Clay-Cation Compositions from Groundwater Chemistry as an Indicator of Depositional Environments, Paleoclimates, and Paleo-Groundwater Flow

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DOCTOR OF PHILOSOPHY

in Geology

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DEDICATION

To my brother, Clay.

ACKNOWLEDGMENTS

I would like to thank my dissertation supervisor, Dr. Regina Capuano, for the dedicated attention, for seeing my potential, and for always putting pressure on me when she knew it was what I needed. She played an equal role in the development of this dissertation and her contribution cannot be overstated. We've built an outstanding working relationship that is not common among professors and their graduate students.

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ABSTRACT

New methods to calculate the cation compositions of clays from equilibrated groundwater are presented and applied in three clay-rich coastal aquifers where significant chemical differences are shown to exist among clays based on their depositional environment and the climate at deposition. River-water analyses show that fluvial deposited sediments are represented by majority $X_{Na} \le 8.0\%$ and marine deposited sediments by majority $X_{Na} > 8.0\%$. In a natural system with fluvial, mixed, and marine environments identified by traditional core, log and paleontological analyses, each depositional environment has a distinguishing range of X_{Na} , X_{Ca} and X_{Mg} consistent with these criteria. Differences in X_{Na} are related to climate of deposition among clays deposited in a fluvial environment, where a larger portion of the fluvial clays deposited in a semi-arid paleoclimate have elevated X_{Na} compared to those deposited in a humid subtropical paleoclimate.

Perturbations in these trends were compared to elements in the groundwater not involved in ion exchange to identify areas of upwelling and halite dissolution. Massbalance calculations show that the effect of cation exchange on each pore volume of fluid that flows in the aquifer is large, whereas the effect on the clay composition is small, so clays will not only retain the signature of their depositional setting, but changes in the clay exchange composition can be used to identify the aquifer's past chemical evolution and historical-flow paths. These relationships might be used to aid stratigraphic interpretations based on well logs, sediment samples, and paleontology in distinguishing fluvial, marine, and mixed fluvial-marine depositional environments.

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CHAPTER 1: INTRODUCTION TO THE DISSERTATION

1.1 History and Development of this Dissertation

In the Fall of 2016, after spending two years mudlogging on various rig sites in the Permian, Woodbine, and Eagle Ford basins and working for my Father's company (American Oil Tools), I enrolled in the master's degree program in Geology at the Department of Earth and Atmospheric Sciences at the University of Houston. I earned my B.S. in Geology from Texas A&M University in 2014 and began applying to graduate schools shortly thereafter to further separate myself in such a competitive industry.

Although I began the master's program with a strong geologic background, I realized that if I was to fully utilize the knowledge of my advisor, Dr. Regina Capuano, I had much to learn in terms of hydrology, which I was not required to take during my undergraduate study at Texas A&M. With her help inside and outside of the classroom, I quickly gained the basic knowledge I needed to begin conducting research in this field.

My initial research was generally a learning process as I still lacked the breadth of knowledge to consider certain problems that could stand as significant counterevidence to my theses. As a guide, Dr. Capuano would notify me of these problems, which lead me to delve deep into many genres of hydrology and geochemistry including fluid-mineral equilibria, low temperature thermodynamics, and of course, cation-exchange. As this process continued, my arguments became increasingly interesting to Dr. Capuano who began having a harder time figuring out why they could be scrapped. It wasn't long until we had multiple potential papers outlined and I had a decision to make. It was one year into my master's program, and it seemed I had approached the research in a way that would require a PhD to properly carry out. Although I still had much to learn, and still lacked the mindset a PhD student must adopt, in 2017 I decided to switch from the MS program to the PhD program of the UH department of Earth and Atmospheric Sciences.

The main ideas and evidence presented in this dissertation originated from our early study of groundwater in equilibrium with montmorillonite clays contained in the Chicot/Evangeline Aquifers of the Texas Gulf Coast. The original approach was thermodynamic, where we noticed our groundwater data sets in equilibrium with montmorillonite yielded different activity coefficients than those cited in the literature, which were almost entirely limited to pure-endmember phases. We attributed this to the mixed-phase montmorillonites encountered in a natural setting, which are constantly involved in rapidly occurring cation exchange reactions. Upon further study of cationexchange equilibrium, which has been surprisingly limited to laboratory experiments and simulations, we began to formulate the methods to understand clay-cation exchange equilibrium in natural setting, which is one of the main concepts presented in this dissertation.

1.2 Outline and Organization of this Dissertation

This dissertation contains three chapters that contain large datasets of groundwater chemical analyses sourced from clay-rich siliciclastic formations of the Texas Gulf Coast from which equilibrated clay-cation compositions are calculated. The main scientific themes for all three chapters include, 1) Defining the chemical compositions of clays deposited in specific geologic and environmental settings and establishing criteria for their interpretation based on laboratory measurements, 2) Recognizing which features are exclusive among the clays that share a geologic setting and what chemical transitions occur between clays from different settings, 3) Comparing the results to previous interpretations based on other sources of data.

Chapter 2, 3, and 4 were written in the format of journal articles. Chapter 2 on groundwater chemical evolution and paleo-groundwater flow was submitted to the AGU journal "Water Resources Research," and was published in 2020 with my advisor Dr. Regina Capuano as first author. Chapter 3, on fluvial versus marine sediments, was submitted to the AGU journal "Geochemistry, Geophysics, Geosystems" and is under review at time of writing. Chapter 4, on wet versus dry paleoclimate, was submitted to the Elsevier journal "Applied Geochemistry," and is being revised at time of writing. Dr. Capuano coauthored both chapters 3 and 4.

CHAPTER 2:

CATION EXCHANGE IN GROUNDWATER-CHEMICAL EVOLUTION AND PREDICTION OF PALEO-GROUNDWATER FLOW: A NATURAL SYSTEM STUDY

Chapter Two Published As:

Capuano, R.M., and Jones, C.R. (2020) Cation exchange in groundwater-chemical evolution and prediction of paleo-groundwater flow: a natural-system study. Water Resources Research, 56, e2019WR026318. <u>https://doi.org/10.1029/2019WR0</u>

2.1 Summary

The first aquifer-wide calculations of the clay-cation compositions in equilibrium with the present-day groundwater in a clay-rich coastal aquifer are provided and downgradient changes in Ca on the clay-exchange site identified three sequentialdowngradient zones, Updip (95-80% Ca), Transition (80-60% Ca), and Downdip (60-40% Ca). These zones form a cation-exchange front which extends from a meteoric-water plume, with clays near equilibrium with the fresh-recharge water (Updip Zone), to clays that are increasingly equilibrated with seawater downgradient (Transition and Downdip Zone). The sediments progress from predominantly fluvial clays in the Updip Zone, to shallow-marine clays downdip. Updip-Zone clays are Na poor, with cation exchange downdip progressively dominated by more Ca in the water exchanging for Mg on the clays. In the Transitional and Downdip Zones which have Na on the clays from the original seawater equilibrium, Ca, and further downdip Mg, in the water exchange for Na on the clays. Perturbations in these trends were compared to elements in the groundwater not involved in ion exchange to identify areas of upwelling and halite dissolution. Massbalance calculations show that the effect of cation exchange on each pore volume of fluid

that flows in the aquifer is large, whereas the effect on the clay composition is small, so the changes in the clay exchange composition can be used to identify the aquifer's past chemical evolution and historical-flow paths. This understanding coupled with tracers of modern flow (such as Cl), can be used to recognize areas of modern perturbations, such as contamination or salt dissolution.

2.2 Introduction

Cation concentrations are traditionally thought to have limited use as tracers of groundwater flow and mixing because they are involved in numerous mineral and cationexchange reactions too complex to quantify. However, a study of cation-exchange in a freshening clay-rich coastal aquifer, where the only reactant phases are montmorillonite and minor calcite, shows that cation proportions on the clay-exchange site, and the water in cation-equilibrium with these clays, provide a record of paleo-groundwater flow. These data combined with groundwater tracers controlled only by present-day flow (such as Cl) can be used to recognize areas of flow perturbations and modern contamination.

In the study of cation exchange in aquifers, the exchange of calcium (Ca) in recharging-meteoric water, for sodium (Na) on clays in clastic aquifers is well established (Foster, 1942; Back, 1966; Kreitler et al., 1977; Chapelle, 1983; Whittemore, 1995; Stumm and Morgan, 1996; Drever, 1997; Appelo and Postma, 2005). There are numerous numerical simulations of the progressive changes in groundwater chemistry as a consequence of cation exchange (e.g. Grove and Wood, 1979; Valocchi et al., 1981a and b; Dance and Reardon, 1983; Schulz and Reardon, 1983; Miller and Benson,

1983; Cederberg et al., 1985; Charbeneau, 1988; Wilkinson et al., 1992; Bjerg et al., 1993; Bjerg and Christensen, 1993; Appelo, 1994a; Engesgaard and Traberg, 1996; van Breukelen et al., 1998; Martinez and Bocanegra, 2002; and Eeman et al., 2017). However, these studies often include a limited number of reactions, with most studies limited to Na-Ca exchange, and only two employing a full chemical-speciation model, Appelo (1994a) and Eeman et al. (2017). In addition, none of these studies include calculation of the cation-exchange front that develops within the clay-exchange complex and its contribution to downgradient changes in the groundwater composition.

Because of the complexity of cation exchange and limited modeling, the development of an exchange front in the groundwater chemistry is poorly understood. Even less is known of the coupled development of the exchange front within the clay matrix. This is despite the importance of cation exchange on the evolution of groundwater chemistry in space and time, and the usefulness of this information in predicting and tracing groundwater flow and mixing (e.g. Appelo and Postma, 2005). With a poor understanding of the effects of exchange on the groundwater's cation composition, cation concentrations are seldom used alone as tracers for groundwater flow or mixing, but in combination with more conservative tracers (e.g. Richter and Kreitler, 1993; Kehew, 2001; Appelo and Postma, 2005) or they are used as reactive tracers (e.g. Reimus et al., 2018).



Figure 2.1 Aquifer map of the study area (after Texas Water Science Center, 2014) showing the locations of well-water analyses used in this study, pre-pumping steady-state hydraulic head contours (after Dutton, 1994), and salt domes present in the Chicot/Evangeline aquifers (Beckman and Williamson (1990).

Because of the complexity of cation exchange and limited modeling, the development of an exchange front in the groundwater chemistry is poorly understood. Even less is known of the coupled development of the exchange front within the clay matrix. This is despite the importance of cation exchange on the evolution of groundwater chemistry in space and time, and the usefulness of this information in predicting and tracing groundwater flow and mixing (e.g. Appelo and Postma, 2005). With a poor understanding of the effects of exchange on the groundwater's cation composition, cation concentrations are seldom used alone as tracers for groundwater flow or mixing, but in combination with more conservative tracers (e.g. Richter and Kreitler, 1993; Kehew, 2001; Appelo and Postma, 2005) or they are used as reactive tracers (e.g. Reimus et al., 2018).

To better understand the contributions of cation exchange on the evolution of groundwater chemistry, this study provides the first aquifer-wide calculations of the cation composition of the clay-exchange site in equilibrium with the present-day groundwater. To provide information on cation exchange without the involvement of other mineral reactions, the aquifer chosen for this study is a clastic aquifer with a simple primary mineralogy (clay minerals and trace calcite as the only primary reactant phases) and with a relatively uniform hydrology of downgradient flow of meteoric-recharge water. In these exchange calculations, in addition to the more commonly considered sodium (Na) and calcium (Ca) exchange the contributions of magnesium (Mg), potassium (K), and strontium (Sr) exchange were also considered. Furthermore, attention is given to the shift in the importance of Mg versus Ca exchange downgradient, which is commonly neglected in previous studies. These results provide an understanding of the coupled development and migration of the cation-exchange fronts in both the groundwater and in the clay matrix, and how this information can be used to trace fluid flow and identify areas of contamination.

2.3 Study Area

The chemical composition of well-water samples used for this study were collected from the Chicot and Evangeline aquifers from the Texas Gulf Coast, located approximately 70 to 155 km southwest of Houston, Texas (Figures 2.1 and 2.2). The samples were collected from a 140 km wide transect extending from the inland outcrops of the Chicot and Evangeline aquifers to the coastline (Figure 2.1). The Chicot and Evangeline aquifers are sand aquifers that form the upper-most units of the Gulf Coast Aquifer System, a coastward thickening wedge of sand/clay units which dips toward to the coastline (Sellards et al., 1932; Baker, 1995; Chowdhury and Turco, 2006) (Figure 2.2). In the study area, both aquifers range in thickness from approximately 150 m upgradient to 300 m downgradient at the coastline (Figure 2.2). There are no clear differences in the sedimentary features or in the composition of the sediments that separate the Chicot aquifer from the underlying Evangeline aquifer in the study area (Kreitler et al., 1977; Ryder, 1988; Dutton, 1994; Knox et al., 2006), so they are treated together in this study as the "Chicot/Evangeline aquifers". The Chicot/Evangeline aquifers are underlain by the clay-rich Burkeville-confining layer (Figure 2.2). Inland, the Chicot and Evangeline aquifers are unconfined where they outcrop, becoming confined downdip toward



Figure 2.2 Geologic-cross section of the study area (after Baker, 1979, 1995) showing the transition from fluvial to shallow marine sediments, hydraulic head contours (after Dutton, 1994) and depths of water analyses used in this study. Well and cross-section locations are given in Figure 2.1.

the coast where they are overlain by the Beaumont Formation, a clay-rich confining layer (Figures 2.1 and 2.2). The Chicot/Evangeline aquifers contain abundant clay layers interbedded with the sands. These layers are generally thin (less than 6 m thick) but can be up to 15 m thick (Gabrysch and Bonnet, 1975; Gabrysch, 1984), with the percentage of clay increasing downgradient from a minimum of about 20% to up to 75% at the coastline (Kreitler et al., 1977; Ryder, 1988; Dutton, 1994; Knox et al., 2006).

Fluid flow in the Chicot/Evangeline aquifers is generally lateral flow down gradient and perpendicular to the coastline (Figures 2.1 and 2.2), although pumping in the last forty years has resulted in some drawdown in the southwest portion of the study area (Dutton, 1994). The aquifers are saturated almost to the surface, with artesian conditions prior to recent drawdown. Interconnection of the sands allows unhindered lateral flow in the aquifers, but the numerous clay beds locally hinder vertical flow (Gabrysch and Bonnet, 1975; Gabrysch, 1984, pg. 254; Gabrysch and Coplin, 1998). Recharge is predominantly meteoric water infiltration in the inland outcrop areas, with natural discharge as diffuse-upward flow toward the coast where the aquifers are confined by the Beaumont Formation (Dutton, 1994; Kasmareck and Robinson, 2004).

Although there are irregularities in the groundwater chemistry of the Chicot aquifer downdip in the study area, it generally progresses from dilute (less than 500 mg/L dissolved solids) calcium bicarbonate type water updip, to more concentrated (500-750 mg/L dissolved solids) calcium-sodium bicarbonate to sodium bicarbonate water downdip and finally to saline (750-1250 mg/L dissolved solids) sodium-chloride type water at the coastline (e.g. Dutton, 1994). This trend persists vertically except near the

base of the Beaumont formation, where the aquifer water progresses more rapidly to the more saline sodium-chloride type water. As there is some uncertainty where the base of the Beaumont formation occurs, it is also possible this more saline water is from the Beaumont formation. To avoid this water that might be affected by infiltration of Beaumont water into the aquifer or from the Beaumont formation, samples for this study are only selected from a depth of greater than 61 m.

Sediments of the Chicot/Evangeline aquifers were deposited in a transitional coastal fluvial environment updip grading to a shallow marine environment downdip and are characterized by cyclic deposition of fine sand and clays during the transgressiveregressive events of the Cenozoic (Sellards et al., 1932; Knox et al., 2006). The location of the transition from predominantly fluvial floodplain and meander-belt deposits to predominantly shallow marine deposits downdip within the Chicot aquifer is shown in Figure 2.2 (Knox et al, 2006). The sands of the Chicot/Evangeline aquifers in the study area are predominantly fine to medium grained composed of quartz with few to trace feldspars and little to no calcite cement (Sellards et al., 1932). The clay beds in the area are predominantly composed of montmorillonite, with smaller amounts of illite and kaolinite (Gabrysch and Bonnet, 1975; Gabrysch, 1984; Gabrysch and Coplin, 1998). Although small amounts of chlorite were described by some (Gabrysch and Bonnet, 1975; Gabrysch, 1984; Gabrysch and Coplin, 1998), a more detailed study of shallow samples to a depth of 1,000 m by Burton et al. (1987) found no chlorite. Growth faults occur in the study area parallel to the coastline but are not offset enough to affect the regionalgroundwater flow (Hosman and Weiss, 1991; Chowdhury and Turco, 2006).

Several salt domes occur within the study area, but only one contains halite at a location and depth that might affect the water samples in this study, the Hawkinsville Dome (Figure 2.1). With halite up to a depth of 137m (Beckman and Williamson, 1990), it has halite at depths comparable and up the hydrologic gradient from water samples used in this study. The Gulf Dome is present within the Chicot aquifer but is down the hydrologic gradient from samples used in this study. The Boling Dome has salt at depths below the Chicot aquifer, but sulfur- and carbonate-rich caprock occurs within the Chicot aquifer. The Markham, Clemens and Allen Domes are only present in the underlying Evangeline aquifer and are located down the hydrologic gradient from all the Evangeline aquifer water samples used in this study.

2.4 Methodology

Chemical analyses of well-water samples used for this study were obtained from the Texas Water Development Board's (2018) groundwater database. The samples used were chosen along a downgradient section of the Chicot/Evangeline aquifers extending from the aquifer outcrop to the coastline outside of the area affected by groundwater pumping for the city of Houston (Figure 2.1). In addition, samples were not used from areas cut by incised-valley fill or adjacent to present day rivers to avoid the possibility of local recharge at these locations. Water samples collected from a depth of less than 61 m were omitted to exclude samples only recently recharged or, as discussed above, water that might be affected by infiltration of water from the overlying Beaumont Formation. Samples from the Chicot aquifer based on the drillers log, but incorrectly labeled as from the Beaumont Formation were identified and included in the data set. An aqueous-species distribution using PHREEQC and the LLNL database (Parkhurst and Appelo, 1999) was performed on each analysis to determine the charge-balance error, ion activities in solution, and mineral-saturation indices. Only analyses with pH and all major anions and cations that have a charge-balance error of less than 2% were used in this study. The remaining 103 water analyses were then used to calculate the cation-exchange composition of equilibrated montmorillonite. The Chicot aquifer analyses are given in Table 2.1. The Evangeline aquifer analyses are in Capuano and Jones (2020). Sample temperatures range from 20 to 25°C.

2.4.1 Calculation of the clay-exchange composition

The sum of the mole fractions (X_i) of Ca, Mg, Na, K, and Sr on the montmorillonite $(X_i)_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 \cdot nH_2O$ exchange complex (X_i),

 $X_{Ca} = m_{Ca}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{Mg} = m_{Mg}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{Na} = m_{Na}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{K} = m_{K}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ and $X_{Sr} = m_{Sr}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$

is equal to one,

 $X_{Ca} + X_{Mg} + X_{Na} + X_K + X_{Sr} = 1. \quad Eq. 1$

Table 2.1 Chicot aquifer water chemistry from the Texas Water Development Board (2018) and mole percent, X_i , of the designated element on the clay exchange site calculated in this study.

| | Dist. | Depth | HCO ₃ | Ca | Cl | K | Mg | Na | SO ₄ | X _{Ca} | X _{Na} | X _{Mg} | XK |
|---------|--------------|-------|------------------|------|------|------|------|-------|-----------------|-----------------|-----------------|-----------------|-----|
| Well | km | feet | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | % | % | % | % |
| 6637203 | 36.1 | 419 | 195 | 92 | 155 | 2 | 7 | 60 | 21 | 90.4 | 2.1 | 7.3 | 0.2 |
| 6636604 | 37.5 | 403 | 281 | 110 | 160 | 1.1 | 8.5 | 76 | 17 | 90.2 | 2.4 | 7.3 | 0.1 |
| 6631203 | 37.8 | 447 | 128 | 48 | 42 | 0.9 | 2.4 | 18 | 5 | 94.0 | 0.9 | 5.0 | 0.1 |
| 6637703 | 43.1 | 360 | 228 | 168 | 356 | 1 | 16 | 124 | 56 | 88.0 | 3.2 | 8.7 | 0.1 |
| 6631905 | 48.9 | 397 | 165 | 61 | 57 | 1 | 5.7 | 25 | 9.1 | 89.9 | 1.1 | 8.9 | 0.1 |
| 6645601 | 54.1 | 429 | 239 | 108 | 206 | 1 | 12 | 96 | 31 | 87.5 | 1.4 | 10.8 | 0.2 |
| 6640105 | 54.1 | 560 | 218 | 73 | 74 | 2.1 | 8.6 | 37 | 13 | 86.8 | 3.1 | 10.1 | 0.1 |
| 6646814 | 65.6 | 335 | 329 | 84 | 64 | 2.4 | 9.7 | 55 | 9.2 | 87.1 | 2.0 | 10.6 | 0.3 |
| 6652902 | 65.8 | 230 | 275 | 85 | 61 | 1.4 | 5 | 42 | 13 | 92.6 | 1.6 | 5.7 | 0.2 |
| 6660201 | 66.8 | 671 | 217 | 52 | 40 | 1 | 6.2 | 40 | 14 | 87.0 | 1.9 | 11.0 | 0.1 |
| 6640904 | 68.7 | 212 | 289 | 88 | 110 | 2.8 | 14 | 52 | 13 | 83.9 | 1.8 | 14.0 | 0.3 |
| 6655112 | 72.0 | 482 | 324 | 140 | 220 | 2.8 | 11 | 48 | 72 | 80.8 | 1.7 | 12.2 | 0.3 |
| 6654509 | 74.0 | 222 | 290 | 140 | 230 | 2.4 | 15 | 62 | 7.2 | 00.0 | 2.5 | 0.7 | 0.5 |
| 6541602 | 74.2 85.7 | 255 | 206 | 75 | *0 | 2.5 | 14 | 72 | 10 | 76.2 | 2.5 | 20.1 | 0.5 |
| 6541807 | 86.3 | 612 | 243 | 40.9 | 31.2 | 2.24 | 11.7 | 47.5 | 19.6 | 74.9 | 2.3 | 22.5 | 0.2 |
| 6662711 | 87.4 | 792 | 404 | 75 | 96 | 3.5 | 24 | 84 | 22 | 72.4 | 2.9 | 24.3 | 0.4 |
| 6541925 | 89.3 | 450 | 294 | 79 | 350 | 2 | 19 | 222 | 29 | 73.6 | 7.6 | 18.6 | 0.2 |
| 6541933 | 90.4 | 580 | 283 | 30.6 | 102 | 1.55 | 7.72 | 123 | 13.6 | 73.4 | 6.8 | 19.5 | 0.3 |
| 6664102 | 90.7 | 314 | 364 | 93 | 190 | 3.3 | 22 | 130 | 41 | 76.6 | 4.2 | 18.9 | 0.3 |
| 6542701 | 91.5 | 869 | 326 | 28 | 166 | 1.6 | 7.3 | 190 | 14 | 69.6 | 10.8 | 19.3 | 0.3 |
| 6550101 | 94.2 | 820 | 326 | 46 | 700 | 1.9 | 13 | 500 | 11 | 61.1 | 20.5 | 18.2 | 0.2 |
| 6550102 | 94.2 | 822 | 334 | 68 | 725 | 2.2 | 19 | 483 | 12 | 64.1 | 16.7 | 18.9 | 0.2 |
| 8006407 | 97.3 | 925 | 319 | 42 | 172 | 3.5 | 17 | 159 | 17 | 65.0 | 7.0 | 27.6 | 0.5 |
| 6549703 | 97.5 | 627 | 312 | 63 | 64 | 2 | 18 | 55 | 16 | 75.0 | 2.1 | 22.6 | 0.2 |
| 8007402 | 101.0 | 960 | 270 | 22 | 76 | 2 | 10 | 112 | 17 | 62.6 | 6.8 | 30.2 | 0.4 |
| 8007314 | 102.7 | 292 | 338 | 20.6 | 98.9 | 1.42 | 8.27 | 150 | 1 | 63.3 | 9.4 | 27.0 | 0.3 |
| 8014101 | 103.2 | 650 | 324 | 48 | 66 | 2.3 | 18 | 80 | 18 | 69.1 | 3.4 | 27.2 | 0.3 |
| 6550605 | 104.0 | 354 | 350 | 78 | 520 | 2.4 | 33 | 317 | 20 | 62.2 | 10.0 | 27.6 | 0.2 |
| 6550601 | 104.1 | 875 | 386 | 27 | 515 | 2.3 | 8.7 | 430 | 0.2 | 57.6 | 22.4 | 19.7 | 0.4 |
| 6550807 | 105.7 | 208 | 478 | 124 | 205 | 2.3 | 31 | 131 | 53 | 76.2 | 3.7 | 19.9 | 0.2 |
| 6550805 | 107.3 | 238 | 350 | 64 | 171 | 2.4 | 26 | 127 | 24 | 66.6 | 4.6 | 28.5 | 0.3 |
| 8008504 | 108.7 | 690 | 292 | 27.9 | 38.5 | 1.73 | 11 | 87 | 16.6 | 67.2 | 4.8 | 27.8 | 0.3 |
| 6559202 | 109.5 | 300 | 206 | 30.3 | 429 | 2.2 | 9.95 | 250 | 20.4 | 62.2 | 9.5 | 21.5 | 0.2 |
| 8101102 | 111.4 | 1022 | 261 | 20 | 420 | 2.2 | 12 | 339 | 3.0 | 70.7 | 10.5 | 20.9 | 0.3 |
| 8014607 | 112.7 | 550 | 319 | 38 | 51 | 25 | 11 | 97 | 18 | 72.7 | 4.0 | 274.2 | 0.3 |
| 6557902 | 113.0 | 450 | 259 | 29 | 156 | 2.6 | 86 | 154 | 0 | 60.3 | 8.5 | 21.8 | 0.4 |
| 8101405 | 114.4 | 1051 | 268 | 17 | 29.5 | 1.7 | 9 | 93.82 | 21 | 60.0 | 6.3 | 33.3 | 0.3 |
| 8101402 | 116.8 | 443 | 314 | 22 | 49 | 2 | 7.5 | 121 | 18 | 67.6 | 7.6 | 24.4 | 0.4 |
| 8015701 | 118.1 | 850 | 375 | 47 | 148 | 2 | 12 | 172 | 21 | 72.5 | 7.7 | 19.5 | 0.3 |
| 8015702 | 119.9 | 671 | 342 | 12.2 | 78 | 2 | 5.7 | 163 | 17 | 58.0 | 12.8 | 28.7 | 0.5 |
| 8016305 | 120.8 | 829 | 300 | 8.2 | 120 | 1.05 | 2.97 | 182 | 9.82 | 59.5 | 17.4 | 22.7 | 0.3 |
| 8016301 | 120.9 | 823 | 305 | 11.2 | 86 | 1 | 4 | 150 | 11 | 63.0 | 12.8 | 23.9 | 0.3 |
| 8022302 | 121.2 | 649 | 322 | 10 | 52.5 | 0.8 | 3 | 154 | 24 | 64.1 | 14.6 | 21.1 | 0.2 |
| 6559602 | 121.7 | 615 | 364 | 27 | 415 | 1.4 | 7.8 | 356 | 0.4 | 61.8 | 19.1 | 18.8 | 0.2 |
| 8023102 | 124.0 | 637 | 339 | 6.27 | 71.4 | 1.53 | 2.55 | 164 | 14.6 | 56.8 | 17.9 | 24.7 | 0.5 |
| 8103203 | 126.1 | 500 | 308 | 18 | 280 | 1.6 | 5.7 | 266 | 3.6 | 61.7 | 17.4 | 20.6 | 0.3 |
| 8103204 | 127.1 | 585 | 265 | 27.2 | 437 | 2.33 | 10.5 | 327 | 6.5 | 58.7 | 17.0 | 23.9 | 0.4 |
| 8023302 | 128.2 | 331 | 331 | 11.6 | 52 | 2 | 5.1 | 145 | 11 | 58.9 | 12.1 | 28.5 | 0.5 |
| 8104201 | 133.0 | 525 | 332 | 22 | 430 | 3 | 9.1 | 355 | 0.4 | 55.2 | 20.1 | 24.3 | 0.5 |
| 8109802 | 134.1 | 828 | 545 | 5.2 | 253 | 2 | 1.1 | 367 | 4 | 47.4 | 41.0 | 11.0 | 0.7 |
| 8109908 | 134.3 | 450 | 517 | 4.8 | 65 | 2 | 3.5 | 221 | 4 | 41.7 | 24.2 | 33.4 | 0.7 |
| 8110203 | 134.4 | 268 | 400 | 11.6 | 182 | 4 | 2.2 | 158 | 2 | 12.4 | 3.8 | 21.3 | 0.4 |
| 8024701 | 134.4 | 451 | 200 | 10.6 | 422 | 2 | 5.2 | 1994 | | 47.2 | 37.8 | 21.2 | 0.5 |
| 8117201 | 137.1 | 300 | 599 | 10.6 | 124 | 2 | 5.8 | 312 | 4 | 30.3 | 14.7 | 31.3 | 0.5 |
| 8104514 | 137.5 | 600 | 365 | 18 | 511 | 2.83 | 8.82 | 418 | 1 | 49.3 | 23.5 | 25.6 | 0.7 |

Table 2.1 cont.

| | Dist. | Depth | HCO ₃ | Ca | Cl | K | Mg | Na | SO ₄ | X _{Ca} | X _{Na} | X _{Mg} | X _K |
|---------------|-------------|-------------|------------------|---------------|---------------|----------|------|------|-----------------|-----------------|-----------------|-----------------|----------------|
| Well | km | feet | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | % | % | % | % |
| 8104805 | 140.6 | 578 | 375 | 13.8 | 325 | 2.96 | 7.07 | 317 | 1 | 50.4 | 21.6 | 27.4 | 0.6 |
| 8104907 | 143.0 | 576 | 505 | 26.3 | 156 | 1.53 | 17.9 | 228 | 1 | 51.4 | 11.4 | 37.0 | 0.2 |
| 8104906 | 145.5 | 520 | 692 | 22 | 515 | 3.6 | 13 | 544 | 2.4 | 43.9 | 27.9 | 27.7 | 0.5 |
| 8112101 | 146.4 | 470 | 423 | 18 | 454 | 4 | 9 | 421 | 4 | 48.9 | 24.7 | 25.8 | 0.7 |
| 8105705 | 146.6 | 455 | 615 | 18 | 507 | 5.4 | 11 | 530 | 7 | 42.5 | 29.2 | 27.4 | 0.9 |
| 8112402 | 147.5 | 473 | 520 | 18 | 405 | 4 | 11 | 407 | 6 | 46.2 | 23.3 | 29.8 | 0.7 |
| 8112502 | 149.3 | 567 | 520 | 21 | 925 | 6 | 12 | 749 | 21 | 39.0 | 36.6 | 23.5 | 0.9 |
| 8105801 | 150.9 | 618 | 670 | 18 | 560 | 5.2 | 13 | 565 | 0.8 | 39.1 | 30.0 | 30.0 | 0.8 |
| Note. The dis | stance is d | owngradient | from the bas | se of the Chi | cot aquifer o | outcrop. | | | | | | | |

The mole fraction of each cation on a montmorillonite exchange complex in equilibrium with a water sample was calculated following the Gaines-Thomas convention with the following equations, derived using procedures described in Stumm and Morgan (1996) and Appelo and Postma (2005),

$$X_{Ca} = X_{Na}^{2} \cdot \frac{M_{Ca}^{2+}}{K_{Na/Ca}^{2} \cdot M_{Na^{+}}^{2}}$$
, Eq. 2

$$X_{Mg} = X_{Na}^{2} \cdot \frac{M_{Mg}^{2+}}{K_{Na/Mg}^{2} \cdot M_{Na^{+}}^{2}}$$
, Eq. 3

$$X_{K}=X_{Na} \cdot \frac{M_{K^{+}}}{K_{Na/K} \cdot M_{Na^{+}}}$$
, and Eq. 4

$$X_{Sr} = X_{Na}^2 \cdot \frac{M_{Sr^{2+}}}{K_{Na/Sr}^2 \cdot M_{Na^+}^2}$$
, Eq. 5

where, M_{Mg2+} , M_{Ca2+} , M_{Na+} , M_{K+} , and M_{Sr2+} are the mole/L concentrations of the ions in the water calculated using PHREEQC with the LLNL database (Parkhurst and Appelo, 1999), and $K_{Na/Ca}$, $K_{Na/Mg}$, $K_{Na/K}$, and $K_{Na/Sr}$ are the exchange constants (ion-exchange coefficients) for the exchange reactions:

Na⁺ + ¹/₂ [Ca²⁺R₂^{2⁻}] ↔ ¹/₂Ca²⁺ + [Na⁺ R], Na⁺ + ¹/₂ [Mg²⁺R₂^{2⁻}] ↔ ¹/₂Mg²⁺ + [Na⁺ R], Na⁺ + [K⁺ R⁻] ↔ K⁺ + [Na⁺ R], and Na⁺ + ¹/₂ [Sr²⁺R₂^{2⁻}] ↔ ¹/₂Sr²⁺ + [Na⁺ R], respectively, where R is the negatively charged network of the cation exchanger. X_{Na} is then solved for by combining Equations 1 through 5 to give:

$$X_{Na}^{2} \left(\frac{M_{Mg^{2+}}}{K_{Na/Mg}^{2} \cdot M_{Na^{+}}^{2}} + \frac{M_{Ca^{2+}}}{K_{Na/Ca}^{2} \cdot M_{Na^{+}}^{2}} + \frac{M_{Sr^{2+}}}{K_{Na/Sr}^{2} \cdot M_{Na^{+}}^{2}} \right) + X_{Na} \left(\frac{M_{K^{+}}}{K_{Na/K} \cdot M_{Na^{+}}} + 1 \right) - 1 = 0$$
 Eq. 6

which is solved as a quadratic equation, and then X_{Ca} , X_{Mg} , X_K and X_{Sr} are back calculated using equations 2, 3, 4 and 5.

Ion concentrations (M_i) are used rather than ion activities to solve Equations 2 through 5, because there is no similar activity-coefficient correction for the ions on the clay-exchange complex. Using an activity correction for ions in solution, but not for ions on the clay-exchange complex, was found to result in errors (Stumm and Morgan, 1996; Appelo and Postma, 2005). It was found more reliable to calculate the fractions of cations on the clay-exchange complex using ion concentrations in solution, rather than using ion activities, and proposed that this is the case because the activity corrections for both the ions in the water and the ions on the clay-exchange complex are similar, (e.g. Appelo, 1994b; Stumm and Morgan, 1996; Appelo and Postma, 2005).

The clay-exchange constants used in this study to solve Equations 2 through 5 are $K_{Na/Ca} = 0.4$, $K_{Na/Mg} = 0.5$, $K_{Na/K} = 0.2$, and $K_{Na/Sr} = 0.35$ taken from Appelo and Postma (2005, Table 6.4, after a compilation by Bruggenwert and Kamphorst, 1979). Although Appelo and Postma (2005) do not list the clay mineral, these constants represent the exchange of montmorillonite/illite. Bruggenwert and Kamphorst (1979) note that their compilation

includes predominantly data for montmorillonite clays as most exchange studies in the literature are of montmorillonite because of its relatively large exchange capacity. Further, the exchange constants for montmorillonite and illite are the same for water within the ionic-strength range of the groundwater considered in this study (0.001 to 0.01) (Bruggenwert and Kamphorst, 1979). Kaolinite exchange is not important in considering cation exchange in this study because its cation-exchange capacity (<0.05 mole/kg) is so low compared to that of montmorillonite (0.7 to 1.7 mole/kg) and illite (0.2 mole/kg) (Sposito, 2008). Based on the dominance of montmorillonite and illite exchange capacities can be applied to either montmorillonite and illite, the results of the exchange calculations in the following text are referred to as calculations for montmorillonite or clay exchange.

The exchange constants used in these calculations were generally measured for systems with typical groundwater pH's ranging from near neutral to slightly basic (Bruggenwert and Kamphorst, 1979). Solutions with a very acidic pH can alter the cation-exchange constants away from those measured in a groundwater setting (Stumm and Morgan, 1996). The pH of the Chicot/Evangeline aquifer groundwater in this study ranges from 7 to 8.5, so pH is not a factor in the calculated-downgradient changes in the compositions of the clay cation-exchange complexes.

No other cations besides Ca, Mg, Na, K, and Sr were considered in the clay-exchange calculations because none are present in the groundwater in concentrations greater than 1 mg/L.

Divalent cations (Ca and Mg) are favored on the clays over the monovalent-cation, Na. Of the divalent cations, Ca is favored on the clays over Mg (Appelo, 1994a; Stumm and Morgan, 1996; Appelo and Postma, 2005). Thus, when the monovalent cation, Na, is present in relatively low concentration in the clay compared to Mg, then Ca in the water will exchange for Mg on the clay in addition to Na. The preference of clays for divalent cations over monovalent cations is more pronounced when the water has low-ion concentrations (such as meteoric water) compared to when the water has high-ion concentrations (such as seawater) (Appelo, 1994a; Stumm and Morgan, 1996; Appelo and Postma, 2005). In this study, the groundwater has relatively low ion concentrations (total dissolved solids range from 200 mg/L to 2,000 mg/L) compared to seawater (35,000 mg/L), so this effect is small and not a factor controlling downgradient changes in the composition of the cation-exchange complex.

Cation-exchange between clays and water is rapid, occurring in less than 10 minutes (Nachod and Wood, 1945), so the pore water and clays will be in exchange equilibrium.

2.5 Results

The mole-percent Ca, Mg, and Na on the clay-exchange complex in equilibrium with the water samples are plotted in Figure 2.3a (Table 2.1 and Capuano and Jones, 2020). K (at less than 1mg/L in the groundwater) and Sr (at less than 0.5 mg/L in the groundwater) comprise less than 1% and 0.5%, respectively, of the cations on the clay-exchange site for all the samples, so they are not shown on Figure 2.3a and are not considered further. Ca, Mg and Na show clear trends with a general inverse-linear relationship between Ca and Na, and to a lesser extent between Ca and Mg (Figure 2.3a). The relationships between Ca, Mg and Na, however, are not entirely linear, with the changes in slope suggesting the presence of three cation-exchange groups based on the percentage of Ca on the clay-exchange complex (see Figure 2.3a, Table 2.2);

- 95 to 80% Ca,
- 80 to 60% Ca, and
- 60 to 40% Ca.

Although defined by percent Ca on the clay-exchange site, comparison with the downgradient distribution of the percent Ca on the clay exchange site plotted in cross section (Figure 2.4, Table 2.2) shows that these three cation-exchange groups represent three sequential-downgradient zones,



Figure 2.3 (a) Mole-percent Ca on the clay exchange complex versus mole-percent Ca, Mg, and Na on the clay-exchange complex in equilibrium with the water in the Chicot and Evangeline aquifers, (b) distance downgradient versus mole-percent Ca, Mg, and Na on the clay-exchange complex in equilibrium with the water in the Chicot aquifer. See text for the method of calculation. The ranges in composition of the cations on the clay-exchange complex for montmorillonite and montmorillonite/illite in equilibrium with seawater are from Sayles and Mangelsdorf (1979; Table 2).

Table 2.2 The Clay Cation-Exchange Zones in the Chicot Aquifer Based on the Calculated-Mole-Percent of Ca (XCa) on the Clay Cation-Exchange Complex in Equilibrium with the Aquifer Water in that Zone, with the Range in Mg (XMg), Na (XNa), and K (XK) on the Clay-Exchange Complex, the Dominant Exchange Process and the Dominant Clay-Cation Composition in the Zone.

| | X _{Ca} (%) | X _{Mg} (%) | X _{Na} (%) | X _K (%) | Dominant exchange | Clay-cation Composition |
|---------------------------|---------------------|---------------------|---------------------|----------------------|---|-------------------------|
| Cation-exchange zones | | | | | | |
| Updip Zone | 95-80 | 16-5 | 3-0.9 | 0.3-0.1 | Ca _{water} ⇔Mg _{clay} | Ca-mont. |
| Transition Zone | 80-60 | 33-16 | 20-2 | 0.2-0.5 | Ca _{water} ↔Na _{clav} Ca _{water} ↔Mg _{clav} | Ca,Mg-mont. |
| Downdip Zone ^b | 60–39 ^b | 37–23 ^b | 30–11 ^b | 0.3–0.9 ^b | Ca _{water} ↔Na _{clay} Mg _{water} ↔Na _{clay} | Ca,Mg,Na-mont. |
| Exchange composition | n of clay equil | ibrated with sea | water ^a | | | - |
| Mont. | 4–1 | 40-39 | 55-53 | 4 | - | Na,Mg-mont. |
| Mont./Illite | - | 32 | 56 | 7 | - | Na,Mg-mont. |
| Illite | 11 | 24 | 47 | 17 | - | Na,Mg-mont. |

Note. Also listed is the composition of the clay exchange complex in equilibrium with seawater. Mont. = montmorillonite. a From Sayles and Mangelsdorf (1979, their Table 7). Calculations in this study show XSr in seawater is less than 0.5%. b This range does not include samples affected by halite dissolution (samples 1 and 2 on Figure 2.5; see text).

Figure 2.4 Sample locations depicted in cross section by values for mole-percent Ca on the clay-exchange complex (calculated in this study using equations 2 through 6) and the respective cation-exchange zone of each sample specified by the color (blue = Updip Zone, green = Transition Zone, and red = Downdip Zone). Well and cross-section locations are given in Figure 2.1.

- Updip Zone (95-80% Ca),
- Transition Zone (80 to 60% Ca), and
- Downdip Zone (60 to 40% Ca),

that form a cation-exchange front. The location of the Updip Zone coincides with the zone of Fluvial Dominated sediments, whereas the Transitional and Downdip zones coincide with the zone of Shallow-Marine Dominated sediments.

Within the Chicot aquifer there is only one sample that does not fit into this downgradient pattern (Figure 2.4). In contrast, within the underlying Evangeline aquifer there are several exceptions to this downgradient pattern (Figure 2.4). The exceptions to this downgradient pattern in the Evangeline aquifer all occur along its base. These exceptions in the Evangeline aquifer are likely due to upwelling of water from the underlying clay-rich Burkeville-Confining layer, particularly in the updip portion of the Evangeline aquifer where it pinches-out stratigraphically. This pinch-out has likely disrupted meteoric-water recharge in that area which allowed upwelling from the underlying clay-rich Burkeville-Confining layer. Because of the likely influx of water from below and limited data available downgradient for the Evangeline aquifer, the following discussion of the relative controls on cation exchange downgradient in the cation-exchange zones as a result of meteoric water flushing is limited to the Chicot aquifer samples.


Figure 2.5 Ternary plot of the composition (mole %) of the clay-exchange complex in equilibrium with the Chicot aquifer water samples. Black circles represent clay-exchange compositions equilibrated with seawater measured by Sales and Mangelsdorf (1979) for montmorillonite (closed circles), montmorillonite/illite solid solution (half closed circle), and illite (open circle). Dotted lines show the clay-exchange pathways through cation exchange with the most upgradient groundwater sample and the corresponding seawater equilibrated clay. The clay-exchange composition in equilibrium with underlying saline formation water (calculated in this study using the brine composition for the study area from Capuano, 1990 and Hyeong & Capuano, 2001) is shown by the black triangle and in equilibrium with NaCl is shown by the black diamond.

Shifts in the downgradient composition of the clay-exchange complex in the Chicot aquifer samples are shown in Figure 2.3b and in the ternary diagram in Figure 2.5. On clay-exchange of these diagrams the compositions montmorillonite. montmorillonite/illite and illite in equilibrium with seawater (from Sayles and Mangelsdorf, 1979) are shown. The clay-exchange compositions are trending downgradient toward equilibrium with these seawater-equilibrated clays. Clays in the aquifer were deposited in a shallow-marine environment downdip, and thus it is anticipated they were originally equilibrated with seawater upon deposition. In addition, it is expected that seawater still resides in the aquifer downgradient (Dutton, 1994). So, clays in equilibrium with seawater could be taken as the extreme downgradient end member, or initial composition, of the clays at the start of meteoric water flushing.

Exchange pathways were calculated between the most updip sample of the fresh meteoric-dominated water in the aquifer (fresh-water endmember) and the montmorillonite and illite exchange compositions in equilibrium with seawater. These exchange pathways are drawn as dashed lines on Figure 2.5. They were calculated assuming the incremental exchange of the seawater-equilibrated clay with the fresh-water endmember until achieving the clay composition in equilibrium with the fresh-water end member. These exchange pathways, with few exceptions, mark the upper and lower limits of the exchange composition of the clays in the Chicot aquifer, supporting that this clay exchange process is controlling the clay compositions.

There is a spread in the clay-exchange compositions downgradient. This could be in part a result of compositional differences in the clays downgradient, as the clayexchange compositions of montmorillonite and illite in equilibrium with seawater are different for each mineral. It is noted that the difference in clay-exchange compositions in equilibrium with seawater, which has a high-ionic strength, is in contrast to the discussion above in which the clay-exchange compositions of montmorillonite and illite in equilibrium with low-ionic strength solutions (within the range found in the study area) are the same because their exchange constants are the same. The spread might also be due to changes in the interstitial seawater composition downgradient. It is known that seawater changes composition somewhat within the first few meters of infiltration into the ocean sediments, with a small decrease in Mg, increase in Ca, and no change in Na (Charpentier et al., 2011). Thus, it is possible a shift in the composition of the trapped seawater in buried oceanic sediments, could result in a shift to lower Mg and higher Ca on the exchange site of the original marine clays. Despite these uncertainties, the downgradient-compositional trends in the clay cation-exchange complex are, as expected, generally toward the cation-exchange composition of montmorillonite/illite in equilibrium with seawater (Figures 2.3 and 2.5).

Deviations of samples below the exchange pathways drawn on Figure 2.5, could be caused by mixing of the groundwater with brine possibly from oil-well leakage, vertical migration of saline water from deeper formation along fractures associated with salt domes or growth faults (e.g. Ranganathan and Hanor, 1989; Wendeborn and Hanor, 2013), or possibly exposure of the water to halite (NaCl) dissolution. Brine from oil-well leakage or from underlying formations in this area in all cases have Na concentrations an order of magnitude greater than Mg (e.g. Capuano, 1990; Hyeong and Capuano, 2001) and thus would increase the concentration of Na relative to Mg in the water. Halite dissolution will add Na ions but no Mg ions, so it to would increase the concentration of Na relative to Mg in the water. Both these processes will result in a higher Na/Mg ratio in the water compared to other water in the aquifer unaffected by these processes. The higher Na relative to Mg in the water will reduce the amount of Na relative to Mg in the equilibrated clay-exchange complex and bring the equilibrated clay-exchange composition below the montmorillonite exchange line toward that of water in equilibrium with the oil-field brine or halite. This is shown by an arrow labeled as such on Figure 2.5.

Because of the presence of salt domes in the study area, it is possible that halite dissolution could have affected the groundwater in the aquifer. There is evidence in the data on clay exchange-compositions that two samples were affected by halite dissolution, samples labeled 1 and 2 on Figure 2.5. Both these samples have very high Na/Mg ratios much higher than those of all other samples in the aquifer (Figure 2.6d). These samples are not adjacent to a known salt dome, but there is no certainty all salt deposits in the region have been identified. The clay exchange compositions of these samples also show evidence of the contribution from halite dissolution. On Figures 2.3 and 2.5 (also labeled as samples 1 and 2 on these figures) both these samples are offset from the trends shown by the samples affected only by meteoric water flushing. This can be used as an example of how clay-exchange compositions can be used to aid in identifying local processes, such as salt dome dissolution, that might affect the groundwater composition.

The three exchange zones are shown by different colors on Figure 2.5, with their downdip trends revealing information on exchange in the aquifer. The spread of clayexchange compositions downdip in the samples closest to equilibrium with the original seawater equilibrated clays, narrows updip as the exchange complex approaches equilibrium with the fresh meteoric-sourced groundwater. The point of convergence is at the transition from the sediments with predominantly fluvial deposited clays in the Updip Zone to predominantly shallow-marine deposited clays in the Transition and Downdip zones (Figure 2.4). In the Updip Zone the fluvial-sourced clays deposited in equilibrium with meteoric derived surface or soil water originally would have contained little Na, relative to Ca and Mg. The present-day clays in this Updip zone contain little Na (<3%), and Na shows no uniform change with distance downdip in the aquifer (Figure 2.3b); both of these observations support that the clays originally contained little Na and that currently Na exchange from the clays to the recharging meteoric water is not an important process in the Updip zone. In contrast, Ca increases updip at the expense of Mg producing a linear trend toward 100% Ca on the clay-exchange site.



Figure 2.6 (a) Concentration of Na, (b) Ca/Mg molar ratios, and (c) concentrations of Ca and Mg in the Chicot aquifer groundwater versus distance downgradient. (d) Mole percent Ca on clay-exchange complex versus Na/Mg molar ratio in the groundwater from the Chicot aquifer. Samples affected by halite dissolution are specified.



Figure 2.7 Downgradient changes in (a) pH, (b) HCO3, (c) calcite saturation index, and (d) Cl in the Chicot aquifer groundwater.

In the Transition and Downdip Zones the shallow marine-sourced montmorillonite deposited from seawater originally contained predominantly Na (55-53%), followed by Mg (39-40%), with little Ca (1-4%) (Table 2.2). The present-day clays in these zones trend downdip toward the cation composition in equilibrium with seawater (Figure 2.5). In the Transition Zone, Na exchange from the clays for Ca in the groundwater dominates, whereas Mg either exchanges from the groundwater for Na on the clay, or exchanges from the clay for Ca in the groundwater. In the Downdip Zone, Na and Mg on the clays are exchanging for Ca in the groundwater. Clays in the samples farthest updip in the Transition and Downdip zones have had the most Na, and to a lesser extent Mg, flushed from them by the infiltrating meteoric water, with less and less Na and Mg loss downgradient approaching the original seawater equilibrated values.

After deposition, the updip portion of the Chicot aquifer continued to be exposed to meteoric-water recharge, and eventual lowering of sea level to its present position (Knox et al., 2006) then allowed meteoric water to flush seawater from the marinederived sediments of the Transition and Downdip zones. Subsequently, water in the Downdip zone is predominantly meteoric water but marks the start of downdip seawater mixing. Estimation of seawater mixing based on elevated Cl concentrations (up to 925 mg/L) above that of present day meteoric-sourced groundwater (42 mg/L) (Figure 2.7d) (Richter and Kreitler, 1993; Appelo and Postma, 2005), suggests there is a maximum of 2 to 5% seawater mixed with meteoric water in the Downdip Zone. Thus, the Downdip zone represents where the meteoric water plume begins to mix with the seawater present in the aquifer downgradient.

2.6 Discussion

As the meteoric water infiltrates into the aquifer, the Ca in the meteoric water exchanges for Na and Mg in the originally deposited montmorillonite, producing the downgradient sequence of clay compositions found in today's sediments. A source of Ca in the infiltrating meteoric water is the dissolution of carbonate dust in the air and in the soil zone, which is credited as a major source of Ca in soils and soil water (e.g. McFadden, 2013). Ca is also likely added to the infiltrating meteoric water from the dissolution of the trace calcite in the aquifer. If the sediment contains 0.1% calcite and 23% porosity, complete dissolution of this calcite will add 3,600 mg of Ca to one liter of water. These are possible sources for the Ca in the aquifer water, which has Ca as the major cation and relatively low concentrations of Na and Mg as expected of meteoric-water recharge (e.g. Drever, 1997) (Figures 2.6a and 2.6c).

2.6.1 Reactions within the Cation-Exchange Zones

2.6.1.1 Updip Zone

The Updip Zone contains Ca-montmorillonite clays that were originally deposited in a fluvial environment (Figure 2.4). The water that deposited these clays is likely that of surface water present during flooding events. The composition of this water is expected to have been relatively dilute, Ca and Mg rich and Na poor, typical of surface and shallow groundwater (e.g. Drever, 1997).

These clays have experienced the greatest flushing by meteoric water after deposition and so are nearly stripped of any original Na (3-0.9%). With little Na in these clays, the exchange of Ca in the water for Mg on the clay dominates, resulting in a clear inverse-linear relationship between Ca and Mg downgradient in the clay-exchange complex (Figures 2.3 and 2.5). The Na and Mg on the clays were replaced with Ca provided by the meteoric-recharge water, with Ca increasing in the clays to 95% furthest updip to 80% downdip. At 95% Ca, it is likely that the most upgradient clays are in cation-exchange equilibrium with the meteoric-water recharge and exchange has ceased.

Changes in the clay compositions of this zone are the most uniform, and the most equilibrated with meteoric water, in the study area. The reason for the uniformity in the Updip Zone is because it is furthest from the downgradient seawater-meteoric water mixing front, so meteoric-water recharge fully controls the clay composition. In addition, any original Na has been almost completely flushed from the clays in this zone, and cation exchange is predominantly between only two cations, Ca in the water and Mg in the clay. In the Updip groundwater, Na remains relatively constant in the downdip direction, because little Na was likely present in the clays at deposition and what was present has been flushed from the clays, so there is little Na in the clays to exchange for Ca. Instead, exchange of Ca for Mg on the clay dominates, producing a linear downgradient decrease in the molar ratio Ca/Mg in solution as it equilibrates with clays increasingly enriched in Mg (Figure 2.6b). This produces an inverse-linear trend between Ca and Mg in the water.

The clear inverse linear relationship between Ca and Mg in both the clay and water in this Updip Zone can be used to identify the downdip extent of this fluvial deposited, meteoric water flushed zone within an aquifer. The downgradient extent of the Updip Zone within the Chicot aquifer lies at approximately 80 km (Figure 2.4).

2.6.1.2 Transition Zone

Starting with the Transition Zone, montmorillonite was originally deposited in equilibrium with seawater (Figure 2.4), compared to that deposited from meteoric-sourced surface water updip, so the original clays were rich in Na (53-55%) and Mg (39-40%), with little Ca (1-4%) (Table 2.2). The clays at the front of this zone have experienced the greatest flushing by meteoric water compared to further downdip, and so they contain clays with cation compositions the most altered from the original seawater-equilibrated montmorillonite compared to clays further downdip in the aquifer (Figures 2.3 and 2.5). Meteoric-water recharge has nearly stripped them of almost all the original Na (from approximately 55% to a low of 2%) and Mg (from 40% to a low of 16%) from their original seawater-equilibrated values (Figures 2.3 and 2.5). The Na and Mg

were replaced with Ca provided by the meteoric water, with Ca increasing in these clays from less than 4% in the original seawater-equilibrated values to more than 80% at the most updip portion of this zone.

With greater Na on the original clay-exchange complex, the exchange of Ca in the water for Na in the clays becomes important, producing an inverse linear trend downgradient of increasing Na (from 2 to 20%) coupled with decreasing Ca (from 80 to 60%) on the clay exchange site (Figure 2.3). This cation exchange is reflected in the water, with a downgradient increase in Na coupled with a decrease in Ca (Figures 2.6a and 2.6c). Regarding Mg, there is also an inverse linear trend downgradient compared with Na on the clay exchange site. With greater amounts of Mg on the original clays available to exchange for Ca in the water, there is a small increase in the Mg concentration in the water in this zone (Figure 2.6c).

The change in the clay-exchange complex downgradient in the Transition Zone, with respect to the percent Ca on the clay, shows a greater spread than in the Updip Zone where only Ca and Mg exchange dominates (Figure 2.3). This spread is also apparent on the ternary diagram (Figure 2.5), which allows the combined consideration of the three elements. At the start of the Transition zone, the clay-exchange compositions curve to the right on Figure 2.5 toward greater Na, because of increasing Na in the clays relative to Ca downdip.

In the case of aquifer freshening, the Transition Zone is the closest representation of the final product of an aquifer freshening event and is expected to progress further into the aquifer over time. The longer meteoric-water flushing takes place, and the greater the

volume of meteoric water recharge, the more the groundwater in this zone will become like the meteoric water, and the farther this zone will extend into the aquifer. The Transition Zone in the Chicot aquifer is currently approximately 40 km wide (Figure 2.4).

2.6.1.3 Downdip Zone

Clays in the Downdip Zone are mixed Ca,Mg,Na-montmorillonites, with nearly equal amounts of Mg and Na on the clay exchange complex (Figures 2.3 and 2.5). These clays are the least altered from the original seawater-equilibrated montmorillonite with the highest Na (11-30%) and Mg (23-37%) and the least Ca (39-60%) on the clay-exchange site compared to the clays in the other two zones (Figure 2.3, Table 2.2). These clays are the least altered from the original seawater equilibrated clays, because they have experienced the least flushing by meteoric water compared to the clays updip. Thus, their composition after exchange will be the most controlled by the original exchange composition of the clays prior to flushing, which can explain some of the variation in the exchange compositions in this zone.

With greater Na on the clays, the preference for monovalent to divalent exchange becomes important with the exchange of Na on the clays for Ca in the water dominating, resulting in the downgradient inverse linear trend of increasing Ca with decreasing Na on the clay exchange site (Figures 2.3 and 2.5). The effect on the groundwater composition results in a trend of increasing Na downgradient, with Ca nearly completely removed from the groundwater resulting in the lowest concentrations in the aquifer water of less than 0.7 mmol/L that extend throughout the zone (Figures 2.6a and 2.6c). It is evident that the abundance of Na in the clays available to exchange for Ca in the water extracts all the available Ca from the water, thereby keeping its concentration very low.

Further, because of the large amount of Na on the clays, Mg exchange is reversed in this zone, compared to the Transition Zone. With Na nearly equivalent to Mg on the clay exchange site, the preference for monovalent to divalent exchange again takes preference with Mg in the water exchanging for Na in the clay, rather than the divalent/divalent exchange of Mg in the clay exchanging for Ca in the water as occurs updip in the aquifer. However, because the upstream groundwater concentrations of Mg are so low (less than 1.5 mmol/) compared to Ca (up to 5 mmol/L) (Figures 2.6a and 2.6c), the addition of Mg to the clay as a result of Na-exchange has little impact on the Mg on the clay exchange site compared to the addition of Ca. As a result, there is not a clear trend of increasing Mg with decreasing Na on the clay in this zone.

The effect of the Mg exchange in the groundwater for Na in the clays in this zone influences the Mg concentrations in the groundwater similar to the effect on Ca discussed above. It appears all the available Mg is exchanged out of the water in this zone, with Mg concentrations in the groundwater consistently less than 0.7 mmol/L. Thus, groundwater in the Downdip Zone can be characterized by very low Mg and Ca concentrations of less than 0.7 mmol/L (approximately 20 mg/L), that are nearly equal giving a Ca/Mg molar ratio of approximately 1.

2.6.2 Comparison with other Aquifers

The sequential changes in cation composition downgradient in the Chicot-aquifer groundwater, resulting from cation exchange, are analogous to those found in the hydrogeologically-similar Aquia aquifer in coastal Maryland. Similar to the Chicot aquifer, the Aquia aquifer is a clay-rich quartz-sand aquifer within a coastal-sedimentary wedge composed of interbedded clay, silt and sand that thickens toward the coast (Chapelle, 1983; Chapelle and Knobel, 1983; Appelo, 1994a; Appelo and Postma, 2005). The main mineralogical differences between the two aquifers are that the clay in the Aquia aquifer is glauconite, compared to predominantly montmorillonite in the Chicot aquifer, and the Aquia aquifer contains 1-10% calcite/aragonite (as shells), whereas the Chicot has little primary calcite. The hydrogeology of the Aquia is also similar to the Chicot aquifer, dominated by downgradient flow of dilute Ca-dominated meteoric-recharge water, progressively displacing seawater downgradient (Chapelle, 1983; Chapelle and Knobel, 1983.

The sequential downgradient changes in cation exchange and water chemistry found in the Aquia aquifer were separated by Chapelle (1983) and Chapelle and Knobel (1983) into three Regions (I, II and III). The chemical trends in these three regions correlate well with the three cation-exchange zones in the Chicot aquifer.

• Region 1 in the Aquia aquifer correlates with the Upgradient Zone in the Chicot Aquifer. In both aquifers the groundwater in this zone has the highest Ca and lowest Na concentrations in the aquifer, and both show a trend of decreasing Ca downgradient suggestive of the exchange of Ca from

the water for Na on the clays. The Updip Zone (Region 1) in the Aquia aquifer extends 40 km downgradient, compared to 80 km downgradient in the Chicot aquifer. This difference likely marks different extents of the zone of fluvial-derived clays.

- Region II in the Aquia aquifer correlates with the Transition Zone in the Chicot Aquifer, with the groundwater displaying elevated Mg accompanied by a sharp increase in Na, and a trend of increasing Na with distance downgradient. The Transition Zone in the Aquia aquifer has a small increase in the concentration of K in the groundwater not seen in the Chicot aquifer. This increase in K is probably not seen in the Chicot aquifer because the groundwater in the Chicot aquifer has very low concentrations of K and because the aquifer material lacks a significant source of K. In contrast, K is in higher concentrations in the groundwater throughout the Aquia aquifer, possibly sourced from the glauconite which is an iron-rich mixed-layer illite-smectite with 2 to 8 weight % K on its exchange site (Thompson and Hower, 1975). The downgradient width of the Transition Zone in both aquifers is the same at 40 km.
- Region III in the Aquia aquifer correlates with the Downdip Zone in the Chicot aquifer. Both have the highest groundwater Na concentrations in the aquifer, that are increasing downgradient, coupled with the lowest and near equal Mg and Ca concentrations, suggestive of Na on the clay exchanging for both Ca and Mg in the groundwater.

The similarity of the chemical zones that developed in the Chicot aquifer, which contains predominantly montmorillonite, to the Aquia aquifer which contains predominantly glauconite (an Fe-rich illite-smectite, Thompson and Hower, 1975), supports that the type of smectite present, or the presence of illite and kaolinite does not appreciably change the exchange process in aquifers containing relative dilute (low ionic-strength) water.

2.6.3 Downgradient Changes in the Groundwater Chemistry from Cation Exchange

The sequential changes in the cation-exchange front observed in the clays in the Chicot aquifer are coupled with downgradient changes in the cation composition of the groundwater. Knowledge of these shifts can allow the use of groundwater-cation compositions to predict the presence, and extent, of the cation-exchange front produced by infiltrating meteoric water displacing seawater in a clay-rich clastic aquifer in a geologic setting similar to that of the Chicot aquifer. The relatively uniform decrease in Ca on the clay exchange complex downgradient (Figures 2.3, 2.4 and 2.5) associated with the meteoric-water plume displacing the original seawater in the aquifer, supports that the mole-percent Ca in the clay-exchange complex can be used as a reliable indicator of aquifer freshening, and thereby fluid flow in a coastal aquifer composed of shallow-marine clays.

The clays in the Chicot aquifer have been altered by tens to hundreds of thousands of years of meteoric-water recharge, such that the present-day cation composition of the clays represents the history of multiple pore-volumes of groundwater flow in the aquifer.

In contrast, the present-day groundwater composition represents a snapshot of the current interaction of a single pore-volume of meteoric water flowing into the aquifer and changing composition downgradient as it equilibrates with the matured clays (with the historic signature of previous groundwater flow).

In this setting, changes in the clay composition by a single pore-volume of presentday groundwater are minimal, with each pore-volume of meteoric water making a small incremental change in the clay's cation composition. For example, a pore volume of one liter of water in the aquifer at the entrance to the Transition Zone, given 23% effective porosity (Nobel et al., 1996) and approximately 40% clay (Dutton, 1994), will be exposed to 2.8 kg of clay. If the clay exchange sites contain the maximum Na in seawater equilibrated montmorillonite (55% Na, Table 2.2), and an average cation-exchange capacity of 1.2 mole/kg (ranging from 0.7 to 1.7 mole/kg for montmorillonite, Sposito, 2008), then a total of 42 g of Na are available to exchange from the clay for Ca in the water, which would require 37 g of Ca. Given the concentration of Ca in the water at the start of the Transition Zone of approximately 2 mmol/L (80 mg/L) (Figure 2.6c), a single pore volume (1 liter) of water could exchange out 0.22% of the 42 g of Na available in the clay, or conversely, 460 pore volumes are needed to completely remove the Na on the clay. The greater the clay content, which increases to 80% downgradient, the less Na on the clay is affected by a single pore volume of water. Therefore, as a pore volume of water passes through the sediment in the aquifer and removes all the Na possible from the clay in exchange for Ca, it will have little effect on the relative amount of Ca or Na on the clay but would measurably alter the Ca and Na composition of the water. This estimate does not take into consideration that it is unlikely that all the clay is exposed to groundwater flow and exchange.

With each pore volume of the present-day groundwater flowing through the aquifer having a minimal effect on the cation-exchange composition of the clay, the cumulative effect of long-term flow is required to alter the clay-exchange composition. In contrast, when a single pore volume of water flows through the aquifer, cation exchange can consume most of the Ca in the water and add enough Na, that it has a measurable effect on the water's Na and Ca compositions.

One-dimensional geochemical transport modeling of the freshening of seawater saturated clays in the hydrologically similar Aquia aquifer that is shown above to have experienced similar cation exchange, provides that the present-day pattern of cation exchange could have formed within 100,000 years (Appelo, 1994a). Fresh water flushing of the Chicot aquifer began around 600,000 years ago when sea level receded and deposition of the overlying Beaumont formation began (e.g., Knox et al., 2006). The model calculations suggest there was adequate time to form a cation-exchange front within the Chicot aquifer, although differences in, for example, the original pore water chemistry, percent clay, porosity, exposed clay surface area, and flow rates makes direct comparison between the aquifers uncertain.

Thus, small, or short-term perturbations in flow, such as from modern groundwater pumping, over geologic time will not have a large effect on the clay composition. Long-term flow has resulted in a smoothing effect on the clay-exchange composition, with the present-day clay-cation compositions showing a uniform cation-

exchange front from recharge, downgradient toward seawater-saturated sediments. In contrast, individual cation concentrations in the groundwater can be more irregular, because the mass of cations available on the clay exchange sites in the aquifer far exceed the mass of cations present in a single-pore volume of present-day groundwater passing through the aquifer. Consequently, the change in the cation concentrations in the solution necessary to achieve equilibrium with the clay-exchange complex can result in much larger compositional changes in the groundwater than in the clay. This is best illustrated in the Downdip Zone which contains the most Na-rich clays, where although gradual upstream changes are seen in the clay, the groundwater in equilibrium remains depleted of both Ca and Mg. This deficiency persists until enough pore volumes equilibrate with the clay so Na has been removed and Ca and Mg can remain in the water. Buffering by the clays has been noted to completely change the cation composition of groundwater in an aquifer (e.g., Appelo and Postma, 2005, p 241).

This clay buffering produces sequential changes in the groundwater chemistry of the Chicot aquifer that can be used as indicators of where the sample lies in the cationexchange front. Since the concentrations of all three cations combined (Ca, Mg, and Na) determine the clay-exchange composition, the relative proportions of all three cations in the water sample need to be examined together to evaluate how the exchange process has affected the composition of the clay-exchange complex. This is apparent examining the downgradient concentrations of Ca, Mg, Na and K in the aquifer (Figures 2.6a and 2.6c). Individually the concentrations of these cations show little uniform change downgradient. However, comparing the relative concentrations of all the major cations (Ca, Mg, Na and K) in the groundwater together on the lower-left triangle of the trilinear plot of the Chicot aquifer water (Figure 2.8), shows a smooth downgradient trend that can provide more insight into groundwater flow than individual cation concentrations.

2.6.4 Absence of Na-dominated Montmorillonite in the presence of Na-rich Groundwater

Sodium occurs in the aquifer water in concentrations greater than Ca and Mg in almost all the Chicot aquifer water samples. In contrast, in almost all the equilibrated clays Na is present in percentages less than Ca and Mg. This occurs because the divalent molecules, Ca and Mg, are favored to exchange on the clay-exchange complex over the monovalent ions such as Na (e.g. Stumm and Morgan, 1996; Appelo and Postma, 2005). This is apparent in Equations 2 through 5, which are used to calculate this composition of the clay-exchange complex with the groundwater samples. In these equations, Na is squared and the divalent cations, Ca and Mg, are not. Consequently, their relative concentrations in the water are not comparable to their relative concentrations on the clay-exchange complex. This is most apparent in the Downgradient Zone, where Na is present in concentrations generally an order of magnitude greater than Ca and Mg in the groundwater, but Na is nearly equal to Mg and generally slightly less than Ca in the equilibrated clay-exchange complex (Figures 2.3 and 2.5). Thus, it cannot be assumed that montmorillonite in equilibrium with Na-rich groundwater is predominantly Namontmorillonite, or that the relative proportions of Na to Mg and Na to Ca in the groundwater reflect the relative proportions of Na to Mg and Ca in the equilibrated clays.

2.6.5 Absence of K on the clays

In all samples in all three zones, K contributes less than 1% to the clay-exchange complex (Table 2.2). The unimportance of potassium on the exchange complexes in equilibrium with the Chicot/Evangeline-water samples is a product of the relatively low concentrations of K in the groundwater, always less than 0.16 mmol/L with, in all cases, a concentration an order of magnitude less than Mg and two to three orders of magnitude less than Ca and Na (Figures 2.6a and 2.6c). The low K in the Chicot/Evangeline aquifer water is likely a result of the absence of potassium feldspars in the aquifer matrix or any other external source of potassium. In addition, there is little K (less than 4%) on the exchange sites of the original seawater-equilibrated montmorillonite (Table 2.2). It is possible, however, that in aquifers with a different mineralogy, K can be important in aquifer cation-exchange as has been noted in aquifers with more potassium-rich water than present in the Chicot/Evangeline aquifers (e.g. Chapelle and Knobel, 1983; Appelo, 1994a).



Figure 2.8 Trilinear diagram (Piper, 1944) showing the relative cation and anion concentrations in the Chicot-aquifer water samples and seawater.

2.6.6 Influence of Calcite

Mineral equilibrium calculations using Phreeqc (Parkhurst and Appelo, 1999) indicate almost all the samples are in equilibrium or very near equilibrium, but supersaturated, with calcite (Figure 2.7c). As meteoric water recharges into an aquifer, equilibration with and precipitation of calcite is expected (e.g. Drever, 1997). It is common for groundwater to be supersaturated with calcite because other ions, such as Mg, sulfate, acetate and phosphate can inhibit its precipitation (e.g. Plummer et al., 1990; Appelo and Postma, 2005, Nielson et al., 2016). However, all these ions are present in concentrations too low to inhibit growth, with acetate and phosphate at less than 1 mg/L each, Mg from less than 1 to 20 mg/L (Figure 2.6c), and sulfate from less than one to 40 mg/L. Supersaturation could be the result of errors in analysis and thermodynamic data. For example, pH measurements can be too high if CO₂ is lost prior to measurement. Errors can be caused by the use of a fixed endpoint to analyze for alkalinity, rather than plotting the data to obtain an inflection point (e.g. Oregon Water Science Center, 2013). It is uncertain what caused the supersaturation of the Chicot aquifer with calcite, but with nearly all the samples equilibrated or supersaturated, it is likely saturated, rather than undersaturated, in the groundwater.

With excess clay removing Ca from the groundwater, exchange equilibrium places an upper limit on the Ca concentration of the groundwater, so if calcite dissolves into the aquifer water it cannot not raise the Ca concentration. Clay cation-exchange would consume the new Ca until the groundwater concentration of Ca was again returned to that in cation-exchange equilibrium with the clays. The effect would be to increase HCO₃ in the water while Ca continues to decrease. This pattern is noted in Figures 2.6c and 2.7b. As cation exchange removes Ca from the groundwater downgradient, to maintain calcite equilibrium HCO₃ or pH must increase. The pH of the groundwater varies little, ranging from 7.2 to 8.3 with few exceptions (Figure 2.7a). In contrast, HCO₃ in the water increases from a low of 100 mg/L near recharge to a high of nearly 700 mg/L downgradient (Figure 2.7b). Another source of inorganic carbon to the groundwater besides calcite dissolution, is bacterial degradation of sedimentary organic matter (Chapelle, 2001). Thus, the continued supersaturation of the groundwater with calcite downgradient supports that the HCO₃ concentration in the groundwater is controlled indirectly by cation exchange rather than calcite equilibrium alone. This is evident in the Chicot aquifer groundwater with bicarbonate increasing downgradient as Ca decreases (Figures 2.6c and 2.7b). Recognizing the overriding importance of exchange with the rock matrix by groundwater, despite other mineral-water reactions that are much slower, can help to better understand equilibrium arguments with regard to feldspar equilibrium and other minerals.

2.6.7 Using Cations to Trace Paleo-Groundwater Flow

Reliable tracers of natural groundwater flow are generally conservative elements, compounds or isotopes that show the same flow characteristics as the groundwater. Thus, the preferred inorganic ions used to trace groundwater flow are those not commonly involved in aquifer mineral/water reactions, such as the anions Cl, Br, and I (e.g. Richter and Kreitler, 1993; Kehew, 2001; Appelo and Postma, 2005). Cations are in some cases used as tracers of groundwater flow, but because of their involvement in many mineral and exchange reactions, they are generally used with conservative tracers. Tracers used

in this manner are useful to document the present-day occurrence of uniform groundwater flow from recharge to discharge, and areas where there has been a perturbation in that flow regime, such as from a reversal in flow direction from groundwater use, mixing with water from other sources, oil-well leakage, and surface contamination.

In contrast, with an understanding of cation exchange, the results of this study show that in clay-rich aquifers, rather than using the concentrations of individual cations in groundwater to trace flow, the relative proportions of the major cations (Ca, Mg, Na, and K) in the groundwater and on the clay-exchange site can be used as a tracer. But in this case, rather than tracing present-day groundwater flow, cation proportions in the groundwater are recording the paleo-groundwater flow, because they are equilibrated with the clay cation-exchange compositions which are a product of the exchange with the groundwater over an extended period of groundwater flow. They can also be useful in identifying changes in the depositional environment of the clays, such as fluvial versus marine derived.

For example, in the Chicot aquifer, the cation proportions both on the clays (Figure 2.5) and in the groundwater (Figure 2.8, lower-left triangle) show a uniform shift downgradient, compared to Cl in the groundwater (Figure 2.8) which shows an irregular pattern downgradient (Figure 2.7d). Throughout the aquifer some of the groundwater retains low Cl, less than 200 mg/L, but there are local areas with elevated Cl, such as near the coastline as a result of a zone of irregular seawater mixing, with a high of up to 925 mg/L Cl, and other highs throughout the aquifer, some likely a result of halite dissolution as identified by the cation ratio Na/Mg. These irregular elevated groundwater Cl values

might also reflect the irregular contribution of elevated Cl from the slow diffusion of Cl from the thicker clay layers that originally contained seawater at deposition, a process identified in the Milk River aquifer of Canada (e.g. Fabryka-Martin et al., 1991). Comparing the use of cation proportions to anion proportions on the trilinear plot for groundwater, the cations show a uniform trend downgradient (Figure 2.8 lower-left triangle), whereas the major anions Cl and HCO₃ (there is relatively little SO₄ in these water samples compared to Cl and HCO₃) show no regular trend downgradient (Figure 2.8 lower-right triangle) compared to that of the cations (Figure 2.8 lower-left triangle). Thus, in the case of the Chicot aquifer cation-proportions are useful for identifying long term flow trends, and when used in combination with Cl and cation ratios can identify modern perturbations, such as halite dissolution and seawater mixing.

Thus, with the uniformity of the downgradient changes in the cation proportions compared to other ions in the groundwater, cation proportions can be a useful check on flow predicted using other tracers, or in systems where anion tracers are of questionable use where something other than mixing alters Cl, Br, and I in the groundwater. This often occurs in areas with petroleum resources and their associated brines, or with salt deposits (e.g. Whittemore, 1984, 1995; Davis et al., 1998). Because the cation proportions in the clays, and therefore in the groundwater, are a product of the evolution of cation geochemistry over a long period of groundwater flow, they represent a record of paleogroundwater flow. They are not changed measurably by recent groundwater events that change water volumes or flow directions, such as relatively short-term reversals in flow from groundwater pumping, or changes in recharge from irrigation or a recent climatic event, because these are generally relatively small compared to the long-term recharge and flow that established the current aquifer geochemistry. However, contamination of an aquifer will change the composition of individual cations in the aquifer water and their ratios, for example, a decrease in the Na/Cl ratio and increase in the Ca/Cl ratio in an aquifer water as a result of cation exchange on clays when a saltwater such as road salt or petroleum production brine contaminates a freshwater aquifer. But these perturbations will not shift the cation proportions unless they have occurred long enough to shift the cation proportions in the enclosing clay, such as the areas of halite dissolution in the Chicot aquifer.

Cation proportions could be used to separate long-term historical-groundwater flow in an aquifer from recent local changes in groundwater chemistry, by comparing the relative-cation proportions in the locally contaminated area to those in uncontaminated portions of groundwater that have been buffered by the historic-clay compositions, and also comparing those to changes in other parameters, such as anion tracers, isotopes or contaminants in the groundwater which are controlled by modern processes. This type of comparison could be used to better define, for example, areas of recent contamination, reversals in flow from groundwater use and changes resulting from climate change or tectonic processes.

Knowledge of aquifer porosity, permeability and the abundance and cationexchange capacity of the clays in an aquifer can be used to predict the history of meteoric water recharge into an aquifer, and possible long-term climatic changes in rainfall, or in tectonically active areas to identify aquifers with a changing history of meteoric recharge.

2.6.8 Offset of Cation Proportions to identify Seawater Mixing on Trilinear Diagrams

Understanding the importance of cation exchange to the cation composition of the groundwater also allows better use of the cation chemistry to predict mixing. In using a trilinear diagram, it is common to assume the water composition should tend linearly toward the water with which it is mixing. Since meteoric water is mixing with seawater in the Downdip Zone, it is expected that the cation composition should trend directly toward the seawater composition downgradient in the Chicot aquifer, but it does not; it is shifted down below the seawater composition (Figure 2.8). Cation exchange explains this. Both Mg and Ca in the Downgradient Zone are stripped from the water by cation exchange with the clays for Na, so the percent Ca and Mg in the water in this zone is less than 5%, whereas Na goes to a high of 98%, resulting in a composition offset from that of seawater (Figure 2.8). Thus, while trilinear diagrams can be used to study aquifers when cation-exchange dominates, because of the potential for this type of offset, it cannot be assumed that the cation compositions of mixed water will extend directly between the cation compositions of the two end-member solutions.

2.7 Conclusions

The results of this study show that for a clay-rich aquifer composed of coastalmarine sediments, calculation of the relative-cation percentages on the clay-exchange complexes in equilibrium with the present-day groundwater can provide insight into the aquifer's past chemical evolution and historical-flow paths. The Chicot aquifer, chosen for this study because of its simple mineralogy (quartz, montmorillonite, kaolinite), uniform geologic setting, and historically uniform downgradient flow of meteoric-water recharge displacing saline water downgradient, allowed documentation of the effects of cation exchange without the need to include consideration of complex mineral reactions or flow regimes.

A nearly linear downgradient decrease in Ca on the clay-exchange site was used to identify three sequential-downgradient zones, Updip (95-80% Ca), Transition (80-60% Ca), and Downdip (60-40% Ca), that form a cation-exchange front which extends from a meteoric-water plume, in which the clays are near equilibrium with the fresh-recharge water (Updip Zone), to shallow-marine derived clays that are increasingly equilibrated with seawater downgradient (Transition and Downdip Zone). The zones progressed from predominantly fluvial-derived clays in the Updip Zone, to shallow-marine derived clays downdip. Clays in the updip zone contain little Na, with cation exchange in this zone dominated by progressively more Ca in the water exchanging for Mg on the clays downdip. In the Transitional and Downdip Zone, with Na on the clays from original seawater equilibrium, Ca, and further downdip Mg, in the water exchanges for Na in the clays.

It is demonstrated how deviations from this expected downgradient trend can be used to identify groundwater influenced by sources of contamination such as halite dissolution, mixing with brines from oil-well leakage, and seawater mixing. Cation proportions in both the clays and water, combined with cation ratios and the conservative trace tracers such as Cl, prove reliable indicators of flow and contamination compared to using ions or ion ratios alone in this setting. Cation proportions are shown to be a product of long-term accumulation of ion exchange between the water and clays, and thus a record of paleo-groundwater flow compared to conservative ions, such as Cl, which provide a record of more recent flow. This difference can be used to identify modern contamination and aquifer changes, and to go into the geologic record and understand ancient flow paths and possibly the effects of climatic change on aquifer recharge.

Na-dominated montmorillonite is absent in the aquifer studied, despite that groundwater in the downdip part of the aquifer had Na concentrations almost two orders of magnitude greater than any other cation. This is a product of the clays' strong preference for divalent (Ca and Mg) over monovalent (Na) ions. This suggests that Nadominated montmorillonites are unlikely to occur in natural-aquifer settings due to this strong preference. It was further shown that a clay's preference between the divalent cations (Mg preferred over Ca) is absent when a high concentration of a monovalent ion (Na) is present. It was determined that the general preference for Ca allows the mole percent of Ca on the equilibrated clay to be used as an indicator of the extent of cation exchange and fluid flow.

The chemical trends observed in the Chicot aquifer with respect to cationexchange mirror those of a previous study of the clay-rich Aquia aquifer, which contains a similar downgradient progression, despite minor mineralogical differences. This suggests that cation-exchange processes create a predictable chemical progression that can be applied in the study of all clay-rich aquifers.

The limits imposed by cation-exchange were shown to not only control cation concentrations, but to also affect anion concentrations by influencing other equilibrium reactions. This was most apparent from the increase in bicarbonate in the groundwater downgradient, so as to maintain calcite equilibria in response to the reduction in Ca in the groundwater downgradient by clay cation-exchange. Further study of the overriding importance of cation-exchange on the cation chemistry of groundwater in a clay-rich environment can help understand equilibrium with regard to other minerals, such as feldspars, in an aquifer setting.

2.8 Acknowledgments, Samples, and Data

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2.9 Chapter 2 Bibliography

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CHAPTER 3:

CLAY-CATION COMPOSITIONS FROM GROUNDWATER CHEMISTRY AS AN INDICATOR OF FLUVIAL VERSUS MARINE SEDIMENTS Cole R. Jones and Regina M. Capuano

Submitted to "Geochemistry, Geophysics, Geosystems" and currently under review.

3.1 Summary

This study demonstrates that the cation compositions of clay minerals in a siliciclastic coastal aquifer can aid in locating the transition from fluvial to marine deposited sediments. In this study, the clay-cation compositions (XCa, XMg, and XNa) in two clay-rich siliciclastic coastal aguifers were calculated from the cation compositions of groundwater in equilibrium with the clay minerals, and compositional differences were found between clays deposited in the fluvial and marine environments. River-water analyses show that fluvial deposited sediments are represented by XNa \leq 8.0%, whereas marine deposited sediments are XNa>8.0%. In a natural system with fluvial, mixed fluvial/marine and marine environments identified by traditional core, log and paleontological analyses, each depositional environment has a distinguishing range of XNa, XCa and XMg consistent with these criteria. The fluvial depositional environment is identified by low XNa < 15% (with 92% of the samples with XNa of fluvial origin and XNa ≤8.0%) and high XCa from 55 to 98%. Compared to the marine depositional environment which is identified by greater than 86% of the samples of marine origin (XNa>8.0%) with higher maximum values as high as 39% and lower XCa ranging from 5 to 39%. The mixed fluvial/marine transitional environment has values overlapping the fluvial and marine end members, with 59% fluvial and 41% marine origin clays, and XCa ranging from 45 -

98%. These relationships can be used to augment traditional stratigraphic interpretations based on well logs, sediment samples, and paleontology in distinguishing fluvial, marine, and mixed fluvial-marine depositional environments.

3.2 Introduction

Previous studies have attempted to identify patterns in the mineralogy of the clays present in different depositional environments (Freed, 1980; Ingles and Anadon, 1991; Ingles and Ramos-Guerrero, 1995), however, it has been recognized that clay mineralogy is generally a product of the source material with little coincidence between specific clay minerals (montmorillonite, kaolinite, etc.) and depositional environment. Instead, it is the secondary processes taking place during diagenesis that reflect the character of the depositional environment (Weaver, 1958). This study provides evidence from two siliciclastic aquifers, both deposited in a coastal environment, that the cation compositions of clay minerals, rather than mineralogy, are reliable indicators of the transition of the depositional environments from fluvial, to fluvial-marine transition, to marine. For this study the cation composition of the clay minerals in the aquifer material are calculated from the groundwater chemistry (e.g., Capuano and Jones, 2020). Using the groundwater chemistry to obtain the cation compositions of the clay minerals avoids the problem of a lack of core available for study, whereas groundwater samples are easily obtained allowing for the study of a large area of a sedimentary unit.

It has long been recognized that calcium (Ca) in meteoric water recharging a siliciclastic aquifer will exchange for sodium (Na) in the clays resulting in a downgradient increase in Na and decrease in Ca in the groundwater (Foster, 1942; Back, 1966; Kreitler

et al., 1977; Chapelle, 1983; Whittemore, 1995; Stumm and Morgan, 1996; Drever, 1997; Appelo and Postma, 2005)) with Capuano and Jones (2020) concluding that the cation compositions of the clay minerals at the time of deposition are an important control on this process. In the present study, calculation of the cation compositions of clays in exchange equilibrium with the groundwater in two coastal aquifers shows that fluvialderived sediments occurring updip contain clays that are Ca-Mg rich, where in contrast, the shallow-marine derived clays occurring downdip contain clays that are Na-Mg rich. Because of these different clay-cation compositions in the fluvial versus marine sediments, cation exchange with the meteoric water recharging a coastal aquifer is dominated initially by Ca exchange for Mg and lesser Na in the updip zone of fluvialderived sediments, followed by Ca and Mg exchange for Na on the marine-derived sediments. This results in a pronounced transition downdip in the clay-cation chemistry and the groundwater composition. The clay-cation compositions transition downdip from increasing Mg and Na at the expense of Ca in the zone of fluvial-derived clays, to increasing Na at the expense of Ca and Mg in the zone of marine-derived clays. These changes in the clay-cation composition, are coupled with comparable zoning in the groundwater-cation composition downdip, with groundwater in the fluvial zone becoming more Mg-rich as Ca exchanges with the clays, progressing to groundwater in the marine zone becoming more Na rich as Ca and Mg exchange with the clays (Capuano and Jones, 2020). Understanding the relationship between depositional environment and changes in aquifer-cation chemistry can be useful in tracing aquifer fluid flow, identifying areas fluid influx from outside, and also in identifying the transition from fluvial to marine sediments in studies focused on stratigraphy and depositional environment.

3.3 Study Area

The well water chemistry from two siliciclastic aquifers composed of coastal fluvial/marine sediments were used in this study; 1) the combined Chicot/Evangeline aquifers which occur adjacent to the coastline and form the uppermost aquifers of the Gulf Coast Aquifer System and 2) the stratigraphically deeper and more inland Wilcox aquifer of the Carrizo-Wilcox Aquifer System (Figures 3.1 and 3.2). Both occur in Texas and are Gulfward thickening wedges of transgressive-regressive sequences of predominantly sand-shale units (Sellards et al., 1932; Baker, 1995; Chowdhury and Turco, 2006). Aquifers in both study areas are composed of clastic sediments deposited in a fluvial environment updip that transitions to a coastal marine environment downdip (Figure 3.3). Both have a history of a relatively uniform hydrologic flow downgradient of meteoric-water recharging updip where the aquifers are unconfined, which then flows downdip to where the aquifers become confined by overlying less permeable sediments (Figures 3.1 and 3.2).

Figure 3.1 Map of the Chicot/Evangeline and Wilcox study areas showing the locations of groundwater samples (Texas Water Development Board, 2020) (blue circles for $X_{Na,clay} \le 8.0\%$ and red circles for $X_{Na,clay} > 8.0\%$, see text), river water samples (black boxes) (United States Geological Survey, 2020), salt domes (white circles) (Beckman and Williamson, 1990), Chicot/Evangeline and Wilcox aquifer outcrops shaded grey (Texas Water Science Center, 2014), hydraulic head contours (blue lines) for the Chicot/Evangeline aquifer (after Dutton, 1994) and the Simsboro formation of the Wilcox aquifer (after Dutton, 1999), the inland extent of the marine transgressions at the top and at the bottom of the Chicot/Evangeline aquifer (after Knox et al., 2006) (shown in shades of pink), the inland extent of the shore zone in the Wilcox Group found in outcrops in Bastrop County (after Yancey et al., 2012, 2013; Denison et al., 2017) (red triangle), and the Texas county lines (solid grey lines).





Figure 3.2 Geologic cross section of the Chicot/Evangeline and Wilcox aquifer study areas showing stratigraphy (after Baker, 1995), aquifers (after Dutton, 1994; Dutton, 1999), water sample locations and depths, and hydraulic gradients (after Dutton, 1994; Dutton, 1994; Dutton, 1999). Cross section location shown on Figure 3.1.



Figure 3.3 Geologic cross section of the Chicot/Evangeline aquifers showing water sample depths and their fluvial (blue) or shallow marine (red) classification based on the cutoff of $X_{Na} \le 8.0\%$ for fluvial-deposited clays and $X_{Na} > 8.0\%$ for marine-deposited clays (see text). Cross-section geology after Baker (1995), aquifers after Dutton (1994, 1999). Cross section location shown on Figure 3.1. The maximum-seawater transgression and regression are shown by bold solid black lines (after Knox et al., 2006).

3.3.1 The Chicot/Evangeline aquifers

The Chicot and Evangeline aquifers are within the Pliocene-Pleistocene sands of the Lissie, Willis and Goliad formations (Sellards et al., 1932). The Chicot and Evangeline are both sand aquifers and combined in this study as the "Chicot/Evangeline aquifers", because they have no clear sedimentary or compositional differences to separate them (Kreitler et al., 1977; Ryder, 1988; Dutton, 1994; Knox et al., 2006). They are unconfined inland where they outcrop and become confined downdip toward the coast by the clayrich Beaumont Formation (Figures 3.1 and 3.2). They are confined below by the Burkeville confining layer (Figure 3.2). Thin clay layers up to 15 m thick are interlayered within the sands (Gabrysch and Bonnet, 1975; Gabrysch, 1984), and comprise from 20% of the aquifers updip, to up to 75% of the aquifers at the coastline (Kreitler et al., 1977; Ryder, 1988; Dutton, 1994; Knox et al., 2006).

Historically fluid flow in the Chicot/Evangeline aquifers has been laterally downgradient and relatively perpendicular to the strike of the aquifer outcrop and coastline (Figures 3.1 and 3.2), with some drawdown in the southwest portion of the study area due to pumping in the last forty years (Dutton, 1994). The aquifers are recharged by meteoric water (rain) in the inland outcrop areas, and discharge naturally as diffuse-upward flow toward the coast (Dutton, 1994; Kasmareck and Robinson, 2004). Within in the study area, there is no evidence of seawater intrusion into the Chicot/Evangeline aquifers downgradient since deposition (Chowdhury et al., 2018).

Sediments of the Chicot/Evangeline aquifers are cyclic deposits of fluvial and shallow-marine sediments. The locations of the highest level (most landward)

transgression, most downgradient regression, and the transition from predominantly fluvial floodplain and meander-belt deposits to predominantly shallow-marine deposits downdip are shown in Figure 3.3. The locations of the transgression and regression maximums were identified primarily through the interpretation of well log data, percent sand mapping, and to a lesser extent by the presence of marine fossils (Knox et al, 2006). The highest level of transgression is shown on the plan map (Figure 3.1). Because this level changed through time occurring further inland with increased depth, the most landward transgression near the top of the aquifers is shown and labeled "Upper", and that of most landward transgression near the bottom of the aquifers is shown and labeled "Lower".

The sands of the Chicot/Evangeline aquifers in the study area are predominantly fine to medium grained composed of quartz with few to trace feldspars and little to no calcite cement (Sellards et al., 1932). The clay beds in the area are predominantly composed of montmorillonite, with minor illite and kaolinite (Gabrysch and Bonnet, 1975; Gabrysch, 1984; Gabrysch and Coplin, 1998) and no chlorite (Burton et al., 1987). Growth faults parallel to the coastline are present but not offset enough to affect the regional-groundwater flow (Hosman and Weiss, 1991; Chowdhury and Turco, 2006). While numerous salt domes occur in the study area, only one is known to contain halite at a location and depth that might affect the water samples in this study by salt dissolution, the Hawkinsville Dome (Figure 3.1). All the rest of the known salt domes occur either below or down the hydrologic gradient from the water samples used in this study.

3.3.2 The Wilcox aquifer

The Wilcox aquifer in the study area is composed of the Eocene sands of the Calvert Bluff, Simsboro, and Hooper formations of the Wilcox Group, and lies stratigraphically below the sedimentary units that host the Chicot/Evangeline aquifers (Figure 3.2) (Sellards et al., 1932). The Wilcox aquifer sediments were deposited in the Eocene, 50 to 60 million years ago along the coastal margin of the Gulf of Mexico when it was 240 to 320 km further inland than it is today (Mace et al., 2000). The Wilcox aquifer is confined from below by the marine clays of the Midway Formation. Above the Wilcox aquifer occur the sands of the Carrizo Formation, which forms the base of the Claiborne Group and hosts the Carrizo aquifer (Figure 3.2). Flow in the Carrizo aquifer is hydrologically separate from flow in the Willcox aquifer (Dutton 1999; Dutton et al., 2003). In some areas the Carrizo and Wilcox aquifers are separated by the thin clay-rich Sabine Town Formation (also referred to as the Yoakum shale) (Denison et al., 2017).

Sediments of the Wilcox aquifer are composed of a coastward thickening wedge of clay-rich sands paralleling the coastline, that were deposited in transgressive/regressive cycles. In the study area, the sediments are predominantly of fluvial origin updip at the outcrop, grading to a shallow marine origin downdip well outside of the study area (Figure 3.1) (Kaiser, 1978; Thorkildsen and Price, 1991; Xue, 1994). The exception to this is in the southwest portion of the study area, in Bastrop County, where shallow tidal flat and open marine sediments, instead of fluvial sediments, where found in several outcrops of the Calvert Bluff formation (Yancey et al., 2012; Denison et al., 2017) (location marked by a red triangle on Figure 3.1). The confirmation of the presence of coastal marine

sediments in the Bastrop County area studied by Yancey et al. (2012) and Denison et al. (2017) supports that, despite the predominance of fluvial sourced sediments in the Wilcox Group in this part of Texas, marine sediments are present in this portion of the formation.

Sediments of the Wilcox Group are composed of heterogenous units of fine to coarse grained sand and sandstone interbedded with clay and sandy clay (Thorkildsen and Price, 1991), which include the clay-rich Calvert Bluff Formation at the top, underlain by the sandier Simsboro formation followed by the clay-rich Hooper Formation at the base. The Calvert Bluff and the upper portions of the Hooper Formations also contain thin discontinuous beds of lignite and ironstone concretions (Thorkildsen and Price, 1991). The Simsboro formation sands are composed of quartz and feldspar with minor kaolinite and illite, with the clay layers composed of predominantly montmorillonite (Kohls, 1963). The Calvert Bluff and Hooper formations are predominantly clay composed of montmorillonite with some kaolinite, illite and carbonaceous clays (Kohls, 1963).

Rainfall recharges the Wilcox aquifer inland where it outcrops (Figure 3.1). Historically, flow in the aquifer in the study area has been relatively uniform downgradient into the aquifer from the recharge area (Figures 3.1 and 3.2) (Dutton, 1999; Dutton et al., 2003).

The predominant flow in the Wilcox aquifer is in the Simsboro Formation, which acts as the main aquifer unit. The Simsboro Formation is composed of over 80% permeable sand with 20% clay, whereas the less permeable Hooper formation, and to a lesser extent the Calvert Bluff formation, consisting predominantly of mudstone (Kohls, 1963; Ayers and Lewis, 1985; Thorkildsen and Price, 1991). There are no salt domes in this area of the Texas Gulf Coast, and faulting in the area has no major effect on groundwater flow (e.g., Dutton et al., 2003).

3.4 Methodology

Chemical analyses of groundwater samples used in this study (Figures 3.1 and 3.2) were obtained from the Texas Water Development Board's (2020) groundwater database. Water samples from areas cut by incised-valley fill, or adjacent to present day rivers, were excluded to avoid the possibility of local recharge at these locations. Water samples collected from a depth of less than 200 m were also omitted to exclude samples only recently recharged or water that might be affected by infiltration of water from the overlying confining layer. Only samples in the database specified as taken from the Chicot, Evangeline, or Wilcox aquifers were used. An aqueous-species distribution using PHREEQC with the LLNL database (Parkhurst and Appelo, 1999) was performed on each analysis to determine the charge-balance error, ion activities in solution, and mineralsaturation indices. Only analyses with pH and all major anions and cations that have a charge-balance error of less than 2% were used in this study. In the case of a single well location having multiple analyses, the sample used was determined first by selecting the samples with a complete analysis that have a cation-anion balance accuracy within 2%. Then, from those remaining samples the sample with the most recent collection date was used. In addition, two samples from the Chicot/Evangeline study area identified by Capuano and Jones (2020) as likely affected by a halite dissolution and so omitted from their study, were also omitted from this study. After this elimination, 412 water analyses

from the Chicot/Evangeline and 80 from the Wilcox study areas remained and were used for this study. Their sample locations and depths are shown on (Figures 3.1 and 3.2)

The 32 chemical analyses of river water used in this study (Figure 3.1) are from the United States Geological Survey's (2020) surface water quality database. The samples were selected from the near shore areas of the Colorado and Brazos river basins and their tributaries, which are the two major drainage basins that supply water to the Chicot/Evangeline study area. These 32 samples lacked data for potassium. However, analyses of river water from the same area in a report by Hughes and Leifeste (1965) show expected potassium concentrations are less than 5 mg/L. Potassium of 5 mg/L resulted in a calculated clay exchange composition, XK, of less the 1% for the samples, thus low enough not to consider XK further in this study.

3.4.1 Calculation of the Clay-Exchange Compositions

Cation-exchange between clays and water occurs in less than 10 minutes (Nachod and Wood, 1945), so the groundwater in contact with the clays in the aquifer are in exchange equilibrium. The mole fractions (X_i) of Ca, Mg, Na, K, and Sr on the montmorillonite $(X_i)_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 \cdot nH_2O$ exchange complex (X_i) in equilibrium with the groundwater and river water samples were calculated as the mole fractions (X_i) of Ca, Mg, Na, K, and Sr on the montmorillonite (X_i), where,

 $X_{Ca} = m_{Ca}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{Mg} = m_{Mg}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{Na} = m_{Na}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{K} = m_{K}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ and $X_{Sr} = m_{Sr}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$

and their sum is equal to one,

$$X_{Ca}+X_{Mg}+X_{Na}+X_{K}+X_{Sr}=1$$

Then, using the Gaines-Thomas convention with the following equations, derived using procedures described in Stumm and Morgan (1996) and Appelo and Postma (2005),

$$X_{Na}^{2} \left(\frac{M_{Mg^{2+}}}{K_{Na/Mg}^{2} \cdot M_{Na^{+}}^{2}} + \frac{M_{Ca^{2+}}}{K_{Na/Ca}^{2} \cdot M_{Na^{+}}^{2}} + \frac{M_{Sr^{2+}}}{K_{Na/Sr}^{2} \cdot M_{Na^{+}}^{2}} \right) + X_{Na} \left(\frac{M_{K^{+}}}{K_{Na/K} \cdot M_{Na^{+}}} + 1 \right) - 1 = 0 \text{ Eq. 1}$$

(Capuano and Jones, 2020) where,

- M_i = the concentration of the i^{th} ion in solution
- K = the clay exchange constant, where K_{Na/Ca} = 0.4, K_{Na/Mg} = 0.5, K_{Na/K} = 0.2, and K_{Na/Sr} = 0.35 (Bruggenwert and Kamphorst, 1979; Appelo and Postma (2005); Capuano and Jones, 2020).

As summarized in Capuano and Jones (2020), ion concentrations in solution (M) are used rather than ion activities in solution to solve Equations 1, because there is no similar activity-coefficient correction for the ions on the clay-exchange complex. Using an activity correction for ions in solution, but not for ions on the clay-exchange complex, was found to result in errors (Appelo & Postma, 2005; Stumm & Morgan, 1996,). It was found more reliable to calculate the fractions of cations on the clay-exchange complex using ion concentrations in solution, rather than using ion activities, and proposed that this is the case because the activity corrections for both the ions in the water and the ions on the clay-exchange complex are similar (e.g., Appelo, 1994b; Appelo & Postma, 2005; Stumm & Morgan, 1996).

The clay-exchange constants used in this study to solve Equations 2 through 5 are KNa/Ca = 0.4, KNa/Mg = 0.5, KNa/K = 0.2, and KNa/Sr = 0.35 taken from Appelo and Postma (2005, their Table 6.4, after a compilation by Bruggenwert and Kamphorst, 1979). Although Appelo and Postma (2005) do not list the clay mineral to which these exchange constants apply, Bruggenwert and Kamphorst (1979) note that their compilation includes predominantly data for montmorillonite clays as most exchange studies in the literature are of montmorillonite because of its relatively large exchange capacity. Clays in the formations studied are predominantly montmorillonite with only minor to trace illite and kaolinite. In addition to their minor presence, the importance of illite and kaolinite on exchange in the systems studied is further reduced because their cation-exchange capacities are so much less than that of montmorillonite. Compared to montmorillonite's exchange capacity of 0.7 to 1.7 mole/kg, illite's cation-exchange capacity at 0.2 mole/kg is

almost half that of montmorillonite, and kaolinite's (<0.05 mole/kg) is more than an order of magnitude less than that of montmorillonite (Sposito, 2008).

No other cations besides Ca, Mg, Na, K, and Sr were considered in the clay-exchange calculations because none are present in the groundwater in concentrations greater than 1 mg/L (with the exception of 1 sample from the Chicot/Evangeline study area with 1.7 mg/L of Fe and 5 from the Wilcox study area with Fe ranging from 1.2 to 5.7 mg/L). In addition, the calculated mole-percent K and Sr (XK and XSr) in the equilibrated clays for all the river and groundwater samples considered in this study were less than 1% (with the exception of 6 samples with values from 1.1 to 1.5%) and so not considered further.

3.4.2 Comparison of Calculated Clay-Cation Compositions and Laboratory Measurements

To check the validity of Equation 1 and the uncertainty of the exchange constants used in Equation 1, the cation compositions of clay in equilibrium with seawater and Mean World River Water (Livingstone, 1963) were calculated in this study using Equation 1 and compared with the cation compositions of natural montmorillonite samples that were equilibrated in the laboratory with seawater and Mean World River Water by Sayles and Mangelsdorf (1979). The results are given in Table 3.1.

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Table 3.1 Mole percent of cations on the exchange site of montmorillonite equilibrated with seawater and Mean World River Water¹ in the laboratory (Sayles and Mangelsdorf, 1977) and calculated using Equation 1 (see text).

| Mole percent of cations on the clay exchange site when equilibrated with Mean World River Water ¹ | | | | | | | | | | | |
|---|-----------------------|---------------------------------------|-------|---------|---------|-------|----|--|--|--|--|
| | Natural- equilibra | Calculated with Eq. 1 ³ | | | | | | | | | |
| mole % | Arizona | Dakota | Texas | Wyoming | Average | Range | | | | | |
| Xca | 62.4 | 67.5 | 73 | 65.8 | 67 | 10.6 | 76 | | | | |
| X _{Na} | 2 | 3.6 | 2.9 | 4 | 3 | 2 | 1 | | | | |
| Хмд | 34.3 | 28.7 | 23.3 | 29.7 | 29 | 11 | 22 | | | | |
| Хк | 1.3 | 0.2 | 0.8 | 0.5 | 0.7 | 1.1 | 1 | | | | |
| Xca + X _{Mg} | 96.7 | 96.2 | 96.3 | 95.5 | 96.2 | 1.2 | 98 | | | | |

| Mole percent of cations on the clay exchange site when equilibrated with seawater | | | | | | | | | | | |
|---|----------------------|------------------------------------|---------|-------------------|---------|-------|----|--|--|--|--|
| | Natural- equilibr | Calculated with Eq. 1 ³ | | | | | | | | | |
| mole % | Dakota | Texas | Wyoming | Wyoming (dup.) | Average | Range | | | | | |
| X _{Ca} | 26 | 19 | 1 | 4 | 12.5 | 25 | 9 | | | | |
| X _{Na} | 50 | 55 | 55 | 53 | 53.25 | 5 | 54 | | | | |
| X _{Mg} | 22 | 22 | 40 | 39 | 30.75 | 18 | 31 | | | | |
| Хк | 2 | 3 | 4 | 4 | 3.25 | 2 | 6 | | | | |
| X _{Ca} + X _{Mg} | 48 | 41 | 41 | 43 | 43.25 | 7 | 40 | | | | |

- 1. Mean World River Water: Na = 6.29 mg/L, Ca = 15.0 mg/L, Mg = 4.10 mg/L, K = 2.35 mg/L (Livingstone, 1963)
- 2. Clay-cation compositions of natural-montmorillonite samples equilibrated with Mean World River Water or seawater in the laboratory by Sayles and Mangelsdorf (1979).
- 3. Clay-cation compositions in equilibrium with Mean World River Water or seawater calculated in this study using Equation 1 (see text).

The cation compositions of the four montmorillonite samples equilibrated with Mean World River Water in the laboratory have good agreement for XNa and XK, which have narrow ranges of 2% and 1.1% respectively. There are wider ranges of XCa and XMg (10.6% and 11%), but as pointed out by Sayles and Mangelsdorf (1979) the combined percentages (XCa + XMg) have a narrow range of 1.2%.

The values for the mole percent of cations for clays in equilibrium with the Mean World River Water calculated using Equation 1 lie slightly out of range (1 to 3 mole %) compared to the values determined experimentally for all the cations except K (Table 3.1). Because the calculated values were close, but outside the range, the Dixon's Q-test (Rorabacher, 1991) was used to determine if the calculated value would be an outlier when included as part of the experimental data set. For the Q-test, a Qstatistic value is determined for the calculated cation percent for each cation (Qstatistic = $(x^2 - x^1) / (xn - x^2)$ x1)) (Table 3.1), where x1 is the calculated value in question, x2 is the closest laboratory value to the calculated value, and xn is the furthest laboratory value from the calculated value. The Qstatistic value is then compared to the Qcritical value for small data sets at a 95% confidence level which is 0.71 for a data set of five. Using the Dixon's Q-test criteria, all of the cation percentages calculated for equilibrium with Mean World River Water test as non-outliers when included in the laboratory data set, because Q statistic < 0.71 for all the cations (Table 3.1). Thus, Equation 1 calculates the clay cation compositions within reasonable limits compared to the accuracy of laboratory analyses for the cation compositions of clays equilibrated with a typical river water.

Similar to the montmorillonites in equilibrium with Mean World River Water, the cation compositions of the four montmorillonite samples equilibrated with seawater in

the laboratory have narrow ranges for XNa and XK, 5% and 2% respectively, with wider ranges for both XCa and XMg (25% and 18%), whereas the range in XCa + XMg is smaller at 7% (Table 3.1). For the case of equilibrium with seawater, the cation mole precents calculated using Equation 1 are all within the range of the experimental values, with the exception of XK and XCa + XMg which are slightly out of range (1 to 2 mole%) (Table 3.1). When subjected to Dixon's Q-test, the XK and XCa + XMg, percentages calculated for equilibrium with seawater are determined to be non-outliers when included in with the experimental data set. Thus, clay cation compositions calculated using Equation 1 for seawater give cation compositions that are also within reasonable limits compared to the accuracy of laboratory analyses of the cation compositions of clays equilibrated with seawater.

Thus, the compositions calculated in this study are shown to either lie inside of the ranges for each individual cation or are tested statistically as non-outliers when compared to the experimental data set. This agreement supports that Equation 1 and the exchange constants predict values within the limits of laboratory experimental results. Also of note, since the same equation and exchange constants are used to calculate the equilibrated clay-cation compositions of all the samples in this study, and this study provides a relative comparison of the results showing large differences when comparing the calculated results from one sedimentation zone compared to another addition, the uncertainties in the absolute values would not change the results of this study.

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3.5 Results

3.5.1 Fluvial-Origin Clays

Cation exchange between clays and water is almost instantaneous (Nachod and Wood, 1945), so fluvial clays and river water will be in exchange equilibrium at deposition. To calculate the cation compositions of clays that would deposit from river water in the fluvial portions of the Chicot/Evangeline and Wilcox aquifers using Equation 1, the present-day composition of river water from the coastal portions of the Brazos and Colorado rivers and their tributaries in the vicinity of the Chicot/Evangeline study area (Figure 3.1) were used and the results presented on the ternary diagram in Figure 3.4a. The present-day cation compositions of river water in the Chicot/Evangeline study area are likely representative of those of the river water that deposited the fluvial sediments of the Chicot/Evangeline and Wilcox aquifers, because rivers in the near-shore environment at the time these aquifers formed drained the same source areas as present-day rivers in the study area.

Figure 3.4 A) Calculated mole-percent Ca, Mg, and Na (X_{Ca}, X_{Mg} and X_{Na}) on the clayexchange complex in equilibrium with the local present-day river water (small open squares, this study) and Mean-World river-water (Open black boxes are for clay samples equilibrated with Mean World River Water in Sayles and Mangelsdorf's (1977) experiments; large black "X" is calculated in this study from the composition of Mean World River Water), seawater (large black filled circles are for clays equilibrated with seawater in Sayles and Mangelsdorf (1977) experiments; large black filled triangle is calculated in this study from seawater composition), and clay in equilibrium with pore water from bay sediment from a depth of 200 ft (a large bold "B") (from Texas Water Development Board, 2020). B) Calculated mole-percent Ca, Mg, and Na (X_{Ca}, X_{Mg} and X_{Na}) on the clay-exchange complex in equilibrium with Chicot/Evangeline aquifer groundwater samples (this study) and C) Calculated mole-percent Ca, Mg, and Na (X_{Ca}, X_{Mg} and X_{Na}) on the clay-exchange complex in equilibrium with Wilcox aguifer groundwater samples (this study). For the groundwater samples, the blue circles represent fluvialdeposited clays based on a cutoff of $X_{Na} \leq 8.0\%$ (those in the blue shaded area), whereas the red circles represent marine-deposited clays based on a cutoff of $X_{NA} > 8.0\%$ (those in the pink shaded area) (see text).



A River Water and Seawater Equilibrated Clay

For comparison with other river water in the world, the cation-compositions of four clay samples equilibrated in the laboratory (Table 3.1) with Mean World River Water (MWRW) (Livingstone, 1963) by Sayles and Mangelsdorf (1977) are plotted on Figure 3.4. In addition, in this study the composition of clay in equilibrium with the Mean World River Water (MWRW) (Livingstone, 1963) was calculated (Table 3.1) and is also plotted on Figure 3.4a. A plot of the compositions of the local present-day river water and the Mean World River Water on a water-composition trilinear diagram, show they plot in comparable locations on the cation triangle of the diagram (Figure 3.5a).

For further comparison with other river waters of the world, the river water from the study area and the Mean-World River Water are plotted on a Gibbs diagram (Gibbs, 1970) which shows the relationship between the total dissolved solids content versus weight ratios of Na/(Na+Ca) of river waters of the world (Figure 3.6). River water from this study area plot within the area for river-waters with compositions controlled by reactions with the rock and soil in the enclosing basin. This is the composition expected of rivers in a climate that is neither desert where evaporation-dominated river compositions would plot, nor tropical where rivers with rain-dominated compositions would plot. The climate in the study area during deposition of the Chicot/Evangeline and Wilcox aquifer sediments were neither desert nor tropical. The climate setting of the northern Gulf of Mexico has generally remained a warm, subtropical climate since the Oligocene (Galloway, 2008), so their location on the Gibbs plot further supports that the proportions of Na and Ca during deposition of the aquifers studied would be similar to that of the present-day river water.



Figure 3.5 Trilinear plots (Piper, 1944) of A) river water, B) Chicot/Evangeline aquifer water, and C) Wilcox aquifer water samples used in this studied. Blue circles are water samples in equilibrium with a clay with a cation composition of $X_{Na} \le 8.0\%$, red circles are water samples in equilibrium with a clay with a cation composition of $X_{Na} \ge 8.0\%$, black circles are river water samples. MWRW=Mean World River Water from Livingstone (1963). Seawater is from Hem (1985).



Figure 3.6 Gibbs diagram (Gibbs, 1970) of the weight ratio of Na/(Na+Ca) versus total dissolved solids showing the present-day river-water compositions from the study area (black dots), Mean World River Water (MWRW, red dot). The area outlined represents the composition of world river waters from Gibbs (1970) noting the composition of river water whose composition is controlled by reaction with rocks (Rock Dominated), dilution rain in a tropical climate (Precipitation Dominated), concentration by evaporation in a dry climate (Evaporation Dominated) and mixing with seawater (Seawater).

The clay-cation compositions in equilibrium with the local river water and the Mean-World River Water plotted on Figure 3.4a show a uniform and narrow range in compositions. In all samples XCa is dominant (64 to 93%), followed by XMg (5 to 30%), and XNa always less than 8% (ranging from 0.7% to 8%). There is an inverse linear relationship between XCa and XMg, with a slight increase in XNa as XMg increases.

Of note, comparison of the cation compositions of the river water to that of the equilibrated clays shows an apparent disproportionate amount of Na relative to Ca and Mg in the river water (Figure 3.5a) compared to that in the equilibrated clays (Figure 3.4a). Na on the equilibrated clays in all cases comprises a small precent of the cations on the clays, ranging from 0.7 to 8%, of the total cations (Figure 3.4a), whereas, the proportion of Na in the paired water sample is always a higher percentage of the cations in the water, ranging from 14 to 68% of the total cations in the water (Figure 3.5a). This disproportionate amount of Na in the water compared to Na on the equilibrated clay is expected because of the cation exchange properties of clay minerals in which the divalent cations (Ca and Mg) are favored over the monovalent cations (Na) on the clays (Appelo and Postma, 2005). This disproportionate relationship supports why using the equilibrated clay-cation proportions is more useful to differentiate clay origin than groundwater cation proportions.

Based on XNa of less than 8.0% for all clays equilibrated with present day river water, 8.0% was used as a cutoff for the composition of clays of fluvial origin (river origin) that would have formed in the fluvial portions of the Chicot/Evangeline and Wilcox aquifer sediments. A line was drawn at XNa = 8.0% on Figure 3.4a to represent this maximum XNa expected for clays of fluvial origin, and thus the upper limit of XNa

expected from rivers clays deposited in a climate other than desert or tropical climate, as was the climate present in the study areas at the time of deposition of the aquifer sediments. Thus, it is expected that the cation compositions of the clays that originally deposited from rivers when forming fluvial sediments of the Chicot/Evangeline and Wilcox aquifers should plot to the left of this XNa 8.0% maximum.

Of note, the XNa of less than 8.0% was present in all river waters independent of total dissolved solids which ranged from 99 to 709 mg/L for the river samples in this study and plotted on Figure 3.5a. Rivers in high flow flood stage are expected to have higher total dissolved solids than in low flow. This independence of XNa of the equilibrated clays on fiver flow stage supports that XNa of clays deposited in flood stage would be in the range of XNa <8%.

For a clay to have an XNa > 8.0%, and thus plot to the right (outside) of the area of fluvial-origin clays, would require a higher Na to Ca ratio in the water than expected of river water in the area at the time of deposition. In a coastal setting, which is the focus of this study, sea water would have this higher ratio (Figure 3.4a and 3.5a), as would water in environments in which river water is mixed with sea water, such as found in the nearshore and marginal-marine environment (e.g., estuaries, lagoons, tidal flats, deltas, inland bays, barrier complexes, shoreface, peri-tidal extremes of tidal estuaries and wetlands).

3.5.2 Marine to Marginal-Marine Origin Clays

The cation composition of clays in equilibrium with seawater both calculated with Equation 1 and experimentally determined by equilibrating clay samples (montmorillonite, mixed-layer montmorillonite/illite, illite, and kaolinite) with seawater are shown in Figure 3.4a. As expected because of the high percentage of Na relative to Ca and to a lesser extent Mg in sea water compared to river water (Figure 3.5a), the seawater-equilibrated clays have high XNa values ranging from 40 to 60%, compared to the Fluvial-Origin Clays which have values of less than 8% (Figure 3.4a). In contrast, XCa of the seawater equilibrated clays are extremely low, less than 25%, compared to the very high values of the Fluvial-Origin Clays with XCa ranging from 72 to 93%. Finally, XMg is similar in the seawater equilibrated clays ranging from 23 to 41% and the Fluvial-Origin Clays ranging from 5 to 35%.

The proportion of cations in seawater are generally constant (Wilson, 1975) but the proportion near the coastline and in coastal environments will shift as a result of dilution by mixing with river water runoff from the continents. Dilution of present-day seawater off the coast of the northern Gulf of Mexico resulting a salinity as low as 27,000 mg/L, compared to 35,000 mg/L in undiluted seawater, has been found (Orlando et. al, 1993). Greater dilution is expected in the marginal marine setting, such as coastal bays and estuaries.

This is likely the result of changes in the composition of seawater subsequent to burial. The pore water in shallow marine sediments have been shown to increase in Ca by up to 6 mmol/kg (a 60% increase) (Hammond, 2001) relative to the other ions which includes Na and Mg. This increase in Ca, relative to Na and Mg, in shallow marine sediments is likely the result of calcite dissolution (Froelich et al., 1979). Thus, it is expected that clays equilibrated with this shallow pore water after deposition in the marine environment would have higher Ca values relative to Na and thus plot in the region between river water and seawater on the clay triangle in Figure 3.4, as would groundwater later equilibrated with those clays. This is further supported by an analysis of pore water collected from coastal bay sediments from a depth of 200 ft from north of the study area (Texas Water Development Board, 2020). The equilibrated clay-cation composition of that bay pore water sample plots within the area for marginal-marine origin clays between the seawater equilibrated clay and river water clay shown as "B" on Figure 3.4.

With little to no seawater infiltration occurring in the study area, the only significant source of Na is from meteoric water influx (Chowdhury et al., 2018), which cannot account for the Na content of the Na-rich clays in the marginal-marine zone of the study area. Further, the Cl content of the groundwater in equilibrium with the marginal-marine clays is not increased when compared to the groundwater in equilibrium with the fluvial deposited clays (Figure 3.5). Several recent studies document the chemical changes in groundwater that result from seawater infiltration induced by heavy pumping in coastal and island aquifers and show a coupled increase in Cl and Na in the groundwater progressing toward seawater in both the cation and anion portions of the trilinear diagram (Figure 3.5) (Sun et al., 2015; Aris et al., 2021; Heyddy et al., 2014).

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3.5.3 Cation Composition of Clays in Equilibrium with the Present-Day Groundwater

The mole-percentages of Ca, Mg and Na (XCa, XMg and XNa) on the clay-exchange site in equilibrium with the groundwater samples from the Chicot/Evangeline (Figure 3.4b) and Wilcox aquifers (Figure 3.4c) were calculated using Equation 1 and plotted on the clay triangles. With few exceptions, all the cation compositions of clays in equilibrium with the aquifer-water samples plot either in area for Fluvial-Origin Clays or Marginal-Marine Origin Clays. The exceptions to this are four samples from the Chicot/Evangeline aquifers that plot outside these areas (Figure 3.4b). Of these four outliers, three had one or more earlier water analyses in the database that were not used for this study, but would have plotted in the area of Marginal-Marine Origin Clays, suggesting the most recently analyses which are the ones used in this study may have analytic errors or been contaminated. Since the four outliers comprise less than 1% of the 492 samples used in this study, and since they are likely in error they are not considered further and not included on any other figures.

The clays in the study area that plot on Figure 3.4b and 3.4c in the area of Fluvial-Origin Clays, XNa \leq 8%, with few exceptions, show a strong inverse linear relationship between XCa and XMg and a much smaller inverse linear relationship between XCa and XNa, similar to that of the present-day river water clays. In comparison, and as expected, the clays that plot on Figures 3.4b and 3.4c in the area pf Marginal-Marine Origin Clay, XNa > 8%, bend away from the area of Fluvial-Origin Clays and trend toward the composition of clays in equilibrium with seawater. This results in the samples that plot in the area for Marginal-Marine Origin Clay having an inverse linear relationship between XCa and XNa (Figures 3.4b and 3.4c).

Based on the XNa cutoff of 8% the calculated depositional environment of the clays predicted from the groundwater chemistry the samples were separated into Fluvial-Origin Clays (blue on Figures 3.4b and 3.4c) and Marginal-Marine Origin Clays (hereafter referred to as Marine-Origin Clays, red on Figures 3.4b and 3.4c).

3.5.4 Geographic Distribution of the Fluvial, Mixed, and Marine Derived Sediments based on Stratigraphic Data

The predicted environment of deposition of the clays, fluvial versus marine, in the study area will be compared to the actual environment of deposition of the sediments in which they occur.

3.5.4.1 Chicot/Evangeline Study Area

The environment of deposition of sediments that compose the Chicot/Evangeline aquifers in the study area reported in Figures 3.1 and 3.3 were determined by Knox et al. (2006) using 140 geophysical well logs, and outcrop and micropaleontological data. Percent-sand distributions calculated from the well logs were used to map sand distributions and determine depositional facies. Micropaleontological evidence was used to confirm marine sediments.

The sediments of the Chicot/Evangeline aquifers were identified as cyclic deposits of fluvial and shallow-marine sediments. The locations of the most landward ocean transgression (rise in sea level) and most downgradient ocean regression (reduction in sea level) were determined for each geologic unit and are shown on the cross section in Figure 3. The sediments beyond these transgressive and regressive extremes will be referred to as the Fluvial Zone and Marine Zone. Between these maximum and minimum limits of sea-level rise and decline lies a transition zone composed of repeated cycles of fluvial and marine sediments, which will be referred to as the Mixed Zone.
3.5.4.2 Wilcox Study Area

The depositional environment of the sediments of the Wilcox aquifer in the study area is fluvial (Kaiser, 1978; Thorkildsen and Price, 1991). The exception to this is in the southwestern portion of the study area (in Bastrop County) where tidal flat and shallowmarine sediments are found in the Calvert Bluff Formation (Yancey et al., 2012, Denison et al., 2017), which is the shallowest unit of the Wilcox aquifer. This area is marked by a red triangle on Figure 3.1. The presence of this small area of Marine sediments is based on paleontological data from outcrop samples. Samples of both tidal sediments which could mark the fluvial-marine transition zone and samples of open marine sediments were found.

3.6 Discussion

3.6.1 Sediment Depositional Environment based on Geographic Location compared with that predicted by the Clay-Cation Compositions (calculated from the Groundwater Chemistry)

Water sample locations and depths are shown on the Chicot/Evangeline cross section (Figure 3.3) color coded to indicate those samples whose composition identifies them as deposited from river water, with XNa \leq 8% (Fluvial-Origin Clays) in blue and those identified as deposited from marginal-marine water, with XNa >8% (Marine-Origin clays), in red. Each water sample was then grouped based on its location as to whether the sample occurred within the geographic zone of Fluvial, Mixed (Fluvial/Marine), or Marine Deposited Sediments as shown on Figure 3.3. XNa values of the clays within each depositional zone were plotted separately on Figure 3.7 showing the number and percentage of samples within each unit division of XNa. These results are summarized in Table 3.2.



Figure 3.7 Frequency distribution of X_{Na} values of clay (calculated using Equation 1) equilibrated with figure A river water and B to E groundwater. The number above each bar represents the percentage of total samples within that category. For the Chicot/Evangeline plots the samples are separated into the three depositional zones B) Fluvial, C) Mixed, and D) Marine based on their location in the aquifer as shown in Figure 3.3. For the Wilcox plot (E) all the samples are shown in one plot, with a box denoting the marine samples from Bastrop County (see text).

Table 3.2 Chicot/Evangeline study area, range in values of X_{Na}, X_{Ca} and X_{Mg}, and mean and percent of X_{Na}, of river water, and clays from each of the three geographic/depositional zones, Fluvial, Mixed Fluvial/Marine and Marine (see Figures 3.7 and 3.8).

| | X _{Na,clay} (%) | | | | XCa,clay (%) | Хм _{g,clay} (%) |
|--------------------|--------------------------|--------|--|--|--------------------|--------------------------|
| | range ¹ | median | % of samples of fluvial origin (X _{Na} ≤ 8%) | % of samples of marine origin (X _{Na} >8%) | range ¹ | range ¹ |
| River water | 0.7-8 | 2 | 100 | 0 | 60-98 | 2-40 |
| Depositional Zones | | | | | | |
| Fluvial Zone | 0.5-15 | 2 | 92 | 8 | 55-98 | 2-35 |
| Mixed Zone | 1-31 | 7 | 59 | 41 | 45-98 | 2-35 |
| Marine Zone | 5-39 | 19 | 14 | 86 | 40-70 | 18-38 |

1. range of 99% of the samples

The distribution of Fluvial-Origin Clays (XNa \leq 8.0%) and Marine-Origin Clays (XNa > 8.0%) in Figure 3.7, and summarized in Table 3.2, shows a pattern that can be related to the maximum-ocean transgression and regression in the Chicot/Evangeline study area (Figure 3.3). Above the maximum transgression, where only fluvial clays would have deposited, the majority of the clays (92%) have cation compositions indicating they have a fluvial origin, with XNa \leq 8%. In the zone beyond the maximum regression, where only Marine-Origin Clays should occur, the majority of the samples (86%) have XNa > 8% indicating they are of marine origin. In the mixed (transition) zone between the maximum transgressions and regressions the samples are a near equal mix of fluvial origin (XNa \leq 8%), 59%, and marine origin (XNa > 8%), 41%.

Further, it is apparent that the range in values and median values of XNa within each sediment depositional zone can potentially be used as an indicator of sediment depositional environment (Figure 3.7 and Table 3.2). Clays from the Fluvial Sediment Zone have the lowest values 0.5 to 15% with a median of 2%. As expected, these values are comparable to that of the river deposited clays ranging from 0.7-8% and with the same median of 2% supporting that the majority of the samples have similar values. While some of the clays in the fluvial sediments have values over the maximum of 8% for the river water clays, those high values only represent 7% of the samples from the Fluvial Zone, so the majority of the river water clays and clays from the Fluvial Zone are within the same range.

Clays from the Marine Zone with a range of XNa from 5 to 39% and median of 19%, are greater than the bulk of the samples from the Fluvial Zone, with 50% of the Marine

Zone samples having values greater than the second highest statistically significant value measured in the Fluvial Zone, 14% (note there is one extreme outlier from the fluvial zone of 22%).

Clays from the Mixed Zone, with XNa ranging from 1 to 31% with a median of 7%, as expected have values for XNa that are intermediate to, and span those of samples from both the Fluvial and Marine Zones. However, the marine samples in the Mixed Zone which have the highest XNa of 31%, do not reach the highest values present in the Marine Zone of XNa =39%. Further in the Mixed Zone approximately half the samples (59%) are fluvial origin (XNa \leq 8.0%) and the rest (41%) marine origin (XNa >8.0%). This reflects that the sediments in this zone deposited along the coastline in a transitional fluvial to marine environment.

To further show the distribution of the calculated values of XCa, XMg and XNa for the clays within each geographic zone, the results are plotted on a clay-cation triangle which in this case is color coded to show the clay values within each geographic zone (Figure 3.8) and are summarized in Table 3.2. Clay values from the Fluvial zone are in blue, from the Mixed Fluvial/Marine zone are in grey, and from the Marine zone are in red. These data show that, while there is some overlap in XCa, XMg and XNa between the three geographic zones, there are clear differences in the clay-cation compositions within each zone. In addition to the differences in XNa described above, XCa is highest in samples from the Fluvial Deposited Zone, 55-98%, the lowest in the Marine Deposited Zone, 40-70%, and the Mixed Deposited Zone with XCa ranging from 45 to 98% it overlaps the most with the Fluvial Deposited Zone and less with the Marine Deposited Zone. In contrast, XMg is

the lowest, and has a similar range, in the Fluvial and Mixed Zones, 2 - 35%, and is somewhat higher ranging from 18-38% in the Marine Zone.

These results strongly suggest a relationship between the clay-cation composition and the depositional environment of the aquifer sediments. Sediments above the maximum transgression were deposited in a fluvial-flood plain, those beyond the maximum regression were deposited in a shallow-marine to marine setting, and the sediments between these two zones, were deposited in a mix of flood plain environment and shallow-marine to marine environment as sea level changed through time.

A similar relationship was seen in the Wilcox aquifers sediments, although the study area did not include a full sequence with the transition from fluvial to shallow marine. Instead, the majority of the Wilcox aquifers samples are from fluvial sediments, with a small portion of the study area having evidence of marine sourced sediments which were found in several outcrops only in the Bastrop County area (marked with a red triangle on Figure 3.1). The marine sediments were found in the Calvert Bluff formation from the Wilcox Group, and it was concluded they are evidence of more extensive marine sediments in the area.

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Figure 3.8. Calculated-clay compositions from the Chicot/Evangeline study area grouped based on their location with the three depositional zones designated on Figure 3.3 (Fluvial, Mixed, Marine). The range in cation composition of clays deposited by river water and seawater area are outlined with solid black lines

Comparison of the predicted environment of deposition of the clays in the Wilcox aquifer based on XNa of the equilibrated-clay composition, shows the majority of the samples are of fluvial origin (XNa \leq 8.0%), with the exception of seven samples that are of marine origin (XNa > 8.0%). The marine origin samples include one sample from the far northeast side of the study area and a cluster of six samples from Bastrop County in the southwestern portion of the study area (Figure 3.1). There is no explanation for the lone marine sample from the northeast portion of the study area where fluvial sediments occur. As it is one sample out of 77 fluvial samples in this area, it is possible the water sample from this location is contaminated or there is an error in the sample depth, and it is sourced from another aquifer.

In contrast the other six samples of Marine origin are from Bastrop County and from the Calvert Bluff Formation, a similar location and the same formation as the marine sediments found in the Bastrop County outcrops. This good agreement between the geographic location of the Wilcox samples with a fluvial origin in the area of fluvial deposited sediments, and the clays with a marine origin only in the area where marine sediments have been found, supports the relationships between clay cation composition and depositional environment found in the Chicot/Evangeline aquifer area.

Further, the XNa values for marine sediments from Bastrop County range from 17 to 40%, which is within the range of XNa of clays from Marine Deposited sediments in the Chicot/Evangeline study area (Figures 3.3 and 3.7). The XNa value of the lone marine sample from the northeastern portion of the study area that is 15% is likely local contamination of the groundwater from oil field brine upwelling or another source, or possibly an error in reporting the sample depth so it is from a different aquifer.

3.6.2 Comparison with the Aquifer-Water Chemistry

The chemical composition of the water samples from the Chicot/Evangeline and Wilcox aquifers used for this study are shown on the trilinear diagram (Piper, 1944) in Figure 3.5. The trends show the groundwater associated with fluvial origin clays range from Ca to Na as the dominant cation, whereas the water associated with clays of marine origin are all Na dominant. No trend is seen in the anion compositions (HCO3, Cl and SO4) of the groundwater that can be related to a fluvial or marine origin. This decoupling of the cation and anions was also described and explained in Capuano and Jones (2020).

As the clay-cation compositions calculated from the groundwater can be used to predict depositional environment, it is evaluated whether the cation composition of the groundwater can be used to do the same. Figure 3.9 is a plot of just the cation triangle of the trilinear diagram (Piper, 1944) for the Chicot/Evangeline water samples, color coded to show which of the three depositional zones shown on Figure 3.3 each water sample was obtained.

Chicot/Evangeline Groundwater – Depositional Zones



Figure 3.9 Cation triangle from the trilinear plot (Piper, 1944) of Chicot Evangeline Groundwater with color coding showing the samples collected from the depositional zones designate on Figure 3.3, blue for the Fluvial Zone, black for the Mixed (transition) Zone, and red for the Marine zone. In addition, an arrow labeled "flow" showing approximately where these samples fit into the direction of downgradient flow of recharging meteoric (rain) water in the aquifer.

There are trends and regions of groundwater cation composition that can be associated with a depositional environment, but they have a lot of overlap so do not give as clear a separation as the clay cation compositions calculated from the groundwater compositions. A couple of relationships stand out that could allow groundwater cation composition to be used in a limited way to predict the depositional environment of the enclosed formation. Groundwater from the Fluvial Depositional Zone has the lowest percent Na and higher percent Ca, with a zone that does not overlap with the other two zones, that has greater than 50% Ca. The other relationship is that the Marine Zone samples with few exceptions have greater than 70% Na and less than 15% Ca, although it does overlap with water from the Mixed (Transition) Zone. However, if samples are from the Mixed (Transition) zone than a wider range of values would be expected that overlap with a portion of the Fluvial and the Marine Zones. Thus, groundwater cation compositions might be used as a preliminary assessment but would not be as reliable as clay-cation compositions.

3.6.3 Evolution of the Clay-Cation Composition after Deposition and Identification of Fluvial versus Marine Sediments

After deposition of these coastal aquifers, with their continued outcrop exposure on the surface, cations in recharging (rain)meteoric-water will exchange with the cations in the clays in the aquifer material as the water and clays achieve cation-exchange equilibrium. Ca in the Ca dominated rainwater will exchange with Mg in the fluvial sourced clays first, then as it flows downgradient Ca and Mg will exchange with Na in the marine clays of the mixed fluvial/marine then marine zones. This results in the cation composition of the ground water progressing downgradient from Ca dominant, to Ca-Mg dominant within the fluvial sediment zone to Na dominant in the Mixed Fluvial/Marine to Marine sediment zones. This is seen in the cation triangle of the trilinear plots of the Chicot/Evangeline and Wilcox groundwater compositions (Figure 3.5). Similar to that discussed in Capuano and Jones (2020), there is no comparable downgradient relationship noted in the anion (HC03-CO3, SO4, Cl) chemistry of the groundwater (Figure 3.5).

The clays in the Chicot aquifer have been altered by tens to hundreds of thousands of years of meteoric-water recharge, such that the present-day cation composition of the clays represents the history of multiple pore-volumes of groundwater flow in the aquifer. However, in this setting, changes in the clay composition by a single pore-volume of present-day groundwater are minimal, with each pore-volume of meteoric water making a small incremental change in the clay's cation composition. For example, given the average effective porosity of 23% (Nobel et al., 1996) and approximately 40% clay (Dutton, 1994) 1 liter of water will be exposed to 2.8 kg of clay. If the clay exchange sites contain the maximum Na in seawater equilibrated montmorillonite (55% Na, Table 3.1) which has an average cation-exchange capacity of 1.2 mole/kg (ranging from 0.7 to 1.7 mole/kg for montmorillonite, Sposito, 2008), then a total of 42 g of Na are available to exchange from the clay for Ca in the water, which would require 37 g of Ca to remove all the Na from the clay. Given the concentration of Ca in the mean world river water of approximately 0.38 mmol/L (15 mg/L) (Table 3.1), a single liter of water could exchange out only 0.04% of the 42 g of Na available in the clay, or conversely, 2,500 liters are needed to completely remove the Na on the clay. The greater the clay content, which increases to 80% downgradient, the less Na on the clay is affected by a single volume of water. Therefore, as the water passes through the sediment in the aquifer it will have little effect on the relative amount of Ca or Na on the clay, but would measurably alter the Ca and Na composition of the water. In addition, it is unlikely that all the clay is exposed to groundwater flow and exchange. The cumulative effect of long-term flow is required to alter the clay-exchange composition. However, despite this there is a downgradient trend in elevated Na in the clays that coincides with the transition from fluvial to marine depositional environments. Therefore, in the setting of this study area, flushing has not been adequate to remove the characteristic elevated Na of greater than 8% in the clays deposited in the marine and transitional fluvial-marine settings. This progression in groundwater composition from the Fluvial to the Marine sediments is expected to occur in other coastal sourced aquifers with a similar climatic, geologic and hydrogeologic setting. Thus, the progression in groundwater cation chemistry, and the coupled equilibrated clay-cation compositions, can potentially be used to aid sedimentologic studies with the purpose of identifying fluvial, fluvial to marine transition and marine depositional environments.

Further, the results of this study show that groundwater composition and the equilibrated clay-cation compositions (calculated with Equation 1) can also potentially be used as diagnostic criteria to determine the environment of deposition of siliciclastic coastal sediments. In addition, groundwater chemistry is more commonly available and more easily obtained than sediment samples that require the acquisition of core which is seldom collected due to extra drilling expense and, if collected, may not be readily available. Moreover, cation analyses of groundwater samples and calculation of the equilibrated clay compositions can be easily automated providing a rapid overview of a large area of study.

Comparison with a traditional sedimentological study of the same area by Knox et al. (2006) highlights the potential value of using groundwater cation composition to delineate the fluvial from marine sediments and their transition. The Knox et al. (2006) study required acquisition, interpretation, and correlation of 140 geophysical well logs, outcrop data and micropaleontological data to define the occurrence of fluvial versus marine sediments and the transition zone. The Knox et al. (2006) study was itself a reinterpretation of the topic, emphasizing the necessity of paleontological data, which are commonly not available, and describes some of the difficulties and uncertainties in using geophysical logs to determine depositional environments. Numerous studies show how the mineralogy of clays (not their cation composition) and their fraction of the sediment can be used as indicators of depositional environments to differentiate marine from nonmarine conditions (e.g. Griffin and Parrot, 1964; Gibbs, 1977; Lonnie, 1982), but this requires acquisition of sediment samples which are not always readily available. In contrast, the groundwater geochemistry data required for the methods proposed in this study, are easier and less expensive to obtain, and require fewer resource to analyze.

In addition, if core samples are available from a sedimentary unit, analysis of the cation composition of the clays could possibly be used to aid in the determine the depositional environment or to augment a sedimentological/mineralogical based study.

3.7 Conclusions

Calculation of the cation composition of clays deposited from river water demonstrates that XNa is a key discriminator of sediments of fluvial origin, with all river water deposited clays having XNa \leq 8.0% versus clays of marginal marine to marine origin having an XNa > 8.0%. Using this criteria clay cation compositions (XCa, XMg, and XNa) calculated for present-day groundwater from the Chicot/Evangeline aquifer show a strong correlation between groundwater composition and clay XNa, and to a lesser extent XCa and XMg, and the depositional environments of the host formation as determined independently based on micropaleontological, core, and petrophysical log data.

Three depositional environments were identified from stratigraphic analyses of the area (Knox et al., 2006). These consist of a fluvial flood plain zone up-dip of the maximum transgression (Fluvial Zone), a shallow-marine to marine zone down-dip of the maximum regression (Marine Zone), and a mix of flood plain and shallow-marine to marine sediments between these two zones (Mixed Zone). Within each of these zones, XNa and XCa values showed clear distinctions that could be used to identify the depositional origin of sediments from the clay cation equilibrium calculated from the groundwater:

Fluvial Zone:

XNa: 92% of the samples from this zone have a river water origin with XNa \leq 8.0% ranging from 0.5 to 15% with a median of 2%

XCa ranges from 60-98% and in all cases is greater than XMg (2 – 35%) and XNa (0.5 - 15%) and agrees well with the fluvial origin, with all the values within the range for river water.

Marine Zone:

XNa : 86% of the samples from this zone have a marine origin with XNa > 8.0%, with values ranging from 5.0 to 39% with a median of 19%. Also, 50% of the Marine Zone samples have XNa values greater than the highest value in the Fluvial Zone of 15% (excluding the one extreme outlier of 21%).

XCa and XMg are within the range of river water and Fluvial Zone samples, leaving XNa as the key discriminator of these samples.

Mixed Fluvial/Marine Zone:

XNa values are mixed. Nearly half, 59%, have a fluvial origin (XNa \leq 8.0%) and half, 41%, have a marine origin (XNa > 8.0%). Values range from 1 to 31% and have a median of 7%. The highest values of XNa in the Mixed Zone, 31%, do not reach the highest values present in the Marine Zone of 39%.

XCa and XMg approximately overlap with both those in the Fluvial and Marine Zones.

A similar relationship was observed in the Wilcox aquifers sediments, although the study area did not include a full sequence from fluvial to shallow marine.

Due to present-day outcrop exposure of the aquifers, cations in recharging (rain)meteoric-water will exchange with the cations in the clays in the aquifer material as the water and clays achieve cation-exchange equilibrium. Ca in the Ca dominated rainwater will exchange with Mg in the fluvial sourced clays first, then as it flows downgradient Ca and Mg will exchange with Na in the marine clays of the mixed fluvial/marine then marine zones. This results in the cation composition of the ground water progressing downgradient from Ca dominant, to Ca-Mg dominant within the fluvial sediment zone to Na dominant in the Mixed Fluvial/Marine to Marine sediment zones (Figure 3.5). In contrast, there is no similar downgradient relationship in the anion (HCO3-CO3, SO4, Cl) chemistry of the groundwater (Figure 3.5) (Capuano and Jones, 2020).

This progression in groundwater composition from the fluvial to the marine sediments is expected to occur in other coastal source aquifers with a similar climatic, geologic and hydrogeologic setting. This progression in groundwater cation chemistry, and the coupled equilibrated clay-cation compositions, can potentially be used to aid sedimentologic studies with the purpose of identifying fluvial, fluvial to marine transition and marine depositional environments.

3.8 Acknowledgments, Samples, and Data

Authors have no conflict of interest. FAIR Data standards data availability statement: This research uses data from https://www2.twdb.texas.gov/apps/WaterDataInteractive/GroundWaterDataViewer, https://data.tnris.org/collection/79a18636-3419-4e22-92a3-d40c92eced14, and https://waterdata.usgs.gov/nwis/dv/?referred_module=sw, accessed 2020-9-15

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CHAPTER 4:

CLAY-CATION COMPOSITION OF RIVER SEDIMENTS AS EVIDENCE OF WET VERSUS DRY PALEOCLIMATE Cole R. Jones and Regina M. Capuano

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4.1 Summary

Cation compositions (X_{Na}, X_{Ca}, X_{Mg}) of clays are shown to reflect the composition of surface water at the time of deposition, with clays deposited from surface water in a semiarid climate (evaporation > precipitation) having an X_{Na} >8%, compared with X_{Na} < 8% for clays deposited under wetter conditions (evaporation < precipitation). This is a product of the effect of evaporation in the dry climate resulting in an increase in Na relative to Ca and Mg in the surface water. This trend is shown in fluvial sediments from the Texas Gulf Coast where both the present-day climate, and the climate during Late Pleistocene deposition, have a gradient from wet humid subtropical (mild temperate) in the north, to dry semi-arid subtropical in the south with evaporation exceeding precipitation much of the year. The possibility that the clay-cation compositions could have been altered by meteoric water recharge after deposition was considered by comparing the ratios of the conservative ion Cl against Na which is undergoing cation exchange. It was found that the Na-rich clays currently present in the south are releasing Na to the groundwater, so it is enriched in Na relative to Cl strongly supporting their original deposition as Na rich rather than Na poor clays in the dry environment. This trend was not present in the northern sediments with the wetter climate, supporting their deposition as Na poor clays. These results support that the Na content relative to Ca and Mg in clays deposited from surface

water in a terrestrial environment can be used as paleoclimate proxies to predict a wet versus dry climates.

4.2 Introduction

The climate of the Texas Gulf Coast progresses from wetter humid subtropical in the north to drier semi-arid subtropical in the south, while the geologic and hydrologic settings of the fluvial portion of the Beaumont Formation of the Gulf Coast Aquifer System are relatively uniform from north to south. This allows for a comparative study of the effect of climate on the composition of clays deposited in a wet versus a dry fluvial environment.

While there are numerous studies of the effects of climate on the quantity, character, and distribution of clay assemblages in fluvial sediments and their use as indicators of the whether the environment of deposition is fluvial or marine (e.g., Ingles and Ramos-Guerrero, 1995; Macklin et al., 2012), no study has related the cation composition of clays deposited in a fluvial environment to the wet versus dry character of the climate at the time of deposition.

In this study, it is shown that surface water in the northern Texas Gulf Coast is precipitation dominated (Gibbs, 1970) and thus more enriched in Ca and Mg relative to Na, compared to the surface water in the southern Texas Gulf Coast which is generally evaporation dominated (Gibbs, 1970) and thus more enriched with Na relative to Ca and Mg, and has higher total dissolved solids (TDS). The calculated cation composition of clays that would be deposited by the surface water in northern versus southern regions of the study area have similar cation compositions to the actual clays equilibrated with the groundwater in the Beaumont formation in each region. Fluvial sediments deposited in the cooler-wetter northern Texas Gulf Coast are enriched in Ca, and to a lesser extent Mg, relative to Na, such that Na comprises less than 8% of the cation content of the clays. In contrast, in fluvial sediments deposited in the warmer-drier southwest Texas Gulf Coast, Na comprises greater than 8% of the cation content of the clays relative to Ca and Mg on the clays.

4.3 Study Area

The focus of this study is the Late Pleistocene aged (120,000-20,000 bp) Beaumont Formation deposited along and parallel to the Texas Gulf Coast, extending approximately 280 km from approximately the San Jacinto River to the Nueces River (Figure 4.1). The Beaumont Formation is the youngest, uppermost geologic unit of the Gulf Coast Aquifer System, which is a wedge of seaward thickening Cenozoic sediments that outcrop parallel to the Texas coastline (Sellards et al., 1932; Aronow, 1971). The Beaumont Formation lies in outcrop at the top of this Cenozoic wedge, and itself is also a coastward thickening wedge that extends to the shoreline (Aronow, 1971; Garcia, 1991) (Figures 4.1 and 4.2). It is underlain by the predominantly quartz-rich sands of the Lissie Formation, and below that the Willis Formation which together comprise the Chicot Aquifer (Aronow, 1971; Baker, 1995). The Beaumont Formation acts as a confining layer to the Chicot Aquifer (Sellards et al., 1932; Baker, 1995; Chowdhury and Turco, 2006;). On the surface, the Beaumont Formation generally forms a smooth flat topography, gently dipping toward the coastline. It is cut locally by modern rivers, where it is filled with recent river alluvium.



Figure 4.1 Plan map of the study area showing the locations of the fluvial (in white) and marginal-marine (in pink) portions of the Beaumont Formation outcrop (after Young et al., 2010; Solis, 1981), the groundwater and river water samples, NADP rain collection sites (NADP, 2021), salt domes that present within in the Beaumont Formation (after Beckman and Williamson, 1990), climate regions C1, C2 and C3 (see text), and cross sections A-A', B-B', and C-C'. The groundwater sample colors represent blue for XNa < 8% and red for XNa > 8% (see text for method of calculation). The green highlighted areas show the locations of the Selected Wedge and the Salt Dome Free Area of C1 used for the Cl and Na Mass Balance Calculations.



Figure 4.2 Generalized cross sections (after Solis, 1981) for climate regions A) North-C1 (A-A'), B) Central-C2 (B-B'), and C) South-C3 (C-C') (Figure 4.1) showing the maximum depth of the Beaumont Formation within each climate region and the downdip location of the transition from fluvial to marginal-marine sediments (after Solis, 1981). Hydrologic head contours (light grey lines) for C1 are from Dutton (1994), and for C2 and C3 are from Ryder and Ardis (1991).

The Beaumont Formation is a regressive sequence of coastal sediments deposited during the sea water decline that began at the end of the glacial high stand approximately 135,000 years ago (Winkler, 1979). The Beaumont Formation was deposited during this interglacial period from approximately 120,000 to 20,000 years ago, during which time the gradual fall in sea level resulted in deposition of sediments transitioning from fluvial to fluvial-deltaic inland to near-shore marine toward the coastline (Winkler, 1979, Garcia, 1991). The depositional style of the Beaumont Formation has remained constant throughout its formation regardless of the rate or magnitude of sea level change or fluctuation (Winkler, 1979). Sea level is thought to have been approximately 6 m higher during deposition of the Beaumont Formation compared to sea level today (Aronow, 1971).

The Beaumont Formation consists of a series of adjacent and overlapping units progressing toward the coastline of fluvial, fluvial-deltaic, and shallow marine origin (Aronow, 1971). The overlapping fluvial units consist of meander belt deposits of sand, silt, and in places gravel, in a matrix of clay-rich flood-plain and back-swamp deposits. The meander belt deposits crisscross toward the coastline ending in small to large deposits of clay-rich deltas that prograde into shallow marine water where overbank and interdistributary muds were deposited (Aronow,1971; Garcia, 1991). The location of the transition from fluvial (fluvial-channel sand and floodplain mud) to marginal marine (facies of bayhead delta sand and bay-fill mud) is shown as a dashed line on Figure 4.1 (Solis, 1981; Knox et al., 2006; Young et al., 2010). The focus of this study is the fluvial portion of the Beaumont Formation. The Beaumont Formation is predominantly composed of greater than 75% clay and less than 25% very fine to fine sand (Aronow, 1971; Garcia et al., 1991; Tuck 1991). The clay fraction is montmorillonite, and the silt/sand fraction is predominantly quartz with minor to trace kaolinite, plagioclase and mica (Gabrysch and Bonnet, 1975; Garcia et al., 1991; Tuck 1991). In the southern portion of the study area, Region C3 (Figure 4.1), cementation with calcite and accumulations of calcareous nodules are common in the silt/sand fraction (Aronow, 1971).

Groundwater flow in the Beaumont Formation is generally uniform flowing toward the coastline (Figure 4.2). The hydraulic conductivity measured by tracer and aquifer tests give 3 x 10-3 cm/sec for the of the Beaumont Formation with porosity ranging from 35 to 41% (Capuano and Jan, 1996).

The source of sediments for the Beaumont Formation in both study areas throughout the Late Pleistocene deposition and today was consistently from the northwest, originating from continental erosion and runoff from the interior of Texas extending to the Rocky Mountains (Galloway, 2005; Chowdhury and Turco, 2006; Galloway et al., 2011). There are no evaporite beds in the source area or in the present day drainage basins that could have resulted in high-Na river water (Aronow, 1971; Galloway, 2005; Chowdhury and Turco, 2006; Galloway et al., 2011), with the exception of three salt domes present in the Beaumont Formation in the Northern-C1 study area (Figure 4.1).

The overlapping relict delta plains of the Beaumont Formation in the study area were produced by precursors of the present-day Brazos, Colorado, Guadalupe, and Nueces Rivers (Aronow, 1971). In the northern portion of the study area (C1), the drainage basins of the larger rivers dominate sedimentation. In this area (C1) the Brazos-Colorado alluvial plains and deltas are large, suggestive of rivers rivaling the size of the Rio Grande in the past. In contrast, in the southern portion of the study area (C2 and C3) the drainage basins of the larger rivers narrow as they pass through the Beaumont Formation, covering less area, and their sediments make up a smaller proportion of the Beaumont Formation. In this southern area (C2 and C3) the drainage basins of numerous smaller-local rivers are increasingly important, filling their local basins with sediments and comprising a greater portion of the Beaumont Formation than the major river sediments. Thus, fluvial sediments of the Beaumont Formation in the south portion of the study area (C2 and C3) are predominantly a product of the smaller more local river deposits.

Numerous salt domes underlie the Beaumont Formation in the northern portion of the study area (Region C1), however only three of these domes (Blue Ridge, Hawkinsville and Orchard) have halite at a depth shallow enough to occur in the Beaumont Formation (Figure 4.1) (Beckman and Williamson, 1990). No salt domes occur in Regions C2 and C3.

4.4 Methodology

4.4.1 Groundwater Analyses

The chemical compositions of groundwater collected from the Beaumont Formation that are used in this study were obtained from the Texas Water Development Board's (2021a) groundwater database. Only analyses with pH and all major anions and cations, with a charge balance error of less than 2%, calculated using PHREEQC and the LLNL database (Parkhurst and Appelo, 1999), and located more than 5 km from the coastline or bays were used. For the case in which multiple analyses from a single well passed the above criteria, the analysis with the most recent sample date was used. After this elimination, 304 samples remained. The sample locations and depths are shown on Figures 4.1 and 4.2.

4.4.2 River Water Analyses

Two datasets were used to represent the chemistry of river water in this study, a Complete Elemental Analysis dataset which includes only river water analyses with complete chemical analyses (all major and minor ions and pH) and the Electrical Conductivity (EC) dataset which includes only electrical conductivity measurements of the river water. The data in both data sets was obtained from the Texas Commission on Environmental Quality (2021).
The Complete Chemical Analysis river-water dataset was used for calculation of all river water cation equilibrium and mass balance calculations. For this dataset, only those analyses with all major anions and cations, pH, and with a charge balance error of less than 2% (calculated using PHREEQC and the LLNL database) (Parkhurst and Appelo, 1999) were used. River water analyses from within the zone of the daily tidal surge or collected from lakes or reservoirs were excluded from this dataset. For the case of sample locations that had river water samples collected over multiple years (1959-2020) and had multiple chemical analyses available, all sample dates were used that met the above criteria. This Complete Chemical Analysis river-water dataset includes 2870 chemical analyses of river water from 40 river locations (Figure 4.1). The Electrical Conductivity river-water dataset was included in this study because it provides data on the relative ion concentrations at many more locations, 206 locations (Figure 4.3), compared to the 40 (Figure 4.1) location in the Complete Chemical Analysis dataset. This Electrical Conductivity dataset provides average EC data for the 206 locations calculated from 39,797 EC measurements taken from 1969 to 2021 (Figure 4.3). This EC dataset does not include river water samples collected from within the zone of the daily tidal surge or collected from lakes or reservoirs.



Figure 4.3 Average specific-electrical conductance (EC) (μ s/cm at 25C) of river water samples at the locations shown in the study area. Data obtained from the Texas Commission on Environmental Quality (2021).). The location of the humid subtropical to semi-arid subtropical climate boundary is after Narasimhan et al. (2008) and Texas Water Development Board (2012).

4.4.3 Rainwater Analyses

The annual wet deposition of Cl and Na in rainwater in the study area was obtained from the National Atmospheric Deposition Program data base (NADP, 2021) for the four NADP sample locations in the study area.

4.4.4 Calculation of the Clay Cation-Exchange Equilibrium Compositions

Clay minerals and water achieve cation-exchange equilibrium within 10 minutes (Nachod and Wood, 1945)., so groundwater will be in exchange equilibrium with the clays in the aquifer sediments, and fluvial deposited clays will be in exchange equilibrium with the surface water from which they are deposited (e.g. Capuano and Jones, 2020). Thus, given a water analysis, the cation composition of the clay in contact with that water can be calculated. Fluvial clavs are in contact with the surface water that carries them, so fluvial clays will be in cation-exchange equilibrium with the surface water from which they are deposited. After deposition, clays in the aquifer will undergo exchange equilibrium with the groundwater. However, because of the dual porosity nature of clays, groundwater in clays will flow along preferential pathways (macropores), bypassing the water in the matrix (micropores) (e.g., Glaus et al., 2010, Tetre et al., 2015). Water in the macropores will maintain cation exchange equilibrium with the clays on the surface of the macropores. Diffusion of cations in the clay matrix is relatively rapid, dispersing into a 5 to 6 cm clay plug within 20 days (e.g., Tertre et al., 2015; Gimmi and Kosakowski, 2011; Krejci et al., 2021; Baborová et al., 2021), giving a rate of about 0.3 cm/day. At this rate, cations would diffuse thoughout the 2 m maximum thickness of the clay layers in the

Beaumont Formation (van de Lageweg et al., 2018; Chowdhury and Turco, 2006) within a year. Since there will be macropores within the clay layers (e.g., Saravanathiiban, 2014; Muddle and Briggs, 2019), cation diffusion within tens of days is likely. Also, since the velocity of groundwater flow in the Beaumont Formation of 0.37 cm/day (given the hydraulic conductivity of 10-3 cm/sec and porosity of 35%, Capuano and Jan, 1996; and hydraulic gradients shown in Figure 4.2) is similar to the cation diffusion rate of 0.3 cm/day, there will be time for cations in the flowing groundwater to diffusion into the clay layers resulting in a homogenization of the cations in the aquifer water and thus an opportunity for exchange equilibrium of these cations with the majority of the clays in the formation.

The cation compositions of clays in equilibrium with the groundwater and river water samples were calculated as the mole fractions (X_i) of Ca, Mg, Na, K, and Sr on the montmorillonite (X_i) $_{0.33}$ Al_{2.33}Si_{3.67}O₁₀(OH)₂·nH₂O exchange complex (X_i), where

 $X_{Ca} = m_{Ca}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{Mg} = m_{Mg}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{Na} = m_{Na}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ $X_{K} = m_{K}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$ and $X_{Sr} = m_{Sr}/(m_{Na}+m_{Ca}+m_{Mg}+m_{K}+m_{Sr}),$

and their sum is equal to one,

$$X_{Ca} + X_{Mg} + X_{Na} + X_K + X_{Sr} = 1.$$
 Eq. 1

Then, using the Gaines-Thomas convention with the following equations, derived using procedures described in Stumm and Morgan (1996) and Appelo and Postma (2005),

$$X_{Ca} = X_{Na}^{2} \cdot \frac{M_{Ca}^{2+}}{K_{Na/Ca}^{2} \cdot M_{Na^{+}}^{2}},$$
 Eq. 2

$$X_{Mg} = X_{Na}^2 \cdot \frac{M_{Mg}^{2+}}{K_{Na/Mg}^2 \cdot M_{Na^+}^2}$$
, Eq. 3

$$X_{K}=X_{Na} \cdot \frac{M_{K^{+}}}{K_{Na/K} \cdot M_{Na^{+}}}$$
, and Eq. 4

$$X_{Sr} = X_{Na}^2 \cdot \frac{M_{Sr}^{2+}}{K_{Na/Sr}^2 \cdot M_{Na^+}^2}$$
, Eq. 5

where, M_{Mg2+} , M_{Ca2+} , M_{Na+} , M_{K+} , and M_{Sr2+} are the mole/L concentrations of the ions in the water calculated using PHREEQC with the LLNL database (Parkhurst and Appelo, 1999). $K_{Na/Ca}$, $K_{Na/Mg}$, $K_{Na/K}$, and $K_{Na/Sr}$ are the ion-exchange coefficients for the exchange reactions:

respectively, where R is the negatively charged network of the cation exchanger. X_{Na} is then solved for by combining Equations 1 to 5 to give

$$X_{Na}^{2} \left(\frac{M_{Mg^{2+}}}{K_{Na/Mg^{*}M_{Na^{+}}}^{2}} + \frac{M_{Ca^{2+}}}{K_{Na/Ca^{*}}^{2} M_{Na^{+}}^{2}} + \frac{M_{Sr^{2+}}}{K_{Na/Sr^{*}}^{2} M_{Na^{+}}^{2}} \right) + X_{Na} \left(\frac{M_{K^{+}}}{K_{Na/K^{*}} M_{Na^{+}}} + 1 \right) - 1 = 0 \quad \text{Eq. 6}$$

which is solved as a quadratic equation, and then X_{Ca} , X_{Mg} , X_K and X_{Sr} are back calculated using equations 2 through 5 (Capuano and Jones, 2020).

Ion concentrations (M_i) in the water are used rather than ion activities to solve Equations 2 through 5. Because there are no similar activity-coefficient corrections for the ions on the clay-exchange complex, it was found more reliable to calculate the fractions of cations on the clay-exchange complex using ion concentrations in solution, rather than using ion activities (Stumm and Morgan, 1996; Appelo and Postma, 2005). The reason for this is likely because the activity corrections are similar for both the ions in the water and the ions on the clay-exchange complex (e.g., Appelo, 1994; Stumm and Morgan, 1996; Appelo and Postma, 2005).

The clay-exchange constants used in this study to solve Equations 2 through 5 are $K_{Na/Ca} = 0.4$, $K_{Na/Mg} = 0.5$, $K_{Na/K} = 0.2$, and $K_{Na/Sr} = 0.35$ taken from Appelo and Postma (2005, their Table 6.4, after a compilation by Bruggenwert and Kamphorst, 1979). Although Appelo and Postma (2005) do not list the clay mineral, these constants represent the exchange of montmorillonite/illite. Bruggenwert and Kamphorst (1979) note that their compilation includes predominantly data for montmorillonite clays as most exchange studies in the literature are of montmorillonite because of its relatively large exchange capacity. Clay in the Beaumont Formation is montmorillonite. However, if kaolinite is present its exchange is not important in considering cation exchange in this study, because its cation-exchange capacity (<0.05 mole/kg) is so low compared to that of

montmorillonite (0.7 to 1.7 mole/kg) and illite (0.2 mole/kg) (Sposito, 2008). Based on the dominance of montmorillonite and illite exchange compared to kaolinite, and because the exchange coefficients used in these calculations can be applied to either montmorillonite and illite, the results of the exchange calculations in the following text are referred to as calculations for montmorillonite or clay exchange.

The exchange constants used in these calculations were generally measured for systems with typical groundwater pH's ranging from near neutral to slightly basic (Bruggenwert and Kamphorst, 1979). Solutions with a very acidic pH can alter the cation-exchange constants away from those measured in a groundwater setting (Stumm and Morgan, 1996). The pH of the groundwater used in this study ranges from 6.5 to 9 and the pH of the river water ranges from 5.8 to 9.1 (with one sample at 10.2), none of which are very acidic. So, pH is not a factor in the calculated clay-exchange compositions.

Only Ca, Mg, Na, K, and Sr were considered in the clay-exchange calculations because no other cations are present in the water samples in concentrations greater than 1 mg/L. For the groundwater and river water samples for which Sr and K analyses were available the cation ratios on the clays were less than 1% (with only two exceptions), so Sr and K are not considered further in this study.

To test the validity of Equation 6, it was used to calculate the cation composition of clay in equilibrium with Mean World River Water (Livingstone, 1963), and the results were compared to the composition of montmorillonite equilibrated with Mean World River Water in the laboratory (Sayles and Mangelsdorf, 1979) (Table 4.1). There is good agreement for X_K. The four samples measured in the laboratory cover a narrow range in X_K from 0.2 to 1.3% and $X_K = 1\%$ calculated with Equation 6 lies within that range (Table 4.1). For the remaining cations, Na, Ca, and Mg, the range of the laboratory analyses, of $X_{Na} = 2.0-4.0\%$, $X_{Ca} = 62.4-73.0\%$, and $X_{Mg} = 23.3-34.3\%$, do not include the calculated values $X_{Na} = 1\%$, $X_{Ca} = 77\%$ and $X_{Mg} = 22\%$ (Table 4.1). However, application of the Dixon's Q-test, used to determine outliers in small data sets, shows that the calculated values for X_{Na} , X_{Ca} , and X_{Mg} would not be outliers when added to the laboratory data set, thereby supporting the use of Equation 6. In addition, the calculated value of $X_{Na} = 1\%$ is close to the narrow range of X_{Na} in the laboratory montmorillonite samples further supporting the use of Equation 6.

| Clays Equilibrated with | Clay cation compositions (%) | | | | |
|--|------------------------------|------|------|-----|-----------------------------------|
| Mean World River Water ¹ | X _{Na} | Xca | Хмд | Хк | X _{Ca} + X _{Mg} |
| Lab - Az. mont. ² | 2.0 | 62.4 | 34.3 | 1.3 | 96.7 |
| Lab - Dk. mont. ² | 3.6 | 67.5 | 28.7 | 0.2 | 96.2 |
| Lab - Tx. mont. ² | 2.9 | 73.0 | 23.3 | 0.8 | 96.3 |
| Lab - Wy. mont. ² | 4.0 | 65.8 | 29.7 | 0.5 | 95.5 |
| Calculated using Equation 6 ³ | 1 | 77 | 22 | 1 | 99 |

Table 4.1 Comparison of clay-cation compositions equilibrated with Mean World River Water¹ determined experimentally and calculated with Equation 6.

1. Na = 6.29 mg/L, Ca = 15.0 mg/L, Mg = 4.10 mg/L, K = 2.35 mg/L (Livingstone, 1963).

- Natural montmorillonite samples were flushed with Mean World River Water until complete exchange was achieved. The equilibrated clay sample was then analyzed for cation fractions. Az.= Arizona, Dk.= Dakota, Tx. = Texas, Wy. = Wyoming, mont.
 = montmorillonite, which are normalized to 100%. From Sayles and Mangelsdorf (1979)
- 3. Calculated in this study for Mean World River Water using Equation 6 (see section 3.4).

Most important to this study, as will be shown below, is the relative percent of X_{Na} compared to $X_{Ca} + X_{Mg}$, rather than the absolute values of X_{Ca} and X_{Mg} . Thus, the large range of 11% in the laboratory measured X_{Ca} and X_{Mg} (X_{Ca} 62.4-73.0% and X_{Mg} 23.3-34.3%) is not a problem in this study, because their sums compare well. The sum of $X_{Ca} + X_{Mg}$ of the laboratory analyses covers a narrow range, from 95.5 to 96.7%, and it is in good agreement with the sum of X_{Ca} and X_{Mg} calculated with Equation 6 of 99%, further supporting the use of Equation 6 to calculate $X_{Ca} + X_{Mg}$.

These results shows that the low percentages calculated for river water deposited clays discussed below for wet climate (<8%) are likely reliable (Figure 4.4), and support that the remainder of the cations in the clays, as predicted by Equation 6, are Ca and Mg. The relative error in the ratio of Ca compared to Mg is not a concern for this study, as the focus in this study is on the relative amounts of Ca plus Mg compared to Na on the clays.



Figure 4.4 Ternary diagrams of the clay-cation compositions in equilibrium with the groundwater and river water from regions D) C1, E) C2 and F) C3 calculated using Equation 6 (see text). On all figures blue symbols represent samples with $X_{Na} < 8\%$ and red symbols represent samples with $X_{Na} > 8\%$ (see text section 3.4 for method of calculation).

Further, since in this study all the clay cation percentages are calculated with the same equation, they are uniformly consistent. That is, the calculated values are used only to compare to relationships within the study area and to samples determined using the same equation, rather than to values determined by other methods. So, they are all comparative to one another, and the relative relationships determined would still apply even if they are offset from the absolute values of the samples.

4.5 Results and Discussion

Clay minerals carried by surface water and then deposited with fluvial sediments will be in cation-exchange equilibrium with the water because the exchange reaction is nearly instantaneous. Thus, cation composition of surface water can have an important effect on the composition of clays that accumulate in fluvial sediments.

Surface water compositions as (weight) ratios of cations, Na/(Na+Ca), and anions, Cl/(Cl+HCO3), relative to total dissolved solids (TDS) have been shown to be dependent on the local climate (Gibbs, 1970). In the very-wet tropical-climates, surface-water compositions are controlled by the composition of the abundant atmospheric precipitation, resulting in Na- and Cl-rich (Na/(Na+Ca) \geq 0.5 and Cl/(Cl+HCO3) \geq 0.2) and low TDS (<50mg/L) surface water (Figure 4.5).



Figure 4.5 River water samples from the study area plotted on Gibbs diagrams (Gibbs, 1970) for Na/(Na+Ca) versus total dissolved solids (TDS) for regions A) North-C1 and B) South-C3 and Cl/(Cl+HCO3) versus total dissolved solids (TDS) for regions C) North-C1 and D) South-C3.

In dry desert-climates, surface water compositions are controlled by evaporation, resulting in Na- and Cl-rich water (Na/(Na+Ca) ≥ 0.5 and Cl/(Cl+HCO3) ≥ 0.2) but with elevated TDS > 500 mg/L) (Figure 4.5). In contrast, surface water in other climates controlled by reactions with the rock and reflect the composition of the rocks, so they are Ca and HCO3 enriched (Na/(Na+Ca) ≤ 0.5 and Cl/(Cl+HCO3) ≤ 0.2) with intermediate TDS (ranging from approximately 50 to 500 mg/L) (Figure 4.5).

Since surface water compositions can be controlled by climate, climate can then control the cation compositions of fluvial-deposited clays at the time of deposition. Upon burial, later reactions with the groundwater could change these compositions but that would be dependent on adequate mass of groundwater and ions in the groundwater to effect this change. Further, if surface water recharge is the primary source of the groundwater then the climate effect on surface water could also have an important effect on the composition of the groundwater and the effect on the composition of the buried clays. Taking into account the later effects of groundwater on clay composition, it is possible that the cation compositions of clays in fluvial sediments could be used as evidence of the climate at the time the fluvial sediments were deposited.

4.5.1 Present-day climate and net precipitation

The fluvial deposits of the Beaumont Formation in the study area provide a location to evaluate the effect of the present and past climate on the surface water composition, and in turn the surface water composition's effect on groundwater and claycation compositions. Within the study area, there is a large progression in the current climate from wet, humid subtropical (also referred to as warm temperate or mild temperate) in the north to dry semi-arid subtropical in the south (Figure 4.6) (Narasimhan et al., 2008; Texas Water Development Board, 2012). The Köppen climateclassification scheme describes the north as C_{fa} (humid subtropical without a dry season, hot summers, constant moist rainfall through all months of year such that precipitation is distributed evenly throughout the year; rainy, mild winters) and south as B_{Sh} (dry semiarid and hot and dry year-round) (Köppen, 1900; Rohli and Vega, 2015). Humid subtropical is also referred to as a mild temperate climate.



Figure 4.6 Location of the Beaumont Formation outcrop (after Young et al., 2010; Solis, 1981), and contours of the present-day average-annual temperature, average-annual precipitation, average-annual lake evaporation, and humid subtropical to semiarid subtropical climate boundary (after Narasimhan et al., 2008; Texas Water Development Board, 2012).

Based on this climate transition, the study area was divided into three regions; North-C1 entirely within the humid subtropical climate, Central-C2 which is within the transition from humid subtropical to semi-arid subtropical climate, and South-C3 which is entirely within the semi-arid subtropical climate. In the north (C1), compared to the south (C3), it is wetter with annual precipitation of 52-43 in/yr, and evaporation is less, with lake-surface evaporation of 50-54 in/yr (Figure 4.6). These wetter conditions result in an overall positive net precipitation (precipitation – evaporation) for the year, and for the Fall and Winter months (Table 4.2). In contrast the Spring and Summer months have negative net precipitation, but this evidently is not enough for the annual 12-month net precipitation to be negative. Hence, there is overall greater annual precipitation than evaporation in the northern (C1) study area. **Table 4.2** Average-daily net precipitation (mm/day) for 12 months, Summer, Winter, Spring and Fall for present day (1954-2020) and for winter and summer 120,000 yr. before present (BP).

| | Present Day (1954-2020) Net Precipitation (mm/day) ¹ | | | | | Approximate Change in | | Predicted net | |
|-------|---|----------|-------------|---------|------------------------------------|-----------------------|-----------|---------------|---------|
| | | | | | | Net Precipitation | | precipitation | |
| | | | | | | (125,000 yr BP minus | | 125,000 yr BP | |
| | | | | | Present Day) (mm/day) ² | | (mm/day)3 | | |
| | 12-month | Winter | Spring | Summer | Fall (Sept | Winter | Summer | Winter | Summer |
| | (Jan-Dec.) | (DecFeb) | (March-May) | (June- | Nov.) | (DecFeb) | (June- | (Dec | (June- |
| | | | | August) | | | August) | Feb) | August) |
| North | 0.11 | 1.01 | -0.52 | -0.81 | 0.72 | -0.7 | -1 | 0.31 | -1.81 |
| South | -1.19 | -0.12 | -1.30 | -2.85 | -0.51 | -0.7 | -1.5 | -0.82 | -4.35 |

1. Calculated from reported monthly net evaporation obtained from the Texas Water Development Board (2021c).

2. Montoya et al. (2000) data only available for Winter and Summer.

3. Net precipitation 125,000yr BP = Present Day Net Precipitation + Change in Net Precipitation

In comparison, in the southern study region (C3) annual precipitation is much less at 38 to 28 in/yr compared to the north with 52-53 in/yr. In addition, lake surface evaporation is greater in the south, 54 to 56 in/yr, compared to 50 to 54 in/yr in the north. Combining these extremes of less precipitation and more evaporation in the south results in a net precipitation (precipitation – evaporation) that is negative annually (12-month period) and negative for all four seasons (Winter, Spring, Summer and Fall) (Table 4.2). Thus, evaporation has significantly less effect on the surface water composition in the north compared to the south. In the south evaporation greatly exceeds precipitation, such that evaporation has an important effect on the surface water composition, ultimately resulting in greatly reduced amounts of meteoric water recharge.

4.5.2 Climate and net precipitation during Late Pleistocene deposition of the Beaumont Formation

The Beaumont Formation was deposited during a drop in sea level that occurred during the Late Pleistocene between 20,000 to 120,000 yr BP (Winkler, 1979). World climate simulations for the winter and summer months at the start of the Late Pleistocene (125,000 yr BP) show that net precipitation (gross precipitation minus gross evaporation) in the study area was approximately 0.7 to 1.5 mm/day less than net precipitation today (Table 4.2) (Montoya et al., 2000). More recent world climate simulations for the Late Pleistocene by Otto-Bliesner et al. (2013) and Rybaka et al. (2018), while not providing detailed results for the study area, are consistent with those of Montoya et al. (2000) Net precipitation in the northern (C1) and southern (C3) regions of the study area during the summer and winter months of the Late Pleistocene were calculated from the results of the climate modeling (Table 4.2). The results for net precipitation for 125,000 yr BP shows that a similar gradient in net precipitation, from a wetter north to a drier south, occurred in the Late Pleistocene, similar to present-day. Also, similar to present-day, at 125,000 yr BP the southern study area was dry with slightly negative net precipitation during the winter, and very strongly net negative precipitation in the summer (Table 4.2). Thus, evaporative effects would dominate surface water composition in the south 125,000 yr BP, as occurs today. In the northern study area, the present-day trend of positive net precipitation in the winter months and slightly negative net precipitation in the summer months was also present 125,000 yr BP (Table 4.2), resulting in a similar effect of evaporation on the surface water composition 125,000 yr BP as is expected in present day.

Further, the dominance of large river deltas in the Beaumont Formation in the north, compared to the thinner and smaller delta deposits to the Beaumont Formation in the south, support that the climate was wetter in the north with more river runoff compared to the drier south with less precipitation and less river runoff during deposition of the Beaumont Formation (Aronow, 1971). The difference in river discharge during the Late-Pleistocene is mirrored by the present-day river discharge., In the present-day north, where the climate is wetter with less evaporation, the annual runoff ranges from approximately 1.9 to 5.9-million-acre feet annually. In contrast, in the present-day south, where there is less precipitation and more evaporation, the annual runoff is only approximately 0.4 to 1.0 million acre feet (Texas Water Development Board, 2021b). In addition, the presence of carbonate cement and calcareous nodules, common developments of a dry climate (Aronow, 2917), only in the southern portion of Beaumont (Aronow, 1971), further support the presence of a drier climate in the south during deposition of the Beaumont Formation.

4.5.3 Present-day River Water Compositions

The similar climate and climate gradients of the present day and the Late Pleistocene discussed above support that river water compositions in the Late Pleistocene should have been affected by the same gradients in evaporation and precipitation, and thus have similar compositional trends between north and south. This supports that the present-day river compositions can be used as analogs to the Late Pleistocene river compositions during deposition of the Beaumont Formation.

The chemical compositions of present-day river water from the three regions (C1, C2, and C3) plotted on trilinear diagrams (Piper, 1944) diagrams (Figure 4.7) and Gibbs diagrams (Gibbs, 1970) (Figure 4.5) show a significant change from north to south. The river water in the north (C1) is predominantly Ca-HCO3 type with lesser Na-Cl type, whereas river water in the south (C3) is predominantly Na-Cl type with lesser Ca-HCO3 type. The central region (C2) has compositions ranging between C1 and C3. This transition in the river water compositions from predominantly Ca-HCO3 type in the north to Na-Cl type in the south is



Figure 4.7 Trilinear diagrams (Piper, 1944) showing river water and groundwater chemistry for climate regions C1 (A and C) and C3 (B and D).

also evident in the Gibbs diagrams plotted for the river water compositions which compare Na/(Na+Ca) and Cl/(CL+HCO3) with total dissolved solids (TDS) (Figure 4.5).

On the Gibbs diagrams these compositional differences result in the river water from the north, C1, plotting predominantly in the rock-dominated area (i.e., composition controlled by reaction with the country rock) where Ca is greater than Na and HCO₃ is greater than Cl (Figure 4.5). In comparison, the river water compositions in the south, C3, span from the rock-dominated area into the evaporation-dominated area on both the Na-Ca and Cl-HCO₃ Gibbs diagrams, with the majority of the samples in the evaporationdominated area of the diagrams (Figure 4.5).

The relationships on the Gibbs diagrams show that the river water samples in the north have lower TDS and are more enriched in Ca relative to Na compared to the river water in the south, which is more enriched in Na relative to Ca and higher in TDS. Gibbs (1970) suggests this trend is a result of increased TDS and Na in the samples with increased evaporation, while the proportion of Ca relative to Na is decreased because of coupled carbonate mineral precipitation. Calculation of calcite saturation in river water from the south, C3, using Phreeqc and the LLNL.dat database (Parkhurst and Appelo, 1999) shows that the majority of the samples are saturated to supersaturated with calcite and is thus consistent with the possible loss of calcium with evaporation from these samples. The groundwater in the southern region (C3) occurs well below the ground surface and thus is not thought to contribute water to the rivers in the southern region (e.g. Myers and Dale, 1966), supporting that the higher TDS, and increased Na relative to Ca in the southern rivers is a product of increased evaporation rather than groundwater discharge. A map of average specific electrical conductance (EC) of river water samples

(Figure 4.3) supports the importance of evaporation in the south. It shows a trend of higher EC, which indicates an increase in TDS and thus greater evaporation in samples from the south where evaporation dominates compared to the north where evaporation is much less important (Figure 4.3).

In the north, with greater rainfall and less evaporation, the net precipitation (precipitation-evaporation) available to supply water to the rivers is greater than in the south, resulting in an average river water concentration of 56.7 mg/L Na, 56 mg/L Ca, and 12.4 mg/L Mg. where rainfall is less and evaporation is greater. Rivers in the north with greater discharge and less evaporation show minimal evidence of evaporation compared to rivers from In the south, where the rivers which have less discharge which that is compounded by more greater evaporation, there is a lower available water supply resulting in an average river water concentration of 315.8 mg/L Na, 122.7 mg/L Ca, and 22.8 mg/L Mg. ultimately resulting in theUltimately the river water chemistry in the southern region showing shows significant changes in response to evaporation. This difference in the importance of evaporation between the northern and southern rivers is a product of the change in climate from north to south.

River water compositions during deposition of the Beaumont Formation during the Late Pleistocene are expected to be similar to present-day river water compositions, because as shown above, net precipitation in the north and south regions during the Late Pleistocene is similar to that of present-day (Table 4.2). The expected similarity between Pleistocene and present-day surface water-cation compositions supports that clays deposited by these surface water both during the Pleistocene and present-day would have similar cation compositions.

4.5.4 Cation Compositions of Clay Minerals Deposited from Present-day River Water

The cation compositions of X_{Ca} , X_{Mg} and X_{Na} of clays in equilibrium with the presentday river water from the study area were calculated using Equation 6, and plotted on ternary diagrams for the climate region (C1, C2 or C3) in which the river occurs (Figure 4.4). Since cation exchange is nearly instantaneous, these clay-cation compositions represent the cation composition of clays that would deposit from the surface water in each region. There is a clear increase in X_{Na} of the river equilibrated clays from north to south. Most notable is that in the north region (C1), where 99% of the all the river water locations have equilibrated clays with $X_{Na} < 8\%$, whereas in the south region (C3), only 55% of the river water locations have equilibrated clays with $X_{Na} < 8\%$. River water samples in the central region, C2, would deposit clays with X_{Na} intermediate between that of regions C1 and C3, supporting that there is a progressive change in X_{Na} of river water clay compositions from the wet north to the dry south.

The northern region (C1) occurs where the climate is humid subtropical (mild temperate) and where river compositions plot predominantly in the Na poor rock-dominated region of the Gibbs Diagram (Figure 4.5). Thus, the prediction of very low X_{Na} ($X_{Na} < 8\%$ and XCa + XMg > 92%) in over 99% of the sample locations, (strongly supports that surface water in this type of climate (humid subtropical/mild temperate) will deposit clays depleted in Na with $X_{Na} < 8\%$ relative to Ca and Mg. This well-defined X_{Na} maximum of 8% represents the maximum possible X_{Na} for fluvial-deposited clays in a the humid subtropical (mild temperate) climate, and will be used as a cutoff in the following sections. The deposition of clays with X_{Na} greater than 8% requires river water richer in Na relative

to Ca and Mg than what is present in the rock-dominated river waters of region C1, as is seen in the southern region C3.

The southern region (C3) occurs where the climate is dry (semi-arid subtropical) with evaporation exceeding precipitation much of the year (Table 4.2), and where the river water samples plot predominantly in the Na-rich evaporation-dominated portion of the Gibbs Diagram (Figure 4.5). The elevated Na in these river water samples results in 45% of the sites having X_{Na} greater than the 8% cutoff set for rivers in the wetter climate. Thus, the results for the south region (C3)show that a climate where evaporation exceeds precipitation for most of the year can produce the type of surface water composition that allows for deposition of clays with $X_{Na} > 8\%$. This evaporation effect and increase in X_{Na} above 8% would be enhanced in floodwaters that disperse on the flood plain and deposit the majority of the clays in fluvial deposits, where they would be exposed to further evaporation.

Since the majority of sediment deposition in a fluvial setting takes place during high flows and flooding events, and because periods of high flows are less common than periods of low flow, it is important that the high Na concentrations in C3 relative to C1 are not restricted to low flows. The average Na concentrations (mg/L) from the river water from both regions C1 and C3 were plotted with respect to the month of sampling in Figure 4.8, where the maximum precipitation (cm) from 1941-2021 is overlain for each month of the year (Texas Water Development Board 2021c). The contrast between the evaporation dominated river water in region C3 and the rock dominated river water in region C1 is further evidenced in Figure 5, where the Na concentrations of C3 river water are dependent on precipitation patterns, and the Na concentrations in C1 river water appear to be relatively independent from rainfall. Although the average C3 Na concentrations reach yearly minimums during the periods of high flow, the river water in C3 during the months of high flow still have average Na concentrations at least triple the average Na concentrations during high flow in C1.

In addition, evaporation of surface water during infiltration into the soil zone will increase the concentration of Na relative to Ca and Mg and the subsequent Na enrichment, thereby further increasing the X_{Na} of these clays to values greater than 8%. Together, these processes will produce clays with predominantly $X_{Na} > 8\%$ when deposited in a semi-arid climate. Ultimately , surface and soil water in the dry semi-arid environment are expected to produce a large region of clays deposited with $X_{Na} > 8\%$.



Figure 4.8: Average Na concentrations (mg/L) for each month of the year in regions C1 and C3 compared to maximum monthly precipitation for quadrangle 910 (Texas Water Development Board 2021c).

4.5.5 Cation compositions of clay in the fluvial deposited portion of the Beaumont Formation

The Late Pleistocene climate in the study area is predicted to be similar to the present-day climate with regard to the wetter climate in the north (C1) and dryer in the south (C3) (Table 4.2), thus it is expected that clays deposited in the Late Pleistocene sediment of the Beaumont Formation in the north would have $X_{Na} < 8\%$, and those deposited in the south would have predominantly $X_{Na} > 8\%$. The next section looks at the clay-cation compositions present in the fluvial portion of the Beaumont Formation today.

Because cation exchange is nearly instantaneous, the groundwater in the Beaumont Formation in exchange equilibrium with the clays, allowing the use of the groundwater compositions to predict the clay-cation compositions in the formation. A plot of the groundwater compositions in the fluvial sediments of the Beaumont Formation shows that the proportions of Na in the groundwater compared to Ca and Mg increases from the north region (C1) to the south region (C3) (Figure 4.7). Clay-cation compositions calculated using Equation 6 show a similar progression from the north region (C1) where $X_{Na} < 8\%$ for 96% of the samples, to the central region (C2), where $X_{Na} < 8\%$ for only 50% of the samples, to the southern region (C3), where $X_{Na} < 8\%$ for as few as 9% of the samples (Figure 4.4). The distribution of the samples with $X_{Na} < 8\%$ and $X_{Na} > 8\%$ on the plan map and cross sections further show this clear shift from $X_{Na} < 8\%$ in the north to X_{Na} >8% in the south (Figures 4.1 and 4.2).

It is evident from the composition of clays equilibrated with surface water in the two climate zones present in the study area, that the cation compositions of clays deposited in fluvial sediments will reflect the climate in which the sediments are deposited. Fluvial clays deposited in the humid subtropical (mild temperate) climate, such as present in the northern study area (C1), will have $X_{Na} < 8\%$ and $X_{Ca}+X_{Mg} > 92\%$. In contrast, fluvial clays deposited in a semi-arid climate where evaporation exceeds precipitation, such as in the southern study area (C3), will have the majority of the clays with $X_{Na} > 8\%$ and $X_{Ca}+X_{Mg} < 92\%$. This is the relationship present in the present-day clay-cation compositions in the fluvial sediments of the Beaumont Formation in regions C1 and C3 (Figure 4.4). The agreement between the predicted and actual clay cation compositions supports that the fluvial sediments of the Beaumont Formation were deposited from surface water with a cation composition similar to that of the surface water present in northern (C1) and southern (C3) regions today. This further supports that the climate of these two regions, C1 and C3, were similar and had a similar gradient in composition during deposition of the Beaumont Formation as is present today. This supports the results of climate simulations discussed above (Montoya et al., 2000) (Table 4.2).

4.5.6 Potential Effect of Meteoric Water Recharge on X_{Na} of the Clays after Deposition

It is possible that the present-day clay-cation compositions do not reflect the cation composition of the clays at the time of deposition. The source of water in the Beaumont Formation today and in the past has been meteoric water recharging at the surface (Chowdhury et al., 2018). This influx of recharging meteoric water will exchange with the clays in the formation and can alter their cation compositions.

Although the clays present in the geologic and hydrologic settings used in this study have retained enough Na since deposition to posses a chemical signature of the climate at deposition, it must be noted that this should not be a universal case, especially for much older formations. Since cation-exchange equilibrium between clays and surrounding pore-water is ongoing, it is not only the depositional waters that have influence over the present-day cation compositions of the clays, but all subsequent flowing groundwater that has come in contact with and presumably exchanged cations with the clays. This groundwater induced transformation of the clay cation chemistry will take a substantial amount of time given the typical volume of cations contained by a 1 kg of clay compared to the exchangeable cations present in a single 1L pore-volume of typical low-TDS groundwater, nonetheless, it is assumed that all deposited clays will be limited to a window of geologic where the methods applied in this study can be successfully performed. This window of time can be estimated for sediments by taking into account the time since deposition, the abundance of clay in the sediments, and the estimated volume of post-depositional water the sediments have likely come in contact with.

Capuano and Jones (2020) show that recharging meteoric water infiltrating into an aquifer would not contain enough Ca to significantly decrease the Na in clays with X_{Na} > 8%, which is the range of X_{Na} expected for the clays deposited in region C3. The aquifer they studied contained less clay available for exchange, with a lower percentage of clay (40%) than the Beaumont Formation (80%). The aquifer was also older than the Beaumont formation, so it had sustained a longer period of meteoric water recharge and thus more time for exchange reactions to take place. It was shown that the clay in the formation had such a large reservoir of cations compared to the recharging water, that the clay-cation compositions controlled the cation composition of the groundwater, rather than the clay-cation compositions being controlled by the groundwater. A similar relationship is expected in region C3 which therefore retained its Na-enriched clay-cation compositions since deposition.

Although these indications presented in this study are still present in the clays of the C3 region, these are likely time-constrained due to cation exchange reactions over geologic time which will eventually alter the original compositions completely to where they can no longer provide a signature of the original depositional waters. For example, if the clays in the C3 region had been exposed for 250,000 years, given the hydrologic setting, the elevated Na in the clay used to identify Na-rich depositional waters would no longer exist. Because of this, this type of study can possibly only be applied to relatively younger formations that have been exposed to relatively shorter periods of meteoric water flushing. Much care must be taken in the evaluation of the hydrologic and geologic setting that this is applied to.

In contrast, calculation of Na mass balance in the present study site show that there is not enough Na in the meteoric water recharge to have created the high Na concentrations presently in the wedge of sediments in the C3 study area.

For these calculations Na mass balance was compared to the mass balance for the conservative ion Cl in thenorthern (C1) and southern (C3) regions of the fluvial deposited Beaumont Formation, by comparing the Na/Cl ratio of the recharge water to that of the groundwater in each region. Cl in the meteoric water recharge is expected to behave conservatively (it does not undergo exchange or mineral reactions) (e.g. Richter and

Kreitler, 1991) once in the aquifer, whereas Na does not behave conservatively and undergoes cation exchange with the clays. Consequently, the ratio of Na/Cl in the recharge water compared with that in the groundwater can be used as a measure of whether Na has been added or removed from the recharge water by cation exchange after infiltration into the formation. If Cl behaves conservatively in the recharge water but Na is lost to the clays, then the ratio of Na/Cl in the groundwater will be less than the ratio in the recharge water. In contrast, if Cl is conservative and Na is gained from the clays, then the Na/Cl ratio of the groundwater will be greater than the ratio in the recharge water.

The addition of Na to the groundwater after recharge would support that there is excess Na in the clays relative to the recharge water. In contrast, depletion of Na from the groundwater after recharge would support that the clays are depleted in Na relative to the recharge water. For clays to have excess Na compared to the recharge water, then Na would have to have been sourced from the clays by cation exchange. This would support that the clays were deposited as Na enriched, $X_{Na} > 8\%$. If Na is removed from the groundwater relative to Cl, then it supports the clays were originally depleted in Na at deposition, $X_{Na} < 8\%$. Recharge water to the Beaumont Formation in the study area is river water and rainwater (e.g., Scanlon et al., 2011). The molar ratio of Na/Cl in rainwater (wet deposition) in the study area is 0.88 (Table 4.3) (Figure 4.9). This value was determined from the Na/Cl molar ratios in rainwater samples collected from four NADP (2021) collection sites located in the study area (Figure 4.1) (Table 4.3). The molar ratio of Na/Cl for river water from regions C1 and C3 were determined from the slope of the straight line fit to all the river water data for that region plotted on a graph of Na versus Cl (Figure 4.9). This gives a Na/Cl molar ratio for river water in region C1 of 0.96 and for river water in regions C3 of 0.85 (Figure 4.9). The line used to determine the Na/Cl ratios for the river water data displayed an excellent straight-line fit for both regions, with R² of .93 and .95 for C1 and C3 respectively (Figure 4.9).

| NADP Collection Site (Location) ¹ | Years Collected ² | Average Annual Na Wet Deposition ³ (kg/ha) | Average Annual Cl Wet Deposition ⁴ (kg/ha) | Annual Na/Cl Molar Ratio in Wet Deposition ⁵ |
|---|---------------------------------|---|---|--|
| TX-03 (Beeville) | 1984-2020 | 3.27 | 5.68 | 0.8896 |
| TX-10 (Sealy) | 1984-2020 | 3.75 | 6.58 | 0.8782 |
| TX-39 (Corpus Christi) | 2002-2006 | 11.96 | 21.34 | 0.8673 |
| TX-53 (Victoria) | 1980-1988 | 4.41 | 7.86 | 0.8679 |
| | | | Average ⁶ | 0.8757 |

Table 4.3 Wet Deposition of Na and Cl and Na/Cl Molar Ratio at the NADP Collection Sites in the Study Area

1. National Atmospheric Deposition Program (NADP) collection site number (NADP, 2021), and closest city (see Figure 4.1).

2. Range of years for which annual wet deposition data is available for the specified NADP collection site.

3. Average of all annual Na wet deposition values for the years with data available for the specified NADP collection site.

4. Average of all annual Cl wet deposition values for the years with data available for the specified NADP collection site.

5. Average of all calculated Na/Cl molar ratios (Cl: 35.543 g/mole, Na: 22.9897 g/mole) for each year of available data for the specified NADP collection site.

6. Average of the Annual Na/Cl molar ratios of wet deposition at the four NADP collection sites listed in this table (NADP, 2021).



Figure 4.9 Na and Cl in and river water (USGS, 2021) and Beaumont Formation groundwater (TWDB, 2021) in regions north-C1 and south-C3. For the groundwater in region C1, only samples in the "no salt" region (Figure 4.1) are included on this figure and in the slope calculations. The red dashed lines show the Na/Cl molar ratio of rainwater of 0.88 (NADP, 2021) from Table 4.3.

The Na/Cl molar ratio for the groundwater in region C1 of 0.19 and for region C3 of 0.92 were also obtained from the slope of the straight line fit of the groundwater data on a plot of Na versus Cl (Figure 4.9). For region C1 the groundwater analyses used for the calculation of the Na/Cl ratio were taken only from the southern portion of regions C1 where there are no salt domes in the fluvial portion of the Beaumont Formation (labeled "no salt" on Figure 4.1). There are no salt domes in region C3 so all the groundwater data from the fluvial Beaumont Formation was used. The straight-line fit used to determine the Na/Cl ratio for groundwater in region C3 was adequate with R²=0.72, but the straight-line fit used to determine the Na/Cl ratio for groundwater in region C1 was not adequate with R²=0.28 (Figure 4.9). So, the Na/Cl ratio for C1 groundwater is not a reliable value.

For the southern region C3, there is a clear difference between the Na/Cl molar ratio of the recharge water 0.85-0.88 and that of the groundwater 0.92 (Figure 4.9), with the higher ratio of the groundwater supporting there is excess Na in the groundwater compared to the recharge water. This relationship is displayed on Figure 4.9, with the majority of the groundwater samples in region C3 plotting above the data river water data and the Na/Cl ratio of the rainwater. The higher Na/Cl ratio of the groundwater compared to the recharge water (rain and river water), strongly supports that the clays in region C3 have excess Na relative to the recharge water. For this to happen, the clays have excess Na relative to the recharge water and are exchanging it into the groundwater when the recharge water enters the formation. Thus, the recharge water is not bringing in excess Na and exchanging that Na from the groundwater into the clays, while removing Ca or Mg from clays originally enriched in Ca and Mg. This supports that these clays were enriched in Na at deposition, with $X_{Na} > 8\%$, and are currently releasing that Na to the groundwater.
An original clay composition in region C3 of $X_{Na} > 8\%$ supports that the sediments were deposited in a dry climate similar to that present in region C3 today, where evaporation is important and net precipitation generally negative.

In the north region C1, the Na/Cl molar ratios for the rainwater (0.88) and river water (0.96) are close, but do not match as well as those in region C3 (Figure 4.9). In addition, the Na/Cl molar ratios of the groundwater for regions C1 vary widely, resulting in a poor fit of the data to a straight line (R^2 =.28) (Figure 4.9). This is not a concern because, in contrast to region C3, the groundwater in region C1 does not clearly show an excess of Na. Rather then plotting well above the lines of the river and rain recharge ratios as seen for regions C3, the groundwater samples in region C1 are scattered closely to the lines including many below the lines. This strongly supports that the sediments in the northern region C1 do not have excess Na to contribute to the groundwater, and that that the sediments of this region contain clays that are not enriched in Na ($X_{Na} < 8\%$) which were deposited in a climate different from the dry evaporation-controlled climate of region C3. The clays of region C1 were deposited in a wetter climate where surface water compositions were more rock dominated as is the climate present in region C1 today.

4.5.7 Excess Na in C3 Groundwater as Product of Cation-Exchange

In region C3, the elevated Na/Cl ratio of the groundwater compared to the recharge water supports that there is another source of Na in the Beaumont Formation of region C3 besides the input from meteoric water. In the case that this excess Na is sourced from cation exchange with Na-enriched clays, this would be possible if the climate models for 125,000 BP are accurate, and the evaporation/precipitation conditions predicted for C3 in the late Pleistocene (evaporation>precipitation) resulted in the deposition of Naenriched clays in the Beaumont Formation which have subsequently exchanged Na for Ca to reach equilibrium with meteoric water recharge. This would mean that the surface water conditions 125,000 years ago are consistent with today's surface water conditions which are shown to deposit Na-enriched clays (appx 50% with X_{Na} >8%) from today's river water (Figure 4.4). This contrasts with the comparative Na/Cl ratios for the northern region C1, where there is no apparent excess Na relative to Cl. This contrast between C1 C3 is also consistent with late Pleistocene climate models and the evaporation/precipitation conditions which resulted in the deposition of Na-depleted clays in the C1 Beaumont Formation (evaporation<precipitation) where only minor, if any, exchange of Na for Ca in meteoric water has occurred since deposition, which is consistent with the present-day C1 river water compositions that are shown to deposit mostly Na-depleted clays (96% with $X_{Na} < 8\%$).

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4.6 Conclusions

The results of this study show that the cation composition of clays deposited in a fluvial environment reflect the cation compostion of the surface water present in the area at the time of deposition. In turn, the cation composition of the local surface water is controlled by the climate at the time of deposition. Na-rich surface water that develops in a dry climate where evaporation is important deposits Na-enrich clays ($X_{Na} > 8\%$). In constrast, Na-poor surface water that occurs in wetter climates (where evaporation is less important relative to precipitation) deposits Na-poor clays ($X_{Na} < 8\%$). If these cation compositions persist in the geologic record, they can be used as evidence of past wet versus dry climates.

The Beaumont Formation of the Texas Gulf Coast selected for this study has a uniform fluvial sourced environment of deposition and hydrogeologic conditions throughout the study area with a present-day climate gradient from wet humid subtropical (mild temperate) in the north to dry semi-arid subtropical in the south with evaporation exceeding precipitation much of the year. Climate modeling supports that the same climate with a transition from north to south has occurred in the study area since the start of Beaumont Formation deposition in the Late Pleistocene.

Present-day river water compositions were found to reflect the climate gradient in the study area, with rock-dominated, Ca and HCO3 enriched river water compositions in the wetter north, trending toward evaporation dominated, Na and Cl enriched and higher TDS river water compositions in the dry south. Calculation of the cation-compositions of clays in equlibrium with this river water, and thus the composition of the clays that would deposit from this water, shows that the northern clays are relatively low in Na ($X_{Na} < 8\%$) compared to Ca and Mg, while the southern clays have more Na ($X_{Na} > 8\%$) compared to Ca and Mg.

Calculation of the composition of clays in the Late Pleistocene fluvial Beaumont Formation in the study area shows that the clays in the formation have a similar shift in composition from north to south as the clays in equilibrium with the present-day river water in the north and south. In the northern study area Beaumont Formation clays have relatively low Na ($X_{Na} < 8\%$) compared to Ca and Mg, compared to the clays in the south which have more Na ($X_{Na} > 8\%$) compared to Ca and Mg. This chemical similarity of the current composition of surface water deposited clays and the Pleistocene clays currently in the formation supports that the present day climate and the climate during Late Pleistocene formation of the fluvial Beaumont Formation where the same, consistent with climate modeling.

The possiblity that the Beaumont Formation clay cation compositions could have been altered by meteoric water recharge after deposition was considered. As the only source of recharge to the sediments in the study area is surface water, comparison of the ratio in the groundwater of the conservative ion Cl, with Na which is undergoing cation exchange with the clays, allowed consideration if Na is being added to the recharge water by exchange with Na-rich clays after infiltration, or removed by exchange with Na-poor clays. The Na/Cl ratios show that in the southern region there is excess Na in the groundwater that is sourced from the clays. This is evidence that the clays were originally deposited as Na enriched clays ($X_{Na} > 8\%$) rather than Na poor clays, and that the presentday Na-rich character of the clays represents their original composition at deposition. In contrast in the northern region the Na/Cl ratio in the groundwater did not show evidence of sodium rich clays at deposition, supporting that the clays in the north were originally deposited as Na-poor clays (XNa < 8%) as are currently present in the Beaumont Formation in the north.

Further, these results support that the Na content of clays deposited in a fluvial environment can be used as paleoclimate proxies that can aid in identifying the wet versus dry character of a past climates. The climatic effect on the surface water composition in the case of a wet versus dry climate, can be reflected in the composition of the clays at the surface and can potentially be retained in the clays after deposition. It is likely that the trends presented in this study will be evident in any depositional environment in which clays are deposited from surface waters in a terrestrial sedimentary environment, such as an alluvial plain or lake.

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4.8 Chapter 4 Bibliography

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