.11)
\]
As usually accepted, the likelihood function used to assess for the quality of a model \( m \) is Gaussian distributed:

\[
P(d|m) = \frac{1}{[(2\pi)^N \det C_d]^{1/2}} \exp \left[ -\frac{1}{2} (g(m) - d)^T C_d^{-1} (g(m) - d) \right],
\]

(4.12)

where \( g(m) \) is the forward modeling operator corresponding to the solution of the Laplace equation for the complex-valued electrical potential (see previous section). It connects non-linearly the components of the complex tensor to the observed electrical potential so that \( g(m) \) corresponds to the predicted data, \( d \) is an \( N \)-vector of the observed complex potential data. Matrix \( C_d \) corresponds to the data covariance matrix, which comprises the measurements errors, assumed uncorrelated and to obey Gaussian distributions. They are determined from the standard deviation on the measurements and determined at each frequency over three cycles.

The prior distribution on the model parameters is also taken as Gaussian, i.e.,

\[
P_0(m) = \frac{1}{[(2\pi)^M \det C_m]^{1/2}} \exp \left[ -\frac{1}{2} (m - m_{\text{prior}})^T C_m^{-1} (m - m_{\text{prior}}) \right],
\]

(4.13)

where \( m_{\text{prior}} \) is the prior value of the model parameters and \( C_m \) denotes the model diagonal covariance matrix incorporating the uncertainties related of the prior model. We can choose a null-prior as information on the model parameters.

In the classical Bayesian approach, the model parameters \( m \) that fit the observations \( d \) maximizes the posterior probability density \( \pi(m|d) \). The problem is to explore the posterior probability density \( \pi(m|d) \). The Markov chain Monte Carlo (McMC) family of algorithms is well-suited for Bayesian inference problems (Mosegaard and Tarantola, 1995, Malinverno and Torres-Verdin 2000). McMC algorithms consist of random walks where different states (i.e., different values of a model vector) are visited and where the choice of the next state depends only on the value of the current state. After an initial period in which the random walker moves
toward the highest a posteriori probability regions, the chain returns a number of model vectors
sampling the a posteriori probability density $\pi(m|d)$. We can fit $\pi(m|d)$ with a Gaussian
distribution and determine the mean and the standard deviation from the set of realization
obtained after convergence of the chain.

The Metropolis-Hastings algorithm follow a two-step procedure: (1) the current model $m$
is modified randomly to obtain a candidate vector. This candidate is drawn from a proposal
distribution $q(m,m')$ where the choice of $m'$ depends on the current vector $m$. (2) the candidate
model is accepted with the acceptance probability (Malinverno, 2002),

$$
\alpha(m;m') = \min\left[1, \frac{\pi(m'|d) q(m|m')} {\pi(m|d) q(m'|m)}\right],
$$

$$
= \min\left[1, \frac{P_0(m')} {P_0(m)} \frac{P(d|m')} {P(d|m)} \frac{q(m|m')}{q(m'|m)}\right],
$$

$$
= \min\left[1, (\text{Prior ratio}).(\text{Likelihood ratio}).(\text{Proposal ratio})\right].
$$

(4.14)

If the candidate is accepted, the state of the chain is changed to $m'$, otherwise the chain stays at
$m$. The acceptance probability depends only on the proposal, likelihood, and prior functions at
the current and candidate models, all of which can be easily computed. Assuming that the
proposal distribution is symmetric, $q(m|m') = q(m|m')$ (e.g., a Gaussian distribution centered at
the current point), the acceptance probability reduces to:

$$
\alpha(m;m') = \min\left[1, \frac{P(m'|d)} {P(m|d)}\right].
$$

(4.15)

This algorithm is known as the original Metropolis algorithm (Metropolis et al., 1953; Tamminen, 2004).

To improve the performance of the standard Metropolis algorithm, Haario et al. (2001)
introduced an algorithm, called the Adaptive-Metropolis Algorithm (AMA). An important
advantage of the AMA algorithm is that it starts using the cumulative information right at the
beginning of the simulation. The rapid start of the adaptation ensures that the search becomes more effective at an early stage of the sampling, which diminishes the number of realizations needed to reach the convergence of the chain. We assume now that we have sampled the states \((\mathbf{m}^0, \ldots, \mathbf{m}^{i-1})\) where \(\mathbf{m}^0\) corresponds to the model vector of the initial state (for instance given by the peak probability of the prior). Then a candidate model \(\mathbf{m}'\) is sampled from the Gaussian proposal distribution \(q\) with mean point at the present model \(\mathbf{m}^{i-1}\) and with the covariance,

\[
C^i = \begin{cases} 
C^0, & \text{if } i \leq n_0, \\
\sigma_n^2 K^i + s_n \varepsilon I_n, & \text{if } i > n_0,
\end{cases}
\]  

(4.16)

where \(I_n\) denotes the \(n\)-dimensional identity matrix, \(K^i = \text{Cov}(\mathbf{m}^0, \ldots, \mathbf{m}^{i-1})\) is the regularization factor (a small positive number that prevents the covariance matrix from becoming singular), \(C^0\) is the initial covariance matrix that is strictly positive, \(s_n = (2.4)^2 / n\) is a parameter that depends only on the dimension of the vector \(\mathbf{m} \in \mathbb{R}^n\) (Haario et al., 2001). The candidate model \(\mathbf{m}'\) is accepted with the acceptance probability

\[
\alpha(\mathbf{m}^{i-1}; \mathbf{m}') = \min \left[ 1, \frac{\pi(\mathbf{m}'|\mathbf{d})}{\pi(\mathbf{m}^{i-1}|\mathbf{d})} \right].
\]  

(4.17)

If the candidate model vector is accepted, we update the model according to \(\mathbf{m}^i = \mathbf{m}'\), otherwise we choose \(\mathbf{m}^i = \mathbf{m}^{i-1}\).

The AMA algorithm was written in a MATLAB routine coupled with the forward modeling made in Comsol Multiphysics 4.3a. The data vector is written as \(\mathbf{d} = [E_{\theta_1}, \ldots, E_{\theta_N}]\), where \(E_{\theta_i}\) represents a measurement of the electrical field at a given azimuthal angle \(\theta_i\). The vector of model parameters, \(\mathbf{m}\), comprises the eigenvectors and eigenvalues of the complex conductivity tensor. In our experiments, because of the alignment of the core with the symmetry of the samples, the model vector is simply given by the three complex-valued eigenvalues of the
complex conductivity tensor $\mathbf{m} = [\log \sigma_{11}^*, \log \sigma_{22}^*, \log \sigma_{33}^*]$. Therefore, we assume that we know the eigenvectors perfectly and that we are looking for the three eigenvalues of the tensor. The log transform for the model parameters is used to enforce positiveness of the model parameters and the probability density will be therefore log-normal distributed (Fouskakis, 2012).

**Acquisition system**

We use the impedance meter described by Zimmermann et al. (2008a) (Figure 4.1) characterized by a sensitivity of 0.1 mrad in phase lag for frequencies below 100 Hz (see benchmark tests in Revil and Skold, 2011). The system comprises a four-channel acquisition array and the frequency range 1 mHz - 45 kHz. A current $I_0$ is excited in the sample by an applied voltage $U_1$ between two non-polarizing Ag/AgCl electrodes 1 and 4 (or A and B), located at the top and bottom faces of core sample. Diagrams of the acquisition geometries are shown in Figures 4.1 and 4.2. We approximate the resistance in the medium as a linear circuit using the constitutive equation $Z_m = U_m / I$, where $Z_m \approx Z_s$ denotes the true impedance in ohms, $U_m \approx U_s$ denotes the potential difference between the measuring electrodes 2 and 3 (M and N) in volts (V). In the voltage range 1 V to 10 V, the impedance has been checked to be independent of the current magnitude $I_x$ (Jougnot et al., 2010a). The impedance is estimated as $Z_m = U_m / I_x = R_s U_m / U_s \approx Z_s$ for a current excited by a 5 V difference in applied voltage, we have $I_x \approx I_s = U_s / R_s = 5$ mA, where $R_s = 1$ kΩ is the resistance at the shunt resistor.

**Electrodes**

Due to their robustness, we use sintered silver chloride (Ag/AgCl) electrodes and various types of medical electrodes including electrocardiogram ECG and transcutaneous nerve stimulation TENS electrodes. These electrodes can be used as potential electrodes in SIP measurements. Ag/AgCl sintered electrodes consist of a pure silver core coated in a porous
Figure 4.2  Azimuthal array for anisotropic SIP measurements. a. Perspective viewpoint (electrodes shown detached from the sample to illustrate the size and shape). AB are the current electrodes and MN the voltage electrodes. b. Top view. Electrodes are distributed radially about the core (axis coincident with the isotropic plane) to sample the change in potential field distribution over the surface. Measurements of the complex voltages can be inverted for the full electrical tensor and the rotation vectors. c. Methodology flowchart.
crystalline matrix of poorly soluble silver chloride salt. In our experiments, we used 2.0 mm
sintered Ag/AgCl pellet ECG electrodes arranged azimuthally about the core axis (Figure 4.2a, b). We also used an amplifier with input impedance that needs to be at least 10 times the sample
impedance (JFET OP AD825 with an input resistance of 1 GΩ), connected by characterized tri-
axial cables with driven, grounded shields (Morrisson, 1977) to minimize leakage currents and
capacitive coupling.

**Core samples**

We use a lathe, milling machine, cutting tools and bits, as well as dimensioning and
positioning machines, to cut, shape, and instrument the cores to within sub-millimeter accuracy.
We selected cylindrical samples from whole core from the Haynesville and Bakken shale
formations. The samples were then cut using a lathe, rotary indexer, and various carbide cutting
tools to dimension it, and to position and align the sensors. Cutting was performed under dry
conditions, without water or lubricant.

Mineral orientations within the samples were determined prior to machining through core
analysis via X-Ray Diffraction (XRD) (Table 4.1), Computed Tomography (CT) X-ray imaging
(Figure 4.3), Scanning Electron Microscope (SEM) imaging (Figure 4.4), as well as ultrasonic
measurements (not discussed here). The CT and SEM data provided an estimate of the

<table>
<thead>
<tr>
<th>Mineral fraction (wt%)</th>
<th>Median</th>
<th>Maximum</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 clay</td>
<td>45.0</td>
<td>57.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>28.0</td>
<td>31.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Calcite</td>
<td>14.0</td>
<td>38.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>5.0</td>
<td>11.0</td>
<td>3.0</td>
</tr>
<tr>
<td>TOC</td>
<td>3.5</td>
<td>6.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2.0</td>
<td>4.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Pyrite</td>
<td>2.0</td>
<td>7.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 4.1 Representative mineralogy of the Haynesville samples from QXRD analysis. The
median, maximum and median mass fractions (in percent) are provided in different columns.
Figure 4.3 Computed Tomography (CT) images of a Haynesville core showing clear alignment of decompression fractures (dark linear features), calcified bedding planes (light linear features), bedding planes (subtle gray scale striations), and disseminated pyrite (bright spots and lines). **a.** Image of a cross-section of the sample. **b.** Vertical slice through a 3D volume of stitched cross section images (the location of the image in panel a is indicated by a stippled black line. The white “x” marks the approximate point of azimuthal coincidence between panels a and b. The interpreted in-plane and transverse directions are indicated by the white and black arrows, respectively.

Macroscopic deviation of the bedding planes from the symmetry axis, whereas the ultrasonic measurements provided a dynamic measurement of elastic anisotropy. Mineralogical composition was obtained from XRD. While none of these methods share a causal link to electrical anisotropy, we could infer from imaging and mineral data that the core samples should be characterized by a transverse anisotropy (therefore with a plane of isotropy). This finding was further substantiated by ultrasonic measurements.

**Saturation and pore fluid**

We discuss three different approaches to saturate shale cores: (a) pressurized infiltration, (b) imbibition and molecular diffusion, and (c) vapor adsorption under controlled humidity conditions (Figure 4.5). The low porosity and permeability of unconventional hydrocarbon-bearing shales (typically, $\phi \leq 0.05$ and $k \leq 100 \mu D$ where $1 D = 0.987 \times 10^{-12} \text{ m}^2$) pose significant
time constraints when acquiring reliable measurements. It took us over a year to perform the measurements reported in the present paper. Potential effects of reactive minerals and saturating fluids must also be accounted for in each experiment (e.g., demineralized water is highly reactive in shales and clay rocks and would dissolve some of the minerals, changing the porosity of the core samples; see Revil et al., 2005).

Pore water solution

The composition of the electrolyte used to saturate the porous material needs to be modeled to estimate equilibrium concentrations of soluble mineral fractions. Imbalanced solutions will dissolve soluble minerals, especially calcite or aragonite (CaCO₃), affecting the composition and petrophysical properties of the medium, including mineral surface area, cation exchange capacity, porosity, and permeability. The open-source aqueous geochemical modeling
Figure 4.5  Schematic diagrams of the pressure vessel and vacuum chambers used to saturate core samples by pressurized fluid injection and by imbibition and diffusion. a. High pressure system for forced fluid saturation: a hydrostatic load is applied to a degassed sample (reduced capillary entry pressure), effectively increasing saturation rate. b. Low vacuum system for diffusion/imbibition driven saturation: the degassed brine is dripped onto the sample under low vacuum, allowing the pore fluid to naturally saturate the material, and providing a high degree of control over the saturation state. We have also utilized humidity chambers and bell jars (not shown) to saturate samples by vapor adsorption. Samples are simply placed into a controlled humidity environment and allowed to equilibrate with the ambient conditions.

Software PHREEQC (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/) was used to estimate solution chemistry in equilibrium with the mineral paragenesis. For the Haynesville, we used 6.65 g of a sample in 8.5 L of deionized water. Equilibrium molar concentrations were 8.312×10^{-7} (Al), 1.157×10^{-3} (C), 5.8×10^{-4} (Ca), 5.692×10^{-15} (O), and 7.515×10^{-5} (Si), with a carbonate fraction comprising CO_{2(aq)}, H_{2}CO_{3}, HCO_{3}, and CO_{3}^{2-} (see Table 4.1; plagioclase and chlorite could be neglected and the oxidation of pyrite was ignored). We conclude from this test that dissolution effects are not negligible due non-equilibrium reactions with the clay fraction of the sample and soluble minerals. An equilibrium solution was obtained from mixing a small fragment of the sample with deionized (DI) water. Soluble minerals equilibrate naturally with the
water producing a chemically balanced saturating fluid (equilibration time was typically 12 to 24 hours in agreement with numerical modeling with PHREEQC).

In the present work, we vary NaCl concentration for some of the experiments. Changing the salinity allows to separate the effects of bulk and surface conduction in Equation 4.3. The solutions were first degassed to remove dissolved oxygen, which may oxidize ferrous minerals such as pyrite. In addition, using degased solutions is a good way to remove trapped air bubbles in the sample during the saturation process. Active monitoring of the samples and the saturating fluid should be maintained to ascertain when the cores have reached saturation, determine changes to the pore fluid chemistry, and estimate the pore fluid volume in the saturated sample. We performed regular monitoring of pH, relative humidity, salinity, and sample mass to secure reliable measurements.

**Saturation protocols**

Our experiments include unsaturated and saturated measurements with three brines of known salinity and pH. In the following, we outline three methods for saturating low permeability samples by pressurized fluid injection, imbibition and diffusion, or vapor adsorption. Diagrams of the apparatus used for fluid injection and imbibition are provided in Figure 4.5. The pressurized forcing of fluid into the pores accelerates the saturation of the macro- and meso-porosity under elevated hydrostatic load; however, care must be taken to ensure that the sample is not damaged or fractured due to high entry pressure or an imposed differential stress (e.g., from uneven fluid distributions). We point out that our samples were never stored completely dry, which could have resulted in problems such as the formation of cracks but they were also not preserved in their pristine conditions. We used a 50 mm stainless steel (high pressure) transfer vessel to both evacuate and saturate the core. The vessel was assembled with
3.175 mm or 1.5875 mm steel tubing, high-pressure compression fittings, and isolated with a high-pressure needle or regulating valve (Figure 4.5a). The core samples were placed under vacuum for a period of several hours (up to 24 hours in tight rocks: a nominal gas diffusivity of $10^{-8}$ to $10^{-9}$ m$^2$ s$^{-1}$ yields a time constant ranging from 2 to 24 hours) to degas the core, and to enhance fluid imbibition through the capillary suction force imposed by vacuum in the pores. The vessel is sealed under vacuum, and incrementally opened to the pressurized fluid line to fill the vessel; a designated pressure ramp is applied to the sample. We found that a gradient of $\leq 7$ kPa minute$^{-1}$ is acceptable for most rock types. The choice of maximum confining pressure depends on the nature of the pore space of the specimen. In particular, the meso- and micro-scale porosity, the characteristic pore throat size, and the relative permeability to the fluid, are the properties that govern the capillary entry pressures at the various length scales of the porous network. Additionally, adsorbed or trapped gas volumes may dissolve in the degassed fluid. It is not always possible to overcome the entry pressure in tight, micro-porous regions within a sample; nevertheless, we found this approach was generally effective to saturate cores for SIP experiments.

An alternative approach allows for the natural imbibition and diffusion of the fluid in the sample under near ambient pressure conditions. A chamber is connected to both fluid and vacuum lines to evacuate the sample prior to introducing the fluid (Figure 4.5b). The time scale of this procedure is governed by the permeability $k$ and hydraulic diffusivity $D$ of the sample (generally, $k \in [10^{-19} \text{ to } 10^{-16}]$ m$^2$; $D \in [10^{-14} \text{ to } 10^{-12}]$ m$^2$ s$^{-1}$), often taking several weeks to fully saturate the core. This method has the advantage of allowing the fluid to achieve equilibrium saturation, which can be more ubiquitous than the pressurized method for high tortuosity materials (Zhang and Knackstedt, 1995). Also, the same approach allows for regular monitoring
of the fluid properties as well as gravimetric analysis. The chamber is evacuated for a period of several hours to allow the sample to degas. Next, the chamber is isolated under vacuum, and the pore fluid is dripped onto the sample until the desired level of immersion is attained. The upper portion of the core is left exposed to vacuum, as this will help to draw the fluid into the sample and allow remaining sorbed or trapped gases to escape.

To saturate by vapor adsorption, the sample is placed in a closed environment under controlled relative humidity RH. This procedure can be carried out either under vacuum or at atmospheric conditions utilizing an environmental chamber or desiccant slurry of a pure salt to control the ambient humidity. The advantage of this method is that it allows for precise control of the saturation state of the material, which is relevant for measurements of unsaturated samples. Also, vapor diffusivity is generally several orders of magnitude greater than the hydraulic diffusivity in the liquid state (Jougnot et al., 2010b). These systems can also be used to store saturated samples at or near the dew point to reduce evaporation (both for storage and during measurement) and limit the need for complete immersion of the sample, which may rapidly dissociate samples with high swelling clay fractions.

All three methods were used for the samples presented in this work. A general flowchart is shown in Figure 4.2c. We found the following protocol to be effective: 1) Samples are evacuated under low vacuum and pressure saturated with a characterized brine. The pressurization is repeated regularly until the samples reach a constant, saturated mass. 2) The imbibition and diffusion method is used to resaturate of samples with different brines. The conductivity and pH of the saturating fluid are monitored until they are shown to be in equilibrium with the sample. 3) Humidity chambers are used both for storage of saturated samples and used to house the samples during data acquisition to mitigate evaporation effects.
Experimental determination of the complex conductivity tensor

In order to validate the stochastic inversion of the components of the complex conductivity tensor, we measured both the azimuthal spectra and the spectra of eigenvalues (single-component method) of Bakken and Haynesville core samples. This single component approach has been previously discussed in the literature in a couple of studies on clay-rich materials (Cosenza et al., 2007; Ghorbani et al., 2009; Jougnot et al., 2010). Spectral data were acquired at log-distributed frequencies ranging 1 mHz to 45 kHz. We remark that we have been working with unpreserved samples which may have been damaged. That said, the method that we have developed would work for preserved shales.

Azimuthal surface sampling and inversion of distributed electrical potential data

A set of cylindrical Haynesville cores samples was used to validate the azimuthal approach. We measure the multicomponent electrical field and invert the tensor components from the complex potentials utilizing an azimuthal array of potential electrodes, distributed radially about the axis at 0°, 45°, and 90° (referenced to the plane of the mineral fabric, Figure 4.2). The inversion of the components of the complex conductivity tensor was performed with the McMC sampler discussed above. The experimental protocol requires at least three separate acquisitions about a core axis aligned in the bedding plane (the isotropic symmetry plane), with current electrodes coincident with the core axis at facing ends (Figures 4.1 and 4.2).

Azimuthal SIP measurement protocol

We tested different saturation protocols were implemented on the Hayneville samples: one sample was subjected to a fluid injection protocol under hydrostatic load; remaining samples were saturated at low vacuum in a bath of degassed chemically balanced solution, and later desaturated by vapor desorption using a chamber and desiccant salts. The upper limit at or near the dew point corresponds to \( \text{RH} \approx 1.0 \). The lower saturation limit
Figure 4.6  Gravimetric monitoring of the characteristic imbibition and desorption behavior of several Haynesville shale samples. a. Imbibition of the degassed pore fluid. b. Desorption of the pore fluid in a constant humidity chamber. The controlled humidity saturation protocol provides precise control of the humidity in the sample.

corresponds to RH = 0.336±0.003 for which we used a MgCl desiccant at 25 °C. This low relative humidity implies that the saturation corresponds approximately to a monolayer of water covering the surface of the minerals (Woodruff and Revil, 2012). The first sample was pressurized at 10.34 MPa for a period of 72 hours, and left to equilibrate within a saturated jacket for an additional 120 days (flooded with a drained, saturated pore line, $P_p = 0$ Pa). The saturation state was determined by gravimetric monitoring and calculated as $S_w = \phi \nu_m \rho \rho_w^{-1}$, where $\phi$ is the total connected porosity, $\nu_m$ is the gravimetric water content obtained from the monitoring procedure (in g g$^{-1}$), $\rho$ is the mass density of the bulk sample, and $\rho_w$ is the density of water (in kg m$^{-3}$), respectively. Immersion and adsorption saturation protocols were tested on the remaining cores (Figure 4.6). For the Azimuthal SIP measurement, we used 14 Ag/AgCl electrodes. Potential electrodes were separated by 31.75 mm. The cylindrical surface was painted
outside the location of the electrodes to electrically insulate the sample. We found epoxy and quick dry nail polish to have favorable insulating properties, with good resistance to moisture and immersion in water, and are easy to use for this purpose; however, the coating is not permanent and may degrade if exposed to water for extended periods of weeks or months.

**Direct measurement of the eigenvalues of the impedance tensor**

In addition to the azimuthal measurements that are inverted with the McMC sampler, we performed direct measurements of the components of the complex conductivity tensor. The goal was to check whether the McMC inversion yields the correct solution. Shale plugs must allow for the measurement along one of the two principal axes of a TI medium, or along each of the three principal axes for a sample with orthorhombic symmetry, using pairs of orthogonal cylindrical cores, core triplicates, or cubic (parallelepiped) specimens. In our case, we assume that the eigenvectors are perfectly known and we can directly measure the eigenvalues of the complex impedance tensor. If the measurements are aligned with the principal eigenvectors, the six-component tensor reduces to three independent components in the general case (two for TI symmetry) in the directions of the tensor bases. Measurements are acquired using a current density in the direction of the eigenvectors of the porous material. The approach used to measure the eigenvalues of the impedance tensor is described further in Appendix D.

We designed a set of benchtop experiments to measure the eigenvalues of the impedance tensor in shale core samples. These samples comprised both cored pairs with corresponding axes both coincident (in-plane) and transverse to the isotropic bedding plane in the samples. Core samples were saturated with an equilibrium fluid of 0.05 mM CaCl$_2$, at incremental pore fluid pressures of 0.7 MPa, 3.45 MPa, 6.89 MPa, and 10.34 MPa. The SIP measurements were performed at each fluid pressure to characterize the saturation effect (see Figure 4.7). The
Figure 4.7 Influence of the change of water content on complex conductivity in the orthogonal Bakken B core pair. a. In-plane measurements. b. Transverse measurements. The data show a monotonic concomitant increase of the in-phase and quadrature conductivity independent of the anisotropy. Indeed, changes in saturation only affect the magnitude; the anisotropy ratio remains consistent throughout the experiment (7.1±0.9 at 1 Hz for the in-phase and quadrature components). Saturations estimated from gravimetric monitoring as $S_w = \phi v_w \rho_{w}^{-1}$ over the course of the saturation sequence.
samples were then resaturated in solutions of 0.5 M and 0.05 M NaCl. Stabilization at the high and intermediate concentrations of 0.5 M and 0.05 M took more than 50 days, consistent with a diffusion constant of $2.5 \times 10^{-11}$ m$^2$ s$^{-1}$ for the salt (CaCl$_2$) which yields 46 days for an average sample radius of 10 mm. The value of the diffusion coefficient for the salt is consistent with values obtained for instance by Revil et al. (2011) for the Calovo-Oxfordian clayrock of the Paris basin. Table 4.2 describes the mass, pH and fluid conductivity monitoring data.

In these experiments, we used TENS surface electrodes with the same radius than the core sample to inject the current with a single component current density (see electrodes A and B in Figure 4.1). 2.0 mm sintered Ag/AgCl pellet electrodes were used to measure the complex voltages (see electrodes M and N in Figure 4.2). Due to the symmetry of the electrode array, there is no azimuthal dependency of the gradient of electrical potential distribution within the sample.
Validation

The complex conductivity tensor is inverted from the complex voltages (amplitude and phase) measured on the surface of the sample. We show that data acquired in alignment with the bedding plane (i.e., the principal basis) can be used to obtain the complex eigenvalues of the conductivity tensor. Similarly, the single-component protocol developed in Appendix D effectively isolates the complex conductivity eigenvalues, enabling the direct measurement of the tensor through the full polarization of the specimen in a directional electric field.

The acquisitions were made in the principal directions of the samples, such that the model comprises the three complex conductivity eigenvalues \( \mathbf{m} = \left[ \log \sigma_{11}, \log \sigma_{22}, \log \sigma_{33} \right] \) of the (diagonal) tensor \( \boldsymbol{\sigma}^* \); the data vector of complex-valued electrical field measurements at a set of frequencies \( \mathbf{d} = \left[ \mathbf{E}_0, \mathbf{E}_{45}, \mathbf{E}_{90} \right] \) in the 0°, 45°, and 90° directions relative to the isotropic plane for the distributed azimuthal data, and \( \mathbf{d} = \left[ \mathbf{E}_1, \mathbf{E}_3 \right] \) corresponds to the in-plane and transverse directions for the single-component data. The complex-valued voltage represents the potential difference and associated phase lag measured between electrodes M and N (Figure 4.1), according to Ohm’s law,

\[
\left| U_x \right| e^{i(\omega t + \phi_U)} = \left| I_s \right| \left| Z_x \right| e^{i(\omega t + \phi_I)}, \quad (4.18)
\]

\[
\left| U_x \right| = \left| U_2 - U_3 \right|, \quad (4.19)
\]

and

\[
\phi_U = \phi + \phi_I \quad (4.20)
\]

where \( \omega \) (rad s\(^{-1}\)) denotes angular frequency. We decompose the data vector into a scalar magnitude voltage \( \left| U_x \right| \) in volts and phase shift, computed as the lag between the current and the potential \( \phi = \phi_U - \phi_I \) in radians, and invert the magnitude and phase independently. Because we
are only interested in the phase lag of the complex impedance, $\varphi$, the choice of phase parameterization is somewhat arbitrary for the forward operator, as long as it is consistent with Equation 4.11. In the present examples, we compute $\varphi_U$ directly from the complex-valued potential differences $U_2$ and $U_3$, resulting in a nonzero phase in the current $\varphi_I$; however, it is equally accurate to reference the phase to any one of the three variables, e.g., $\varphi_I \equiv 0$ and $\varphi = \varphi_U$.

The current is calculated from the potential at electrode B in volts as $I_s = U_4 / R_s$ in Amperes, which grounds across the shunt resistor (see Figure 4.1). The in-phase and quadrature components of the complex conductivity are also inverted independently, resulting in the following data and model vectors:

$$d = \begin{bmatrix} \log \sigma_{11}', \log \sigma_{22}', \log \sigma_{33}', \log \sigma_{11}'', \log \sigma_{22}'', \log \sigma_{33}'' \end{bmatrix} \quad (4.21)$$

and

$$m = \begin{bmatrix} [U_{x1}, U_{x45}, U_{x90}, \varphi_{U_1}, \varphi_{U_{45}}, \varphi_{U_{90}}], \text{azimuthal} \\ [U_{x1}, U_{x3}, \varphi_{U_1}, \varphi_{U_3}], \text{single-component} \end{bmatrix} \quad (4.22)$$

We performed 10,000 stochastic realizations of each model to define the posterior probability density for the complex conductivity tensors of the Haynesville-092 cores (azimuthal method, one sample) and Bakken A (single-component method, two directional plugs). The posterior probability density functions (PDF) of the in-phase and quadrature conductivities are determined with the last 1000 realizations. To start the MCMC chain, we use a broad likelihood function with a standard deviation of $\log_{10}(\sigma)$=2 S m$^{-1}$, assigning greater weight to the data in the estimation of $\pi(m|d)$. Properties of the sample are given in Tables 4.3 and 4.4; the inversion is performed using data acquired on a saturated core with a pore water salinity of 50 mM NaCl.

Figure 4.8 shows the posterior probability density of the in-phase and quadrature...
Table 4.3 Characteristics of the shales used in the polarized SIP study. The eigenvalue spectra for these samples are provided in the figures. Porosities from hydrogen porosimetry have been corrected for the mass fraction of kerogen, which accounts for a much larger volume fraction of the material (roughly double the wt%, see Prasad et al., 2011; Revil et al., 2013).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>φ</th>
<th>Density (kg m⁻³)</th>
<th>TOC (wt%)</th>
<th>TOC (vol%)</th>
<th>HI</th>
<th>Maturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakken A</td>
<td>2630</td>
<td>0.017</td>
<td>1,990</td>
<td>20.1</td>
<td>60</td>
<td>584</td>
<td>II</td>
</tr>
<tr>
<td>Bakken B</td>
<td>3098</td>
<td>0.018</td>
<td>2,220</td>
<td>12.1</td>
<td>48</td>
<td>436</td>
<td>III</td>
</tr>
<tr>
<td>Bazhenov A</td>
<td>3824</td>
<td>0.038</td>
<td>2,510</td>
<td>5.0</td>
<td>19</td>
<td>422</td>
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<td>11</td>
<td>288</td>
<td>IVa</td>
</tr>
<tr>
<td>Woodford A</td>
<td>4343</td>
<td>0.011</td>
<td>2,190</td>
<td>8.0</td>
<td>26</td>
<td>572</td>
<td>II</td>
</tr>
</tbody>
</table>

Table 4.4 Ratios of the in-plane to transverse impedance spectra. All of the data sets exhibit anisotropy on the order of 10 for in-phase and quadrature components. A higher degree of variability exists for the quadrature conductivities, due to the sensitivity of the phase measurement to noise. Both mean anisotropy in the frequency band (0.1 Hz – 2 kHz) and the anisotropies at 1 Hz are provided along with the standard deviation (for the 1 Hz value, the standard deviation was computed for \( f \in [0.2, 1, 5] \) Hz). The values given for the Haynesville sample represent changes to the impedance magnitude in the 0° and 90° azimuths (i.e., not independent tensor components), whereas, Bakken A and B anisotropies correspond to tensor eigenvalues.

<table>
<thead>
<tr>
<th>Sample</th>
<th>In-phase, ( \lambda' ) (10 point mean)</th>
<th>Quadrature, ( \lambda'' ) (10 point mean)</th>
<th>In-phase, ( \lambda' ) (at 1 Hz)</th>
<th>Quadrature, ( \lambda'' ) (at 1 Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakken A, 0.5 mM</td>
<td>8.80±0.03</td>
<td>6.14±0.83</td>
<td>8.82±0.01</td>
<td>6.25±0.42</td>
</tr>
<tr>
<td>Bakken A, 0.05 M</td>
<td>8.64±0.05</td>
<td>6.51±0.56</td>
<td>8.66±0.03</td>
<td>6.26±0.59</td>
</tr>
<tr>
<td>Bakken A, 0.5 M</td>
<td>7.86±0.08</td>
<td>13.29±2.86</td>
<td>7.83±0.03</td>
<td>16.36±4.23</td>
</tr>
<tr>
<td>Mean value</td>
<td>8.43±0.05</td>
<td>8.64±0.94</td>
<td>8.43±0.02</td>
<td>9.62±1.75</td>
</tr>
<tr>
<td>Bakken B, 0.5 mM</td>
<td>7.04±1.02</td>
<td>6.85±0.08</td>
<td>7.04±0.03</td>
<td>6.82±0.02</td>
</tr>
<tr>
<td>Bakken B, 0.05 M</td>
<td>10.03±2.12</td>
<td>7.59±0.53</td>
<td>10.04±0.03</td>
<td>7.58±0.23</td>
</tr>
<tr>
<td>Bakken B, 0.5 M</td>
<td>3.43±2.10</td>
<td>7.90±1.49</td>
<td>3.42±0.03</td>
<td>7.92±1.14</td>
</tr>
<tr>
<td>Mean value</td>
<td>6.43±1.54</td>
<td>7.45±0.64</td>
<td>6.83±0.02</td>
<td>7.44±0.46</td>
</tr>
<tr>
<td>Haynesville 092</td>
<td>3.45±0.04</td>
<td>9.32±0.53</td>
<td>3.42±0.01</td>
<td>9.40±0.30</td>
</tr>
<tr>
<td>Haynesville 247</td>
<td>7.82±0.42</td>
<td>5.52±2.36</td>
<td>7.76±0.15</td>
<td>4.77±1.87</td>
</tr>
<tr>
<td>Haynesville 251</td>
<td>9.85±0.04</td>
<td>13.51±2.51</td>
<td>9.80±0.14</td>
<td>14.73±2.79</td>
</tr>
</tbody>
</table>
Table 4.5 Characteristics of the shales used in the polarized SIP study. The eigenvalue spectra for these samples are provided in the figures. Porosities from hydrogen porosimetry have been corrected for the mass fraction of kerogen, which accounts for a much larger volume fraction of the material (roughly double the wt%, see Prasad et al., 2011; Revil et al., 2013).

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</tr>
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Conductivities using the stochastic inversion. Results are validated with the direct eigenvector determination within a difference <5%. The posterior PDF for the complex conductivity eigenvalues at 2 Hz is \( N([7.3+0.06i, 6.5+0.04i, 0.8+0.004i], [1.7+1.95i, 1.32+1.91i, 1.38+2.04i]) \) mS m\(^{-1}\), yielding geometrical factors \( K_1=0.04 \) m in-plane and \( K_3=0.032 \) m transverse, whereas the direct measurement of the complex conductivity tensor, at the same frequency, was \( \text{diag}(\sigma_{ij})=[6.5+0.04i, 6.5+0.04i, 0.8+0.004i] \) mS m\(^{-1}\). Figure 4.9 shows the data misfit and compares the prior and posterior models for seven frequencies \( f \in [2, 5, 10, 20, 30, 70, 130] \) Hz. Both model and data show excellent agreement, validating the accuracy of our general stochastic algorithm to invert the components of the complex conductivity tensor in shales.

We perform a similar stochastic inversion of a data set acquired azimuthally on the Haynesville 092 core. Tables 4.4 and 4.5 describe the properties of the core. The prior model is taken with a broad standard deviation of \( \log_{10}(\sigma)=1 \) S m\(^{-1}\). Results for the posterior probability densities were obtained for the in-phase and quadrature conductivity eigenvalues (Figure 4.10).

Figure 4.11 shows a near perfect reproduction of the data together with the model obtained from the resampled posterior data distribution for seven frequencies \( f \in [0.1, 0.2, 0.5, 1, 2, 5, 10] \). A consequence of the resampling is that the uncertainty of the
Figure 4.8  Probability density functions for the complex conductivity eigenvalues of the Bakken A sample at 1 Hz. The mean posterior likelihood of the tensor components accurately reproduced the values obtained analytically with a geometric factor $K=A L^{-1}$, validating the single-component method. The analytical complex conductivity $\text{diag}(\sigma_\text{ij})=[6.5+0.04i, 6.5+0.04i, 0.8+0.004i]$ mS m$^{-1}$, falls near the mean of the posterior Probability density function, defined by the (base 10) lognormal distributions $N([7.3+0.06i, 6.5+0.04i, 0.8+0.004i]$ mS m$^{-1}$ and $[1.7+1.95i, 1.32+1.91i, 1.38+2.04i])$ mS m$^{-1}$.

- **a.** Posterior probability density functions for the in-plane and transverse complex conductivity (the in-plane conductivity is shown as the joint probability of the 1:1 and 2:2 directions).
- **b.** Prior and posterior probability density functions for the in-phase conductivity.
- **c.** Prior and posterior probability density functions for the quadrature conductivity.

Observed anisotropy

We observe a clear directional dependence in the spectral induced polarization response of the shales measured in this study (information about the samples can be found in Tables 4.3 and 4.5). Figure 4.12 describes the characteristic impedance spectra. Anisotropy ratios are
Figure 4.9 Inversion results for the single-component data obtained from the Bakken A orthogonal core samples saturated with 0.05 M NaCl. a. Data misfit of the amplitude and phase in the in-plane and transverse directions showing excellent agreement between the measurement and the synthetic. b. Comparison of prior and posterior models. The prior model represents the complex conductivity calculated from the impedance measurement using an analytical geometric factor; the posterior probability density obtained from the AMA clearly substantiates the analytical result.
Figure 4.10  Posterior PDF’s for in-phase (solid lines) and quadrature (stippled lines) conductivity, showing reasonable agreement to first order between the analytical estimate computed from the in-plane (0°) and transverse (90°) acquisitions; however, the posterior model clearly exhibits a shift of the mean values, which can be interpreted as the most likely value of the respective tensor eigenvalue.

reported in Table 4.6. The anisotropy ratio is typically on the order of 10, which means a formation factor or a bulk tortuosity approximately ten times larger in the direction normal to bedding by comparison to values observed in the bedding plane. Cosenza et al. (2007) also found an anisotropy ratio of ~10 for the amplitude of the conductivity between the measurements parallel and perpendicular to the bedding plane of shales. While the conductivity spectra may vary by several orders of magnitude, the governing anisotropy exhibits only small variations among the different cores and for different frequencies. We ascribe this consistency within the sample set to characteristically low porosities $\phi \leq 0.05$ and to the fact that all of the samples exhibit TI symmetry (Table 4.4).
Figure 4.11 Comparison between the measured data and the data determined from the model characterized by the highest posterior probability. a. Data misfit obtained from the resampled posterior PDF, showing an excellent reproduction of the measurements. b. The posterior model corresponding to the maximum likelihood data fit. The uncertainty of the posterior model increases due to the resampling of the posterior probability density; however, the model is still in good agreement with the joint posterior likelihood of the model shown in Figure 4.10.
Figure 4.12 Typical impedance spectra for Haynesville and Bakken cores. **a.** Azimuthal data represent a radial sampling of the electric field about an axis of symmetry. The data correspond to the incremental change of the full-field (current and potential) response of the medium, which is used to invert the full anisotropic complex conductivity tensor. **b.** Eigenvalue spectra acquired with the polarized field method. The single component field results in the direct measurement of the characteristic directional dependence of the sample.
Figure 4.13  a. In-phase and b. quadrature eigenvalue spectra for two pairs (Bakken A and Bakken B) of orthogonal Bakken core samples oriented. The anisotropy ratio for both A and B sets is on the order of 10^1, evidencing the dependence of the anisotropy on the textural properties through the formation factor and tortuosity tensor.

Figure 4.13 shows complex conductivity eigenvalue spectra for two distinct Bakken shales originating from different parts of the Williston Basin. Although both samples exhibit similar anisotropy, responses vary considerably due to contrasting material properties (see Table 4.3).

**Salinity of the pore water**

The formation factor can be obtained by measuring the conductivity at different salinities, thereby providing an ideal basis to study the directional dependence of shales through the characterization of the textural properties. Figure 4.14 shows the salinity dependence of the complex conductivity at 0.5 mM, 0.05 M and 0.5 M NaCl. The in-phase conductivity increases with salinity and exhibits a strong surface conductivity component as discussed by Revil et al. (2013c). The quadrature conductivity depends only weakly on the salinity.
Figure 4.14 Complex conductivity spectra for Bakken core Sample A. a. In-phase electrical conductivity versus frequency at three salinities (0.5, 0.05, and 0.005 M NaCl). b. Quadrature electrical conductivity versus frequency at three salinities (0.5, 0.05, and 0.005 M NaCl).

Having measurements at different salinities, we can use Equation 4.3 to decompose the in-phase conductivity into a bulk component (associated with conduction through the interconnected porosity) $F_j \sigma_w$ and a surface conductivity $\sigma_{ij}^s$ associated with conduction in the electrical diffuse layer:

$$\sigma_{ij}' = F_j \sigma_w + \sigma_{ij}^s$$  \hspace{1cm} (4.23)

The POLARIS model predicts a relationship from the quadrature conductivity and the surface conductivity as discussed recently by Revil (2013b) and Weller et al. (2013). We plot in Figure 4.15 the surface conductivity versus the quadrature conductivity for the database used by Weller et al. (2013) and the data corresponding to the Bakken core Samples A and B. We observe that the relationship determined by Revil (2013b) and Weller et al. (2013) can be extended to oil and gas shales. This opens interesting perspective in interpreting downhole measurements for instance.
Figure 4.15  Comparison between the surface conductivity and the quadrature conductivity. We compare here our data for the transverse and in plane surface conductivity and quadrature conductivities of the Bakken samples A and B with the database discussed by Weller et al. (2013). This dataset is extended to much lower values in Figure 4.16.

In Figure 4.16, we go one step further. We consider all the quadrature conductivity for the Bakken Sample B. These measurements include in-plane and transverse measurements, measurements at different saturations, and measurements at different salinities. All the data plot on the same linear trend, which is consistent with the prediction of the model developed by Revil (2013b) with R the dimensionless number connecting the surface conductivity to the quadrature conductivity (we obtain R = 0.022 independent on saturation, direction, and salinity).

**Saturation effects**

Figure 4.7 shows the complex conductivity spectra as a function of water saturation $S_w$; with marked changes in the conductivity magnitude, we observe a constant anisotropy ratio of 7.1±0.7 independent of the saturation as predicted by the model discussed above. A complete analysis of the saturation effect can be found in Revil et al. (2013c) and will not be repeated here.
Conclusions

We developed a protocol based on stochastic inversion to determine the full complex conductivity tensor of anisotropic hydrocarbon-bearing shales. This protocol is more general than the classical method of single-component measurements, which requires knowledge of the plane of symmetry of the core sample. The protocol was successfully validated with direct measurements of the eigenvalues of the complex conductivity tensor in the case where eigenvectors are known and measurements are performed in the main direction of anisotropy.

We observed that Bakken and Haynesville core samples are transversely isotropic (TI) with an anisotropic ratio on the order of 10. The in-phase conductivity tensor is found to be poorly dependent on frequency, at least up to 100 Hz. The magnitude of the components of the quadrature conductivity tensor increases with frequency in the frequency range 1 to 45 kHz.
Table 4.6  Anisotropy ratios of the Bakken A and Haynesville 092 cores obtained from inversion. Both the transverse and in-plane ratios are provided, evidencing the hexagonal (TI) symmetry observed in the cores. These results agree with the measured anisotropy (Table 4.4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>In-phase, $\lambda'$</th>
<th>Quadrature, $\lambda''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakken A</td>
<td>$\sigma_{11}' / \sigma_{33}'$</td>
<td>$\sigma_{11}' / \sigma_{22}'$</td>
</tr>
<tr>
<td>9.56±0.06</td>
<td>1.17±0.01</td>
<td>9.65±0.79</td>
</tr>
<tr>
<td>Haynesville 092</td>
<td>3.23±0.53</td>
<td>0.92±0.01</td>
</tr>
</tbody>
</table>

They appear to reach a plateau below 1 Hz. This transition is likely related to the transition between the double layer polarization at low-frequency and the Maxwell-Wagner polarization at high frequencies.

The in-phase conductivity is sensitive to pore water conductivity and this dependence can be used to determine surface conductivity. Quadrature conductivity depends only weakly on pore water conductivity. Both components are sensitive to pore water saturation. We found that the surface conductivity and quadrature conductivity can be related to each other. This relationship is independent of the saturation, salinity, and direction as predicted by the recently derived Stern layer polarization model.

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CHAPTER 5
MEASUREMENTS OF ELASTIC AND ELECTRICAL PROPERTIES OF AN UNCONVENTIONAL ORGANIC SHALE UNDER DIFFERENTIAL LOADING

A paper submitted to Geophysics

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Abstract

We developed an experimental approach to simultaneously measure the stress dependence of ultrasonic wave velocities at 1 MHz, and therefore the components of the undrained elastic stiffness tensor, as well as the components of the complex conductivity tensor in the frequency range 100 mHz to 10 Hz. A cylindrical core sample of gas shale is used for this purpose. The core sample originates from the Haynesville formation (porosity ~0.08 and clay content, mostly illite, ~30-40 wt.%). Experiments are performed under controlled confining and pore fluid pressures, achieving differential pressure states representative of autochthonous reservoir conditions. Directional measurements were made using independent acquisition arrays (piezoelectric crystals and non-polarizing electrodes) distributed azimuthally on the core sample external surface, the bedding plane being along the axis of the cylindrical core sample.

Ultrasonic waveforms were recorded on a high-resolution oscilloscope and complex impedance spectra were recorded with a four-electrode acquisition system using an impedance meter with a precision of 0.1 mrad. Experiments were repeated under drained and undrained conditions, over both loading and unloading sequences. Measurements show strong stress dependence on both ultrasonic and complex conductivity measurements, which can be ascribed to the opening and closing of cracks within the samples. The data are used to estimate the anisotropic electrical and elastic effective pressure coefficients of the core sample, resulting in
effective stress coefficients smaller than one for both elastic and electrical properties. These effective stress coefficients are also smaller for both electrical and acoustic properties once the cracks have closed. The anisotropy ratio for the components of the complex conductivity tensor is on the order of 30 while it is only 2 for the compressional components of the stiffness tensor.

**Introduction**

The role of rock mechanics and the connection between different petrophysical measurements (permeability, mechanical and electromagnetic properties) and the state of stress of oil and gas shales is gaining increasing importance in the multi-scale exploration, characterization, and production of unconventional oil and gas reservoirs (Yang and Zhang 2002; Kachanov and Sevostianov 2005; Josh et al., 2012). Such reservoirs are characterized by low porosities, very low permeability (<< 1 mD), and the presence of kerogen. The goal of these studies is to understand the anisotropic effects of local and regional stresses acting in situ on these formations, the existence of sweet spots that can be produced at affordable costs, and the evolution of the transport properties during production (Vernik and Liu 1997; Johansen et al., 2004; Chalmers et al. 2012). The knowledge of the electromagnetic properties (conductivity and permittivity) of oil shales is also required to determine the efficiency of radio frequency dielectric heating (Sweeney et al., 2007).

Ultrasonic and electrical measurements can be used to assess the effect of stress state and describe the poroelastic (undrained) response of a core sample. The study of the propagation of seismic waves in fluid-saturated porous media was pioneered by Frenkel (1944) and Biot (1955, 1956, 1962). Extension of the poroelastic theory to anisotropic media can be found in Carroll (1979) and Cheng (1997). In shales and mudstones, clay and kerogen contents and the effect of
textural anisotropy are expected to impact the measured P- and S-waves velocities (Prasad et al., 2011) and the corresponding components of the undrained stiffness tensor.

The complex electrical conductivity tensor of oil and gas shales has been modeled recently by Revil et al. (2013) and a validation of this model has been discussed by Woodruff et al. (2014) using a broad dataset of experimental measurements. In the case of acoustic and electrical measurements, oil and gas shales can be treated as transversely isotropic (TI) materials with the plane of isotropy corresponding to the foliation plane.

In the context of the production of unconventional reservoirs, the response of the anisotropic acoustic and electrical properties to differential stress levels in drained and undrained conditions remains poorly understood (Passey et al., 2010, Kuila et al., 2014). To study the corresponding effects of the mechanical response of shales, we developed a new measurement protocol incorporating the simultaneous acquisition of ultrasonic and spectral induced polarization datasets on a core sample of gas shale (Haynesville gas shale), characterized by transverse isotropy (Woodruff et al., 2014). For transport properties, it is usually possible to define an effective stress law with an effective stress coefficient (e.g., Bernabé, 1987; Coyner, 1984). Our goal is to study the effective stress coefficient for these properties, which are measured simultaneously for the first time on the same core sample and to look for the effect of the closure of the cracks on the effective stress response.

**Effective stress equations**

In the context of porous materials with a Newtonian pore fluid and a linear elastic isotropic skeleton, the effective pressure of poroelasticity $P^*$ (Pa) is given by

$$P^* = P_c - \alpha P_p,$$

(5.1)
where \( P_c \) (in Pa) defines the confining stress, \( P_p \) (in Pa) the pore fluid pressure, and \( \alpha \) (dimensionless) denotes the Biot coefficient, which obeys \( 0 \leq \alpha \leq 1 \). In the linear poroelastic framework, the Biot coefficient of an isotropic material is given by \( \alpha = 1 - K / K_s \leq 1 \), where \( K \) is the static bulk modulus of the porous material in drained conditions (the frame bulk modulus) while \( K_s \) denotes the static bulk modulus of the solid phase (Biot and Willis, 1957). In soils, where the compressibility of the skeleton is much smaller than the compressibility of the solid grains, the Biot coefficient can approach unity (de Boer and Ehlers, 1990). On the other hand, in very stiff rocks (e.g., crystalline rocks), \( \alpha \) can be close to zero. In anisotropic formations, the Biot’s coefficient is a second-rank symmetric tensor (e.g., Giot et al., 2012).

It is also customary to introduce effective stress laws for transport properties (Todd and Simmons, 1972; Bernabé, 1987; Coyner, 1984). These laws involve effective stress coefficients that are not necessarily similar to the effective stress coefficient defined above. In other words, the effective stress coefficient may be different for different petrophysical properties of porous media such as electrical conductivity, permeability, and mechanical/elastic properties (Bernabé, 1987; Coyner, 1984). The effective stress state for a given property is often difficult to quantify because the effective stress coefficient, \( \alpha \), may be also stress-dependent when deformation is considered over large pressure drops (e.g., Ghabezloo et al., 2008).

Our goal is to gain better insight regarding the effective stress coefficient for the undrained stiffness and complex conductivity tensors of a transversely isotropic gas shale. The elastic and electrical properties can be measured at various differential pressure states in order to obtain the changes of a measured response with respect to an effective stress law. Todd and Simmons (1972) showed that the effective stress coefficient for a given physical property, \( \chi \), can be estimated as (see Appendix E),
\[ \alpha^{\chi} = 1 - \frac{\partial \chi}{\partial P_p} \bigg|_{P_p}, \]  

(5.2)

In the present work, we will apply equation 2 to the components of both the undrained stiffness and complex conductivity tensors.

**Stiffness elastic tensor of transverse isotropic media**

In an anisotropic porous material such as gas shale, the poroelastic equations in drained conditions can be written in incremental form as (e.g., Giot et al., 2012),

\[ d\Sigma = C : d\epsilon - A dP_p, \]  

(5.3)

\[ dm = \rho_f A : d\epsilon + \left( \frac{1}{M_p} + \frac{\phi}{K_f} \right) dP_p, \]  

(5.4)

where \( M_p \) denotes the solid Biot modulus, \( \phi \) denotes the (Lagrangian) porosity, \( m \) (kg m\(^{-3}\)) denotes the pore water mass exchanged between the core sample and the reservoirs, \( K_f \) (Pa) and \( \rho_f \) (kg m\(^{-3}\)) denote the bulk modulus and mass density of the pore fluid, respectively, \( \Sigma \) (Pa) denotes the second-rank stress tensor, \( U \) (dimensionless) is the second-rank strain tensor, and finally \( C \) (components in Pa) denotes the fourth-rank (drained) stiffness elastic tensor. The confining pressure is defined by \( P_c = -(1/3) \text{Tr} \Sigma \) where \( \text{Tr}(.) \) denotes the trace of the matrix representation of the tensor. We note \( e_i \) (\( i = 1, 2, 3 \)) the basis vectors of the Cartesian frame of reference and we assume that \((O, e_3)\) will be the axis of symmetry, normal to the foliation or bedding plane of the material. In our case this direction will be normal to the centerline of the cylindrical core sample as discussed further below.
The stiffness tensor is related to its components \( C_{ijkl} \) by \( C = C_{ijkl} e_i \otimes e_j \otimes e_k \otimes e_l \), where \( e_i \cdot e_j = \delta_{ij} \) where \( \delta_{ij} \) is the Kronecker delta, while \( a \otimes b \) denotes the tensorial product between the two vectors \( a \) and \( b \). This stiffness tensor is characterized by two Young’s coefficients (\( E_1 \) and \( E_3 \)), two Poisson coefficients (\( \nu_{12} \) and \( \nu_{13} \)), and a shear modulus (\( G_{13} \)) (see for instance Giot et al., 2012). Assuming that the core sample is transverse isotropic, the second rank Biot tensor \( A \) entering equations 3 and 4 is expressed as,

\[
A = \alpha_1 (e_1 \otimes e_1 + e_2 \otimes e_2) + \alpha_3 e_3 \otimes e_3. \tag{5.5}
\]

Therefore the matrix representation of this tensor is,

\[
A = \begin{bmatrix}
\alpha_1 & 0 & 0 \\
0 & \alpha_1 & 0 \\
0 & 0 & \alpha_3 \\
\end{bmatrix} \tag{5.6}
\]

where \( \alpha_1 \) and \( \alpha_3 \) are the Biot coefficients in the bedding plane and in the transverse direction.

The incremental change of porosity can be written as (e.g., Giot et al., 2012):

\[
d\phi = A : d\epsilon + \frac{1}{M_\phi} dP_p \tag{5.7}
\]

Note however that equation 7 accounts only for the reversible change of porosity associated with the poroelastic deformation of the porous material. We will see that the deformation of the core sample in our experiments is characterized by a small component of irreversible deformation (damage).

The experiments that will be described below are made in both drained and undrained states. However we will not try to measure the deformation of the sample or the mass of fluid exchanged between the sample and the reservoirs. Instead, we will measure the stiffness tensor using ultrasonic measurements. At a given compaction state, the ultrasonic measurements probe
the undrained stiffness tensor of the material (i.e., the pore fluid has no time to flow in response to the stress solicitation associated with the passage of the seismic waves). In an undrained porous material, the mechanical constitutive equation corresponds to another form of Hooke’s law, which is written in incremental form as,

\[ d\Sigma = C^u : d\epsilon \] (5.8)

where \( C^u \) denotes the fourth-rank undrained stiffness elastic tensor (with components \( C^u_{ijkl} \)).

The relationships between the components of the undrained stiffness tensor and those of the drained stiffness tensor can be found in Cheng (1997) under the assumption that the macroscopic anisotropy is due to the arrangement of the pores and not the anisotropy of the solid phase. In the present paper, we will only provide and discuss the components of the undrained stiffness tensor.

Equation 8 can be written as \( \Sigma_i = C^u_{ij} \epsilon_j \) (with Einstein convention) using the Voigt matrix representations (indices \( i \) and \( j \)) of the stiffness elastic tensor connecting the components \( \Sigma_j \) of the stress tensor to the components \( \epsilon_{kl} \) of the strain tensor of the solid phase (Backus, 1962). In the following all the stiffness tensor components will be undrained components and we will drop the superscript “u” for simplicity.

In transverse isotropic materials with index 3 indicates the axis of symmetry, Hooke’s law is given by,

\[
\begin{bmatrix}
    d\Sigma_1 \\
    d\Sigma_2 \\
    d\Sigma_3 \\
    d\Sigma_4 \\
    d\Sigma_5 \\
    d\Sigma_6 \\
\end{bmatrix} =
\begin{bmatrix}
    C_{11} & C_{11} - 2C_{66} & C_{13} & 0 & 0 & 0 \\
    C_{11} - 2C_{66} & C_{11} & C_{13} & 0 & 0 & 0 \\
    C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
    0 & 0 & 0 & C_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & C_{44} & 0 \\
    0 & 0 & 0 & 0 & 0 & C_{66} \\
\end{bmatrix}
\begin{bmatrix}
    d\epsilon_1 \\
    d\epsilon_2 \\
    d\epsilon_3 \\
    d\epsilon_4 \\
    d\epsilon_5 \\
    d\epsilon_6 \\
\end{bmatrix}.
\] (5.9)
The complex conductivity tensor

Oil and gas shales being anisotropic materials, their complex conductivity tensor is expected to be direction-dependent. Very few works have investigated the complex conductivity of anisotropic materials (e.g., Zisser and Nover, 2009; Zisser et al., 2010; Revil et al., 2013, Woodruff et al., 2014) or in comparing the anisotropy behavior of ultrasonic P-wave velocity and electrical conductivity (Louis et al., 2003). In water-saturated porous materials, the electrical constitutive equation of interest is the generalized Ohm’s law, which can be obtained from non-equilibrium thermodynamics and Ampères law as (Vinegar and Waxman, 1984):

\[ J = \sigma^* \cdot E, \]  \hspace{1cm} (5.10)

where \( J \) (A m\(^{-2}\)) is the total current density and \( E \) (V m\(^{-1}\)) the electrical field. The complex conductivity tensor \( \sigma^* \) is related to its complex-valued components \( \sigma_{ij}^* \) by \( \sigma^* = \sigma_{ij}^* e_i \otimes e_j \) in S m\(^{-1}\)) where \( e_i \) (\( i = 1, 2, 3 \)) correspond to the basis vectors of the Cartesian frame of reference. Equation 10 can integrate also the displacement current and so the complex conductivity an integrate dielectric effects such as Maxwell-Wagner polarization mechanisms (see Revil, 2013a, b for further discussions).

Each component of the complex conductivity tensor is a complex number and can be written as

\[ \sigma_{ij}^* = \sigma_{ij}' + i \sigma_{ij}'', \]  \hspace{1cm} (5.11)

where \( i^2 = -1 \) (\( i \) denotes the pure imaginary number). In a transverse isotropic material (with axis 3 being the axis of symmetry, normal to the foliation plane), the complex conductivity tensor is,

\[ \sigma^* = (\sigma_{11}' + i \sigma_{11}'') (e_1 \otimes e_1 + e_2 \otimes e_2) + (\sigma_{33}' + i \sigma_{33}'') e_3 \otimes e_3, \]  \hspace{1cm} (5.12)

and therefore the generalized Ohm’s law is given by
\[
\begin{bmatrix}
J_1 \\
J_2 \\
J_3
\end{bmatrix} = \begin{bmatrix}
\sigma'_{11} + i\sigma''_{11} & 0 & 0 \\
0 & \sigma'_{11} + i\sigma''_{11} & 0 \\
0 & 0 & \sigma'_{33} + i\sigma''_{33}
\end{bmatrix} \begin{bmatrix}
E_1 \\
E_2 \\
E_3
\end{bmatrix}, \quad (5.13)
\]

in a Cartesian framework aligned with the eigenvectors of the complex conductivity tensor (axis 3 normal to the foliation plane).

The components \( \sigma'_{ij} \) represent the real (in-phase) components of the complex conductivity tensor and these components describe electromigration phenomena affecting the charge carriers. Electromigration occurs both in the bulk pore space and in the electrical double layer coating the surface of the grains. This electrical double layer comprises the Stern layer of counterions sorbed on the surface of the grains and the diffuse layer in which the counterions and co-ions are bound to the mineral surface through Coulombic interactions. The components \( \sigma''_{ij} \) denote the imaginary (out-of-phase, quadrature or imaginary) components. These components describe the polarization or capacitive effect of the core sample, or, in other words, the reversible storage of electrical charges in the porous material. In addition, these quadrature components can be affected by dielectric polarization phenomena such as the Maxwell-Wagner or high frequency polarization effects (see Revil, 2013a, b).

Revil (2013a) developed a complex conductivity model obtained by volume-averaging the Nernst-Planck equation in isotropic porous media. At high porosities, this model is consistent with the Waxman and Smits (1968) equation of electrical conductivity and the Vinegar and Waxman (1984) model of polarization. That said, Revil’s (2013a) model seems more accurate at low porosities (see Woodruff et al., 2014). In this model, the quadrature conductivity is mostly controlled by the polarization of the Stern layer of counterions. Neglecting Maxwell-Wagner polarization, Revil et al. (2013c) extended this model to the anisotropic case and provide
analytical expressions describing the in-phase and quadrature components of the complex conductivity tensor as

\[
\sigma_{ij} ' \approx F_{ij} \sigma_w + T_{ij} \rho_s \left[ \beta_{(+)} (1 - f) + \beta_{(+)}^S f \right] \text{CEC},
\]

\[
\sigma_{ij} " = T_{ij} \rho_s \beta_{(+)}^S f \text{CEC},
\]

respectively. In the above equations, \( F_{ij} \) denotes the components of the (symmetric second-rank) conductivity formation factor tensor for the conductivity, \( F \), and \( T_{ij} \) denotes the components of the (symmetric second-rank) tortuosity tensor of the pore space, \( T \). For transverse isotropic materials, these two tensors are defined as,

\[
F = \frac{1}{F_1} (e_1 \otimes e_1 + e_2 \otimes e_2) + \frac{1}{F_3} e_3 \otimes e_3,
\]

\[
T = \frac{1}{\tau_1} (e_1 \otimes e_1 + e_2 \otimes e_2) + \frac{1}{\tau_3} e_3 \otimes e_3,
\]

and \( F_1 = \tau_1 / \phi \) and \( F_3 = \tau_3 / \phi \). The terms \( F_{1,3} \) are analogous to the classical (resistivity) formation factors (>1) while the terms \( \tau_{1,3} \) are analogous to the classical tortuosities (>1) of the pore space in the foliation plane (directions 1, 2) and normal to the foliation plane (direction 3).

The partition coefficient, \( f \) entering equations 14 and 15 (dimensionless, typically in the range 0.85 to 0.99, see Revil, 2012, 2013a, b), denotes the fraction of counterions in the Stern layer, \( \rho_s \) denotes mass density of the solid phase (typically 2650±50 kg m\(^{-3}\) for the crystalline framework of clay minerals), \( \sigma_w \) (S m\(^{-1}\)) denotes the conductivity of the pore water, and CEC (see equations 14 and 15) corresponds to the cation exchange capacity of the material (expressed in C kg\(^{-1}\)). The parameter \( \beta_{(+)} \) denotes the mobility of counterions in the electrical diffuse layer while \( \beta_{(+)}^S \) denotes the mobility of counterions in the Stern layer (both are expressed in m\(^2\)s\(^{-1}\)V\(^{-1}\)).
For clay minerals, the mobility of counterions in the diffuse layer is equal to the mobility of the same counterions in bulk pore water (e.g., \( \beta_+^{(\text{Na}^+, 25^\circ\text{C})} = 5.2 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1} \), see Revil, 2012; Revil, 2013a, b) while the counterion mobility in the Stern layer is substantially smaller, \( \beta_+^{(\text{Na}^+, 25^\circ\text{C})} \approx 1.5 \times 10^{-10} \text{ m}^2\text{s}^{-1}\text{V}^{-1} \) for clay minerals (Revil, 2012, 2013a, b; Revil et al., 2013).

**Stiffness tensor and mechanical compaction**

Pictures of the core sample used in this study are shown in Figures 5.1 and 5.2 and the position of the foliation plane with respect to the sample axis is shown in Figure 5.2 and Figure 5.3 (the 90° angle-direction is normal to bedding). The components of the stiffness elastic tensor can be derived from azimuthal velocities (as measured from the isotropic reference plane) of the compressional velocity, \( v_p \), and the fast horizontal and vertical shear wave velocities, \( v_{SH0} \) and \( v_{s90} \), respectively (see Figure 3). The six independent (undrained) stiffness coefficients in Equation 9 can be obtained from five directional velocity measurements (e.g., Hornby, 1988), namely,

\[
C_{11} = \rho v_{p0}^2 \\
C_{33} = \rho v_{p90}^2 \\
C_{44} = \rho v_{s90}^2 \\
C_{66} = \rho v_{SH0}^2 \\
C_{12} = \rho \left(v_{p0}^2 - v_{SH0}^2\right) = C_{11} - 2C_{66}
\]

where the vertical translational component is obtained from \( C_{11} \), \( C_{33} \), \( C_{44} \) and an off-axis compressional or shear velocity measurement (typically at 45 incidence to the foliation plane)

\[
C_{13} = -C_{44} + m \sqrt{(C_{11} + C_{44} - 2\rho v_{45}^2)\left(C_{33} + C_{44} - 2\rho v_{45}^2\right)},
\]
Figure 5.1 Photomicrographs of the Haynesville gas shale showing its microstructure. We generalize the textural properties of the Haynesville core according to the microscopic features which have the greatest impact on the ultrasonic and spectral induced polarization measurements. **a.** Microscopic decompression fractures. **b.** Preferential alignment of clay minerals. **c.** Heterogeneous pore network ranging from intergranular porosity, mesoporosity and microporosity in the clay laminations, and kerogen porosity. In each set of images, the right-hand panel shows the area outlined in white in the left-hand image at 10× magnification.
Figure 5.2 Vertical and horizontal slices obtained from X-Ray tomograms depicting the pervasive decompression fracture distribution in the core sample. Fractures are aligned predominantly in the foliation plane, but exhibit some conchoidal features. The fracture networks have pronounced effects on both ultrasonic and electrical measurements. Dashed lines indicate where horizontal slice (a) intersects the vertical slice (b). The white X’s collocate the images azimuthally, white arrows are oriented in-plane and black arrows transverse to the fracture plane.

taking $m=-1$ for off-axis compressional velocity and $m=1$ if the off-axis shear velocity is used. In these equations $\rho$ (kg m$^{-3}$) denotes the mass density of the material (2450 kg m$^{-3}$ from Figures 5.1 and 2 of Jiang and Spikes, 2013 and where the velocity subscripts indicate both the wave type (subscripts P and S denote compressional and shear waves, respectively), and direction (subscripts 0 and 90 denote the horizontal and vertically propagating waves, see Figure 5.3). The vertical shear wave and the horizontal shear wave polarized in the vertical plane ($v_{S90v}$) are assumed equal and are denoted by $v_{S90}$. Shear sources and the measured arrivals are polarized,
Figure 5.3  Azimuthal array for anisotropic ultrasonic and spectral induced polarization measurements. Electrodes are distributed radially about the core (axis coincident with the isotropic plane) to sample the change in electrical potential field distribution over the surface. Impedance measurements can be inverted for the full electrical tensor and the rotation eigenvectors. The axis 1 and 2 are along the bedding/foliation plane while the axis 3 is normal to the bedding/foliation plane.

thus allowing for the isolated measurement of the velocities along each of the independent directions defined by the stiffness tensor. For a differential pressure increment and therefore an associated compaction increment of the material, the effective stress laws for the stiffness coefficients are discussed in Appendix F.

As previously emphasized, the complex conductivity and ultrasonic wave velocities are both dependent on the effective pressure applied to the porous medium. This pressure state is in
turn related to the consolidation of the material through the compaction of the pore space and the
deformation of minerals. The nature of mechanical behavior of microstructure in rocks is
complex (e.g., deformation and elongation of pores and micropores, closure of the cracks,
realignment of platy minerals, irreversible creep or pore collapse to list a few). Nevertheless, the
macroscopic effect of mechanical compaction in the quasilinear elastic regime can be described
according to changes in the bulk textural properties used to define the elastic and electrical
properties in the preceding sections. We will also assume that the deviations between the
electrical and elastic tensor eigenvectors are small and can be neglected. The bulk density and
the components of the undrained elastic tensor $C_{ijkl}^u$.

**Complex conductivity tensor and mechanical compaction**

In anisotropic conditions, we obtain the components of the two textural tensors $\mathbf{F}$ and $\mathbf{T}$
from the in-phase and quadrature conductivities from equations 14 and 15, as follows. The
components of the formation factor tensor can be obtained as:

$$F_{ij} = \sigma_{ij}^{-1} \left[ \sigma_{ij}^1 - \sigma_{ij}^2 \left( 1 - \frac{\sigma_d}{\sigma_S} \right) \right], \quad (5.24)$$

while the components of the tortuosity tensor are obtained according to

$$T_{ij} = \frac{\sigma_{ij}^2}{\sigma_S} \quad (5.25)$$

In equations 24 and 25, the conductivities of the Stern and diffuse layers are given by
$\sigma_S = \rho_S \beta_{s(+)} f \text{CEC}$ and $\sigma_d = \rho_S \beta_{d(+)} (1 - f) \text{CEC}$ and
$\sigma_d / \sigma_S = \beta_{s(+)} (1 - f) / [\beta_{s(+) f} \eta]$ (see equations
14 and 15). The CEC of the Haynesville formation is comprised between 13.9 and 3.6 meq/100g
(Breeden et al., 2011, equivalent to 13,000 to 3,400 C kg$^{-1}$). Kuila (2013) measured the CEC of
several samples from the Haynesville formation. His data are shown in Figure 5.4 together with
Figure 5.4 Relationship between the clay content and the cation exchange capacity of core samples from the Haynesville formation (data from Kuila, 2013, and Breeden et al., 2011). Meq means milliequivalent and $\phi_w(\%)$ expresses the clay content in weight %.

the data from Breeden et al. (2011). The linear trend between the CEC and the clay content shown in Figure 5.4 will be used to estimate the CEC from the clay content of our core sample, which is done in the next section.

**Description of the experiments**

The acoustic velocity measurements were acquired at 1 MHz (ultrasonic frequency) while the electrical impedance spectroscopic data was acquired in the frequency range 100 mHz to 10 Hz. The ultrasonic frequency 1 MHz is used to generate wavelengths compatible with the laboratory scale of the core sample while the low-frequency of the complex conductivity measurements is justified by the occurrence of electrical double layer polarization processes at this frequency range (Revil et al., 2013; Woodruff et al., 2014).
Table 5.1  Representative mineralogy of the Haynesville samples from QXRD (Quantitative X-Ray Diffraction) analysis. The median, maximum, and median mass fractions (in percent) are provided in different columns.

<table>
<thead>
<tr>
<th>Mineral fraction (wt%)</th>
<th>Median</th>
<th>Maximum</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 clay</td>
<td>45.0</td>
<td>57.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>28.0</td>
<td>31.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Calcite</td>
<td>14.0</td>
<td>38.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>5.0</td>
<td>11.0</td>
<td>3.0</td>
</tr>
<tr>
<td>TOC</td>
<td>3.5</td>
<td>6.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2.0</td>
<td>4.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Pyrite</td>
<td>2.0</td>
<td>7.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

A detailed description of the core preparation protocols (machining, fluid synthesis and saturation), laboratory equipment and measurement protocols are provided in Woodruff et al. (2014) and the readers are directed to this paper for the details. In the present paper, we used a cylindrical plug (sample H251; see Table 5.1 for its mineralogical composition and Table 5.2 for the porosity) from a whole core specimen of the Haynesville shale formation, encased in a jacket of our own design for joint acoustic/electrical measurements under effective hydrostatic load. We control the pore and confining pressures with syringe pumps (Teledyne ISCO model 100DM), enabling precise control of differential stress ranging from 0 to 34.5 MPa at increments of 3.45 MPa per stage.

**Description of the Haynesville core sample**

The Haynesville formation is located in the Texas-Louisiana Salt Basin. The Haynesville shales are generally characterized as silty, argillaceous or calcareous mudstones, and dolomitic mudstones and dolostones with a strong vertical transverse anisotropy (Horne et al., 2012; Jiang and Spikes, 2013). The formation varies compositionally, depending on the position in the stratigraphic column. In situ sampling indicates clay content of 30% (± 10%), 15% (± 10%) calcite, and 4% (± 3%) TOC (total organic content), by mass (Spain and Anderson, 2010, their
Table 5.2  Haynesville core sample description from standard core analysis including the mass fraction of the predominant mineralogy and porosity as obtained from pulverized samples (Gas Research Institute, GRI, method) and from Archimedes’ method (Water Immersion Porosity WIP, \( \phi \), see Kuila, 2013, Kuila et al., 2014). Additional petrophysical studies of downhole measurements are consistent with these observations. TOC denotes Total Organic Content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quartz (wt%)</th>
<th>Carbonate (wt%)</th>
<th>Sum Clay (wt%)</th>
<th>TOC (wt%)</th>
<th>( \phi ) (GRI)</th>
<th>( \phi ) (WIP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H251</td>
<td>21</td>
<td>32.5</td>
<td>29.6</td>
<td>5.38</td>
<td>0.087</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Table 5.1). Chalmers et al. (2012) report a TOC of 4.2 % (Type II kerogen distributed in the rock). Chalmers et al. (2012) reported a mean pore diameter of 4.9 nm, a porosity of 6.2%, a clay content of 44% in weight (essentially illite and some chlorite). Elgmati et al. (2011) reported a mean pore size of 6.5 nm (Hg-porosimetry), a porosity of 10.3%, and a permeability of \( 1.4 \times 10^{-4} \) mD.

The texture of the Haynesville mudstone exhibits laminated fabrics ranging on both the scale of the mineral foliations, as well as that of the depositional bedding planes. Environmental (Scanning Electron Microscope) SEM images taken from the Haynesville core confirm the microstructure visible on the surface of the core (Figure 5.1), showing clay laminations, mineral heterogeneity, kerogen distribution, and the presence of cracks.

Recovered Haynesville samples are fissile and exhibit usually decompressional stress-related cracks. These cracks are shown by X-Ray computerized axial tomography to be predominantly aligned in the plane of mineral foliations (Figure 5.2), some of them traversing the entire core with some conchoidal character. As we will show below, such fractures have pronounced effects on both the ultrasonic and complex conductivity measurements, exhibiting characteristic changes resulting from the closure of the cracks. Due to the relatively ubiquitous volume fraction of clay and homogeneous water saturation, both porosity and density are also tied closely to the calcite distribution (Skelt, 2011).
The core sample was machined to improve the accuracy of sample dimensioning and sensor placement; bulk samples were well characterized prior to machining through standard core analysis, X-ray diffraction, CT imaging, SEM imaging, as well as ultrasonic measurements in order to determine the bases of the material properties. The dry sample was evacuated under vacuum and pressure saturated with an equilibrium solution prepared in balance with the characterized mineralogy of the sample (see Woodruff et al., 2014, for a detailed description of the saturation procedure). It was pressurized at 10.34 MPa for a period of 72 hours, and left to equilibrate within a saturated jacket for an additional 120 days (flooded with a drained, saturated pore line, at 0 Pa).

For the sample investigated in the present work, a clay content of 30% yields a CEC value of 3.8 meq/100g (3,700 C kg⁻¹) according to the relationship determined in Figure 5.4. The conductivity of the equilibrium solution was determined with PHREEQC (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/PHREEQC) to be 88 µm cm⁻¹ (~0.0088 S m⁻¹). The equilibration time was typically 12-24 hours (see Woodruff et al., 2014). It follows that using the following values, \( \sigma_w = 0.01 \text{ S m}^{-1} \), \( \beta_{(+)} = 5\times10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1} \) (mobility of sodium in water at 25°C), \( \beta_{(+)}^S = 0.05 \beta_{(+)} \) (default value for the mobility of sodium in the Stern layer at 25, see Revil, 2013a), and default value of the partition coefficient \( f = 0.90 \) (see Revil, 2013b), we obtain \( \sigma_S = 0.0221 \text{ S m}^{-1} \) and \( \sigma_d = 0.049 \text{ S m}^{-1} \). This indicates very clearly that applying Archie’s law for the electrical conductivity without a correction from the surface conduction is not an appropriate choice since surface conductivity appears as a very important component of the overall conductivity of the porous material. Note that the independent measurements of the formation factor (from the in-phase and quadrature conductivities) and the tortuosity tensor (from the quadrature conductivity alone) can also be used to estimate the porosity at a given compaction
state. At the end of this paper, we will try to perform such a computation for different differential pressures.

**Jacketed core assembly**

A jacket was designed to encase the sample and the affixed sensors, as well as to provide a closed pressure system. The core assembly allows for anisotropic characterization of cylindrical plugs with a height of 51 mm, and diameter 38 mm, with an axis aligned in the foliation plane, corresponding to the isotropic plane of symmetry. It was designed for the measurement of electrical potentials and acoustic wave velocities, utilizing three separate azimuthal arrays distributed about the circumference of the sample (see Figure 5.3).

The jacketed assembly incorporates both 2.0 mm sintered Ag/AgCl pellet Electrocardiography (ECG) electrodes and Lead Zirconate Titanate (PZT) ceramic piezoelectric crystals for joint acquisition of spectral induced polarization and ultrasonic measurements. These sensors were arranged azimuthally about the core axis. Figures 5.3 and 5.5 depict the core, sample jacket, acquisition geometry, and sensor locations with respect to the foliation plane of the core sample. Prior to placing the sensors, additional precision machining was performed to prepare the surface of the sample for instrumentation (14 Ag/AgCl electrodes; 12 PZT crystals). We drilled 2.0 mm diameter sockets in the center of the top and bottom surfaces to house the current electrodes, and pairs of sockets radially about the core at precise angles of 0°, 45° and 90° relative to the foliation plane (0°, demarking the isotropic plane, was estimated prior to machining, see Figure 5.3).

For the ultrasonic array, we machined parallel surfaces for the ultrasonic wave propagation experiments along the same azimuths. Electrodes are separated by 31.75 mm. The cylindrical surface is painted to electrically insulate the sample; we have found Revlon, clear
Figure 5.5 Sketch of the jacketed core assembly. Feedthroughs are distributed radially in the outer ring and the removable center plug is threaded for the NPT pore line fittings. The removable plug enables saturation of the sample after the sample is encased in the jacket. Dimensions in mm. A and B denote the current and M and N denote the potential electrodes, while P and S denote the compressional and shear piezoelectric crystals.

cloth and quick dry nail polish to have favorable insulating properties, with good resistance to moisture and immersion in water. Both the top and bottom surfaces, as well as the inner surfaces of the electrode sockets are left clean. The end caps are affixed and a bead of epoxy is placed along the contacting edges to seal the inner and outer portions of the assembly and prevent leakage around the outside of the sample. Sensors are coupled to the sample with conducting silver epoxy; leads soldered to feed troughs in the end cap. The exterior of the sample, including the sensors and lead wires are encased in a highly compliant resin.
Measurement systems

A steel pressure vessel filled with a low compressibility, low conductivity oil is used to apply hydrostatic pressure to confine the sample under a prescribed load and electrically insulate the sensor leads on the immersed sample. Two Teledyne ISCO model 100DM syringe pumps are used to modulate the opposed confining pressure $P_c$ (MPa) in the vessel and pore line pressure $P_p$ (MPa) inside the sample jacket.

A Tektronix TDX 3014C oscilloscope is used to acquire the acoustic waveforms. The acoustic source is controlled by an electronic pulser, which modulates both the voltage (300 V at full range) and pulse width of the electrical current in the piezoelectric crystal exciting a resonant frequency of 1 MHz in the crystal. We measure the traveltime $t$ ($\mu$s) between the pulse and the source and receiver crystals for both P-wave and S-waves. Velocity is calculated as $v = 2r / t$ (km s$^{-1}$) where $r = 3.81$ cm is the radius of the core sample. Data are acquired and travel time for the acoustic waves are picked using the Spec4Win software developed for the Center for Rock Abuse at the Colorado School of Mines.

Regarding the determination of the complex conductivity, we use the ultrasensitive impedance meter designed by Egon Zimmermann (Zimmermann et al., 2008a, b) instrumented with sintered Ag/AgCl electrochemical (non-polarizing) electrodes and configured according to the protocols published recently by Woodruff et al. (2014). The system comprises a four-channel acquisition array and nominal frequency range of 1 mHz to 45 kHz. Figure 5.6a shows a sketch of the spectral induced polarization acquisition system characterized by a sensitivity of 0.1 mrad in phase shift. A current $I_0$ is excited in the sample by an applied voltage $U_1$ between two stimulus electrodes 1 and 4 (or A and B), located at the top and bottom faces of core sample (Figures 5.3 and 5.5). We approximate the resistance in the medium as a linear circuit using
Figure 5.6  Impedance measurement and typical complex conductivity spectrum for the Haynesville core sample. a. Circuit diagram of the impedance measurement. The stimulus voltage $U_1$ and current $I_0$ are modulated over at a set of predesigned frequencies ranging from 100 mHz to 10 Hz, grounded across the sample at the locations 1 and 4. The true sample impedance, $Z_x$, is calculated from the transfer current $I_x$ in the sample, the potential drop $U_x$ between the potential electrodes, 2 and 3, and the known resistance $R_s$ of the shunt resistor (1 kOhm). Electrode contact impedances $Z_e$, and the known input impedance $Z_v$ (~1 GOhm) of the acquisition system are also depicted. Current, impedance and voltage are measured in A, Ohm and V, respectively. b. Typical complex conductivity spectrum (in-phase and quadrature conductivity versus frequency) for the Haynesville core sample.
\[ Z_m = U_m / I, \] where \( Z_m \approx Z_x \) denotes the true impedance in ohms, \( U_m = U_x \) denotes the potential difference between the Ag/AgCl measuring electrodes 2 and 3 (voltage electrodes M and N) in volts (V) and \( I \) is the electrical current in Ampères. For shales, in the voltage range 1 V to 10 V, the impedance has been checked to be independent of the current magnitude \( I_s \) (Jougnot et al., 2010). The impedance is estimated as \( Z_m = U_m / I_s = R_s U_m / U_s \approx Z_x \) for a current excited by a 5 V difference in applied voltage, we have \( I_s = U_s / R_s = 5 \) mA, where \( R_s = 1 \) KOhm is the resistance at the shunt resistor. The expression of the complex impedance can be written as,

\[ Z^*(\omega) = |Z^*(\omega)| e^{\varphi(\omega)} \] (5.26)

where \(|Z^*(\omega)|\) is the impedance magnitude in Ohms, and \(\varphi(\omega)\) is the frequency dependent phase angle in milliradians, obeying Ohm’s law as \(Z(\omega) = U(\omega)I(\omega)^{-1} \). Once the impedance is obtained, we determine the geometrical factor (see Woodruff et al., 2014) and the in-phase and quadrature conductivities of the core samples in the different directions (Figure 5.6b).

**Experimental Results**

Isothermal electrical and elastic data sets were jointly acquired such that the properties derived from the two data sets are directly comparable at a given stress state. The Joule dissipation effect associated with the current was too small to generate notable change in the temperature of the core sample so all the measurements can be considered to have been done in isothermal conditions. These data yield a direct measure of the components of the complex conductivity and undrained stiffness tensors, which both depend on the textural changes in the sample due to the mechanical deformation proportional to the known effective pressure imposed in each experiment. The confining pressure \(P_c\) (MPa) is applied external to the jacket and the
Figure 5.7 Sketch of the pressure matrix in pore fluid pressure / confining pressure space. Drained experiments correspond the line $P_p=0$. Undrained experiments comprise all of the stages shown. Measurements are made in sequence obeying the condition $P_p \leq P_c$ to ensure that the sample is not subjected to negative differential stress $P_d < 0$ which may fracture the sample depending on its tensile strength. Data is first acquired along lines of constant pore pressure in increments of 3.45 MPa (solid arrows); ultimately, the zero differential stress loop $P_d = 0$ is acquired (dashed arrow). Additional experiments along (diagonal) lines of constant differential stress may be of interest to describe the effective stress dependence of the sample.

Pore pressure $P_p$ (MPa) is controlled inside the jacket during the experiment. This allow use to control the effective pressure, $P^*(MPa)$, applied to the core sample.

Figure 5.7 depicts the pressure matrix of the undrained experiments. Repeated ultrasonic and spectral induced polarization were first acquired for the as-received drained sample under hydrostatic confining pressure $P_c$ from 0 MPa to 34.5 MPa for both loading and unloading sequences. Subsequent undrained experiments were made along lines of constant pore pressure $P_p$ from 0 MPa to 17.25 MPa, over sequential confining pressure $P_c$ loops up to 35.4 MPa at pressure increments of 3.45 MPa or 6.98 MPa per stage. Undrained zero-stress measurements, $P_d=0$ MPa, were made at the same confining pressure interval. At the maximum differential
pressure state of 34.47 MPa, the sample may not behave as a pure poroelastic composite (damage is commonly observed due to the highly heterogeneous nature and fissility in shales). We provide an analysis along lines of both constant pore pressure and differential stress, but the measurements were made only along lines of constant pore pressure.

Experiments were performed with jacketed samples under hydrostatic confinement in hydraulic oil. A nominal gradient of 140 kPa minute$^{-1}$ was used throughout the various acquisitions. The required pressure was reached when pump flow rate fluctuated around 0.1 ml/min for that pressure. Prior to each acquisition, we conditioned the sample in a stress loop from 0 MPa to 13.79 MPa (70 kPa minute$^{-1}$), allowing for stress equilibration at the maximum pressure. Equilibration times were determined during the first few measurements through repeated ultrasonic tests. Measured waveforms were compared until the elastic response stabilized, yielding an equilibration period of 30 minutes per pressure stage. We collected both compressional and shear waveforms and impedance spectra at each of the pressure steps. Data were acquired at log-distributed frequencies ranging from 100 mHz to 10 Hz.

The pressure dependence of both elastic wave velocity and complex conductivity is associated to porosity changes. We observe a monotonic increase in velocity with increasing differential pressure (Figure 5.8) and a corresponding monotonic decrease in complex conductivity (Figures 5.9 and 5.10). The drained measurements were made prior to the undrained measurements. These data comprise the initial stress cycle to which the core was exposed closure pressure (approximately 20 MPa) in order to identify and characterize the poroelastic response before and after closure of these cracks. (loading and unloading from 0 MPa to 34.5 MPa). The sample was taken well beyond fracture (approximately 20 MPa) in order to identify and characterize the poroelastic response before and after closure of these cracks.
Figure 5.8 Drained ultrasonic measurements in the in-plane (0°), oblique (45°) and transverse (90°) directions. a. Compressional (P-) wave velocity. b. Shear (S-) wave velocity. We observe monotonic increases in compressional and shear velocity with increased differential pressure. Higher velocities also evidence damage in the unloading stress stages.

**Interpretation of laboratory measurements**

We describe the ultrasonic and SIP datasets in the context of poroelasticity to obtain the effective electrical and elastic properties of the sample.

**Effective Pressure for the ultrasonic velocity**

Elastic tensor components were obtained from in the in-plane $C_{11}$ and transverse $C_{33}$ compressional and in-plane $C_{66}$ and transverse $C_{44}$ shear wave velocities using equations 5 through 10 (see Table 5.3). We analyze the tensor components along lines of constant differential stress and lines of constant pore pressure in the respective directions. These data are shown in Figures 5.11 and 5.12. We are able to delineate two stress regimes in the elastic properties, the sub-closure (dark circles with solid lines) and super-closure (light circles with dashed lines) fracture closure pressure measurements corresponding to open and closed fracture networks, respectively. While these regimes are analogous to those described in the undrained experiments,
Figure 5.9  Complex conductivity under hydrostatic loading, **a.** drained experiment and **b.** undrained experiment. The in-phase and quadrature conductivities decrease with increased load due to infinitesimal changes in the textural properties, such as the porosity, with compaction. Conductivities represent relative magnitudes calculated from azimuthal complex impedances with a geometric factor $k = 0.323$ (dimensionless); tensor components can be inverted from these data. The full cycle in the differential pressure shows the damage generated in the core sample.
Figure 5.10  Complex conductivity decreases with increased load due to changes in porosity (fracture closure and compaction; drained experiment). Closure is observed as a first-order reduction in conductivity at 20.68 MPa (differential stress exceeds the fracture closure pressure in the shaded regions). a. Textural fabric gives rise to second-order changes in the in-plane slope above closure; the magnitude change in the quadrature component is one quarter the in-phase component ($|\Delta \log_{10} \sigma'|=0.03$; $|\Delta \log_{10} \sigma''|=0.04$) indicating changes in tortuosity are small in correspondence with changes in surface conductivity. b. Changes in transverse slopes are comparable ($|\Delta \log_{10} \sigma'|=0.04$; $|\Delta \log_{10} \sigma''|=0.04$), indicating that the tortuosity normal to the bedding plane correlates with fracture closure and mechanical compaction.
the fracture closure pressure is now somewhere between 10 MPa and 15 MPa, therefore significantly lower than in the drained experiments. We believe that this behavior is the result of changes in the fracture compliance between the experiments; the undrained experiments exhibit much weaker, more compliant fractures than the initial drained experiments (i.e., the sample was strained and possibly fractured by the drained experiments).

Lines of constant differential stress evidence a change in slope with increasing confining stress in the in-plane and transverse moduli, with slopes increasing for compressional moduli ($C_{11}$ and $C_{33}$) and decreasing for shear moduli ($C_{66}$ and $C_{44}$) to constant gradients above fracture closure. The effective stress coefficient was estimated from these gradients for measurements at both sub-closure and super closure differential pressure conditions using Equation 3. Given the scatter in the data, a predominant slope was selected to represent the numerator. For measurements made at low differential stress (below fracture closure) we obtained the following effective stress coefficients for the components of the undrained stiffness tensor: $\alpha_{11} = 0.67$, $\alpha_{33} = 0.90$, $\alpha_{44} = 0.69$, and $\alpha_{66} = 0.93$ (see definition in Appendix F). Measurements made under high differential loading (above fracture closure) yielded significantly lower effective stress coefficients: $\alpha_{11} = 0.02$, $\alpha_{33} = 0.31$, $\alpha_{44} = 0.50$, and $\alpha_{66} = 0.37$. This result evidences the intuitive phenomenon of increased sensitivity of ultrasonic measurements to pore pressure with open fractures when compared to the same sample with closed fractures.

The stress dependence of velocity is dependent on the increase in the density associated with the compaction of the sample under increasing hydrostatic load. Indeed, the dynamic (high frequency) mechanical characteristics of the material are described by elastic moduli (i.e., components of the stiffness tensor) obtained directly from the compressional and shear velocities.
Figure 5.11 Effective stress behavior for the stiffness tensor components. **a.** In-plane $C_{11}$ and **b.** transverse $C_{33}$ compressional moduli along lines of constant differential stress and constant pore pressure. The effective stress coefficient is computed as the ratio of the gradients of differential stress lines to pore pressure lines. Values are obtained below (dark circles with solid lines) and above (light circles with stippled lines) fracture closure. These results evidence a strong dependence of the effective stress response to the fractures in the sample.
Table 5.3 Components of the mechanical stiffness tensor ($C_{ij}$) and electrical formation factor tensor ($F_{ij}$) and tortuosity tensor ($T_{ij}$) from the undrained experiments along the initial loading path, the $P_p=0$ line. Fracture closure values are provided at 10.34 MPa confining pressure, bounded by the values above and below closure at 6.89 MPa and 13.79 MPa, respectively. The in-plane and traverse translational component are determined from equation 15 from Hornby (1998).

<table>
<thead>
<tr>
<th>Confining pressure, $P_c$</th>
<th>6.89 MPa</th>
<th>10.34 MPa</th>
<th>13.79 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stiffness tensor</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}$ (in-plane compressional)</td>
<td>52.38 GPa</td>
<td>53.54 GPa</td>
<td>54.21 GPa</td>
</tr>
<tr>
<td>$C_{33}$ (transverse compressional)</td>
<td>24.29 GPa</td>
<td>26.07 GPa</td>
<td>26.52 GPa</td>
</tr>
<tr>
<td>$C_{66}$ (in-plane shear)</td>
<td>18.87 GPa</td>
<td>19.03 GPa</td>
<td>19.12 GPa</td>
</tr>
<tr>
<td>$C_{44}$ (transverse shear)</td>
<td>15.31 GPa</td>
<td>15.87 GPa</td>
<td>16.30 GPa</td>
</tr>
<tr>
<td>$C_{12}$ (in-plane translational)</td>
<td>14.65 GPa</td>
<td>15.48 GPa</td>
<td>15.97 GPa</td>
</tr>
<tr>
<td>$C_{13}$ (transverse translational)</td>
<td>11.34 GPa</td>
<td>12.66 GPa</td>
<td>12.89 GPa</td>
</tr>
<tr>
<td><strong>Textural tensors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_1$ (in-plane formation factor)</td>
<td>251</td>
<td>261</td>
<td>255</td>
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<tr>
<td>$F_3$ (transverse formation factor)</td>
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<td>3819</td>
<td>5470</td>
</tr>
<tr>
<td>$\tau_1$ (in-plane tortuosity)</td>
<td>15</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>$\tau_3$ (transverse tortuosity)</td>
<td>185</td>
<td>180</td>
<td>227</td>
</tr>
</tbody>
</table>

measured across the sample in different directions relative to the bedding/foliation plane (equations 18 through 23). The mechanical response shows some irreversible deformation. Indeed, a compacted sample will not decompress completely on the time scale of the experiments and may undergo inelastic rheological changes if subjected to sufficiently compressional high stress states. Figure 5.8 shows velocity increases under hydrostatic loading with damage evidenced by higher velocities in the unloading sequence.

We observe fracture closure in the ultrasonic data as a change in slope along the stress path occurring around 20.7 MPa. Above this stress state, the rate of velocity increase with confining (differential) stress decreases in both compressional and shear measurements (Figure 5.8). Compressional and shear energy are sensitive to different properties and components of a porous medium. Because fluids do not support shear motion, the shear energy propagates in the
Figure 5.12 Effective stress behavior for the stiffness tensor components. 

**a. In-plane**

- Lines of constant differential stress
- Lines of constant pore pressure

**b. Transverse**

- Lines of constant differential stress
- Lines of constant pore pressure

Shear modulus, $C_{66}$ (GPa)

<table>
<thead>
<tr>
<th>Pore pressure, $P_p$ (MPa)</th>
<th>Shear modulus, $C_{66}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 MPa</td>
<td>10.3 MPa</td>
</tr>
<tr>
<td>3.45 MPa</td>
<td>13.8 MPa</td>
</tr>
<tr>
<td>6.89 MPa</td>
<td>17.2 MPa</td>
</tr>
</tbody>
</table>

The effective stress coefficient is computed as the ratio of the gradients of differential stress lines to pore pressure lines. Values are obtained below (dark circles with solid lines) and above (light circles with stippled lines) fracture closure, which evidences a strong dependence of the effective stress response to the fractures in the sample.
solid frame, whereas the compressional energy propagates in both fluid and solid phases. Due to this phenomenon, the compressional energy is more sensitive to changes in porosity since this impacts the distribution (and density for compressible fluids) of fluids within the pore and fracture networks. We observe a more pronounced change with closure in compressional data when compared to shear data, which is attributed to the abrupt change in (saturated) fracture porosity above fracture closure pressure. Shear energy is not transmitted in the fluid phase; while fracture closure impacts the effective stress response, shear waves are not sensitive to changes in fluid distribution associated with closure. However, shear energy has higher sensitivity above closure associated with the mechanical coupling of the fracture planes (microscopic misalignment of the roughness of the fracture surfaces).

We can also make observations of the relative sensitivity of the directional measurements to fracture closure to draw inferences about the mechanical response of the sample. The sample is least sensitive to open fractures (low differential stress) for in-plane compressional waves; the change in the corresponding anisotropic effective stress component is most pronounced in this direction, evidencing fracture closure nearly eliminates the pore pressure effect (Figure 5.9). The sample is most sensitive to shear waves polarized in the isotropic (fracture, bedding, foliation) plane (Figure 5.10). This behavior is evidence that macroscopic fractures slow the propagation of shear energy when the fracture surfaces are decoupled in the direction of in-plane shear motion. Similarly, the transverse compressional wave is also sensitive to fractures at low differential pressures when the fracture surfaces are decoupled in the direction of transverse particle motion. Shear waves polarized at 90 degrees to the isotropic plane exhibit the least sensitivity to fracture closure, as this wave is polarized transverse to the fracture sets.
Figure 5.13 Complex electrical conductivity change in the in-plane and transverse directions for equilibrium measurements ($P_d=0$). The electrical poroelastic effect is anisotropic. Normalized increases in in-plane and transverse complex conductivities are calculated as the ratio of the minimum and maximum in-phase and quadrature conductivities. We obtain $\Delta\sigma^* = 2.64 + 1.99i$ in the in-plane direction and $\Delta\sigma^* = 0.89 + 0.91i$ in the transverse direction. This indicates that the electrical response has the highest sensitivity to pore pressure in the foliation plane, probably because the cracks are oriented in this plane.

**Effective Pressure for the complex conductivity**

Figures 5.13 and 5.14 show the components (in-plane and transverse) of the complex conductivity tensor as a function of the equilibrium pressure and confining pressure, respectively. We first analyzed the effective stress response of the complex electrical conductivity as the change in conductivity in the in-plane and transverse directions for equilibrium measurements ($P_d=0$). We found the poroelastic effect associated with the electrical response to be anisotropic, exhibiting a normalized increase in complex conductivity of $\Delta\sigma^* = 2.64 + 1.99i$ for the in-plane and $\Delta\sigma^* = 0.89 + 0.91i$ for the transverse conductivities,
Figure 5.14  Complex electrical conductivity as a function of the confining pressure. **a.** In Plane components of the in-phase and quadrature conductivities. **b.** Transverse components of the in-phase and quadrature conductivities. The crosses represent extrapolated data and are provided estimates as a visual aid.

respectively. This behavior indicates the electrical response is most sensitive to pore pressure in the foliation plane (Figure 5.13). Several spectral induced polarization datasets were considered to be unreliable due to noise level (determined at each frequency on three cycles). As a result, we
Figure 5.15 Complex electrical conductivity effective stress coefficients for the formation factor and tortuosity tensors. The relative magnitude of the effective stress components indicates higher sensitivity in the foliation/bedding plane. Plots identify lines of constant differential ($P_d = 0$) pressure and constant pore fluid pressure ($P_p = 0$).

did not obtain a complete matrix of pore pressure and differential pressure measurements and the analysis is performed as a function of differential pressure, irrespective of the loading-unloading sequence. Anisotropic effective stress coefficients were estimated from the gradients of electrical textural tensor components $F_{ij}$ and $T_{ij}$ only along lines of zero differential pressure and zero pore pressure. We obtained in-plane and transverse poroelastic effective stress coefficients of $\alpha_{11}^F = 0.95$ (in plane) and $\alpha_{33}^F = 0.84$ (transverse) for the formation factor tensor and $\alpha_{11}^T = 0.98$ (in plane) and $\alpha_{33}^T = 0.51$ (transverse) for the tortuosity tensor (see definitions in Appendix F), indicating that the stress dependence for the textural tensors is strongest in the direction transverse to the foliation plane (Figure 5.15).
We know that the in-phase conductivity tensor depends on the series combination of the conduction current in the pore water and the surface conduction in the Stern and diffuse layers, indicating correlation to the conductivity magnitude through the porosity (including the directional dependence of the formation factor and tortuosity tensors), whereas the quadrature conductivity tensor also depends on the textural changes through the tortuosity tensor (refer to the respective in-phase and quadrature forms in equations 13 and 14). Therefore, we expect the first-order stress dependence of the complex conductivity to be tied to the direction of deformation. For a hydrostatic load, this is expected to occur in the direction normal to the bedding plane (transverse direction), i.e., the change in electrical conductivity is greater in the transverse direction, but there is greater sensitivity to the effective pressure change in the plane of isotropy (in-plane).

We observe a decrease in the complex conductivity of a quarter order of magnitude in the undrained in-plane measurements, and a decrease of nearly half an order of magnitude in the transverse direction, with the sample stabilizing at 20.7 MPa in the drained experiments (see Figure 5.9). The stabilization can be attributed to the closing of the fracture porosity observed in the sample. The in-plane measurements exhibit a conductivity change over 1.5 orders greater (approximately a factor 30) than the transverse to bedding/foliation plane.

Figure 5.16 compares the stress dependence for the drained and undrained acquisitions. Here we once more observe evidence of an irreversible component of strain in both acquisitions. Indeed, the undrained experiments appear to follow the measurements along the unloading sequence of the drained measurements, indicating that the sample did not return to its initial condition. The loading path of the complex conductivity follows the drained acquisition and rebounds at a lower complex conductivity in the unloading sequence in both in-plane and
Figure 5.16  Stress-induced strain curves in the complex electrical conductivity for drained (circles) and undrained (triangles) experiments in the a. in-plane and b. transverse directions. Fracture closure occurs at 20 MPa (drained) and between 10 MPa and 15 MPa (undrained) due to changes in the fracture compliance between experiments. The change in slope along the unloading and unloading stress paths indicates that the sample undergoes irreversible changes with successive stress loops (note undrained loading data follow the drained unloading path).
transverse directions. This response is further evidence of damage due to compaction. Both in-phase and quadrature conductivity exhibit a reduced rate of change as the fractures reopen with decreasing differential stress.

We expect the second-order sensitivity to arise because of differences in the in-phase and quadrature conductivities. The in-phase component should be more sensitive to stress (i.e., mechanical compaction) than the quadrature component due to the in-phase sensitivity to changes in conduction in fractures and macroporosity and this sensitivity should increase with salinity as the conduction current increases. Changes in the textural fabric above closure (20.7 MPa) give rise to second-order changes in the slope of the in-plane measurements associated with reduced tortuosity (e.g., the infinitesimal realignment of clay minerals; refer to Figure 5.10). The magnitude change in the quadrature component is one quarter that of the in-phase component ($|\Delta \log_{10} \sigma'| = 0.03; |\Delta \log_{10} \sigma''| = 0.01$), indicating that changes in tortuosity are small in correspondence with the change in surface conductivity. Changes in transverse in-phase and quadrature slopes are comparable ($|\Delta \log_{10} \sigma'| = 0.04; |\Delta \log_{10} \sigma''| = 0.04$), indicating that the tortuosity normal to the bedding plane correlates with fracture closure and compaction.

**Evolution of the anisotropy factor**

In Table 5.3, we can see the values of the formation factor and tortuosities for the in-plane and transverse directions. The complex conductivity anisotropy factor was computed as the ratio of the in-plane and transverse in-phase and quadrature conductivities, respectively (Figure 5.17). From these data, it seems that the realignment of the platy clay minerals is affected by the increased of the mechanical load and therefore complex conductivity anisotropy increases with differential pressure (Figure 5.17). At low differential pressure, the closure of the cracks is also captured by the change in the anisotropy ratio with differential pressure along the respective
Figure 5.17 Complex electrical conductivity anisotropy factor for drained (circles) and undrained (triangles) acquisitions. Fracture effects are captured by the change in anisotropy ratio with differential pressure along the respective loading and unloading paths. Anisotropy remains higher with successive loading (dark) and unloading (light) loops, indicating that the sample does not fully decompress or return to the initial condition. The material behaves elastically above fracture closure, indicating compaction of the sample at these confining pressures is elastic and damage is largely associated with the fractures. The anisotropy factor is calculated as the ratio of the in-plane and transverse in-phase and quadrature conductivities, i.e., \( \lambda' = \frac{\sigma_0'}{\sigma_90'} \) and \( \lambda'' = \frac{\sigma_0''}{\sigma_90''} \) (both dimensionless), respectively.

loading and unloading paths. The anisotropy of the electrical response remains higher with successive loading-unloading stress loop, indicating that the sample does not fully return to the initial condition. Above crack closure, the material behaves elastically.

**Effective stress laws**

Figure 5.18 shows four of the components of stiffness tensor as the function of the effective pressure \( P^* = P_c - \alpha^x P_p \). The left figures show the four components as a function of the effective stress, \( P^* \) assuming that the effective pressure coefficient is independent
Figure 5.18 Effective stress law for the components of the stiffness tensor $C''$ using $\alpha_{11} = 0.67$, $\alpha_{33} = 0.90$, $\alpha_{44} = 0.69$, and $\alpha_{66} = 0.93$ below fracture closure and $\alpha_{11} = 0.02$, $\alpha_{33} = 0.31$, $\alpha_{44} = 0.50$, and $\alpha_{66} = 0.37$ above. On the left side, the effective stress coefficient is independent of differential pressure, while on the right side the effective stress coefficient is dependent on differential pressure.
Constant Biot coefficient, $\alpha$

Stress dependent Biot coefficient, $\alpha$

Compressional modulus, $C_{11}$ (GPa)

Shear modulus, $C_{66}$ (GPa)

Shear modulus, $C_{44}$ (GPa)

Effective pressure, $P^*$ (MPa)
Figure 5.19  Effective stress law for the in-plane and transverse components of the complex conductivity tensor. The crosses correspond to extrapolated data. The values of the pressure dependence effective stress coefficient are provided on the graphs using the effective stress coefficients obtained for the tortuosity, $\alpha_{11}=0.98$ and $\alpha_{33}=0.51$. 
Figure 5.20 Effective stress law for the porosity as determined from the relationship between the components of the formation factor tensor and those of the tortuosity tensor.

dependence with the differential pressure, collapsing the data into a master curve. The effective stress laws for transverse and in-plane electrical conductivity tensor components are shown in Figure 5.19. We see a general decrease of the components of the complex conductivity tensor with effective stress and an effective stress coefficient that is scaled dependent upon the stress state.

Since we did not directly measure deformation in these experiments, we obtain a measure of porosity compaction from the ratios of the textural tensor components $F_{ij}T_{ij}^{-1}$. The porosity mean and standard deviation versus effective stress evidences porosity reduction on the order of 0.03 with increased effective stress as shown in Figure 20. Note that the starting porosity is of
the differential pressure. The different curves do not collapse into a single master curve indicating the effective stress coefficients are stress dependent. The figures on the right side account for the stress consistent with the mass density used in this work (2450 kg m\(^{-3}\)). In future experiments, it will be interesting to measure directly the deformation of the core sample and the amount of fluids released during compaction to have a complete description of the components of the drained stiffness tensor and to obtained therefore a complete characterization of the poroelastic parameters of the material.

Conclusions

We described the effective stress coefficients for the components of the stiffness and complex conductivity tensors of a transverse isotropic core sample taken from the Haynesville gas shale formation. The following conclusions have been reached:

(1) We have found that surface conductivity is a very important contribution to the overall electrical conductivity of the Haynesville. The anisotropy ratio for both the in-phase and quadrature components is comprised between 20 to 50 and depends on the differential stress and shows an increase associated with the closure of the cracks.

(2) Two pressure regimes were identified as delimited by the crack closure pressure (around 10 to 20 MPa in differential pressure). We determined the effective stress coefficients for the components of the undrained stiffness tensor and the components of the formation factor and toruosity tensors. The effective stress coefficients are much higher in the low effective pressure regime (cracks open) than in the high effective pressure regime (cracks closed).

While the results presented in this work should not be generalized to characterize the Haynesville gas shale (since we investigated only one core sample with cracks), they can be broadly applied to better understand the poroelastic behavior of tight, clay-rich shales and
mudstones with microcracks, providing a basis to describe the multi-physical connections between geophysical measurements and the mechanical deformation of unconventional reservoir rocks.

Acknowledgements

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CHAPTER 6
GENERAL CONCLUSIONS AND FUTURE WORK

Oil and gas shales represent more than 70 percent of total hydrocarbon resources worldwide. According to the 2014 US Energy Information Administration (EIA) Annual Report, the United States is the largest producer of unconventional hydrocarbons in the world with over 45 billion barrels of proven shale oil and 665 trillion cubic feet of gas, producing nearly 10 million barrels per day of oil and 3 billion cubic feet per day of natural gas from unconventional plays. Domestic oil and gas production accounts for 20% of the GDP and for up to 40% of state generated revenues some states and has significantly reduced American dependence on imported hydrocarbon fuels and has increased exports. Nevertheless, EIA projections show a decrease in unconventional production over the next 25 years, indicating a steady decline in both proven reserves as well as in anticipation of new discoveries, augmenting the need to better understand these materials and develop new approaches to improve the state of the art in exploration, completion and production of unconventional reservoirs.

Previous chapters detail a multidisciplinary approach to the investigation into the effect of clay surface properties on electrochemistry in shales, electrical and elastic anisotropy and effective stress in organic rich shales. In conclusion of my dissertation, I will provide a brief review of an ongoing study of the effects of the maturation of organics (kerogen) and hydrocarbon generation on the complex conductivity of shales. This work employs the various theories and methodologies presented in this thesis and represents a forward-looking application of this work to a case study performed in conjunction with colleagues at the Colorado School of Mines, the Formation Evaluation Consortium at the University of Texas at Austin and the United States Geological Survey in Denver.
SIP characterization of kerogen maturation in shales

Studying both the processes and the physical nature of the changes caused by kerogen catagenesis is integral to improving our ability to detect, characterize and exploit unconventional oil and gas shale resources. We have developed a comprehensive experimental approach using hydrous pyrolysis and spectral induced polarization to characterize changes in rock properties resulting from kerogen maturation. In the following, I provide a review of the geochemical processes and the resulting electrochemical characteristics associated with polar and hydrocarbon generation in organic rich rocks, followed by a discussion of the effect of thermal maturation on the complex conductivity.

Electrochemical characteristics of bitumen generation

Kerogen cracking during pyrolysis (see Lewan 1983, Behar et al., 2008, and Behar et al., 2010) results in the formation of \textit{n}-alkanes (Leif and Simoneit, 2000, Burdelnaya et al., 2013) broadly referred to as bitumen or pyrobitumen composed of saturates, aromatic hydrocarbons, resins and asphaltenes. These polar molecules are formed of alkyl and aryl compounds bonded with carboxyl groups or other side chains (R-groups), in which the amount of free radicals in the chains is related to the reactivity of functional groups in the polymer chains (Takamura and Chow, 1985, Jada and Salou, 2002). Free radicals in the chains provide active surface sites for ion exchange, depending on thermal maturation history of the material (e.g., Hoering 1984, Lewan 1997, Stalker et al., 1998). At temperatures above 150 C, bitumen can be described as either a colloidal suspension or dispersed fluid (Le Guern et al., 2010 and references therein), which forms a reactive surface in water-bitumen fluid systems (e.g., Wu et al., 1999, Laroche et al, 2002, Rodríguez-Valverde et al., 2003).
Catagenic reactions in bitumen

There are several known reaction pathways for the reduction and hydration of bitumen during thermal aging, which depend on the conditions of catalysis, e.g., kerogen type, hydrous versus anhydrous, fluid chemistry including pH and salinity, as well as the mineralogical composition of the solid (Bjorøy et al., 1987, Seewald, 2001). These reactions can increase the activity of the alkanes and aromatic compounds (e.g., Seewald 2001 and references therein), affecting the composition of the bitumen pyrolysate. Three types of reactions affect the electrochemistry of bitumen-water fluid systems:

(1) the bonding with hydroxyl groups of exposed mineral surfaces resulting in a change in wettability of the mineral surfaces (e.g., Chiappa et al., 1999),

\[
> S^- \overset{\text{H}_2\text{O}}{\text{K}_w} + \overset{\text{R}_\alpha}{\text{K}_a} \overset{\text{K}_w}{\rightarrow} > S^- \overset{\text{R}_\alpha}{\text{K}_a} + \overset{\text{H}_2\text{O}}{\text{K}_w},
\]

where \( S^- \) denotes an active site on the mineral surface and \( \overset{\text{H}_2\text{O}}{\text{H}_2\text{O}} \) denotes water and \( \overset{\text{R}}{\text{R}} \) denotes an \( n \)-alkane polymer (or hydrocarbon) as immiscible polar fluid phases, \( \text{K}_w \) and \( \text{K}_a \) are the equilibrium constants of adsorption for the water \( w \) and the alkane \( a \).

(2) Active ion exchange at the water-bitumen interface (e.g, Takamura and Chow, 1985, and Rodriguez-Valverde et al., 2003),

\[
\overset{\text{R}^0}{\text{R}} \Leftrightarrow \overset{\text{R}^-}{\text{R}} + \overset{\text{H}^+}{\text{H}}+ , \]

\[
\overset{\text{R}^-}{\text{R}} + \overset{\text{Na}^+}{\text{Na}^+} \Leftrightarrow \overset{\text{R}^-}{\text{R}}\overset{\text{Na}^+}{\text{Na}^+}
\]

or in the case of aromatic groups

\[
\overset{\text{RCOOH}^0}{\text{RCOOH}} \Leftrightarrow \overset{\text{RCOO}^-}{\text{RCOO}} + \overset{\text{H}^+}{\text{H}}+ , \]

\[
\overset{\text{RCOO}^-}{\text{RCOO}} + \overset{\text{Na}^+}{\text{Na}^+} \Leftrightarrow \overset{\text{RCOO}^-}{\text{RCOO}}\overset{\text{Na}^+}{\text{Na}^+}
\]
where $R^0$ and $RCOOH^0$ are neutral alkane and carboxyl groups, respectively, $R^-$ and $RCOO^-$ are dissociated alkane and carboxyl groups with active sites.


$$\text{RCOO}^- + \text{H}_2\text{O} \rightarrow \text{HR} + \text{CO}_2(\text{g}) + \text{H}^+(\text{g}) .$$

While Type-1 reactions will lower the electrical conductivity, effectively expulsing the connate water and eliminating the electrical double layer on the mineral surfaces, the other two reaction paths can potentially increase the activity in the resulting water-bitumen emulsion. A current hypothesis is that these reactions result in an additional CEC associated with the bitumen and the formation of a secondary double layer at the bitumen-water interface allowing for a secondary component of surface conductivity as described in the parallel conduction model in Appendix H. Schmutz et al., 2010 and Revil 2011 reported the effects of active $n$-alkane hydrocarbons (wet oil) on the complex conductivity, providing a basis to study the similar interactions of the water with bitumen-water emulsions.

**Effect on the complex conductivity**

We consider two mechanisms affecting electrical conduction in porous media during hydrocarbon generation: (1) changes to the textural properties of the specific surface area of the solid phase, and (2) changes in the electrochemistry of immiscible fluids in the pore space. The cracking reactions in kerogen and bitumen occur at high temperature and elevated pressures, which may generate fractures or otherwise alter the petrophysical or textural properties of the material. These changes affect complex conductivity through the formation factor and tortuosity tensors. Kerogen pyrolysis in hydrocarbon source rocks results in the generation of polar compounds, asphaltenes and resins generally classified as bitumen, which permeate the pore
network. Bitumen is a precursor in the generation of liquid and gaseous hydrocarbon phases during pyrolysis. These polymers effect marked changes to the electrochemical nature of the fluid-solid interface comprising both water wet and bitumen wet systems, as well as the fluid interface between immiscible phases. Revil et al., 2011, have shown that the introduction of wettable oils effects a measureable increase in the complex conductivity, where characteristic dispersion in the quadrature conductivity is associated with a secondary double layer at the oil-water interface.

We observe an increase in the complex conductivity with maturation in the aliquot data sets (Figure 6.1). This increase may be due to an additional excess charge density and surface conductivity at the water-bitumen interface, changes in the textural properties (e.g., increased porosity) or both mechanisms may be occurring simultaneously. Formulations for complex conductivity in both single-phase fluid systems (Chapter 3) and multiphase phase systems are provided (Appendix E).

**Methods**

We measured complex conductivity spectra of organic-rich Woodford chert aliquots to capture the effect of thermal maturation of kerogen by hydrous pyrolysis on the complex conductivity. The single source component method (Chapter 4) was used to measure the full anisotropic characterization of saturated porous media in the frequency range 10 mHz to 45 kHz. Details are provided for sample preparation, the hydrous pyrolysis method, the SIP acquisition system, and the impedance measurement.

**Woodford chert aliquots**

The Woodford chert used in this study is an organic rich siliciclastic mudrock from the upper portion of the Woodford formation, low in clay content with characteristically simple, silicious mineralogy (e.g., see Caldwell 2012), making it an ideal candidate to mitigate the
Figure 6.1 Complex conductivity spectra of the pyrolyzed Woodford aliquots. In-phase conductivity shows a monotonic increase with maturation associated with increased porosity. Quadrature conductivity shows a relaxation at 10 Hz.

effects of surface conduction in the clays. Hence, changes in the complex conductivity of the samples can be ascribed to the changes in the saturating fluids. Rock-Eval pyrolysis, TOC, and XRD mineralogy on similar cores yielded 5.53% organic carbon (TOC; Type-II kerogen), 6.3% carbonate (CaCO₃), >75% silica (SiO₄), <5% phyllosilicate (Si₂O₅), and trace pyrite and K-feldspar fractions <10%, by mass (e.g., Bed 4 in Birdwell et al., 2013). Nuclear magnetic resonance (NMR) measurements yielded a T2 porosity of 0.0415 and a T2 porosity of 0.0395 (Birdwell et al., 2013, and Washburn et al., 2013) for the immature samples.

To make SIP measurements along the various principal directions of the material, identical cubic aliquots were cut from the same massive slab of Woodford chert, collected at Springer outcrop at a road cut on the west side of I-35 near mile marker 44 in Carter County, Oklahoma (N 34° 21.117', W 97° 8.931'). Ten sample cubes were dimensioned with sides of length 3.5±0.06 cm from a homogenous portion of the slab, in close alignment with the visible (isotropic) bedding plane. We follow the approach developed by Woodruff et al., 2014 (Chapter
4 of this thesis). We have shown this degree of precision in sample dimensioning is sufficient to characterize the eigenvalues of the electrical tensor using the SIP method and provided detailed protocols to measure the components of the complex conductivity tensor in the laboratory (Woodruff et al., 2014).

**Hydrous pyrolysis experiments**

Hydrous closed-system pyrolysis experiments were performed on five pairs of the Woodford aliquots, under uniaxial confinement at various prescribed thermal equilibria representing each of the phases of kerogen catagenesis in hydrous conditions: immature kerogen at low temperature, low and peak bitumen generation with increasing temperature, and cracking bitumen to oil and gas at high temperature. We follow the general method for hydrous pyrolysis of Lewan (1985), using a mechanical clamp introduced by Lewan and Birdwell (2013) to confine the samples normal to the bedding plane of the cubic core samples and mitigate changes in porosity during pyrolysis. In order to capture the various stages of kerogen catagenesis, five aliquot pairs were obtained by heating pairs of immature Woodford chert samples in a closed reactor, such that the hydrous conditions maximize water-bitumen reactions in the formation of low molecular weight hydrocarbons (Lewan, 1997). The samples characterize immature kerogen (100 C), thermal maturation at the onset of bitumen generation (300 C), peak bitumen generation (330 C), oil generation (360 C), oil cracking and gas generation (400 C) phases. Equilibrium temperatures were chosen based on previous work by Lewan and colleagues (e.g., Engel and Macko, 1993; Lewan, 1997; Lewan and Roy, 2011).

**SIP measurements**

SIP measurements were made in the frequency range 1 mHz to 45 kHz using a four electrode single source component method (e.g., Vinegar and Waxman, 1984; Woodruff et al.,
6.2 In-phase and quadrature conductivity response with maturation temperature.

2014). The measurements were made immediately (STP) as each aliquot was removed from the reactor to capture an initial condition. The pyrolysate was retained and samples were stored in the remaining equilibrium fluids. The SIP experiments were repeated after 6 months, no changes in the response was observed, indicating the changes in complex conductivity can be ascribed to changes in the material properties associated with kerogen pyrolysis.

**Discussion**

The hydrous pyrolysis experiments produced five pairs of artificially matured aliquots representative of the stages of kerogen cracking to oil under closed, hydrous conditions. Complex conductivity spectra obtained for the artificially matured Woodford aliquots are shown in Figure 6.1. The complex conductivity shows a marked increase with pyrolysis temperature, with the largest increase occurring during bitumen generation (Figures 6.1 and 6.2).

The in-phase conductivity increases monotonically with temperature (note that the impedance spectra were acquired at 25 C, the temperatures used in the discussion and figures refer to the maximum equilibrium temperature reached during pyrolysis). Quadrature
conductivities also appear to increase monotonically, with the exception of the aliquot heated to the point of maximum bitumen generation at 330 °C (Figure 6.2). We also observe a relaxation in the quadrature conductivity between 10 and 100 Hz, which can be attributed to the distribution of the length scales associated with the pore throats and fractures.

The steady increase of the in-phase conductivity indicates textural effects on the electrical response (i.e., the increase in formation factor due to increased porosity, most likely the generation of microcracks resulting from the expansion of the organic matter as it cracks to bitumen at high pressure above 300 °C). While we see a similar monotonic increase in the low temperature data which can be similarly linked to the textural changes in the sample; however, the measurement on the maximum bitumen aliquot at 330 °C exhibits anomalously high quadrature conductivity (Figure 6.2). We hypothesize this is due to an increase in the specific surface area of the sample with the introduction of active alkyl and aryl n-alkane polymers in the pore fluid (corresponding to an increased CEC of the medium). The peak relaxation frequency also appears to both broaden and shift to higher values. This is evidence that the predominant length scale of the saturated voids in the material is changing with maturation and the peak frequency shifts to higher values as a result of the generation microcracks during each successive stage (Figure 6.1).

**Future work**

More work needs to be done to understand the physical and electrochemical nature of the increase in conductivity associated with kerogen maturation. I am currently developing a model to invert the physicochemical parameters, primarily the CEC of both the organics and mineral phases, to determine whether or not some component of the increased complex conductivity can be attributed to bitumen generation. Detailed petrophysical analysis will be performed to both
describe the various aliquots and characterize the results of the pyrolysis experiments. This work presents some exciting prospects and raises interesting questions about the electrochemistry of multiphase fluid systems in unconventional reservoirs.

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APPENDIX A. SEQUENTIAL INVERSION STRATEGY

Two Bayesian analyses were performed in series to obtain independent probabilistic frameworks for the sorption and desorption models upon which the normalized sorption model was built. The first step in the sequence implements an MCMC algorithm to determine the normalized $\overline{\text{CEC}_i}$, followed by strict Bayesian analysis of the normalized isotherm model, Equation 2.19, to determine the following $\overline{V}_m$, $\Gamma$ (for the inversion of the drying curve), and $\bar{\xi}$.

The chosen variant of the MCMC algorithm (Haario et al. 2001; Tamminen, 2004) utilizes a memory mechanism based on a recursive update of the model variance known as the Adaptive Metropolis Algorithm (AMA). This approach is used to compute the posterior Probability Density Function (PDF) of the model parameters (in our case $\overline{\text{CEC}_i}$). This PDF is taken as Gaussian distributed. The PDF is defined from the stochastic sampling of the parameter space once the model variance $\sigma$ has been minimized after running a number of realizations. This process is strictly data driven. No model bias has been introduced in this step. Generalized CEC values are used to constrain the inversion $a$ priori using the additional constraint $\overline{\text{CEC}_k} < \overline{\text{CEC}_i} < \overline{\text{CEC}_s}$ (where the subscripts indicate the clay type, e.g., S for Smectite) using values ranging from 0.001 to 1 meq g$^{-1}$ (see Figure 2.1). Clays for which we have both sorption and desorption data samples the same value for $\overline{\text{CEC}_i}$ is used for both sorption and desorption during each realization. Although, according to our model, we are specifically inverting for $\overline{\text{CEC}_i}$ in this step, actual estimates of the CEC are used as prior constraints to assign higher likelihood to models in which $\overline{\text{CEC}_i}$ approaches CEC. The misfit is defined by the RMS error associated with the resulting scatter of the $\overline{\text{CEC}_i}$-normalized data, and the posterior likelihood is defined according to the
joint probability of the data and model PDFs. The results of this step are presented in Figure 2.8.

To optimize the normalized isotherm, a Bayesian analysis of the parameter space was performed within the following given bounds, $\bar{\nu}_m \in [0.001; 0.1]$; $\Gamma \in [0.001; 0.1]$, and $\bar{\xi} \in [0.1; 20]$. A posterior PDF is computed first for the $\text{CEC}_i$-normalized adsorption data to determine the scaled monolayer parameter $\bar{\nu}_m$ and the normalized sorption constant $\bar{\xi}$. The parameters are again taken as Gaussian distributed, and the posterior likelihood is determined from the misfit of the computed normalized BET line and the normalized data, using Equation 2.19 as the kernel with $\Gamma$ fixed at 0. For the desorption isotherms, the value of $\bar{\nu}_m$ is input from the previous step, and $\Gamma$ is optimized following a similar procedure. These results are shown in Figure 2.9. The normalized model presented in Figure 2.10 is calculated with the values of $\text{CEC}_i$, $\bar{\nu}_m$, $\Gamma$, and $\bar{\xi}$ determined from this sequential inversion using the $\text{CEC}_i$-scaled variant of Equation 2.17. Correlation coefficients were obtained for both $\text{CEC}_i$-normalized sorption data, as well as the transformed data in BET parameter space, indicating a near linear correlation of the scaled sorption data to the predicted values shown in Figures 2.9 and 2.10. Correlation values of 0.94, 0.92 were calculated for $\text{CEC}_i$-normalized adsorption and desorption data, as well as 0.79 and 0.93 for $\text{CEC}_i$-normalized BET lines, respectively (a correlation value of 1 corresponds to a perfectly linear trend).

The mineralogical parameter $\delta_i$ can only be obtained empirically from the data when the true CEC of the samples are known; further inquiry is required to better constrain this parameter. However, estimates of the monolayer water volume and the bound water can be made by simply multiplying the scaled parameters by the scaled CEC, $\nu_m = \bar{\nu}_m \text{CEC}_i$, and $bw = \Gamma \text{CEC}_i$. 

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APPENDIX B. SALINITY DEPENDENCE OF THE PARTITION COEFFICIENT

We introduce a simple model to describe the dependence of salinity on the partition coefficient, \( f \). Consider first the sorption of sodium in the Stern layer of clays and the dissociation of protons according to the following, simplified speciation model:

\[
> \text{SH}_0 \leftrightarrow > \text{S}^- + \text{H}^+, \tag{B-1}
\]

and

\[
> \text{S}^- + \text{Na}^+ \leftrightarrow > \text{S}^- \text{Na}^+ \tag{B-2}
\]

where >S designates the surface (amphoteric) sites attached to the crystalline framework, \( \text{H}_0 \) are protons (which are assumed to be immobile), while weakly sorbed \( \text{Na}^+ \) (which are known to keep their hydration layer) are assumed mobile in the Stern layer. Equilibrium constants for the reactions A1 and A2 are given by,

\[
K_{\text{Na}} = \frac{\Gamma^0_{\text{SNa}}}{\Gamma^0_{\text{S}} \left[ \text{Na}^+ \right]^0} \tag{B-3}
\]

and

\[
K_{\text{H}} = \frac{\Gamma^0_{\text{SH}} \left[ \text{H}^+ \right]^0}{\Gamma^0_{\text{S}}} \tag{B-4}
\]

The conservation equation for the surface species is given by,

\[
\Gamma^0_{s} = \Gamma^0_{\text{SNa}} + \Gamma^0_{\text{S}^-} + \Gamma^0_{\text{SH}} + \Gamma^0_{x} \tag{B-5}
\]

where \( \Gamma^0_{s} \) denotes the total surface site density (including charge associated with isomorphic substitutions in the crystalline framework), \( \Gamma^0_{\text{SNa}} \), \( \Gamma^0_{\text{S}^-} \), and \( \Gamma^0_{\text{SH}} \) designate the surface charge density of the sites >S\text{Na}^+, >S\text{}, and >SH\text{0}, respectively, and \( \Gamma^0_{x} \) represents the number of equivalent sites corresponding to isomorphic substitutions (all expressed in sites m\(^{-2}\)). To
simplify notation, we write pH = -log_{10} [H^+], while [Na^+] = C_f denotes the salinity of the pore water solution. The resolution of equations B-3 to B-5 yields

\[
\Gamma_{SH}^0 = \frac{\Gamma_S^0 - \Gamma_X^0}{K_H \left( 1 + C_f K_{Na} \right)} \left( 1 + 10^{-pH} \right)
\]

(B-6)

\[
\Gamma_S^0 = \frac{(\Gamma_S^0 - \Gamma_X^0)K_H / 10^{-pH}}{1 + K_H / 10^{-pH} (1 + C_f K_{Na})}
\]

(B-7)

and

\[
\Gamma_{SNa}^0 = \frac{(\Gamma_S^0 - \Gamma_X^0)C_f K_{Na} K_H / 10^{-pH}}{1 + K_H / 10^{-pH} (1 + C_f K_{Na})}
\]

(B-8)

All the charged sites that are not compensated in the Stern layer need to be compensated in the diffuse layer. Therefore, the fraction of counterions in the Stern layer is defined by the equations

\[
f = \frac{\Gamma_{SNa}^0}{\Gamma_{SNa}^0 + \Gamma_S^0 + \Gamma_X^0}
\]

(B-9)

and

\[
f = f_M \left\{ \frac{C_f K_{Na}}{f_M (1 + C_f K_{Na}) + (1 - f_M) \left[ 1 + C_f K_{Na} + \frac{10^{-pH}}{K_H} \right]} \right\}
\]

(B-10)

where \(f_M\) designates the highest value of \(f\) reached at high salinities, i.e.

\[
f_M = \lim_{C_f \gg 1/K_{Na}} f = 1 - \frac{\Gamma_X^0}{\Gamma_S^0}
\]

(B-11)

The value of \(f_M\) is approximately 0.99 for kaolinite, 0.90 for illite, and 0.85 for smectite. At high pH values one has

\[
f = f_M \left( \frac{C_f K_{Na}}{1 + C_f K_{Na}} \right)
\]

(B-12)
Therefore, an increase of salinity is responsible for an increase of the partition coefficient, $f$, which in turn is responsible for an increase of the magnitude of the quadrature conductivity (see Revil, 2012).
APPENDIX C. THE GEOMETRICAL FACTOR

The geometrical factor depends on the position of the electrodes and accounts for the effect of the boundary conditions at the surface of the core sample. By definition, $K$ is a purely geometric construct (defined as a dimension of length). It is independent of the material properties including conductivity and the current density. For isotropic media, the geometric factor can be easily obtained numerically. However, estimating the geometric factor in anisotropic measurements is nontrivial. Therefore, we provide below a detailed discussion of the geometric factor, which has central importance in the determination of the complex conductivity anisotropy from AC-impedance measurements.

The solution of the constitutive equation for a current $I$ (in Ampère), is determined from the flux $J_s$ through the surface $A$ bisecting the sample,

$$I = \int_A J_s \cdot \hat{n} \, dA$$

where $J_s$ is in A m$^{-2}$ and $A$ represents the cross section in m$^2$ at the mid-point $H/2$, and $\hat{n}$ denotes the unit vector normal to $A$. Electrical resistance between the potential electrodes is given as the ratio of the potential difference to the current $U_x/I$ in ohms. The geometrical factor is thus,

$$K = \frac{1}{\sigma^* Z^*}$$

where impedance $Z^*(\omega) = |Z^*(\omega)|e^{\phi^*(\omega)}$ is defined by $I = Z^* U_x$, $\sigma^*$ is the known complex conductivity distribution in the model domain.

In order to extend this concept to the anisotropic case, one must consider the effect of anisotropy on the electrical current and potential distribution in the sample. The ohmic assumption holds for a given measurement, but changing the direction of the measurement in repeat acquisitions effectively changes relationship between the voltage $U_m$, and the current $I$. 

through the resistor (i.e., the core sample) in the acquisition circuit. Consider a repeat SIP measurement of an anisotropic sample for which the current electrodes (A and B) are not moved between acquisitions, but the potential electrodes (M and N) are relocated, such that $U_m = U_2 - U_3$ is measured in a different direction. There is an identical response at A and B, yet $U_m$ may differ by a factor $>10$ between the two acquisitions. If the geometry of the electrode array is the same for both measurements, $K$ is the same by definition; however, we must account for the anisotropy of the current flux in order to correlate the two datasets. The anisotropic Ohm’s Law for AC currents is written, in tensorial form, as $I = Z^{-1} \cdot U_x$, which defines the simple proportionality of the electrical current to the complex impedance tensor $I \propto U \propto Z$. We exploit the proportionality of Ohm’s law by normalizing the measurements by the impedance ratios $\zeta_i = \frac{|Z_i|}{|Z_{\text{min}}|}$ obtained from sequential acquisitions, where $|Z_i|$ and $|Z_{\text{min}}|$ represent the impedance magnitudes of the acquisitions $i$ and the minimum impedance (maximum conductance), respectively, and define the anisotropic geometric factor as $\kappa = \zeta K$ and $I = (\kappa Z^*)^{-1} \cdot U_x$. This normalization step correlates the datasets, accounting for the change in voltage by normalizing the impedances relative to the direction of the maximum current density. Here, $\kappa$ (in m) and $\zeta$ (dimensionless) are arrays of length $i$. The equation $I = (\kappa Z^*)^{-1} \cdot U_x$ implies the minimum impedance is aligned with the maximum principal eigenvector-eigenvalue pair of the conductivity tensor, and that this measurement is equivalent to the isotropic case, i.e., $\kappa = K$. This approach yields a good approximation of the anisotropic complex conductivity, adequate to use as prior constraint on an inversion of the true complex conductivity, accounting for any deviation from the alignment and magnitude of this approximation. Although it is possible to invert the complex conductivity tensor without an explicit geometric factor, the solution to the
anisotropic Laplace equation is highly non-unique; uncertainty is reduced greatly by implementing an accurate prior.

If the conduction pathways of the current are linear (e.g., for the single-component method presented in this paper), the circuit is ohmic and the geometric factor can be determined analytically as $K = AL^{-1}$, where $A$ is the cross section (in m$^2$) and $L$ is the length of the sample between the potential electrodes in meters. In this special case, the source current density can be approximated as $|J_s| = J_s \cdot \hat{n} = J_s$; the problem reduces to the dimensions of the sample and the array. This result has been verified numerically using Comsol Multiphysics for a cylindrical domain of radius $R$ and height $H$. A single-component surface current density is simulated at the ends of the domain. For dimensions $R = 0.013$ m, $H = 0.037$ m, and electrode spacing $L = H/3$, the mean squared error between the analytical value and the result obtained by the procedure discussed above is $3 \times 10^{-4}$ m, or 0.7%. The voltage between M and N along the axis $r = 0$ (i.e., the geometric equivalent to the analytical solution) and on the surface of the cylinder $r = R$ differs by <0.1%.
APPENDIX D. THE COMPLEX IMPEDANCE TENSOR

In this section we use the circuit analogy of the vectorial field equations discussed in the main text. Our goal is to describe how to measure directly the components of the electrical impedance tensor, which are then converted to components of the complex conductivity tensor. For alternating currents and isotropic media, Ohm’s law is written as $I = Z^* U$ where $Z^*(\omega) = |Z^*(\omega)| e^{i\varphi(\omega)}$, and $I$ is electrical current (A), $U$ is voltage difference (V), $|Z^*(\omega)|$ is the magnitude of the impedance (ohms), and $\varphi(\omega)$ is the phase angle (rad). In anisotropic media, $Z^* = Z_{ij}^* e_i \otimes e_j$ designates the (complex) impedance tensor of the rock. Vectors $e_i$ ($i = 1, 2, 3$) denote the basis vectors of the Cartesian frame of reference ($e_i \cdot e_j = \delta_{ij}$). For transverse isotropic (TI) symmetry of unknown orientation, we define the acquisition geometry within a Cartesian coordinate space $\{x, y, z\}$ of arbitrary orientation with respect to the principal basis of the conductivity tensor. A tensor defined in the acquisition frame can be rotated to the intrinsic basis $\{e_1, e_2, e_3\}$, thereby collocating the measurement with the intrinsic anisotropy of the sample. The diagonal tensor of eigenvalues represents the characteristic tensor for the medium, oriented within the space defined by the unit dyadic $e_i \otimes e_j$, which is invariant for all possible coordinate transformations. We rewrite the complex conductivity tensor in terms of the eigensystem $\{\mu_{i,j}, v_{i,j}\}$ by $v_i \sigma^* v_j = \mu_{ij} \delta_{ij}$ (no summation) where $\mu_{i,j}$ and $v_{i,j}$ are the respective eigenvalues and (unit) eigenvectors of the principal coordinate system, and $\delta_{ij} = v_i \cdot v_j$. The basis of the acquisition system can be rotated to obtain the diagonal form by a simple tensor transformation, i.e. $\sigma^* = \lambda_{mn} \lambda_{mn}^* \sigma_{mn}^* = \mu_{i,j} \delta_{ij}, \lambda_{ab} = v^a \cdot e_b$ represent the direction cosines of the $m \rightarrow i$ and $n \rightarrow j$ transformations, such that
\[
\nu^j \cdot (\sigma^*_{mn} e_m \otimes e_n) \cdot \nu^i = (\nu^i \cdot e_m) (\nu^j \cdot e_n) \sigma^*_{mn} = \lambda^i_m \cdot \lambda^j_n \sigma^*_{mn}
\]  

(D-1)

In the case where the principal basis is known, \( \lambda_{ab} \) can be calculated analytically; however, this relationship can also be used to invert the principal tensor without prior knowledge of the material being measured. An equivalent approach is to perform a matrix rotation of the tensor through sequential multiplication of single-axis rotation matrices \( R_n \) given by

\[
R_n(\theta_n) = \cos \theta_n I + \sin \theta_n X_n + (1 - \cos \theta_n) x_n \otimes x_n
\]

(D-2)

\[
Q = \prod_{n=1}^{3} R_n
\]

(D-3)

where the rotations correspond to the Euler angles \( \theta_n \) (n=3), yielding dyadic rotation matrices about unit eigenvectors \( x_n = [u, v, w] \), \( X_n \) is the cross-product matrix, \( Q \) is the n-axis rotation matrix corresponding to the product of \( n \) infinitesimal rotations \( R_n \). We can therefore relate the measured tensor \( \sigma^*_{mn} \) to the principal (diagonalized) tensor, \( \sigma^*_{ij} = Q \sigma^*_{mn} Q^T \).

In order to isolate the tensor components, we use a polarized current density given for instance by \( Z^*_{11} I = U_1 = U_2 = Z^*_{22} I_2 \) and \( Z^*_{33} I_3 = U_3^* \). The experiment generates a symmetric, polarized (single-component) current distribution in the sample, with equivalent symmetry in the electrical field. To illustrate the concept, we rewrite the previous equations in matrix form,

\[
\begin{bmatrix}
Z^*_{11} & Z^*_{12} & Z^*_{13} \\
Z^*_{21} & Z^*_{22} & Z^*_{23} \\
Z^*_{31} & Z^*_{32} & Z^*_{33}
\end{bmatrix}
\begin{bmatrix}
0 \\
0 \\
I_3
\end{bmatrix}
= 
\begin{bmatrix}
0 \\
0 \\
U_3^*
\end{bmatrix}
\]

(D-4)

Where only one component of the tensor (the characteristic eigenvalue, e.g., \( Z^*_{33} \)) is measured.
APPENDIX E. EFFECTIVE STRESS COEFFICIENT

In this appendix, we show how the effective stress coefficient can be defined for any transport property \( \chi(P_d, P_p) \) where \( P_d = P_c - P_p \) denotes the differential pressure (see Todd and Simmons, 1972, for the P-wave velocity in the isotropic case). We start with the total differential,

\[
d\chi = \left( \frac{\partial \chi}{\partial P_p} \right)_{P_d} dP_p + \left( \frac{\partial \chi}{\partial P_d} \right)_{P_p} dP_d,
\]  

E-1

Equation (A1) can be written as,

\[
d\chi = \left[ \left( \frac{\partial \chi}{\partial P_p} \right)_{P_d} - \left( \frac{\partial \chi}{\partial P_d} \right)_{P_p} \right] dP_p + \left( \frac{\partial \chi}{\partial P_d} \right)_{P_p} dP_c,
\]  

E-2

\[
d\chi = \left( \frac{\partial \chi}{\partial P_d} \right)_{P_p} \left\{ \left( \frac{\partial \chi}{\partial P_p} \right)_{P_d} - 1 \right\} dP_p + dP_c.
\]  

E-3

Equation (A3) can be written as,

\[
d\chi = \left( \frac{\partial \chi}{\partial P_d} \right)_{P_p} dP^*,
\]  

E-4

where the effective pressure \( P^* \) for the property \( \chi \) is defined as \( dP^* = dP_c - \alpha \chi dP_p \) (effective pressure law), and the effective stress coefficient as,

\[
\alpha = 1 - \frac{\left. \frac{\partial \chi}{\partial P_p} \right|_{P_p}}{\left. \frac{\partial \chi}{\partial P_d} \right|_{P_p}}.
\]  

E-5
We will use this formulation in this paper. In the close vicinity of a stress state, we can consider that the effective stress coefficient is constant (the isolines in the state of stress \((P_p, P_d)\) can be approximated by parallel straight lines) and the effective pressure becomes \(P^* = P_c - \alpha \chi P_p\). Note however that another formulation is possible by using \(\chi(P_c, P_p)\). In this case, we can write the total differential as,

\[
d\chi = \left(\frac{\partial \chi}{\partial P_p}\right)_c dP_p + \left(\frac{\partial \chi}{\partial P_c}\right)_p dP_c ,
\]

\[E-6\]

\[
d\chi = \left(\frac{\partial \chi}{\partial P_c}\right)_p dP_c + \left(\frac{\partial \chi}{\partial P_c}\right)_p \left(\frac{\partial \chi}{\partial P_p}\right)_c dP_p .
\]

\[E-7\]

Therefore we can write the effective pressure law as,

\[
d\chi = \left(\frac{\partial \chi}{\partial P_c}\right)_p dP^* ,
\]

\[E-8\]

where the effective pressure \(P^*\) for the property \(\chi\) is defined as \(dP^* = dP_c - \alpha \chi dP_p\) (effective pressure law), and the effective stress coefficient as,

\[
\alpha \chi = -\left(\frac{\partial \chi}{\partial P_p}\right)_c\left(\frac{\partial \chi}{\partial P_c}\right)_p .
\]

\[E-9\]
In both cases, when the effective stress coefficient is close to one, we recover Terzaghi’s definition of the effective stress (e.g., De Boer and Ehlers, 1990) with the confining and the pore fluid pressures playing opposite role on the variation of the property $\chi$. 
APPENDIX F. EFFECTIVE STRESS COEFFICIENTS FOR THE STIFFNESS TENSOR

Using the results of Appendix A, we can write effective stress law in incremental form for the components of the undrained stiffness tensor,

\[ dC_{11} = \left( \frac{\partial C_{11}}{\partial P_d} \right)_{P_p} (P_c - \alpha_{11} P_p), \]

\[ dC_{33} = \left( \frac{\partial C_{33}}{\partial P_d} \right)_{P_p} (P_c - \alpha_{33} P_p), \]

\[ dC_{44} = \left( \frac{\partial C_{44}}{\partial P_d} \right)_{P_p} (P_c - \alpha_{44} P_p), \]

\[ dC_{66} = \left( \frac{\partial C_{66}}{\partial P_d} \right)_{P_p} (P_c - \alpha_{66} P_p), \]

\[ dC_{12} = \left( \frac{\partial C_{12}}{\partial P_d} \right)_{P_p} (P_c - \alpha_{12} P_p), \]

\[ dC_{13} = \left( \frac{\partial C_{13}}{\partial P_d} \right)_{P_p} (P_c - \alpha_{13} P_p), \]

and where the different effective stress coefficients are defined by Eq. (A5) of Appendix A. Similar equations can be developed for the components of the conductivity formation tensor,

\[ dF_1 = \left( \frac{\partial F_1}{\partial P_d} \right)_{P_p} (P_c - \alpha_{1}^f P_p), \]

\[ dF_3 = \left( \frac{\partial F_3}{\partial P_d} \right)_{P_p} (P_c - \alpha_{3}^f P_p), \]

and for the components of the tortuosity tensor,
\[ d\tau_1 = \left( \frac{\partial \tau_1}{\partial P_d} \right)_{p_p} (P_c - \alpha_i^T P_p). \]  

\[ d\tau_3 = \left( \frac{\partial \tau_3}{\partial P_d} \right)_{p_p} (P_c - \alpha_3^T P_p). \]

In these equations, we have therefore two effective stress coefficients for the formation factor and two others for the tortuosity tensor. All the effective stress coefficients described in this appendix are not necessarily equal or related to the component of the tensor \( \mathbf{A} \) described in the main text, that is to the two effective stress coefficients entering the effective pressure relationship.
APPENDIX G. COMPLEX CONDUCTIVITY IN MULTIPLE POLAR PHASES

The complex impedance tensor is used to determine the complex conductivity tensor of components $\sigma^{*}_{ij} = \sigma^{'}_{ij} + i\sigma^{''}_{ij}$, comprising the real and imaginary components of the complex conductivity, which correspond to the in-phase contribution of the bulk and surface conductivity of the diffuse layer (Revil et al., 2013),

$$\sigma^{'}_{ij} = F_{ij} S_{w}^{n} \sigma_{w}^{n} + T_{ij} S_{w}^{n} \sigma_{diff}^{n}$$ (G-1)

and the out-of-phase, or quadrature, contribution associated with the polarization of the Stern layer,

$$\sigma^{''}_{ij} = T_{ij} S_{w}^{n} \sigma_{Stern}^{n}.$$ (G-2)

Our conductivity model denotes $\sigma_{w}$ as the conductivity of the pore water and

$$\sigma^{n}_{diff} = \rho_{s} \beta_{(+)} (1 - f) CEC$$ (G-3)

$$\sigma^{n}_{Stern} = \rho_{s} \beta_{(+)} f CEC$$ (G-4)

are the surface conductivities in the diffuse layer and Stern layer (denoted by subscripts diff and Stern, respectively), formed along active surfaces in S m$^{-1}$, $S_{w}$ is the water saturation, $p = n - 1$ denote the saturation exponents (see Vinegar and Waxmann, 1984), where $F_{ij} \equiv T_{ij} \phi$ (dimensionless) are the respective formation factor and tortuosity tensors described in Revil et al. 2013 and Woodruff et al., 2013. The partition coefficient $f$ denotes the fraction of counterions in the Stern layer, $\rho_{s}$ denotes mass density of the solid phase (typically 2650±50 kg m$^{-3}$ for the crystalline framework of clay minerals), $\sigma_{w}$ denotes the conductivity of the pore water (in S m$^{-1}$), CEC (expressed in C kg$^{-1}$) denotes the cation exchange capacity of the material, $\beta_{(+)}$ denotes the mobility of counterions in the diffuse layer, and $\beta_{(+)}^{S}$ corresponds to the mobility of counterions
in the Stern layer (typically, $\beta_{(\pm)}(\text{Na}^+, 25^\circ\text{C}) = 5.2 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$, $\beta_{(\pm)}^{\text{S}}(25^\circ\text{C}, \text{Na}^+) = 1.5 \times 10^{-10} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$ for clay minerals; see Revil, 2012, 2013). Note, electrical anisotropy in porous media is governed according to these two textural parameters, which describe the macroscopic effect of the tortuous conduction pathways in the medium.

We consider a multiphase fluid system in which one or more of the pore fluids (denoted by superscript or subscript $k$) are either conductive or constitute polar compounds (such as bitumen polymer chains) that can form additional double layers between fluid phases, Equations 1 and 2 can be represented as electrical conduction in parallel, such that each conductive component is subjected to the same voltage drop across the sample,

$$\sigma^*_{ij} = \sum_{k=1}^{l} \left( F_{ij} S_k \sigma_k + T_{ij}^k S_k^p \sigma_k^{*S} \right),$$

where $\sigma^k_j$ are the conductivities of the fluid phases $k$ (in S m$^{-1}$), and $S_k$ are the relative saturations of the phases $k$, and $\sigma_k^{*S} = \sigma_k^{\text{S,diff}} + i\sigma_k^{\text{S,Stern}}$ is the complex surface conductivity (in S m$^{-1}$) of the respective polar phases, whereby surface conduction can be supported through the formation of a double layer at the interface between immiscible phase. For simplicity, we write the saturation exponents independently of each phase, recognizing this assumption may not hold for all fluids, and assume surface mobility in the polar phases is equivalent to the mobility of the mineral surface, while allowing for distinct cation exchange (by substituting a phase-dependent charge density $Q^k_v = \rho_k \text{CEC}_k$ in C m$^3$ in Equations G-3 and G-4) and independent tortuosities $T_{ij}^k$ governing the surface conduction pathways of each phase. In systems with non-conducting (organic) fluid phases for which water is the sole conducting phase, the first term on the RHS of Equation G-5 accounting for the bulk fluid conductivity reduces to
\[
\sum_{k=1}^{l} F_{ij}^k S_{ik}^n \sigma_k \equiv F_{ij} S_{ik}^n \sigma_w .
\] (G-6)

The relative saturation dependence of all phases in such a system can be negated due to the sole
dependence of the in-phase and quadrature conductivities on the additional ion exchange in the
water, whether it is associated with the active mineral surfaces or the active interface between the
fluids. For example, in a water-bitumen fluid system, we hypothesize a secondary double layer
forms in the water at the water-bitumen interface due to polymer adsorption at surface radical
sites in the bitumen chains and the corresponding mobility of sorbed ions along these surfaces. In
this special case, the complex conductivity can be attributed to a dependence on the textural
tensors \( F_{ij} \) and \( T_{ij} \) (which account for both the mineral and polar surfaces in the medium; the
exponent \( m \) is effectively increased by the additional fluid phases in the pore network) and the
CEC of the active surfaces. For a two-phase system for fluid conductivity, \( l=2 \), in which both the
water-mineral (denoted \( \text{min} \)) and water-bitumen (denoted \( \text{bit} \)) interfaces exhibit a surface
conductance; using Equation 6 for the bulk fluid conductivity, the conductivity model reduces to

\[
\sigma_{ij}^* = F_{ij} \sigma_w + T_{ij}^\text{min} \sigma_{\text{min}}^{*S} + T_{ij}^\text{bit} \sigma_{\text{bit}}^{*S},
\] (G-7)

\[
\sigma_{ij}^' = F_{ij} \sigma_w + T_{ij}^\text{min} \rho_S \beta_{(+)} (1-f) \text{CEC}_{\text{min}} + T_{ij}^\text{bit} \rho_{\text{bit}} \beta_{(+)} (1-f) \text{CEC}_{\text{bit}},
\] (G-8)

\[
\sigma_{ij}^" = T_{ij}^\text{min} \rho_S \beta_{(+)} f \text{CEC}_{\text{min}} + T_{ij}^\text{bit} \rho_{\text{bit}} \beta_{(+)} f \text{CEC}_{\text{bit}},
\] (G-9)

accounting for the bulk conduction in the pore water and the respective surface components.