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Controls on the composition of saline formation waters from coastal and offshore Louisiana

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A Thesis

Submitted to the Graduate Faculty of
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master in Science

in

The Department of Geology and Geophysics

by

Marielle Elaine Ausburn
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ABSTRACT

Geothermal energy is a renewable energy source that can contribute to the U.S. energy mix. As such, new technologies are being explored for lower temperature systems which would open new areas for exploration in Louisiana. Unlike concepts proposed in the early 1980s, in which heat would have been extracted at the land surface from produced overpressured waters, methods currently being proposed would involve engineered down-hole heat exchangers with zero-mass-fluid withdrawal. A re-examination has been made of the controls on the composition of formation waters in south central and offshore Louisiana in the context of providing insight into water-rock reactions that might be expected as a result of lowering reservoir temperatures and mixing native formation waters associated with in situ heat extraction. An evaluation was made of produced waters from several fields in the south-central coastal area of Louisiana, the Weeks Island field, the Bullwinkle offshore field, and a proprietary offshore field called Bellatrix. Thermodynamic analysis suggests that the chemical composition of these waters is being buffered in part by the mineral assemblage albite, illite, smectite, chalcedony, calcite, dolomite, and barite. The waters are highly undersaturated with respect to gypsum, anhydrite, and halite. Thus it should be possible to predict reactions in the subsurface which could occur as a result of removing heat and lowering temperature. Data from Weeks Island, Bullwinkle, and Bellatrix establish the existence of significant spatial variations in formation water compositions within individual reservoir sands or fault blocks. Of most significance, in terms of the potential for precipitation of mineral cements or scale, are the inverse relations of the concentrations of dissolved barium and sulfate and of dissolved calcium and alkalinity. Mixing of waters within these sands could cause the precipitation of barite and/or calcite within a down-hole heat exchanger and/or conventional production tubing.
CHAPTER 1. INTRODUCTION

Geothermal energy production through the development of geopressured brine reservoirs is being investigated for local energy potential in the US Gulf Coast region (Feng, 2012). Historically, active geothermal energy production has been limited primarily to high-grade hydrothermal systems with little emphasis placed on the potential of lower-grade systems, such as geopressed basinal sediments (Plaksina, 2011). High pore fluid pressures, waters of variable salinity, and temperatures in excess of 300 °F (150 ºC) characterize potential targets for development (Plaksina, 2011). Sediments in the southern Louisiana Gulf Coast are representative of these targets.

There was a burst of research activity in evaluating geothermal resources in the Louisiana and Texas Gulf Coast in the late 1970s and early 1980s (e.g., Kumar, 1977; Kharaka et al., 1978; Bebout and Bachman, 1981; Bebout et al., 1983). Potential sources of energy were considered to include the heat in produced formation waters, dissolved methane in these waters, and the mechanical energy released by producing overpressured fluids (e.g., Kharaka et al., 1978; Bebout et al., 1983). There was a general loss of interest in geothermal resource development after this period due in part to potential environmental problems, including land subsidence and the disposing of large volumes of saline produced waters (Fig. 1.1). These environmental risks could possibly be minimized through a new proposed method of heat extraction being investigated by the LSU Department of Petroleum Engineering (Plaksina, 2011; Feng, 2012). This method would involve a down-hole heat exchanger (DHE) with zero-mass-withdrawal of formation waters (Fig. 1.2). In this proposed design, a horizontal well is drilled allowing heat exchange at the bottom hole temperature zone of the geothermal reservoir (Feng, 2012). Formation fluids are circulated through a heat exchanger and immediately returned back into the formation (Feng, 2012). Because there is zero mass withdrawal from the system, seismicity, and subsidence, and problems associated with disposal of produced waters are eliminated.

Geochemical problems involved with this mode of extracting heat include water-rock reactions induced by lowering formation temperatures around the heat exchanger. Potential reactions include precipitation of silica. In addition, mineral cements, such as barite and calcite, could precipitate as a result of mixing of formation waters of variable composition. Reaction of
native formation waters with engineered materials emplaced into the subsurface, such as
cements, is also possible. Anticipating the potential for scale formation is paramount considering
the costs of hydrocarbon production and would be an important factor in assessing the economics
of down-hole geothermal energy extraction. Scaling in a well in the North Sea Miller Field
cause production to fall from 30,000 barrels per day (B/D) to zero in 24 hours (Crabtree et al.,
1999). Scale forms when the solubility limit for a component in a system is exceeded (Crabtree
et al., 1999). Because solubility is both temperature and pressure dependent, constraining these
variables in this study is important. The solubility of calcium carbonate (CaCO₃) increases with
decreasing temperature while the solubility of barite (BaSO₄) increases with increasing
temperature from 25 °C to 100 °C and then decreases as temperatures near 200 °C (Crabtree et
al., 1999).

The study described in this thesis had two main objectives: (1) to develop a better
understanding of the controls on the composition of formation waters in south central and
offshore Louisiana, (2) to understand what water-rock reactions might occur as a result of
lowering reservoir temperatures and mixing of native formation waters. Based on these
objectives two hypotheses were formulated. The first hypothesis is that the chemical composition
of geothermal formation waters in south Louisiana sediments is controlled in part by metastable
equilibrium involving a suite of ambient silicate, carbonate, and sulfate mineral phases. If so,
knowing what water-rock reactions are involved in controlling formation water compositions
will help develop predictions of what could happen geochemically as the reservoir temperature is
lowered during energy extraction. The second hypothesis is there are spatial variations in the
chemical composition of formation waters on a reservoir scale that could induce chemical
reactions, such as mineral precipitation during mixing.
Figure 1.1. Heat extraction with mass withdrawal. Hot, overpressured waters are removed and transported to the surface where heat extraction occurs. The waste water from this process is then injected back into the subsurface (Hanor, personal communication).

Figure 1.2. Heat extraction with proposed down-hole heat exchanger with zero mass withdrawal. A horizontal well is drilled allowing heat exchange at the BHT zone of the reservoir. Formation waters are circulated around the heat exchanger and immediately returned back into the formation where they are reheated by the rock and convect (Hanor, personal communication).
CHAPTER 2. GEOLOGIC SETTING AND STUDY AREAS

2.1. Geologic Setting of the Northern Gulf of Mexico Basin

Formation of the Gulf of Mexico began in the Late Triassic with the breakup of the supercontinent Pangea with continued rifting into the Middle Jurassic (Salvador, 1991). Tensional features formed as a consequence of rifting include a complex system of linear grabens and half grabens (Salvador, 1991). The deep depressions formed by the down dropped grabens allowed for thick accumulations of salt, estimated to reach a maximum thickness of 2,000-3,000 meters (Salvador, 1991). Deposition of the Louann salt began in the later Middle Jurassic due to limited communication with the open ocean causing evaporation to exceed the inflow of marine waters (Salvador, 1991). According to Land and Macpherson (1992), approximately eight percent of the oceans’ NaCl was sequestered due to deposition of the Louann salt. Observed salt structures in south Louisiana, including the domes and allochthonous sheets found in the study area, are the products of continued tectonic activity and sedimentation since deposition of the Louann salt (Salvador, 1991).

2.2. Study Areas

Several studies were made of the geologic setting of overpressured sediments in southern Louisiana during the 1980s as part of the early phase of interest in geothermal-geopressed energy resources in the area. Szalkowski (2003) and Szalkowski and Hanor (2003) characterized the subsurface temperature-pressure regime of a six-parish area in southwestern Louisiana using maps and cross sections derived from data in an atlas of subsurface sediments by Bebout and Gutierrez (1982).

This study focuses on an area of south central Louisiana and two offshore oil and gas fields (Fig. 2.1). These areas were chosen because of the large number of available chemical analyses of produced waters, including analyses of samples from multiple wells in the same producing reservoir; and the proximity of the reservoirs to salt domes. The study areas include: (1) borehole Amoco-Elf Aquitaine S/L 11736 in the Lake Sand field and oil and gas fields in south-central Louisiana (Kharaka et al., 1978), (2) the Weeks Island field with produced water data from Kumar (1979) and USGS (2002), (3) the Bullwinkle field located in offshore Green
Canyon 65 (GC 65) with data from Hanor (1996), (4) and the Bellatrix field located on the offshore Louisiana continental shelf (proprietary) (Fig. 2.1).

2.3. Previous Work

Work done by Szalkowski (2003) and Szalkowski and Hanor (2003) involved the physical and chemical characterization of waters in southwest Louisiana. This study extends Szalkowski’s research to the east in south central Louisiana with applications for geothermal production. Depth to top of overpressure ranges from 11,500-17,700 ft. (Szalkowski and Hanor,
Salinities throughout the study area exhibit significant variability at any given depth with an absolute range of 10-250 g/L (Szalkowski and Hanor, 2003). Despite this variability, salinities less than seawater (35 g/L) were only found in waters deeper than 8,200 ft in all six study area parishes (Szalkowski and Hanor, 2003). Unlike other sedimentary basins where salinities often increase with depth, salinity-depth profiles in the Gulf of Mexico sedimentary basin are more complex and typically exhibit a reversal in salinity corresponding with top of overpressure (Szalkowski and Hanor, 2003). This downward freshening of salinities into the overpressured sediments could in part be a consequence of the smectite to illite transition (Szalkowski and Hanor, 2003).

Collins (1975) examined produced waters in south-central Louisiana in order to determine the relation of water chemistry to normal and abnormally (i.e. overpressured) pressured geologic zones. Previous work in the area by Dickey et al. (1968), found that the occurrence of hyposaline waters coincided with abnormally high pressures. Collins (1975) determined overpressures pressures exist at depths typically below 8,000 ft and are related to shale-dominated sections. Sediments in the upper section (above 8,900 ft) are considerably sandier when compared to the lower section (Collins, 1975). Salinities generally increase with depth; however, dissolved solids in shallower the hydro-pressured zone range from 600-180,000 mg/L while values in the geopressed zone are less saline than seawater and range from 16,000-26,000 mg/L (Collins, 1975). According to Collins (1975), these lower salinities could be caused by water released by Gulf Coast shales in geopressured zones. Results for temperature found the temperature gradient increased from 18 °C/km in the hydro-pressured section to 32 °C/km in the geopressed zone. Na versus Br values provided evidence for dissolution of salt as the primary source of elevated salinity of Louisiana brines (Collins, 1975).

Land et al. (1988) characterized the geochemistry of formation waters from Miocene age reservoirs located on the Gulf Coast continental shelf, offshore Louisiana. Waters are of the NaCl type with a chloride concentration range of 8,000-170,000 mg/L. Similar to Szalkowski and Hanor (2003), salinities exhibit significant scatter with lower salinities associated with deeper samples from the geopressed zone (Land et al., 1988). Cl/Br ratios indicate the most of the dissolved NaCl is derived from the dissolution of diapiric salt. Samples were found to be undersaturated with respect to K-feldspar with all analyses falling within the albite stability field.
(Land et al., 1988). The ratio of Mg/Ca exhibited strong temperature dependence and is likely controlled by equilibrium between calcite and a Ca and/or Fe-rich dolomite (Land et al., 1988).

Esch (1995) studied the compositional systematics of formation waters collected at the Iberia field, Iberia Parish and waters studied by Land et al. (1988), from seven offshore Louisiana fields. Calculated activities were plotted on activity diagrams constructed from the thermodynamic set in Bowers et al. (1984). Paragonite was used as a proxy for Na-illite. Esch found that the concentrations of the monovalent cations Na\textsuperscript{+} and K\textsuperscript{+} plot on 1:1 slopes versus chloride on log-log plots, whereas divalent cations Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, and Sr\textsuperscript{2+}, and Ba\textsuperscript{2+}, showed a 2:1 ratio with chloride. Log (aNa\textsuperscript{+}/aH\textsuperscript{+}) versus log (aH\textsubscript{4}SiO\textsubscript{4}) cluster around the kaolinite – albite – quartz triple point (Fig. 2.2). Log (aNa\textsuperscript{+}/aH\textsuperscript{+}) versus log (aK\textsuperscript{+}/aH\textsuperscript{+}) plot in the muscovite field near an extension of the albite – K-feldspar phase boundary (Fig. 2.3). Esch did not attempt to couple the monovalent and divalent cations. Esch noted that the stability field for a Si-rich analcime would expand the stability field for that phase. He concluded that at least six mineral phases are responsible for buffering formation water compositions: quartz, albite or Si-rich analcime, Na-illite or paragonite, K-feldspar, muscovite, and kaolinite. Missing from Esch’s discussion are the roles of calcite and dolomite in buffering divalent cations.

![Figure 2.2](image.png)

Figure 2.2. Plot of Na/H activity ratios versus activity of dissolved silica. Phase boundaries calculated for 75 °C, PSAT from thermodynamic data from Bowers et al. (1984). Iberia data are from Esch (1995).
Finally, Hyeong and Capuano (2001) determined the Ca/Mg activity ratio of brines from normal and geopressed sediments of the northeast Texas Gulf Coast. The Ca/Mg activity ratios exhibit strong temperature dependence and plot very close to equilibrium for calcite/disordered dolomite suggesting the ratio of Ca/Mg in the system is likely buffered by calcite and disordered dolomite (Hyeong and Capuano, 2001). One exception in the study comes from the results from dolomite-rich carbonates of the Edwards Group with waters plotting closer to calcite and more ordered dolomite (Hyeong and Capuano, 2001). Fluid flow regimes in the study areas also support rock-buffering as a control on fluid chemistry allowing for adequate residence time to achieve equilibrium in the geopressed section where fluid flow is very slow (tens of millimeters per year) (Hyeong and Capuano, 2001).

**Figure 2.3.** Plot of Na/H activity ratios versus K/H activity ratios. Phase boundaries calculated for 75 °C, P_{SAT} from thermodynamic data from Bowers et al. (1984), assuming aH_2O = 1, quartz saturation, and mineral activities = 1.
CHAPTER 3. SOURCES OF DATA AND TECHNIQUES

3.1. Sources of Data

To test the hypotheses of a rock-buffered system and spatial variations of formation waters existing on a reservoir scale that could induce chemical reactions upon mixing, multiple sources of data were utilized. Some data sets contained analyses for more than one field location.

3.1.1. South central coastal Louisiana

The south central coastal Louisiana study area includes a deep borehole site, Amoco-Elf Aquitaine S/L 11736 (API No. 17045208940000), in the Lake Sand field, Iberia Parish, and several fields sampled for produced waters by Kharaka et al. (1978) in Vermilion, Iberia, and St. Mary parishes. The S/L 11736 site is located in southern Iberia Parish, Louisiana in the Lake Sand field (Fig. 2.1). The Lake Sand field is located near the “Five Islands Trend” in Cote Blanche Bay between two salt domes, the Cote Blanche Island and Bayou Sale domes. The general geologic framework for this study area has been summarized by Kumar (1979) and references therein. The Amoco data for S/L 11736 consists of ten XRD analyses of mudstones over the depth interval of 13,500 – 23,500 ft (Appendix I). Chemical whole rock analyses of mudstones, not utilized here, were reported in weight percentages of major oxides and trace elements. An overview of techniques used by Amoco in obtaining and preparing samples is given by Pacheco (2006). A spontaneous potential – gamma ray – resistivity log for this borehole was obtained from the LA Department of Natural Resources SONRIS site.

Kharaka et al. (1978) reported the chemical composition of ten produced water samples from overpressured reservoirs in six separate fields as part of an earlier study of geothermal resources in the area. Fields in their study include Erath, Grosse Isle, Tigre Lagoon, Bayou Sale, Lake Sand, and Weeks Island (Fig. 2.1). Sample depths range from 7,900 ft to 18,800 ft. Analyses were reported in mg/L with additional information on pH, temperature, and pressure. Sampling procedures for these produced waters are described in Kharaka et al. (1978) and Presser and Barnes (1974). All Kharaka et al. (1978) samples were reported to be from Miocene age sediments. Temperatures reported by Kharaka et al. (1978) range from 170 to 320°F. This
data set is particularly useful for the purposes of this research because it includes data on pH and dissolved silica, which are often missing from analyses of formation waters and because of the careful field and laboratory USGS protocols employed.

3.1.2. Weeks Island field

Three main data sets were utilized in characterizing formation waters of the Weeks Island field. These sets are: Kharaka et al. (1978), Kumar (1979), and USGS (2002). Kharaka et al. (1978), as previously mentioned, reported on the chemical composition of ten produced water samples from six separate fields, including the Weeks Island field. Three of the ten analyses were from the Weeks Island field: 77-GG-19, 77-GG-20, and 77-GG-21.

Kumar (1979) reported analyses of 13 samples of formation waters from the Weeks Island field. Samples were obtained from Shell Oil. The produced water samples were acquired along the salt flank margin from a depth range of 3,000-13,800 ft. Analyses were reported in mg/L. Information on pH was missing, which limits thermodynamic modeling. Values for temperature were missing so a temperature gradient calculated from nearby borehole, S/L 4381 (Bebout and Gutierrez, 1982), was assumed to be similar and was used to estimate temperature at depth.

The USGS produced water database (USGS 2002) contains a vast number of both onshore and offshore analyses from produced waters located throughout the United States, including 4,215 analyses from Louisiana. This database is a revision of a previous database compiled at the DOE Fossil Energy Research Center (http://energy.cr.usgs.gov/prov/prodwat/data.htm). The USGS data base for the Weeks Island field lacked analyses for barium and potassium. Data for sodium was reported but may in fact be sodium plus potassium, a common convention in the 1960s, when most of the analyses were made, in this case by Shell.
3.1.3. Bullwinkle field

A large set of chemical analyses of produced waters at the Bullwinkle (Green Canyon 65) field was generated as part of a sampling program by Shell Offshore, Inc. and utilized by Hanor (1996) to characterize the general geochemistry of waters at the field.

3.1.4. Bellatrix field

The “Bellatrix” field is located on the shallow Louisiana continental shelf. Because of a non-disclosure agreement between Louisiana State University Board of Supervisors and the operators of this field, it is not possible to identify its name or location. The field will referred to here as the “Bellatrix” field (Hanor, personal communication). The Bellatrix data set consists of a large number of chemical analyses of produced waters from multiple fault blocks in the study area. The original data set contained over 614 analyses from 270 wells, often with multiple analyses reported for the same well and sand reservoir.

3.2. Techniques

3.2.1. XRD analyses

Sediment mineralogy was previously determined for borehole S/L 11736 by Amoco by XRD analyses. Mineral phases reported include: quartz, plagioclase feldspar, K-feldspar, calcite, dolomite, siderite, halite, barite, pyrite, anhydrite, kaolinite, chlorite, illite, and smectite. Mineral abundances were normalized to 100% barite-free basis on the assumption that most of the barite was drilling mud contamination. Depth intervals for the ten XRD analyses and their associated mineral compositions are reported in Appendix I.

3.2.2. Depositional environments, lithostratigraphy, and age

A log evaluation of sand bodies in borehole S/L 11736 in the Lake Sand Field was conducted in order to determine depositional environments. The analysis was conducted using basic principles outlined by Rider (1996). Sand bodies were classified based on the overall shape of their SP or gamma ray (GR) response, first, on whether it displayed a bell, cylinder (block), or funnel shape. Additional variations within these three basic geometries were then used to
interpret a possible depositional environment. The three basic facies categories include: deltaic-fluvial, marine, and deep-sea environments (Rider, 1996). Within each facies category, more specific depositional environments can be inferred.

The general lithostratigraphy was determined for S/L 11736 using a technique developed by Bray and Hanor (1990) in order to assess the degree of vertical hydrologic compartmentalization in the sediments. Determining the distribution of sand beds versus shale beds was crucial for the interpretation of additional results, including calculated salinity and temperature profiles for. The entire logged interval of the wellbore (3,500-23,500’) was separated into 300-foot intervals. The percent sand beds within each interval was visually estimated from the SP or GR log against a shale baseline. A plot of percent sand beds as a function of depth (ft) was created to view changes in general lithology with depth.

Sediment ages for S/L 11736 were estimated by correlating SP and GR log signatures to a nearby well with known ages, S/L 4381 (API No. 1704501270000). S/L 4381 was selected from the Bebout and Gutierrez atlas (1982) based on its proximity to S/L 11736, adequate depth for correlation, and known sediment ages. Due to poor resolution of the log image in the Bebout and Gutierrez atlas, S/L 4381 was located and downloaded from the SONRIS site in order to improve correlation confidence.

3.2.3. Temperature

Of the six data sets, only Kharaka et al. (1978) provided information on temperature. Information on temperature calculations for the other 5 data sets is provided in subsequent chapters.

3.2.4. Pressure calculations and overpressure

Pore fluid pressures for S/L 11736 were calculated from drilling mud weights using a technique developed by Hanor (1987). Drilling mud weight is continually adjusted during drilling in order to maintain pressure within the borehole to prevent an invasion of formation fluids and gases (e.g. Hanor, 1987). Because increasing mud weight increases costs and
decreases drilling efficiency, drilling engineers try to use a mud weight that maintains bottom hole pressures as close to formation fluid pressures as possible (Hanor, 1987). Because of this, mud weights can be used to estimate pore fluid pressure. Mud weights were obtained from the well log header with reported mud weights for six runs that range from 12 - 19 lb/gal. Pore fluid pressure at specified depths was determined using the following formula from Hanor (1987):

\[
P_{\text{MUD}} \text{(psi)} = \text{MUD WEIGHT (lb/gal)} \times 0.052 \text{(gal/in}^2\text{ft)} \times \text{Depth (ft)}
\]

A conversion factor of 0.052 (gal/in^2ft) allows for units in psi. Depths at which pressure was calculated correspond with the same sand packages identified for temperature and salinity calculations.

3.2.5. Salinity calculations

Two separate methods were used to determine formation water salinities for S/L 11736. Sand packages were chosen based on their thickness (>15 ft in general) and degree of shale interbedding. Salinity for the upper portion of the borehole (3,500-13,400 ft) was determined from the SP log using a method developed by Funayama and Hanor (1997). This method utilizes a program that calculates formation water salinities and \(R_w\) from SP (Hanor, personal communication). The program is based on an SP-salinity algorithm from Bateman and Konen (1977). Information, including depth at maximum SP deflection, sand thickness, and static spontaneous potential (SSP), was compiled for each sand package. Additional information needed to make salinity calculations included mud weight, \(R_m\), and \(R_{mf}\).

Salinities for the lower portion of the borehole (13,400-23,500 ft) were calculated using the dual-conductivity technique of Revil et al. (1998) as modified by Daugherty (2012) and Hanor (personal communication). The Revil salinity technique requires inputs including calculated cation exchange capacity (CEC) of the bulk sediment and porosity. CEC was calculated from the clay mineralogy (normalized values for smectite, illite, kaolinite, and chlorite as determined from the XRD results). In the absence of porosity information, an assumed porosity of 0.30 was used from Hanor and Mercer (2010) for all sediments. This value may be erroneously high for the deepest part of the section and produced calculated salinities which may
be erroneously low. Bebout and Gutierrez (1981, their Figure 14) showed a porosity versus depth graph for Oligocene and Miocene sandstones of south Louisiana. A regression of their graph yields porosities of less than 0.10 below depths of 20,000 ft H, personal communication). These very low porosities, in turn, result in calculated salinities which in general are unreasonably high for overpressured sediments. Porosities in the range of 0.15 to 0.25 yield salinities of 20 to 30 g/L, which is consistent with salinities determined for overpressured sediments in other part of the Gulf Coast (e.g. Moran, 2003) [Moran reference for refs cited: Moran, K. 2003, Compositional Systematics of Deep, Low Salinity Formation Waters in the Upper Wilcox of Southeastern Texas, LSU M.S. Thesis, 148 p. etd-0409103-160833].

3.2.6. Chemical characterization and thermodynamic analysis

The term ‘rock-buffered fluids’ refers here to aqueous fluids which are in stable or meta-stable equilibrium with respect to a suite of ambient mineral phases. In sedimentary basins, these phases are typically rock-forming silicates, carbonates, and sulfates. Two basic techniques were used to assess whether any of the waters evaluated in this study had compositions that can be accounted for by rock buffering: (1) cross plots of major cation concentrations versus chloride concentrations on log-log plots and (2) thermodynamic calculations of mineral-fluid equilibria as described below.

In rock-buffered systems, the concentrations of the major monovalent cations, \( \text{Na}^+ \) and \( \text{K}^+ \) have an approximately 1:1 slope versus the concentration of chloride on log-log plots (Hanor, 1994). In contrast, the concentrations of the major divalent cations, \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) have an approximately 2:1 slope on log-log plots. The underlying reason for this is as follows. Consider a hypothetical simple system in which \( \text{Na}^+ \) and \( \text{Ca}^{2+} \) are the principal cations and \( \text{Cl}^- \) is the only anion. Charge balance constraints require that:

\[
m\text{Na}^+ + 2m\text{Ca}^{2+} = m\text{Cl}^-
\]

where \( m \) is molality. If the fluid is rock-buffered, it can be shown that the cation/hydrogen ion activity ratios are fixed at a given temperature and pressure:

\[
a\text{Na}^+/a\text{H}^+ = b \quad \text{and} \quad a\text{Ca}^{2+}/(a\text{H}^+)^2 = c
\]
where $a$ is activity and $b$ and $c$ are constants. Neglecting the difference between activity and molality, this gives:

$$m\text{Na}^+ = b(a\text{H}^+) \text{ and } m\text{Ca}^{2+} = c(a\text{H}^+)^2$$

Substituting these relations into the charge balance equation gives:

$$b(a\text{H}^+) + 2c(a\text{H}^+)^2 = m\text{Cl}^-$$

It is clear from the quadratic equation that as $m\text{Cl}^-$ increases that the activity of hydrogen ion must increase. If there is a one-order magnitude increase in $a\text{H}^+$, the activity of Na$^+$ must increase by an order of magnitude, but the activity of Ca$^{2+}$ must increase by two orders of magnitude. Hence, the approximately 1:1 slopes for monovalent cations and 2:1 slopes for buffered divalent cations on log-log concentration cross plots with chloride.

The second technique for evaluating controls on fluid compositions involved thermodynamic calculations of fluid-mineral equilibria. Thermodynamic activities for aqueous species were calculated using a program written by Hanor (personal communication) called QuickieComplex. The program determines aqueous speciation using an algorithm similar to that WATAQ (Truesdell and Jones, 1974). QuickieComplex uses the SOLMINEQ88 (Kharaka et al., 1988) data base for aqueous species and both SOLMINEQ88 and Bowers et al. (1984) for mineral hydrolysis equilibrium constants. Calculations were done using in situ temperatures, and pressures were assumed to be along the liquid-vapor saturation curve ($P_{SAT}$). Because there were no data for dissolved aluminum, aluminosilicate equilibria was evaluated using mineral-fluid equilibrium relations in which aluminum is factored out as a variable (see Bowers et al., 1984). Although alkalinity measurements were available for some data sets, there was no information on what fraction of the alkalinity was bicarbonate and what fraction might have been of other weak acid anions, such as acetate and propionate. Carbonate equilibria were therefore evaluated using the equilibrium relations for calcite-dolomite and calcite-disordered dolomite: $2\text{CaCO}_3 + \text{Mg}^{2+} = \text{CaMg(CO}_3)_2 + \text{Ca}^{2+}$, instead of relations such as $\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$.

A phase diagram for equilibrium relations between aqueous solutions and potassium and sodium aluminosilicate minerals was constructed for temperatures of 75°C and 150°C following
procedures outlined by Esch (1995). Thermodynamic data from Bowers et al. (1984) were used for the mineral hydrolysis reactions. Paragonite was selected as a proxy for Na-smectite, and muscovite was selected as a proxy for K-illite.
CHAPTER 4. SOUTH CENTRAL COASTAL LOUISIANA

4.1. Borehole S/L 11736

Based on SP and GR logs, the Lower Miocene section of the logged interval (14,500-23,500 ft) exhibits a series of alternating thick sand and mudstone packages with an increase in the proportion of mudstone packages lower in the section. Middle Miocene (8,960-14,500 ft) sediments are predominately mud-rich with only two prominent sand packages. The Upper Miocene section (6,560-8,960 ft) is also sand-dominated with an increase in the number of thicker sand packages compared to the overlying Pliocene section (3,500-6,560 ft). Significant interbedding of shale is found throughout the Upper Miocene. The Pliocene section of the well is sand-dominated with a few clean sand packages with highly interbedded sandstone and shale sequences separating them.

Depositional environments (Fig. 4.1), as inferred from interpretation of GR and SP responses, vary significantly in S/L 11736. Lower Miocene (14,500-23,500 ft) sediments are dominated by mudstone and are interpreted to consist of prograding marine shelf and fan channel deposits. There is abrupt change in facies in the Middle Miocene (8,960-14,500 ft) with the deposition of deltaic or fluvial deposits and a transition to deep sea inner fan channel deposits at 9,070 ft. The Upper Miocene (6,560-8,960 ft) consists of marine deposits followed by facies dominated by deltaic or fluvial channel-point bar deposits. Pliocene (3,500-6,560 ft) sediments exhibit primarily fluvial or deltaic facies with several channel-point bar deposits.

Temperatures range from 110-340 °F over a depth interval of 3,580-21,100 ft (Fig. 4.2). There is a noticeable increase in the temperature gradient from 1.12 °F/100ft to 1.68 °F/100ft corresponding with top of overpressure at 13,440 ft. There is a decrease in temperature gradient from 1.68 °F/100ft to 0.748 °F/100ft at 18,430 ft. The overpressured zone (OPZ) was determined to begin at approximately 13,443 ft. which corresponds to an increase in mud weight from 12 to 15.5 (lb/gal). Salinity above the top of overpressure varies greatly with values ranging from 40-210 g/L with no systematic changes with depth (Fig. 4.3). All salinity values in this upper section are greater than normal seawater salinity of 35 g/L. A significant drop in salinity is evident at the
top of the overpressured zone around 13,500 ft. Salinities in the overpressured section show a more systematic change with depth and steadily decrease to values below that of seawater.

Samples for XRD analysis were only taken from the overpressured zone. The two dominant mineral phases in the mudstones are quartz and mixed layer illite-smectite with concentrations of the clay minerals sometimes exceeding 50 percent. A plot of salinities calculated using the Revil technique is plotted against total illite abundance on a barite-free basis in Figure 4.4. The relative abundance of illite increases as fluids become less saline.
Figure 4.2. Temperature (°F) (left) and pressure (psi) (right) as a function of depth for borehole S/L 11736. Dashed line indicates top of overpressure at 13,443 ft. Temperature gradients are listed next to their corresponding interval.
Figure 4.3. Salinity (g/L) (left) and percent sand (right) as a function of depth (ft) for borehole S/L 11736. Black dashed lines indicate top of overpressure at 13,443 ft. Vertical red dashed line indicates seawater salinity (35 g/L). In the hydropressed zone (above OPZ), salinities exhibit significant variability with no systematic change with depth. All values are above average seawater salinity. In the overpressured zone, salinities decrease abruptly to below seawater salinity and show a better relation with depth.
The focus of this study is on the compositional systematics of the major rock-forming components in aqueous solution. Log-log plots of Na\(^+\) and K\(^+\) versus chloride for the Kharaka et al. (1978) formation waters exhibit approximately 1:1 slopes, while log-log trends for the major divalent cations, Mg\(^{2+}\) and Ca\(^{2+}\), exhibit approximately 2:1 slopes (Fig. 4.5). Such slopes are characteristic of rock-buffered fluids in sedimentary basins (Hanor, 1994, 2001), but do not by themselves define which specific mineral phases are involved in the buffering.

**Figure 4.4.** Plot of salinity (mg/L) of waters in borehole S/L 11736 as calculated using the Revil et al. (1998) dual conductivity technique versus total illite.
Dissolved silica activities plot near the chalcedony saturation curve, and decrease with decreasing temperature (Fig. 4.6). The waters are supersaturated with respect to quartz and undersaturated with respect to amorphous silica. The Ca/Mg cation activity ratios of the waters plot near the calcite/ordered dolomite boundary and decrease with decreasing temperature (Fig. 4.7). The Na/K cation activity ratios do not show a pronounced variation with temperature but do plot within the albite stability field and apparently above the stability field for K-feldspar (Fig. 4.8). The waters appear to be in equilibrium with the common scale-forming mineral, barite, over a two and a half order of magnitude reciprocal variation in the activities of dissolved barium and sulfate (Fig. 4.9). The waters are generally significantly undersaturated with respect to anhydrite, gypsum, halite, and other scale-forming minerals. The saturation state of the waters with respect to calcite cannot be reliably evaluated directly because it is not known what proportion of the reported alkalinity is bicarbonate and what proportions are volatile fatty acid anions such as acetate and propionate.

**Figure 4.5.** Log-log plots of major cations versus chloride for fields in south central Louisiana (Fig. 2.1). Monovalent cations (Na⁺ and K⁺) plot along 1:1 slopes while divalent cations (Mg²⁺ and Ca²⁺) plot along 2:1 slopes. Data from Kharaka et al. (1978).
Figure 4.10 is a mineral stability diagram for kaolinite and potassium and sodium aluminosilicates at 75°C and 150°C and quartz saturation constructed from thermodynamic data of Bowers et al. (1984). The activities of the mineral phases = 1. Pressure = P_{SAT}. Black diamonds represent the calculated cation/hydrogen ion activity ratios for the Kharaka et al. (1978) data set.

**Figure 4.6.** Log activity SiO$^2$ (aq) versus temperature plot for fields in south central Louisiana from data in Kharaka et al. (1978). Saturation curves are represented by solid, dashed, and dotted lines as calculated from Bowers et al. (1984).
Figure 4.7. Log cation activity ratio of Ca/Mg versus temperature plot for fields in south central Louisiana from data in Kharaka et al. (1978). Equilibrium boundaries are represented by solid and dashed lines as calculated from Bowers et al. (1984).

Figure 4.8. Log cation activity ratio of Na/K versus temperature plot for fields in south central Louisiana from data in Kharaka et al. (1978). Equilibrium boundary between albite and K-feldspar is represented by dashed line as calculated from Bowers et al. (1984).
Figure 4.9. Log-log plot for activities of sulfate versus barium. Activities calculated using QuickiePT2002 using analyses from Kharaka et al. (1978). Log K values for barite equilibrium range from -9.96 to -9.69 over the temperature range of 25 °C to 150 °C (Hanor, 2000). Thus the waters are close to equilibrium with respect to barite.
Figure 4.10. Mineral stability diagram for kaolinite and potassium and sodium aluminosilicates at 75 °C and 150 °C and quartz saturation constructed from thermodynamic data of Bowers at al. (1984). The activities of the mineral phases = 1. Pressure = $P_{\text{SAT}}$. Black diamonds represent the calculated cation/hydrogen ion activity ratios for the Kharaka et al. (1978) data set.
CHAPTER 5. WEEKS ISLAND FIELD

5.1. Geologic Setting

Weeks Island is located in the “Five Islands Trend” in Iberia Parish (Fig. 2.1). Weeks Island is topographically the highest of the five islands with land surface elevations reaching 171 ft above sea-level as a result of diapiric uplift of salt and cap rock (e.g. Kupfer, 1976; Autin and McCulloh, 1995). The top of salt at this piercement dome lies at approximately 85 ft below the surface of Weeks Island. The surface topographic expression of Weeks Island extends over an area approximately two miles in diameter. The flat-topped salt stock has slight overhangs on the north and east flanks and dips about 60-80 degrees on the south and west flanks (Fig. 5.1) (Kupfer, 1976; Smith, 1976). The following discussion is derived from the description of the field by Smith (1976). Extensive faulting is present on the north side of the field resulting in the formation of a graben. While there is limited faulting within this graben, numerous radial faults, which are commonly associated with piercement salt domes, are present outside of the graben leading to the formation of several smaller oil and gas reservoirs. The Weeks Island oil and gas field surrounds the Weeks Island topographic feature with most of the production occurring along the north flank of the salt dome in a swamp and marsh area. Production comes from numerous sands, predominately of Middle and Lower Miocene age. Stratigraphic sections of Weeks Island range in age from recent to Oligocene and are typically composed of sand and shale intervals. Continental sediments present in the shallower section transition into deltaic-shallow marine sediments at intermediate depths and finally into deeper marine facies at greater depth. Sediments gradually thin and eventually pinch out against the flanks of the Weeks Island salt dome as seen in Figures 5.1 and 5.2.

Shell, the principal operator of the field, designated producing sands by letters of the alphabet (Fig. 5.1) Analyses from the USGS (2002) database for Weeks Island were filtered to include only analyses from sand packages having a minimum of five water analyses for the purposes of the reservoir scale study of compositional heterogeneities. Sands with a sufficient number of complete analyses include: CM, I, M, R2, R, and S sands. Values of pH were provided for most of the analyses. Temperature was estimated using the same temperature gradient calculated from borehole S/L 4381. The discussion in this chapter focuses on the R sand
because the number and spatial distribution of data points within the R sand make it ideal for examining spatial variations on a reservoir scale. Results for the other sands, CM, I, M, R2, and S, are presented in Appendix II.

**Figure 5.1.** Composite cross section of the north and west flanks of the Weeks Island salt dome (Kupfer, 1976). Top of salt reaches within 85 ft of the surface. Sands are labeled alphabetically according to Shell Oil Company’s naming convention. This study examined six of these sands: CM, I, M, R, R2, and S.

**Figure 5.2.** Cross section A-A’ through the Weeks Island field. Cross section runs approximately south to north though the north flank. Oil accumulations shown in light gray and gas accumulation in dark gray (Smith, 1976).
5.2.1. Fluid chemistry

In a log-log plot of major monovalent cations (Fig. 5.3), Na\(^+\) and K\(^+\) from the Kumar (1979) data set exhibit an approximate 1:1 slope with respect to Cl. The USGS data set did not include analyses for potassium. The USGS sodium values are really sodium plus potassium. Divalent cations Mg\(^{2+}\) and Ca\(^{2+}\) fall along a 2:1 slope with respect to Cl. There is significant scatter in Mg vs. Cl in the USGS (2002) data set.

**Figure 5.3.** Log-log plots of major cations versus chloride for Weeks Island (Fig. 2.1). Monovalent cations (Na\(^+\) and K\(^+\)) plot along 1:1 slopes while divalent cations (Mg\(^{2+}\) and Ca\(^{2+}\)) plot along 2:1 slopes. Data from Kumar (1979).
A log-log plot of activities of barium versus sulfate (Fig. 5.4) was created only using data from Kumar (1979) because barium was not reported in the USGS (2002) data set. There is an inverse relation in the concentrations of sulfate and barium with almost all values falling within barite saturation field.
5.2.2. Thermodynamic calculations

Fluid equilibrium diagrams were created to determine the role of buffering by certain mineral phases in controlling formation water chemistry in the Weeks Island field.
Activities of dissolved SiO$_2$ plot along the chalcedony equilibrium boundary with one outlier which plots very close to the amorphous quartz equilibrium boundary (Fig. 5.5). In terms of carbonate equilibrium (Fig. 5.6), activity ratios of Ca/Mg plot directly along the calcite/dolomite boundary and decrease with a decrease in temperature. To determine equilibrium with respect to alkaline feldspars, calculated activity ratios of Na/K versus temperature were plotted (Fig. 5.7). Na/K values fall directly above the albite/K-spar saturation curve with all analyses in the albite stability field, with the exception of one outlier. There is a general increase in the Na/K activity ratio with a decrease in temperature.

**Figure 5.6.** Log activity SiO$_2$ (aq) versus temperature plot for Weeks Island from data in Kumar (1979). Saturation curves are represented by solid, dashed, and dotted lines as calculated from Bowers et al. (1984).
Figure 5.7. Log cation activity ratio of Ca/Mg versus temperature plot for Weeks Island from data in Kumar (1979). Equilibrium boundaries are represented by solid and dashed lines as calculated from Bowers et al. (1984).

Figure 5.8. Log cation activity ratio of Na/K versus temperature plot for Weeks Island from data in Kumar (1979). Equilibrium boundary is represented by dashed line as calculated from Bowers et al. (1984).
5.2.3. Spatial variations in dissolved solutes

Multiple contour maps were created in Surfer to show depths to the top of the production interval and spatial variations in dissolved solutes for each reservoir sand. Maps were created for sands CM, I, M, R, R2, and S. Figure 5.8 shows the spatial distribution of these sand units and their relation to salt on a UTM grid. Maps for the R sand are presented here. Maps for the other sand units are presented in Appendix II.

A structure map of the R sand (Fig. 5.9), with a control of 20 well points, shows depth to top of the sampling interval increasing away from salt; depths range from 12,000-14,200 ft. Chloride values (Fig. 5.9), which range from 127,000 -148,000 mg/L, increase with proximity to salt. Average seawater chlorinity is approximately 19,000 mg/L. Sulfate (Fig. 5.10) has a very clear relation with salt with values decreasing away from salt from 236 mg/L to below detection limits (bdl). Although the USGS (2002) data set does not include analyses of barium, it is reasonable to assume there is an inverse spatial relation between barium and sulfate based on Kumar’s (1979) analyses. Results of bicarbonate and calcium (Fig. 5.11) also show an inverse relation. Bicarbonate, with a range of approximately bdl-385 mg/L, increases with proximity to salt while calcium, with a range of 830-13,500 mg/L, decreases with proximity to salt. Table 5.1 summarizes variations in dissolved solutes for the remaining 5 sands (CM, I, M, R2, and S).
Figure 5.9. Map of sands from USGS (2002) selected for analysis. Contour maps of sands were created using depth to top of analyses (ft). General location of salt is shown. Spatial relation of sands shown on a UTM grid.
Figure 5.10. Contour maps of the R sand from the Weeks Island field. Depth to top of sampling interval (ft) (top figure) and spatial variation in chloride (mg/L) (bottom figure). Black points represent sample locations of data from USGS (2002).
Figure 5.1. Contour map of the R sand from the Weeks Island field. Map shows spatial variation in sulfate (mg/L). Based on the log-log plot for activities of sulfate versus barium (Fig. 5.4) from Kumar (1979), there should be an inverse relation between sulfate and barium in the R sand. Black points represent sample locations of data from USGS (2002).
Figure 5.12. Contour maps of the R sand from the Weeks Island field. Spatial variations in bicarbonate (mg/L) (top figure) and calcium (mg/L) (bottom figure). Black points represent sample locations with data from USGS (2002).
Table 5.1. Solute relations for the Weeks Island field determined visually from USGS (2002). Relation of Cl to salt determined. Inverse relations between SO$_4$ versus Ba and HCO$_3$ versus Ca are also given. *Because the USGS (2002) data set did not analyses for barium, there is an assumed inverse relation between sulfate and barium for all six sands based on the log-log plot for activities of sulfate versus barium (Fig. 5.4).

<table>
<thead>
<tr>
<th>Sand</th>
<th>Chloride Increases toward salt?</th>
<th>SO$_4$ vs. Ba* Inverse relation?</th>
<th>HCO$_3$ vs. Ca Inverse relation?</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>no</td>
<td>probably</td>
<td>yes</td>
</tr>
<tr>
<td>I</td>
<td>no</td>
<td>probably</td>
<td>yes</td>
</tr>
<tr>
<td>M</td>
<td>yes</td>
<td>probably</td>
<td>yes</td>
</tr>
<tr>
<td>R2</td>
<td>yes</td>
<td>probably</td>
<td>yes</td>
</tr>
<tr>
<td>R</td>
<td>yes</td>
<td>probably</td>
<td>yes</td>
</tr>
<tr>
<td>S</td>
<td>yes</td>
<td>probably</td>
<td>no</td>
</tr>
</tbody>
</table>
CHAPTER 6. BULLWINKLE FIELD

6.1. Geologic Setting

The following section is derived from a discussion by Hanor (2007). Most of the continental slope along the northern Gulf of Mexico margin is characterized by allochthonous salt tongues or tabular salt bodies with intervening sediment-filled minibasins (e.g., Holman and Robertson, 1994). One such feature is the Bullwinkle minibasin, which is located in blocks 64, 65, 109, and 110 of the Green Canyon protraction area approximately 300 km southwest of New Orleans, Louisiana, USA (Fig. 6.1). The Bullwinkle oil and gas field was discovered in 1983 by Shell Offshore, Inc. and developed between 1988 and 1990 from a 17,360 ft tall fixed-leg platform in 1,350 ft of water. Production began in 1989. Holman and Roberston (1994) provided a detailed account of the field development, depositional model, and production performance of the field.

Figure 6.1. Map showing location of the Green Canyon protraction area (dashed line) and the Green Canyon (GC 65) oil and gas field (Hanor, 2007).
The GC 65 field lies along the northwest margin of a Plio-Pleistocene salt withdrawal basin. Most of the production has been from the prolific “J” sand sequence, a late Pliocene channel and sheet sand turbidite complex. The primary trap is stratigraphic onlap against a lowstand valley. The J sand package consists of four interconnected sand members, the J1, J2, J3, and J4 sands. A cross section of sands with relation to salt within GC 65 is shown in Figure 6.2. The J sands are overlain by 150 m of bathyal shales which serve as a top seal. There has been additional minor production from the overlying I and H sands.

**Figure 6.2.** Cross section through the Bullwinkle field showing producing sand intervals including the prolific “J” sand sequence with relation to salt. The general location of the J2 sand indicated by red circle. Cross section shows hydrocarbon-bearing sands (cross-hatched regions) and Plio-Pleistocene boundary (dashed line) (Hanor, personal communication).
Hanor (2007) reported the results of a detailed study of the spatial variations in formation water salinities in the Bullwinkle minibasin, Green Canyon 65 (GC 65), northern Gulf of Mexico. A large set of chemical analyses of produced waters generated as part of a sampling program by Shell Offshore, Inc. provided a unique opportunity to reconstruct the pre-production spatial variations in formation water salinity on the reservoir scale. This data set will be referred to as Hanor (1996). This study uses the Hanor (1996) data set to continue to examine reservoir-scale variations in chemistry and the role of rock buffering in controlling water chemistry in the Bullwinkle field. Hanor (1996) previously looked at reservoir-scale variations in chemistry in the Bullwinkle field (Fig. 6.4) and found evidence for mixing of sulfate and barium-rich waters due to field production. The focus of this thesis will be on the J2 sand, which has the largest number

**Figure 6.3.** Contour map (ft) of the J2 sand. Block boundaries represented by vertical and horizontal grid lines. Wells with analyses used in this study indicated by red points (Hanor, personal communication).
of analyses. Hanor (1996) provided chemical data for 11 wells (indicated by red data points in Figure 6.3) in the J2 Sand including pH (Appendix I). Temperature was calculated using a temperature gradient determined for the entire Green Canyon protraction area by Hanor and Mercer (2011).

**Figure 6.4.** Cross sections of formation water chemistry from the Bullwinkle field (GC 64). Sands are labeled alphabetically (naming convention used by Shell). Spatial variation in sulfate (top figure) and barium (bottom figure) shown in mg/L (Hanor, personal communication).
6.2. Results

6.2.1. Fluid chemistry

Log-log plots of major monovalent (Na⁺ and K⁺) and divalent (Mg²⁺ and Ca²⁺) cations versus chloride suggest rock buffering as a control on fluid composition at the Bullwinkle Field (Fig. 6.5). For the J2 sand Na⁺ and K⁺ fall along a 1:1 slope while Mg²⁺ and Ca²⁺ trend along a steeper 2:1 slope (Fig. 6.5). There is significant scatter in K, Mg, and Ca, unlike the waters in the Kharaka et al. (1978) and Kumar (1979) data sets. A log-log activity plot of SO₄ versus Ba (Fig. 6.6) was generated to look for any systematic changes. Unlike waters from south central Louisiana and Weeks Island, some of the Bullwinkle waters are significantly supersaturated with respect to barite.

![Figure 6.5](image)

*Figure 6.5. Log-log plots of major cations versus depth for the Bullwinkle field, J2 sand. Monovalent cations (Na⁺ and K⁺) plot along 1:1 slopes while divalent cations (Mg²⁺ and Ca²⁺) plot along 2:1 slopes. Data from Hanor (1996).*

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6.2.2. Thermodynamic calculations

To further evaluate the role of rock-buffering in the Bullwinkle field, a series of equilibrium diagrams were created. Activity ratios of Ca/Mg cluster tightly on the calcite/dolomite equilibrium boundary at about 86 ºC (Fig. 6.7). Feldspar equilibrium (Fig. 6.8), determined through plotted Na/K activity ratios, shows the majority of waters falling just above the albite/K-feldspar saturation curve with a single analyses in the K-feldspar stability field. Note: due to tight clustering of Na/K and Ca/Mg activity ratios, no systematic changes of these ratios in relation to temperature can be inferred. Equilibrium with respect to silica is not provided as Shell did not report dissolved silica values.

Figure 6.6. Log-log plot for activities of sulfate versus barium for the Bullwinkle field, J2 sand. Activities calculated using QuickiePT2002 using analyses from Hanor (1996). Analyses are both saturated and supersaturated with respect to barite.
**Figure 6.7.** Log cation activity ratio of Ca/Mg versus temperature plot for the J2 sand, Bullwinkle field from data in Hanor (1996). Equilibrium boundaries are represented by solid and dashed lines as calculated from Bowers et al. (1984).

**Figure 6.8.** Log cation activity ratio of Na/K versus temperature plot for the Bullwinkle field, J2 sand from data in Hanor (1996). Equilibrium boundary represented by dashed line as calculated from Bowers et al. (1984).
6.2.3. Spatial variations in dissolved solutes

Contour maps display the structure of the J2 sand as well as spatial variations in dissolved solutes. Locations of 11 analyses are located on a x-y grid (ft) to preserve the spatial relation of analyses. Analyses are reported in mg/L and depth in ft (Appendix I). Available analyses for the J2 sand are located on the northwest flank of salt. A structure map (Fig. 6.9) with depth to top of analyses shows sampling depth increases away from salt. Chloride values range from 87,500-187,000 mg/L with the highest values coinciding proximity to salt (Fig. 6.9). Sulfate, which ranges from bdl-225 mg/L, decreases away from salt, forming an inverse spatial relation with barium (30-305 mg/L), which increases away from salt (Fig. 6.10). Both bicarbonate (140-984 mg/L) and calcium (3,060-8,010 mg/L) increase toward the northwest (Fig. 6.11).
Figure 6.9. Contour maps of the J2 sand from the Bullwinkle field. Depth to top of sampling interval (ft) (top figure) and spatial variation in chloride (mg/L) (bottom figure). Black points represent sample locations with data from Hanor (1996).
Figure 6.10. Contour maps of the J2 sand from the Bullwinkle field. Spatial variations in sulfate (mg/L) (top figure) and barium (mg/L) (bottom figure). Black points represent sample locations with data from Hanor (1996).
Figure 6.11. Contour maps of the J2 sand from the Bullwinkle field. Spatial variations in bicarbonate (mg/L) (top figure) and calcium (mg/L) (bottom figure). Black points represent sample locations with data from Hanor (1996).
CHAPTER 7. BELLATRIX FIELD

7.1. Geologic Setting

The final area examined in this study is an oil and gas field located in the shallow offshore Louisiana continental shelf. As noted in Chapter 3, because of a non-disclosure agreement between Louisiana State University and the operators of this field it is not possible to identify its name or location. The field will referred to here as the “Bellatrix” field (Hanor, personal communication). Host sediments are Pleistocene to Upper Miocene in age and overlie or are near a large salt structure. The Bellatrix field is structurally complex and highly faulted.

The Bellatrix data set consists of a large number of chemical analyses of produced waters from multiple fault blocks in the study area. The original data set contained over 614 analyses from 270 wells, often with multiple analyses reported for the same well and sand reservoir. Because the earliest produced water in a given well is most likely to reflect the pre-production properties of the formation fluids, only the earliest analyses for each well were considered for establishing fluid chemistry relations. Well locations were transformed from a latitude-longitude coordinate system to km-km system having an arbitrary (0,0) origin in order to retain spatial relations of the analyses (Fig. 7.1). Well data ranges between 1,000 m to 3,900 m subsea true vertical depth (SSTVD). Concentrations were converted from mg/L to mmol/L. Temperature was calculated using a temperature gradient determined by J. Hanor (personal communication) from equilibrated bottom hole temperatures for the field obtained from the former Minerals Management Services (Hanor and Mercer, 2010). Information on pH was provided for most analyses.

The Bellatrix study area is highly faulted, generally with a single producing well per each sand in a fault block. As a result, fluid chemistry and spatial variations were analyzed on a fault block scale rather than on the scale of individual sands, as was the case for Weeks Island and Bullwinkle studies.
This study focuses on fault blocks designated here as alpha (α), beta (β), gamma (γ), and delta (δ). These fault blocks were chosen based on the large number of analyses from different wells within these blocks and the spatial relation of the fault block to salt. The approximate locations of first analyses for fault blocks α, β, γ, and δ are identified in Figure 7.2 which shows variations in TDS across the entire study area. A plot map showing relative locations of first analyses for fault blocks alpha, beta, gamma, and delta can be found in Figure 7.3.
Figure 7.2. Map showing depth (m) to top of the sampling interval. Produced water samples are indicated by black points. Note depth to sampling mimics the shape of salt.
Figure 7.3. Map showing salinity (mg/L) variations for the first analyses for each well. Average seawater salinity, 35,000 mg/L, is indicated by dashed red line on the scale bar. General location of the four fault blocks analyzed in this study, the alpha, beta, gamma, and delta fault blocks, are shown schematically by polygons (not representative of fault block shape). The beta block is discussed in this text to this thesis and is highlighted in red.
7.2. Results

7.2.1. Fluid chemistry

Results for fault blocks alpha, beta, gamma, and delta reveal the typical major cation versus Cl relations. Major monovalent cations Na\(^+\) and K\(^+\) generally plot along 1:1 slopes with evidence of “tail” branching off the K\(^+\) versus Cl trend (Fig. 7.4). Major divalent cations Mg\(^{2+}\) and Ca\(^{2+}\) fall along 2:1 slopes (Fig. 7.4). There is significant scatter in the K, Mg, and Ca plots, although the general 1:1 and 2:1 trends are clear.

Activities of dissolved barium versus sulfate on a log-log plot (Fig. 7.5) show an inverse relation.

Figure 7.4. Log-log plots of major cations versus chloride for the Bellatrix field. Monovalent cations (Na\(^+\) and K\(^+\)) plot along 1:1 slopes while divalent cations (Mg\(^{2+}\) and Ca\(^{2+}\)) plot along 2:1 slopes.
7.2.2. Thermodynamic calculations

Activities of dissolved SiO$_2$ for the Bellatrix field marks a great departure from previous field areas. Unlike the other areas, dissolved silica exhibits significant scatter and less of a clear relation with temperature (Fig. 7.6). Another departure from previous study areas is the activities of Ca/Mg for carbonate equilibrium (Fig. 7.7). Values trend along the calcite/dolomite equilibrium boundary and vary as a function of temperature although there is significant scatter. A log-log plot of activities Na/K versus temperature was created to examine feldspar equilibrium in the Bellatrix field (Fig. 7.8). Activity ratios of Na/K plot in both the albite and K-feldspar stability fields. The activity ratios plot in a sub-horizontal field, indicating there is no trend in Na/K with respect to temperature.

**Figure 7.5.** Log-log plot for activities of sulfate versus barium for the beta block in the Bellatrix field. Activities calculated using QuickiePT2002. Analyses are primarily saturated with respect to barite with a few analyses in the undersaturated and oversaturated fields.
Figure 7.6. Log activity SiO$_2$ (aq) versus temperature plot for the Bellatrix field. Equilibrium boundaries are represented by solid, dashed, and dotted lines as calculated from Bowers et al. (1984).

Figure 7.7. Log cation activity ratio of Ca/Mg versus temperature plot for the Bellatrix field. Equilibrium boundaries are represented by solid and dashed lines as calculated from Bowers et al. (1984).
7.2.3. Spatial variations in dissolved solutes

A total of 22 analyses from the beta fault block form the control for the solute maps. Analyses from beta block come from a total of 11 different producing sands. Analyses are plotted on a km grid with concentrations in mmol/L. The beta block is located on the northeast flank of salt. Chloride concentrations increase towards salt with a peak salinity of 1,880 mmol/L (Fig. 7.9). As shown in Figures 7.10 and 7.11, there are inverse relations between sulfate and barium as well as bicarbonate and calcium. Although maps for both bicarbonate and calcium exhibit significant scattering of values with pockets of peak concentration levels, peaks of calcium and bicarbonate that are spatially related do vary inversely. Table 7.1 summarizes results for the beta block as well as fault blocks alpha, gamma, and delta (Maps for additional blocks located in Appendix II).
Figure 7.9. Contour map of the beta fault block in the Bellatrix field. Spatial variation in chloride (mmol/L). Black points represent sample locations.
Figure 7.10. Contour maps of the beta fault block in the Bellatrix field. Spatial variations in sulfate (mmol/L) (top figure) and barium (mmol/L) (bottom figure). Black points represent sample locations. Circled areas highlight inverse relation between SO$_4$ and Ba.
Figure 7.11. Contour maps of the beta fault block in the Bellatrix field. Spatial variations in bicarbonate (mmol/L) (top figure) and calcium (mmol/L) (bottom figure). Black points represent sample locations. Circled areas highlight inverse relation between HCO₃ and Ca.
Table 7.1. Solute relations for selected fault blocks in the Bellatrix field determined visually. Relation of Cl to salt determined. Inverse relations between SO$_4$ versus Ba and HCO$_3$ versus Ca also given.

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<th>HCO$_3$ vs. Ca Inverse relation?</th>
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CHAPTER 8. DISCUSSION AND CONCLUSIONS

8.1. Amoco Borehole

Potential targets for development of in situ extraction of sedimentary geothermal energy are characterized by temperatures in excess of 300 °F (150 °C), high pore pressures, and waters of variable salinity (MIT, 2006, Plaksina, 2011, and Feng, 2012). The 300 °F isotherm occurs at a depth of approximately 18,100 ft at the Amoco borehole, or below the top of overpressure at 13,400 ft. There is an increase in the temperature gradient coinciding with top of overpressure (1.12 °F/100 ft to 1.74 °F/100 ft) followed by a decrease to 0.75 °F/100 ft (Fig. 4.2). Kumar (1977) found similar changes in the temperature gradient at comparable depths in the Bayou Carlin-Lake Sand Area, Iberia and St. Mary parishes. Depth to the top of overpressure is comparable to the values of 11,500-17,700 in southwest Louisiana reported by Szalkowski and Hanor (2003). Salinities at the site exceed seawater salinities (35 g/L) in the shallower hydropressured part of the section and decrease significantly with depth below the top of overpressure (Fig. 4.3), a relation typical for much of south Louisiana (Hanor and Sassen, 1990). This reversal to fresher salinities in the overpressured zone is similarly noted in other studies on Louisiana Gulf Coast sediments (e.g. Collins, 1975; Land et al.,1988; Szalkowski and Hanor, 2003). The Amoco site is near several salt domes, and dissolution of salt is probably the process generating highly saline waters. Dissolution of salt domes as a source of elevated salinities of south Louisiana brines is supported by numerous studies (e.g. Collins, 1975; Land et al., 1988). The wide fluctuation in salinities (40-214 g/L) with depth in the hydropressured section may reflect vertical compartmentalization caused by interbedding of sand and mudstone packages (Fig. 4.3). Dewatering caused by the conversion of smectite to illite could lead to dilution and a decrease in salinity in the overpressured zone where there are salinities below that of seawater (35 g/L) (Szalkowski and Hanor, 2003). This explanation is supported by Figure 4.4, which shows a decrease in salinity associated with an increase in illite in mixed layered illite-smectite. However, some of the unusually low salinities may be an artifact of having used erroneously high porosity values in the Revil method (1998) calculations. If the Amoco borehole site is representative, one would expect to encounter a potentially wide range of salinities and fluid compositions in possible targets for geothermal energy extraction in south central Louisiana.
8.2. Evidence for Mineral Buffering of Fluid Compositions

Although numerical modeling of water-rock geochemical reactions that might occur as a result of significantly lowering the temperature of potential geothermal reservoirs in south central Louisiana was beyond the scope of this study, evidence that the composition of the native formation waters are mineral-buffered helps to constrain boundary conditions for such modeling efforts. Several results from this study support the hypothesis that the chemistry of overpressured formation waters in the study area is controlled in part by mineral-buffering. It has been shown by Hanor (1994 and 2001) and Esch (1995) that in rock-buffered waters, major cation concentrations vary in a predictable manner with respect to chloride. The 1:1 and 2:1 cation-chloride slopes documented are a clear reflection of buffering of fluid compositions (Hanor 1994, 2001). These relations are present in all of the data sets investigated here, although these relations by themselves do not identify which minerals are responsible for the buffering. Significant scatter in Mg versus Cl values from the USGS (2002) data set is evident in the form of outliers and “tails” that do not plot on a 2:1 trend line (Fig. 5.4). Two primary data sets were used to characterize waters in the Weeks Island field, USGS (2002) and Kumar (1979). Because Kumar (1979) clearly shows these slope relations with little scatter (Fig. 5.3), it is likely that deviations in the USGS (2002) results are a result of analytical error.

Equilibrium diagrams created for the study areas provide additional support for rock-buffering as well as information on possible scale forming precipitates that could form as a result of lowering temperature during geothermal energy extraction. Diagrams for silica equilibrium show the activity of dissolved SiO$_2$ decreasing along the chalcedony saturation curve as a function of lowering temperature. Lowering the temperature from 150 °C would cause the waters studied here to become supersaturated with respect to chalcedony, resulting in possible silica scaling, but it would require a substantial drop in temperature for them to become supersaturated with respect to amorphous silica. Results for silica equilibrium for the Bellatrix field beta fault block deviate from the other fields in that the activities of dissolved silica exhibit significant scatter and no clear relation with temperature. This departure may be a consequence of the samples analyzed coming from 11 separate sand reservoirs.
Activity ratios of Ca/Mg from all data sets plot along the calcite-dolomite equilibrium curve. Lowering the temperature would cause the waters to depart from calcite-dolomite equilibrium curve with waters regaining equilibrium through precipitation of calcite, which would lower the activity ratio of Ca/Mg. The Weeks Island field has a single outlier that falls above the calcite/dolomite saturation curve. This outlier was derived from sample number FMW1 in Kumar (1979) and is reported to be from the I-4 sand over a depth range of 3,046 – 3,054 ft. Other studies report a depth range of approximately 10,000-11,000 for the I sand (Kupfer, 1976; Kumar, 1979). There may be a discrepancy in the reported depth for FMW1 which would account for the anomalous temperature. The data sets for south central coastal Louisiana (Kharaka et al., 1978) and Weeks Island (Kumar, 1979 and USGS, 2002) provide evidence for potential calcite precipitation. Results for Bullwinkle (Hanor, 1996) cluster too tightly around 85 ºC to show any variation in the activity ratio of Ca/Mg as a function of temperature. Carbonate equilibrium diagrams show that the activity ratios of Ca/Mg plot above calcite/ disordered-dolomite and align closer to calcite/dolomite. Land et al. (1988) showed the ratio of Ca/Mg in waters from the Gulf Coast continental shelf, offshore Louisiana, also exhibit strong temperature dependence with equilibrium being controlled by calcite and a Ca and/or Fe-rich dolomite. Hyeong and Capuano (2001) also used Kharaka et al. (1978) data set to determine equilibrium with calcite/dolomite. Their results vary slightly from the findings of the present study in that activity ratios of Ca/Mg fall closer to their calculated calcite/disordered dolomite equilibrium curve (Hyeong and Capuano, 2001). According to Hyeong and Capuano (2001), disordering of dolomite leads to lower Ca/Mg ratios due to the greater solubility of disordered dolomite. Higher Ca/Mg ratios (ordered-dolomite) associated with dolomite-rich formations is likely due to dedolomitization, or the conversion of dolomite to calcite (Hyeong and Capuano, 2001).

In contrast to the activities of dissolved silica and Ca/Mg activity ratios the Na/K ratios for most of the study areas show no significant variation with temperature. If the waters were buffered by albite – K-feldspar equilibrium, there should be an increase in Na/K ratios with decreasing temperature. An exception is the Weeks Island area where there is evidence for possible buffering by albite and K-feldspar (Fig. 5.7). Most waters from all of the study areas plot within the albite stability field. Analyses from Land et al. (1988) plot exclusively in the
albite stability field. An exception in this study are the waters from Bellatrix where analyses plot in both the albite and K-feldspar stability fields (Fig. 7.8).

The Na/H and K/H activity ratios calculated from the Kharaka et al. (1978) data plot in essentially the same mineral stability fields as data from Esch (1995) for waters from the Iberia field, Iberia Parish, Louisiana (Figs. 2.2, 2.3). Mineral stability fields were calculated from data in Bowers et al. (1984). Esch also plotted activity relations he calculated from analyses of waters from offshore fields by Land et al. (1988). The Land et al. data did not include values for pH, and Esch calculated values assuming equilibrium with calcite. The Kharaka et al. data plot in the general vicinity of the albite (NaAlSi₃O₈) – muscovite (KAl₃Si₃O₁₀(OH)₂) – paragonite (NaAl₃Si₃O₁₀(OH)₂) fields. If we take muscovite to be a proxy for illite (ca. K₀.₆₅Al₂.O₆(Al₀.₆₅Si₃.₃₅)O₁₀(OH)₂) and paragonite to be a proxy for Na-smectite (ca. Na₀.₃₃Al₂.₃₃Si₃.₆₇O₁₀(OH)₂), one could make a case for the activities of Na and K being buffered by the assemblage albite-illite-smectite-chalcedony. The analyses plot outside of the K-feldspar field and mostly above the kaolinite field.

8.3. Evidence for Potential Mineral Precipitation as a Result of Mixing

As potentially significant as a drop in temperature might be in inducing reactions, the mixing of reservoir waters as a result of circulation around a heat exchanger could be of equal or greater importance if there are spatial heterogeneities in formation water compositions. This would be particularly true of the precipitation of barite by mixing of barium-rich and sulfate-rich waters in reservoir sands waters which are in equilibrium with barite, such as the waters in the data sets considered here. Precipitation of barite and calcite is of peak interest due to potential degradation of reservoir properties, including porosity and permeability, in a heat-extraction system dependent on convecting formation waters (Fig. 1.2).

The mixing of sulfate-bearing waters derived from dissolution of anhydrite in salt, and barium-rich waters could lead to precipitation of barite. Several results presented in this thesis provide evidence for the potential for barite precipitation. Activity log-log plots of barium versus sulfate show that the vast majority of waters considered in the study areas are in equilibrium, i.e., saturated, with respect to barite. Some of the waters in the Bullwinkle field are supersaturated
with respect to barite (Fig. 6.6), a likely consequence of mixing of barium and sulfate-rich waters during hydrocarbon production. In addition, maps of spatial variations in dissolved solutes show an inverse relation between barium and sulfate. In lieu of missing barium analyses for USGS (2002), it can reasonably be assumed there is an inverse relation between barium and sulfate evidenced by the activity log-log plot generated from Kumar (1979) which shows areas low in sulfate are high in barium (Fig. 5.4). Results from Bellatrix show significant compartmentalization of dissolved solutes when compared to other data sets. Because analyses are presented by fault block and not specific sands, increased scatter and “bull’s-eyes” in maps is a reasonable expectation. Despite scatter, an inverse spatial relation between barium and sulfate is also evident in the Bellatrix field (Fig. 6.10).

Most of the maps showing spatial variations in bicarbonate and calcium show an inverse relation on a reservoir scale further supporting evidence for potential calcite precipitation if the waters were mixed. However, this relation is not clearly evident in the Weeks Island S sand (Appendix II), Bullwinkle J2 sand (Fig. 6.11), or Bellatrix alpha and gamma blocks (Appendix II). Lack of clear mixing trends in the Weeks Island S sand may be the result of poorly chosen contouring parameters in the Surfer program because all other sands at Weeks Island in from this data set show a clear inverse relation. It is not known what proportions of the reported alkalinity is bicarbonate and what are volatile fatty acids anions, such as acetate and propionate (Workman and Hanor, 1984) for the Bullwinkle field; this could account for the lack of an inverse relation. For Bellatrix, positive relations between bicarbonate and calcium (Fig. 7.11) may an artifact of comparing analyses of waters taken from multiple sands within the fault block.

8.4. Summary

Geothermal energy is a renewable energy source that can contribute to the U.S. energy mix. As such, new technologies are being explored for lower temperature systems which would open new areas for exploration in Louisiana. Unlike concepts proposed in the early 1980s, in which heat would have been extracted at the land surface from produced overpressured waters, methods currently being proposed would involve engineered down-hole heat exchangers with zero-mass-fluid withdrawal. A re-examination has been made of the controls on the composition of formation waters in south central and offshore Louisiana in the context of providing insight
into water-rock reactions that might be expected as a result of lowering reservoir temperatures and mixing native formation waters associated with in situ heat extraction. An evaluation was made of produced waters from several fields in the south-central coastal area of Louisiana, the Weeks Island field, the Bullwinkle offshore field, and a proprietary offshore field called Bellatrix. Thermodynamic analysis suggests that the chemical composition of these waters is being buffered in part by the mineral assemblage albite, illite, smectite, chalcedony, calcite, dolomite, and barite. The waters are highly undersaturated with respect to gypsum, anhydrite, and halite. Thus it should be possible to predict reactions in the subsurface which could occur as a result of removing heat and lowering temperature. Data from Weeks Island, Bullwinkle, and Bellatrix establish the existence of significant spatial variations in formation water compositions within individual reservoir sands or fault blocks. Of most significance, in terms of the potential for precipitation of mineral cements or scale, are the inverse relations of the concentrations of dissolved barium and sulfate and of dissolved calcium and alkalinity. Mixing of waters within these sands could cause the precipitation of barite and/or calcite within a down-hole heat exchanger and/or conventional production tubing.

### 8.5. Future Work

While this study was able to establish mineral-buffering by chalcedony, calcite, dolomite, and barite, it was unable to determine specifically which minerals are controlling Na and K concentrations in the system. Plotted activity ratios of Na/K show no variation with temperature indicating the ratio is not buffered by albite - K-feldspar equilibrium. Illite could be player in buffering this ratio but would have to be further examined.

A better understanding of what is coupling the monovalent (Na\(^+\) and K\(^+\)) with the divalent cations (Mg\(^{2+}\) and Ca\(^{2+}\)) is also of interest. While distinct 1:1 and 2:1 slopes of the rock-forming cations on log-log plots with chloride were evident in all study areas, not all of the buffering mineral phases have been identified.

Despite providing evidence for mineral precipitation, rates of precipitation were beyond the scope of this study and should be established. Understanding how quickly different scales could form would be invaluable for both geothermal energy and oil and gas production planning.
Finally, future work would include a more comprehensive look at relations between water chemistry and sediment mineralogy.
REFERENCES


Kumar, M.B., 1979, Salt mine brines versus formation waters: in, An investigation of the utility of Gulf Coast salt domes for the storage or disposal of radioactive waters: Institute for Environmental Studies, Louisiana State University, E511-02500-A-1.


APPENDIX I. DATA SETS

XRD analyses for borehole S/L 11736 by Amoco. Reported mineral phases include: quartz, plagioclase, feldspar, K-feldspar, calcite, dolomite, siderite, halite, barite, pyrite, anhydrite, kaolinite, chlorite, illite, and smectite. Mineral abundances were normalized to 100% barite-free basis on the assumption that most of the barite was drilling mud contamination.

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Analyses for the J2 sand in the Bullwinkle field as reported in the data set Hanor, 1996.

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APPENDIX II. SPATIAL VARIATIONS IN DISSOLVED SOLUTES MAPS

Contour maps of the CM sand from the Weeks Island field. Depth to top of sampling interval (ft) and spatial variations in dissolved solutes (mg/L). Black points represent sample locations of data from USGS (2002).
Contour maps of the I sand from the Weeks Island field. Depth to top of sampling interval (ft) and spatial variations in dissolved solutes (mg/L). Black points represent sample locations of data from USGS (2002).
Contour maps of the M sand from the Weeks Island field. Depth to top of sampling interval (ft) and spatial variations in dissolved solutes (mg/L). Black points represent sample locations of data from USGS (2002).
Contour maps of the R2 sand from the Weeks Island field. Depth to top of sampling interval (ft) and spatial variations in dissolved solutes (mg/L). Black points represent sample locations of data from USGS (2002).
Contour maps of the S sand from the Weeks Island field. Depth to top of sampling interval (ft) and spatial variations in dissolved solutes (mg/L). Black points represent sample locations of data from USGS (2002).
Contour maps of the alpha block from the Bellatrix field. Spatial variations in dissolved solutes (mg/L). Black points represent sample locations of data.
Contour maps of the gamma block from the Bellatrix field. Spatial variations in dissolved solutes (mg/L). Black points represent sample locations of data.
Contour maps of the delta block from the Bellatrix field. Spatial variations in dissolved solutes (mg/L). Black points represent sample locations of data.
VITA

Marielle Elaine Ausburn was born in 1985 to Susan Huey and Mark Ausburn and is the twin sister (the good twin) of Melissa Ausburn. After bouncing around the country because of her dad’s job as a geologist, Marielle finally settled in New Orleans, where she graduated from Mount Carmel Academy in May 2004. She began college that August and graduated in 2008 with her B.S. in marketing with the intention of going on to law school after taking the LSAT. After a lawyer told her something to the effect “you’re too sweet for this… it will ruin your soul”, Marielle decided to take a semester off and rethink her career choice. At the suggestion of her father and uncle, both of whom are geologists, Marielle made the transition into geology and will receive her M.S. in Geology from Louisiana State University in August 2013. In June 2013, Marielle will move to Houston, Texas where she will be working for British Petroleum as a geologist.