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Geochemical and Isotopic Characterization of Shallow Basinal Brines from the Makgadikgadi Pans Complex, Northeastern Botswana: Determination of the Sources of Salinity

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GEOCHEMICAL AND ISOTOPIC CHARACTERIZATION OF SHALLOW BASINAL BRINES FROM THE MAKGADIKGADI PANS COMPLEX, NORTHEASTERN BOTSWANA: DETERMINATION OF THE SOURCES OF SALINITY

by

Loago N. Molwalefhe

A Dissertation
Submitted to the Faculty of The Graduate College in partial fulfillment of the requirements for the Degree of Doctor of Philosophy Department of Geosciences

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This dissertation is dedicated to my family, and to my fiancée of many years Ms. Tebogo Mmesi for being supportive, patient and loving during the endless years of my career development. The work is an achievement by all of us.

Loago N. Molwalefhe
Isotopes and chemical tracers have been used to constrain the sources and causes of salinity in shallow groundwater brine from the Makgadikgadi Basin, northeastern Botswana. The brine is massively rich in chloride and sodium, and moderately rich in carbonates, sulphate and potassium, and is distinctively poor in divalent cationic species. Various models that have been advanced to explain the origin of the brines include evaporative enrichment at the surface and density-induced infiltration, dissolution of evaporites, and trapped connate water.

This study presents the compositional variability and behaviors of the stable isotopes of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$), dissolved inorganic carbon (DIC) content, chloride, bromide and sodium in the brine from the northern part of Sua Pan, one of the Makgadikgadi Pans Complex. DIC concentrations in the brine reach 5 grams of carbon per liter and $\delta^{13}C_{DIC}$ compositions average -1.6±0.2‰. The values are compatible with dissolution and accumulation of carbon dioxide of geothermal origin. The halogen content of the brine (Cl/Br ratio) is consistent with studies of fluid-inclusion brines from magmatic rocks, and suggests significant magmatic influence in the formation of the brine. The sodium and chloride inventory on the other hand suggests additional sodium comes from intense weathering of silicate rocks. Spatial patterns in DIC concentrations and fluid conductivity show a linear
anomaly of higher conductivity and DIC to the northeast of the study area. The anomaly may correlate with subsurface structural terminus in the bedrock where saline magmatic fluids are forced towards the surface along faults. Stable hydrogen and oxygen isotope relationships show that the brine is a mixture of local meteoric water and magmatic water from below. The conclusion of a deeper source is consistent with the geology and recent seismic evidence that indicates the area is structurally dynamic. Isotope results are also consistent with a climate-driven scenario, in which water is affected by evaporation at the surface prior to infiltration.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ..................................................................................................................... ii

LIST OF TABLES ............................................................................................................................... v

LIST OF FIGURES ............................................................................................................................. vi

CHAPTER

I. INTRODUCTION ............................................................................................................................. 1

1.1 Statement of the Problem ........................................................................................................... 1

1.2 Objectives of the Study ........................................................................................................... 3

1.3 Significance of the Study ......................................................................................................... 4

II. THE STUDY SITE .......................................................................................................................... 5

2.1 Site Location and Site Description ......................................................................................... 5

2.2 Regional Geology and Structural Framework ......................................................................... 8

2.3 Site Geology 2.4 Hydrogeology ............................................................................................... 9

2.4 Hydrogeology ........................................................................................................................... 10

2.5 Previous Studies ....................................................................................................................... 12

III. INVESTIGATIVE METHODS ....................................................................................................... 14

3.1 Overview .................................................................................................................................. 14

3.2 Field Sampling and Experimental Procedures ......................................................................... 25

3.3 Chemical Analyses .................................................................................................................. 26

3.4 Stable Carbon Isotope Analyses ($\delta^{13}$C, DIC) ..................................................................... 27

3.5 Stable Oxygen ($\delta^{18}$O) and Hydrogen ($\delta^2$H) Analyses ...................................................... 27
Table of Contents—continued

3.6 Procedure for the Distillation of Micro-liter Quantities Water From Brine Samples .......................................................... 29

IV. RESULTS AND DISCUSSIONS .......................................................... 33

4.1 DIC and Stable Carbon Isotope ...................................................... 33
4.2 DIC and Fluid Conductivity Measurements ............................... 37
4.3 Cl-Br-Na Systematics ................................................................. 39
4.4 Na/Cl Ratios ............................................................................. 40
4.5 Stable Oxygen and Hydrogen Isotopes ........................................ 43
4.6 Stable Oxygen and Chloride Concentrations ............................... 46

V. SYNTHESIS AND CONCLUSIONS INTRODUCTION ....................... 50

APPENDICES .................................................................................... 52

A. Summary of Field Data for Northern Part of Sua Pan .................. 52
B. Chemical and Isotopic Data for Brines From the Northern Part of Sua Pan ................................................................. 54

REFERENCES .................................................................................. 56
LIST OF TABLES

1. Experimental Test Data on the Efficiency of the Brine Distillation Cell ...... 32

2. Comparisons of DIC Concentrations and Water Chemistries From Other Alkaline Saline Lakes and the Makgadikgadi System. All Concentrations are in mg/L. 2=Jones et al. (1977), 3=Jankowski and Jacobson (1989), 4=Gould (1986) and Current Study................................. 35
LIST OF FIGURES

1. Locality Map of the Makgadikgadi Pans Complex and Study Area, Botswana ................................................................. 6

2. Hydrogeological Cross-section of the Northern Part of Sua Pan Showing the Various Hydro-stratigraphic Units Beneath the Pan; the Upper Confining Clays, Sand-hosted Brine Aquifer, and Lower Confining Sandstone/Basalt Unit .................................................. 10

3. Map of the Northern Part of Showing Sample Locations and Principal Groundwater Flow Paths in the Aquifer .......................................................... 12

4. Schematic Diagram Showing how Various Processes Would Affect Cl/Br Ratio in Natural Waters .................................................. 22

5. Relationship $^{3}H$ and $^{18}$O for Natural Waters Showing Secondary Processes That Modify Isotopic Compositions in Water (Compiled From Taylor, 1974; Coplen, 1993 and Criss, 1999) ...................................... 25

6. Schematic of the Vacuum Cell Used for Brine Distillation .................................................. 31

7. A Contour Map Showing Spatial Patterns in DIC and the Location of a Zone of High DIC in the Northern Part of Sua Pan......................... 38

8. A Contour Map of the Spatial Distribution of Fluid Conductivity in the Northern Part of Sua Pan Showing Anomalous Values in the Northeast that Show High Specific Conductance .................................................. 38

9. Cross Plot of Br vs. Cl for the Makgadikgadi Brine Showing a Co-varying Relationship Between the Ions .................................................. 40

10. Cross Plot of Na vs. DIC for the Makgadikgadi Brine. The Relationship is Positively Correlated Indicating both Might be Derived From Same Processes.................................................. 41

11. Na vs. K Relationship Showing Evolution of Water to Higher Ionic Strength .................................................. 42

12. Aeromagnetic Map of Northern Botswana Showing Various Geological Units, the Basalt Intrusion and the Location of the Makgadikgadi Pans. The Linear Feature in Dark Color is a Swarm of Very Shallow Regional Basalt Intrusions. The Area Marked With a Rectangular Shape is the Location of the Makgadikgadi Pans. Map Not to Scale .................................................. 42

vi
13. Relationship $\delta^2$H versus $\delta^{18}$O; Meteoric Water Line (Filled Circles) and the Sua Pan Brine (Filled Triangles) ............................................................ 44

14. $\delta^2$H versus $\delta^{18}$O Relationship for the Sua Pan Brine..................................... 45

15. Figure 15: Expected Isotopic Compositions of the Brine (filled circles) Reconstructed by Superimposing the Actual Values (filled triangles) on the Meteoric Water Equation......................................................................... 46

16. $\delta^{18}$O versus Cl Relationship for the Sua Pan Brine. Labeled Wells Represents Recharge From the Surface ................................................................. 48

17. $\delta^{18}$O-Cl Relationship for the Isotopically Heavier Water From the Surface ........................................................................................................... 48

18. $\delta^{18}$O versus Chloride for Samples That Fall Along a Line of Mixing ........... 49
CHAPTER I

INTRODUCTION

1.1 Statement of the Problem

Inland salt lakes are common in southern Africa, and many occur in Namibia, Botswana and South Africa (Lancaster, 1978; Shaw, 1988; Seaman et al., 1991). All inland lakes in southern Africa are shallow, and most are ephemeral with salinities of less than 50 gL⁻¹ (Seaman et al., 1991). The buildup of salinity in surface water and groundwater occurs by either loss of water or addition of salts. Loss of water can occur by evaporation and transpiration by plants (Coplen et al., 2000). Addition of salts arises from a probable deep groundwater source, possibly due to weathering of evaporite deposits, or may be connate, diagenetic or geothermal in origin. Evaporation brines are most widespread, occurring in a range of environmental habitats. Evaporation brines are usually associated with very arid regions and discharge areas for regional groundwater flow systems (Jankowski and Jacobson, 1989). In the case of evaporation and transpiration, hydrogen and oxygen isotopes are useful in identifying the sources of water and salt influx (Fontes, 1980; Payne, 1981; Turner et al., 1987; Fritz and Clark, 1997). Magmatic brines are well known as a phenomenon but not so well documented in the literature. Magmatic brines occur in areas of advanced igneous differentiation such as near failed rifts (Vanko and Batiza, 1982). They are also found in areas where the mantle
source region is enriched and within the hydrothermal envelope adjacent to magma chambers (Vanko, 1986).

In the Makgadikgadi Basin, in northeastern Botswana, Africa, basinal brines with salinity up to five times that of seawater are found in the northern part of Sua Pan, one of the Makgadikgadi Pans Complex. The brine occurs as hypersaline pore waters that are rich in chloride, sodium, carbonates, sulfates and potassium (Gould, 1986). Recently, a large-scale production by Botash (Pty) Ltd of common salt (NaCl) and soda ash (Na$_2$CO$_3$) from the brines has been carried out in the northern part of Sua Pan. The plant supplies the sub-Saharan African countries and parts of the Middle East.

The geomorphology of the Makgadikgadi is a result of tectonic and climate changes that took place in the basin during the last 100,000 years (Baillieul, 1979). Ancient shorelines around the Makgadikgadi indicate that the formerly giant lake attained a size of 37,000 km$^2$ (Ebert and Hitchcock, 1978) and had its surface at 946 meters above sea level (Ebert and Hitchcock, 1978; Grey, 1976). Shoreline features shaping the outlines of Sua and Ntwetwe Pans occur at 890 meters above sea level. This suggests that at its maximum the lake had a water depth of 56 meters. Based on $^{14}$C dates from calcretes at these shorelines (Cooke, 1975) and some archeological evidence (Grey, 1976), the lake was at its maximum during the Pleistocene between 14,000 to 17,000 years ago. Drying up of Lake Makgadikgadi after the Pleistocene is attributed to changes in climate from wet to arid, and to tectonic movements along faults (Grove, 1969; Baillieul, 1979) that have impeded the flow of rivers, especially from the north, into the Makgadikgadi. In most of these cases, the downthrown blocks are to the west.
Studies of the provenance and chemical evolution of saline lakes are numerous, for example Lake Magadi in Kenya, Qaidam Lake in China, and Mono Lake in California, yet little research exists about the unusual water chemistry of lakes in southern Africa in general (Seaman et al., 1991).

A number of conflicting models have been advanced in an attempt to decipher the origin and chemical evolution of the brine in the Makgadikgadi Basin. Baillieul (1979) and Gould (1986) suggested that the brine is a relic of the evaporated giant lake that was maintained by inflow from rivers during the Pleistocene times. Other models have been suggested based on the chemical composition of the brine include dissolution of evaporites by advecting groundwater (Gould, 1986; Shaw, 1988) and in situ trapping of connate water (Seaman et al., 1991). The model of evaporative concentration is currently the most widely accepted explanation for the formation of the brine.

1.2 Objectives of the Study

The major activity of this research is to conduct a focused multidisciplinary stable isotope-based study to investigate the sources of the salinity of groundwater brines in the Makgadikgadi Basin. The main tracers that are employed include stable hydrogen and oxygen of the water molecule, the stable carbon isotope of the dissolved inorganic carbon and the halogens (chloride and bromide) in the brine. These should allow tracing of the origin of water, carbon, and dissolved solutes. The above tracers should also allow elucidation of the causes of salinity and quantification of salinity contributions from various sources. The data from this research will provide a framework to constrain the
model(s) that seek to explain the hydrology of Makgadikgadi Basin, represent the aqueous geochemistry of the brine, and evaluate the role of lakes and climate in the formation of the brine deposits.

1.3 Importance of Study

Understanding of the sources and causes of salinity is of great significance both for the public and scientific interest. The results of the research will contribute towards bridging of the critical gaps in our knowledge regarding the processes that control the formation of brines in the Makgadikgadi, and in general, the causes of salinity over a wide range of geological settings. The economic implications are that the data will assist in the process of decision-making concerning the utilization, management and sustenance of the brine as an economic resource. Decisions need to take into account the influence of continued production on the brine quality.
2.1 Site Location and Site Description

This study was conducted at Sua Pan, part of the Makgadikgadi Pans Complexes of northeastern Botswana (see Figure 1). The Makgadikgadi pans are 200 km from east to west and 120 km from north to south and occupy a depression that forms the center of a basin of internal drainage, the lowest point of which is approximately 890 meters above sea level (masl) located at the northeastern corner of Sua Pan. There are two major pans, Ntwetwe to the west and Sua to the east, and numerous small pans, making up the Makgadikgadi Pans Complexes. The investigated site is located in the northern part of Sua Pan between latitude 20° 22' 02"S to 20° 27' 51"S and longitude 25° 54' 22"E to 26° 06' 16"E.

The surface of the pans is not vegetated and is rather flat, covered by a thin salty crust that breaks down easily under wind action. Elevations measured during the fieldwork ranged from 910 to 947 meters above sea level, and the land slopes gently towards the north. There is a distinct area of elevated ground, the Sua “spit”, in the northern part of Sua Pan, which rises 3 meters above the flat pan surface, 3 kilometers wide and 20 kilometers in length. The spit cuts into Sua Pan in a northwesterly direction and is made up of sand that has been stabilized by grass.
The Makgadikgadi area is part of the semi-arid desert environment of western Botswana where moderate tectonic activity has been reported (Reeves, 1972; Fairhead and Girdler, 1969) in the geologically recent past. The pans are a focus for four regional catchments. A watershed bound them to the east, 90 kilometers away, which was formed by uplift along an axis running roughly North-South through Francistown. The Nata River drains the area to the east and northeast of the Makgadikgadi. Other small rivers to
the east also drain into Sua Pan. To the south, the Makgadikgadi rises gently toward an indistinct watershed at approximately 24°S, forming the southern limit of the catchment area. Drainage in the area south of the Makgadikgadi is almost non-existent, but some fossil valleys (Okwa, Letlhakane, etc.) that used to flow in the past are evident. In the west and northwest, the catchment extends into Namibia and Angola via the Okavango system of rivers and delta. In years of above average rainfall in the Angolan mountains, outflow from the Okavango reaches the Makgadikgadi via the Boteti River, and the southern part of the Ntwetwe Pan may be flooded. To the north, the watershed is formed in the Savuti area, rising steadily in the eastward direction. All of the rivers are either fossil or ephemeral, flowing only after heavy rains.

The climate is semi-arid to arid and characterized by a short cool season (May to August), and a longer warm season (September to April). August is the transitional month in terms of temperature. Countrywide, rainfall is erratic and restricted to the warm season (summer) that terminates in March or April. Rainfall occurs mainly as isolated convection showers and varies temporally and spatially from 250 mm per year in the southwest to 650 mm in the northwest with considerable inter-annual variability (Bhalotra, 1987). Annual average rainfall in the Makgadikgadi area is less than 400 mm/year. The cold season is very dry with temperatures averaging 5°C to 20°C; in the warm season the temperature averages 18°C to 34°C with peaks in October/November, that sometimes reach extremes of 42°C. During the cool season (winter), overnight frost may occur particularly in June and July. Winds are calm and restricted to the transition from winter to summer. Average annual potential evapotranspiration (ca. 2000 mm/year) exceeds the average rainfall amount and occurs during periods of peak temperatures.
2.2 Regional Geology and Structural Framework

Rocks around the Makgadikgadi Basin consist of Carboniferous to Jurassic sedimentary deposits of the Karoo Sequence (Stansfield, 1973), and younger Tertiary formations of the Kalahari Beds dominated by aeolian, fluvial, and lacustrine deposits. The stratigraphy of the Karoo in Botswana is described in Smith (1984). Underlying the Karoo is an old metamorphic terrain that consists of Precambrian granitoid formations. The bedrock is buried beneath the Quaternary-age Kalahari sand cover (Baillieul, 1975). The thickness of the Kalahari is variable, and can be as much as 150 meters in some places. Aeromagnetic data over parts of the basin have revealed dominant structural trends to the northeast and west-northeast directions (Baillieul, 1979). Various authors have reported on seismic activity throughout northern Botswana. For example, Fairhead and Girdler (1969) located earthquake epicenters in southern Africa and concluded that rifting of the East African system extends into northern Botswana. Reeves (1972) identified from regional seismic networks two distinct epicenter populations in Botswana, one directly beneath the Okavango Delta to the northwest of the study area, and the other across the central Kalahari region where the pans are located. Baillieul (1979) reported that water borehole yields to the north of the Makgadikgadi Pans were variable over short distances and concluded that the area experienced some recent large-scale faulting.
2.3 Site Geology

The geological history of the Makgadikgadi pans is tied to the tectonic and magmatic events that have affected the area since the Jurassic times, and is continuing today. The rocks surrounding the Makgadikgadi Pans belong to the Kalahari Beds and consist of aeolian sands, sandstones and various fluviatile and lacustrine deposits. The thickness of the Kalahari varies from zero in the eastern and southern margins of the pans to over 100 meters north of Sua Pan (Gould, 1986).

Sediments underlying the pans belong to the Makgadikgadi sediments (Stansfield, 1973) and consist largely of 80 m of unconsolidated sands and sandy clays. Sandstone bedrock that represents the highest member of the Karoo Sequence underlies these unconsolidated materials (Gould, 1986; Baillieul, 1979). Northern Sua Pan is underlain by a sand and clay succession that maintains a roughly constant thickness of 30 m in the study area. The succession is layered and has varying proportions of sand in a clay matrix. Individual layers may vary from 0.3 to 10 m (Gould, 1986) and often contain layers of chalcedonic silica (Bulley and Hammond, 1991). This short succession becomes slightly sandier with depth (Bulley and Hammond, 1991) and overlies an unconsolidated fine to medium grained sand (aquifer). The sediments beneath the Makgadikgadi Pans are lacustrine and occur in a tectonic basin (Figure 2). Reeves (1973) reported the presence of a basalt intrusion in the northern part of Sua Pan at a depth of 100 m. Similar intrusions have been reported by various authors (Mazor et al., 1977; Modisi et al., 2000) in other localities bordering the Makgadikgadi area. This indicates a wide geographical distribution of the basalt intrusion throughout the area and beneath the pans.
Figure 2: Hydrogeological Cross-section of the Northern Part of Sua Pan Showing the Various Hydro-stratigraphic Units Beneath the Pan; the Upper Confining Clays, Sand-hosted Brine Aquifer, and Lower Confining Sandstone/Basalt Unit.

Similar intrusions occur in the central parts of Botswana and date to be coeval (187 Ma) with the major flood basalt that is widespread in southern Africa (Smith, 1984). All the rocks around the pans are highly fractured by post-Karoo faulting and dyke emplacement (Baillieul, 1979).

2.4 Hydrogeology

Based on borehole records (Baillieul, 1979; Gould, 1986) and field data from this research, three hydrostratigraphic units are identified and represented in cross-section of Figure 2. One aquifer (shown as 3 on Figure 2) is bounded by a low permeability clay
unit at the top and by impermeable sandstone/basalt bedrock at the bottom. The aquifer sediments consist of 20 to 50 m of unconsolidated fine-to-medium grained sands. The overlying clays (Figure 2, units 1 and 2) form a confining layer that restricts the downward percolation of water from the surface. However, under normal conditions, the clay unit is saturated to 1 m below ground level, possibly forming a semi-confining layer that provides limited recharge to the underlying aquifer. The water table in the semi-confining clays fluctuates seasonally (Bulley and Hammond, 1991) to as deep as 3 meters below ground level. Water levels in wells that penetrate the sandy aquifer (Figure 2, unit 3) vary from 7 to 19 meters below ground level indicating confined conditions.

Since pumping by Botash (Pty) Ltd (57, 960 m$^3$/day as of 2002) influences current groundwater levels in the aquifer, groundwater flow directions (Figure 3) were obtained from historical data (Gould, 1986). The data indicate that groundwater flow is largely responsive to the topographic slope at the base of the aquifer rather than to changes in the configuration of the water table. The base of the aquifer is very irregular, clearly owing to structural controls, and dips consistently from the southeast toward the northwest (Gould, 1986). Historical pump tests carried out by Paulsen (1971) defined a confined to semi-confined aquifer. Transmissivity values ranged from 261 to 400 m$^2$/day and storage coefficient values from 0.001 to 0.005. These values imply that small quantities of water are able to infiltrate through the clay sediments.
2.5 Previous Studies

The major ion chemistry of the Makgadikgadi Basin brines assembled from several sources by Gould (1986) indicate that the brines are chemically very similar to other high salinity lakes of southern Africa. The Makgadikgadi brines have a total dissolved solid (TDS) content that ranges from 164 to 188 g/l. The bulk of the salinity is
invariably dominated by chloride (44.6%) and sodium (37.7%); typical of coastal source (seawater), and notably rich in carbonates (11.2%), sulfates (5.2%), and potassium (1.3%); typical of continental dust e.g. Drever (1982). The most common pattern of cation variance in high salinity lakes of southern Africa that include Etosha Pan in Namibia (Seaman et al., 1991), Pretoria Salt Pan in South Africa (Ashton and Schoeman, 1993; Seaman et al., 1991) and the Makgadikgadi Salt Pans in Botswana (Gould, 1986) is Na>K>Ca>Mg. In all the pans mentioned above, divalent cation concentrations are distinctly low (0 to 113 mg/L). The abundance of carbonates (HCO$_3^-$ + CO$_3^{2-}$ = 20000 mg/L for Makgadikgadi Pans) may be largely responsible for the high pH (9 to 10).
3.1 Overview

In this study, the stable isotopes of oxygen and hydrogen were used to study the sources of water in the Makgadikgadi brine. Dissolved inorganic carbon (DIC) concentrations and the stable carbon isotope of the dissolved inorganic carbon will be used to investigate the carbon sources in the brine. Finally, the chloride-bromide-sodium systematics will be used to investigate the sources of solutes in groundwater brines.

The pool of DIC ($\text{CO}_2 + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$ plus other complexed species such as $\text{CaCO}_3^{0(aq)}$, $\text{CaHCO}_3^{+(aq)}$, etc.) in surface water and groundwater may come from a variety of sources that include direct addition of CO$_2$ from root respiration, oxidation of organic debris in the sediment (Clark and Fritz, 1997), and dissolution of carbonates, and to a lesser extent from the hydration of atmospheric CO$_2$. In most natural waters in the continent, the gaseous reservoir of CO$_2$ is biogenic soil CO$_2$ and DIC concentrations are controlled by equilibrium between infiltrating water and soil CO$_2$ (partial pressures $10^{-1}$ to $10^{-2}$ ppm) via the following equations (Clark and Fritz, 1997):

\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2^{(aq)} \tag{1}
\]

\[
\text{CO}_2^{(aq)} + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{CO}_3^{(aq)} \tag{2}
\]

\[
\text{H}_2\text{CO}_3^{(aq)} \leftrightarrow \text{H}^+ + \text{HCO}_3^{-} \tag{3}
\]
Below the zone of influence of soil CO$_2$ reservoir, additional sources of DIC may come from mineral weathering processes (Clark and Fritz, 1997) that include dissolution of calcite (equation 5), incongruent dissolution of dolomite (equation 6), dissolution gypsum (equation 7), and weathering of silicate parent material (equations 8 and 9).

\[
\text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}^{2+}_{(aq)} + 2\text{HCO}_3^{-}_{(aq)}. \tag{5}
\]

\[
(\text{Ca, Mg})(\text{CO}_3)_{2(\text{s})} + \text{H}_2\text{O}(l) + \text{HCO}_3^{-}_{(aq)} + \text{Ca}^{2+}_{(aq)} \rightarrow \text{Ca}^{2+}_{(aq)} + \text{Mg}^{2+}_{(aq)} + 2\text{HCO}_3^{-}_{(aq)} + \text{CaCO}_3(s) + \text{OH}^{-}_{(aq)}. \tag{6}
\]

\[
\text{CaSO}_4\cdot2\text{H}_2\text{O}(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} + 2\text{HCO}_3^{-}_{(aq)}. \tag{7}
\]

\[
\text{NaAlSi}_3\text{O}_8(s) + \text{CO}_2(g) + 11/2\text{H}_2\text{O}(l) \rightarrow \text{Na}^+_{(aq)} + 1/2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(s) + 2\text{H}_4\text{SiO}_4^{0}_{(aq)} + \text{HCO}_3^{-}_{(aq)}. \tag{8}
\]

\[
\text{CaAl}_2\text{Si}_2\text{O}_8(s) + 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \rightarrow \text{Ca}^{2+}_{(aq)} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(s) + 2\text{HCO}_3^{-}_{(aq)}. \tag{9}
\]

Also, dissolved organic matter (DOC) transported from the soil zone by infiltrating water into aquifer may evolve via a sequence of redox reaction (e.g. Wassenaar, 1990) and provide a source of DIC to groundwater. The removal of DIC from groundwater may take place by degassing of CO$_2$ or CaCO$_3$ saturation.

In closed basin environments, evaporation is a major control on the build-up of salinity and evolution of water compositions (Eugster and Jones, 1979). The principles of brine chemistry evolution in natural waters are presented by Garrels and Mackenzie (1967), Hardie and Eugster (1970), and Eugster and Jones (1979). Such studies have provided valuable knowledge on the formation and evolution of solute concentrations of...
brines. Modifications of the Hardie-Eugster concepts were later used in various researches, for example Drever (1988), Jankowski and Jacobson (1989), Francois and Fritz (1991), and many more to study patterns in evolution of brines due to evaporation.

Eugster and Jones (1979) have stated that water that enters a closed basin under an arid climate will undergo evaporative concentration leading to the precipitation of a sequence of minerals that remove specific ions from the solution and thus change its chemical composition. The ultimate chemical composition of brines in a closed basin environments is therefore dependent on the initial water composition and on the successive precipitation of minerals during the evolution of brines (Francois and Fritz, 1991). As a result, the chemical characteristics of brines of continental origin should be radically different from those of marine origin.

The stages of the evolution of brine may be worked out in a similar manner to what was introduced by Hardie-Eugster model, which shows how a succession of geochemical divides produces different pathways of brine evolution and formation. Simply put, as water evolves chemically toward higher ionic strength, precipitation of minerals such as calcite (\(\text{CaCO}_3\)), sepiolite (\(\text{Mg}_2\text{Si}_2\text{O}_5\)) and gypsum (\(\text{CaSO}_4\)) occurs. During precipitation, there is enrichment in the ion present in greater relative concentration and depletion in the ion present in lower relative concentration (Drever, 1997). In the initial stages of brine evolution, calcite precipitation would deplete the water of the calcium if the alkalinity (\(\text{HCO}_3^- + \text{CO}_3^{2-}\)) were more than twice the molar concentration of calcium; if \(2m\text{Ca}^{2+}\) is greater than the alkalinity, the a decline of the alkalinity would be observed. At either determination where the composition of the brine follows the alkalinity enriched or calcium enriched branch, a geochemical divide is
observed. Successive geochemical divides would deplete the remaining solution of, for example, Mg\(^{2+}\) and silicic acid (H\(_4\)SiO\(_4\)) during sepiolite precipitation, or Ca\(^{2+}\) and SO\(_4^{2-}\) during gypsum precipitation, and so on. Conversely, if the calcium concentrations are higher than alkalinity, all carbonate species will be used up and the solution will tend toward a SO\(_4^{2-}\)-Cl brine. If alkalinity is more than twice the calcium, the solution would invariably evolve toward a Na-CO\(_3^{2-}\)-SO\(_4^{2-}\)-Cl brine with elevated pH, e.g. Lake Magadi in the East African Rift Valley (Jankowski and Jacobson, 1989). After the first geochemical divide, the evolutionary branch followed by the solution depends on whether calcium concentrations are lower or greater than the carbonate alkalinity. If Mg\(^{2+}\) is in excess, the solution evolves toward a Na-Mg-SO\(_4^{2-}\)-Cl brine with low pH, typical of marine environments. During precipitation of calcite, gypsum and sepiolite, the concentration of the other ions that do not precipitate at lower salinities continuously increases with progressive evaporation (Faure, 1998).

As a result, evaporative concentration of surface water may result in the formation of brines of widely differing chemical compositions through the deposition of minerals that may form non-marine evaporite rocks. The cationic evolution toward sodium dominance is caused by precipitation of alkaline carbonates and Mg-silicates. The anionic evolution away from HCO\(_3^-\) dominance is related to precipitation of carbonates when the Ca\(^{2+}\)/HCO\(_3^-\) ratio in the solution is »0.5. Other processes such as sorption, degassing, and weathering may further concentrate or dilute ions in solution (Jankowski and Jacobson, 1989).

In non-marine brines with an alkalinity load derived entirely from atmospheric CO\(_2\) and dissolution of calcite, the carbonate alkalinity is limited. The anionic evolution
tends to be away from $\text{HCO}_3^- + \text{CO}_3^{2-}$ dominance, and would be rich in Na, Mg, and Cl. Brines due to evaporation of non-carbonated spring water in Australian saline lakes are very low in alkalinity (range: 7 to 595 mg/L $\text{HCO}_3^-$) (Jankowski and Jacobson, 1989). They are either $\text{Na}(\text{Mg})\text{Cl}$ or $\text{Na}(\text{Mg})\text{Cl}(\text{SO}_4)$ dominated. Only two of the lakes that were studied showed other compositions that were biased toward Na-Cl ($\text{HCO}_3^-$); $\text{HCO}_3^- = 10527 \text{ mg/L}$ and $\text{Mg}(\text{Na})\text{HCO}_3(\text{SO}_4)(\text{Cl})$; $\text{HCO}_3^- = 28100 \text{ mg/L}$. There are saline-alkaline lakes around the world that are enriched in carbonates, e.g. Lake Magadi in Kenya ($\text{HCO}_3^- + \text{CO}_3^- = 88000 \text{ mg/L}$), Mono Lake in California, USA ($\text{HCO}_3^- + \text{CO}_3^- = 15710 \text{ mg/L}$). Some lakes are not alkaline e.g. Great Salt Lake, USA ($\text{HCO}_3^- + \text{CO}_3^- = 285 \text{ mg/L}$). Most of the lakes that show high alkalinity have associated volcanic bedrocks.

Associated with DIC transformations are changes in the stable carbon isotopic ratio ($^{13}\text{C}/^{12}\text{C}$). Isotopic ratios are reported using the delta notation ($\delta$) defined by Craig (1957) and Coplen (1996) as:

$$\delta^{13}\text{C} = \left(\frac{^{13}\text{C}^{12}\text{C}_{\text{sample}} - ^{13}\text{C}^{12}\text{C}_{\text{standard}}}{^{13}\text{C}^{12}\text{C}_{\text{standard}}}\right) \times 1000 \text{ per mil}$$

(10)

where $^{13}\text{C}^{12}\text{C}_{\text{sample}}$ and $^{13}\text{C}^{12}\text{C}_{\text{standard}}$ are the carbon isotopic ratios in the sample and standard respectively, measured in per mil units (‰). The standard used for carbon isotopic measurements is the Pee Dee Belemnite (VPDB) carbonate standard.

The type of vegetation occupying a landscape determines the $\delta^{13}\text{C}$ of soil CO$_2$ and infiltrating water (Clark and Fritz, 1997). Three types of plant metabolic pathways are recognized. Plants that use the C$_3$ metabolic pathway dominate temperate and high latitude regions. The respired soil CO$_2$ from these plants has an average $\delta^{13}\text{C}$ value of -
23‰ (range: -22 to -33‰) (Aravena, 1992; Vogel, 1993). The C4 cycle operates in tropical and temperate grasslands and soil CO2 from the vegetation isotopic has isotopic ratios with a mean value of about -12‰ (range: -10 to -20‰) (Deines, 1980; Vogel, 1993). CAM plants dominate in desert ecosystems with an ability to switch from C3 pathway during the day to the C4 pathway at night (Clark and Fritz, 1997). The isotopic composition is usually intermediate between the C3 and C4 plants, i.e. ~ -17‰. The hydration of CO2(gas) by infiltrating groundwater and its transformation to other carbon species is characterized by large isotopic fractionations in the δ13C, roughly +9‰ from CO2(aq) to HCO3⁻ (e.g. Mook et al., 1974). For this reason, groundwater that hosts CO2 from a C3 landscape would have δ13C values around -14‰, C4 plants -4‰, and CAM plants around -7‰. The DIC extracted from water samples would show δ13C values that depend on the original composition of the source CO2 gas (Rose and Davisson, 1996) and on the temperature of equilibration between the carbonate species (Vogel et al., 1970; Mook et al., 1974; Deines et al., 1974; Bottinga, 1968). Clark and Fritz (1997) provided the values of fractionation factors during the transformation of carbon for a range in temperature from 0 to 75°C. For HCO3⁻(aq)-CO2(g) system, the fractionation factors range from 10.9 at 0°C to 3.3 at 75°C; 11.35 to 3.2 for CaCO3-CO2(g) and -1.2 to -0.9 for CO2(aq)-CO2(g). The analyses of DIC and δ13C thus provide essential information in understanding the biogeochemical carbon cycling in hydrologic systems.

Chemical tracers preserve the history and evolution of the inner earth, crust and the hydrosphere, and their uses play a pivotal role in providing the foundation for constraining their sources, and in reconstructing the history of the earth in general. The use of chemicals as tracers of solute origin and fluid chemistry depends largely on their
inert properties during chemical and physical reactions. Most reactive chemicals can also provide useful information. Geochemical techniques for identifying sources of salinization in hydrological systems are described in Davis et al. (1998), Whittemore (1995) and Nurmi et al. (1988). The halogen compositions of fluids may provide information for determining the sources and origins of salinity and fluid transport patterns. Halogen ratios often provide the most conclusive identification of salinity sources (Walter et al., 1990; Fontes and Matray, 1993 I&II; Vengosh et al., 1994; Kesler et al., 1996; Stiller and Nissenbaum, 1997; Davis et al., 1998; Vengosh et al., 1998; Vengosh et al., 1999).

The ratio of Cl/Br or (Br/Cl) is frequently used as an index to distinguish between saline fluids of different origins (Fontes and Matray, 1993a & b) and to determine mixing from different sources (Vengosh et al., 1998; Davis et al., 1998). The Cl/Br ratio for fresh surface water and shallow groundwater varies from 10 to 150 (Davis et al., 1998), seawater is 288 (Mazar, 1997; Whittemore, 1995) and from 1000 to more than 10,000 for brines that result from dissolution of halite (Whittemore, 1995; Kolak et al., 1999). The analyses of small quantities of inclusion fluids trapped in plutonic and basaltic rock samples provide direct evidence of salinity that is related to magmatic processes. Typical Cl/Br ratios in magmatic systems range from 560 to 1000 (Davis et al., 1998; Kolak et al., 1999; Nurmi et al., 1988).

The Cl/Br ratio in natural waters is influenced by a number of factors (Figure 4). The ratio is modified when waters of different Cl/Br ratio mix and will evolve along a mixing curve as shown in Figure 4. Dissolution of halite would contribute more chloride and very little bromide (Fontes and Matray, 1993b) and would cause the Cl/Br ratio to
evolve towards higher values along an overshoot as indicated in Figure 4. On the other hand, the precipitation of halite leads to bromide enrichment in the remaining solution (Kolak et al., 1999), and causes the Cl/Br ratio to decrease. The Cl/Br ratio is unaffected by evaporation and dilution from freshwater inputs as long as no precipitation or dissolution of halite occurs. Water that is affected by evaporative concentration or dilution by fresh waters would evolve along a line of constant Cl/Br ratio as shown in Figure 4. Organic-rich sediments are typically rich in Br. Ten Haven et al. (1987b) and Martini et al. (1993), and degradation of organic matter in sediments adds bromide to groundwater (Gerritse and George, 1988). Where this contribution is significant, the Cl/Br ratio would decrease with increasing salinity. This has been observed for fresh groundwater systems that are impacted by contamination from agricultural, industrial and domestic wastewaters (Vengosh and Pankratov, 1998; Vengosh, 1999; Davis et al., 1998).

In many cases, the Na/Cl ratio is used alongside chloride and bromide to assess the contribution to salinity due to continental weathering and adsorption-exchange reactions. The Na/Cl ratio typically increases in response to diagenetic input of Na from continental weathering (Fontes and Matray, 1993a) in the absence of significant sources for Cl. Comparing the concentrations of these tracers (Cl, Br and Na) in groundwater provides a way to help identify and quantify the sources of salinity.
Figure 4: Schematic Diagram Showing How Various Processes Would Affect the Cl/Br Ratio in Natural Waters.

The stable isotope ratios of oxygen ($^{18}$O/$^{16}$O) and hydrogen ($^{2}$H/$^{1}$H) in the water molecule are commonly used to interpret the origins and circulation patterns of water in the natural environment (Coplen et al., 2000; Gat, 1996). Isotopic ratios are reported in the $\delta$-notation (Craig, 1961) defined as:

$$\delta^{(18}O, 2H) = \left[\frac{R_{sample} - R_{standard}}{R_{standard}}\right] \times 1000$$

(11)
R\textsubscript{sample} and R\textsubscript{standard} denote isotopic ratios $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ in the sample and standard respectively, measured in per mil units (‰), and referenced to VSMOW (Vienna Standard Mean Ocean Water).

The oxygen and hydrogen stable isotope content of atmospheric water in middle and northern latitudes is most strongly controlled by the temperature at the time of precipitation, with isotopically lighter precipitation associated with colder temperatures (Dansgaard, 1964) i.e. due to temperature fractionation. In higher latitudes, the depletion in the hydrogen isotope may be lower than -200‰ and less than -35‰ for oxygen (Rozanski et al., 1993, Gat, 1980); in the tropical regions, the isotopic content of precipitation is empirically correlated to the amount of rainfall (Coplen et al., 2000; Rozanski et al., 1993; Dansgaard, 1964) with heavier rains producing isotopically lighter water. Fractionations related to this effect are not too extreme, i.e. greater or equal to ~ -80‰ for hydrogen, and -15‰ for oxygen. After precipitation, evaporation becomes an important process that modifies the stable isotopic composition of surface waters and soil moisture (Allison et al., 1984). The heavier isotopic species ($^{18}\text{O}$ and $^2\text{H}$) tend to be retained during evaporation and are thus enriched by evaporative processes compared to their lighter counterparts ($^{16}\text{O}$ and $^1\text{H}$). This is due to differences in mass between lighter and heavier isotopes, which causes isotopic fractionation and enrichment during evaporation. Fractionation due to evaporation may produce isotopic values that are far more than 0‰ for both hydrogen and oxygen. Unlike evaporation, the process of transpiration does not discriminate between the lighter and heavier isotopes and thus does not change the isotopic composition of the residual water (Coplen et al., 2000; Gonfiantini, 1986). Determination of the stable isotopic composition of saline waters is a
useful method for discriminating the causes of salinity because water that is saline due to evaporation will be isotopically more enriched (i.e. higher $\delta$ values) than the source water, whereas water that is saline due to salt weathering/addition will not significantly change its isotopic composition.

When plotted against each other, the hydrogen and oxygen isotopic compositions of water produce an array of trends (Figure 5) that are diagnostic of specific processes when compared to the global meteoric water line (GMWL) of Craig (1961). Variations of the GMWL are area-specific and give rise to coefficients that define local meteoric water lines (LMWL) (Figure 5). The different coefficients showing deviation from the GMWL are controlled mostly by local climatic variations. Evaporation produces trajectories that deviate from the meteoric water lines with slopes that are $\leq 5$ (Figure 5). By following evaporation trajectories towards meteoric water lines (LMWL), the $\delta^{18}O$ and $\delta^2H$ values of the source water may be determined, i.e. where a trajectory intersects with a local meteoric water line. Strong evaporative loss from open surface water bodies such as lake surfaces causes salinity increase and isotopic enrichment with respect to the heavier isotopes.

A co-variation between salinity and isotopic enrichment is thus expected when evaporation is the dominant process affecting the salinity of water. Progressive evaporation to extreme salinities causes the precipitation of salts that remove the heavy isotopes from solution and may impart isotopic depletions on the remaining water (Fritz and Clark, 1997). Such depletions mislead the interpretation of $\delta$D and $\delta^{18}O$ in brines (Gonfiantini, 1986).
Figure 5: Relationship $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for Natural Waters Showing Secondary Processes That Modify Isotopic Compositions in Water (Compiled From Taylor, 1974; Coplen, 1993 and Criss, 1999).

3.2 Field Sampling and Experimental Procedures

Data presented in this study were obtained from samples collected from wells within the northern part of Sua Pan. Sampling depths varied from 24.7 m to 42.8 m below ground surface and were within the medium-grained sand aquifer that is confined beneath the clayey pan deposits (Figure 2, unit 3). Groundwater is pumped to the surface using a network of high-capacity electrical pumps. Wells are evenly spaced at 2 km. The water temperature, specific conductance and pH measurements were determined at the wellhead using appropriate electrodes. Titrimetric determinations of alkalinity (Stumm and Morgan, 1996) were not accomplished in the field due to the high concentration of
HCO$_3^-$ and CO$_3^{2-}$ in the samples. Samples for anion and cation analyses were collected unfiltered in high-density polyethylene (HDPE) bottles. Samples for the analyses of cations/metals were acidified to pH of 2 or lower using high purity nitric acid (85% HNO$_3$) to prevent metals from precipitating during storage. The samples were capped without headspace using plastic caps and refrigerated at 4°C until the analyses for major ions.

For stable carbon isotope analysis of DIC, water samples were injected using a syringe into pre-evacuated septum tubes (blood serum vials) that were pre-loaded with 100% phosphoric acid (H$_3$PO$_4$). This method, known as the vacutainer gas evolution technique, is described in Atekwana and Krishnamurthy (1998). For stable isotopes of oxygen and hydrogen analyses, water samples were collected in 20 ml glass vials with inverted cone closures to minimize headspace and potential evaporation (Gat, 1996). Duplicate samples were collected for all analyses for quality assurance.

3.3 Chemical Analyses

Concentrations of anions (Cl$^-$ and SO$_4^{2-}$) and cations (Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$) were analyzed at the Indiana University Perdue University Indianapolis (IUPUI) hydrogeology lab using a Dionex DX-500 ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with a conductivity detector and an AS40 auto sampler. All samples were diluted 500-fold using ultra-pure de-ionized water to bring the concentrations within the calibration range of the standards. KAR Labs in Kalamazoo, Michigan determined bromide concentrations.
3.4 Stable Carbon Isotope Analyses ($\delta^{13}$C, DIC)

The acid-water reaction that proceeds immediately upon injection of water samples into the pre-evacuated septum tubes containing phosphoric acid produces CO$_2$ gas. The evolved CO$_2$ is extracted by agitating samples in an ultra-sonic bath, a slight modification of the technique of Atekwana and Krishnamurthy (1998) and DIC concentrations were calculated from pressure reading of the purified CO$_2$ gas. DIC measurements are reported as milligrams carbon per liter (mg C/L). Isotope ratios of the CO$_2$ gas were determined using a Micromass Optima isotope-ratio mass spectrometer.

Before samples were run in the mass spectrometer, the efficiency of the ultrasonic technique was tested using a calibrated internal laboratory standard made by dissolving 248 mg of Na$_2$CO$_3$ in 100 ml of de-ionized water. Approximately 96% DIC recovery was achieved through this method. All isotope measurements agreed with values (-7.5±0.1‰) that were obtained by Atekwana and Krishnamurthy (1998), in which CO$_2$ extraction was achieved by heating to 50°C and simultaneously stirring using a magnetic stir bar. The analytical precision of the $\delta^{13}$C measurements is ±0.2‰.

3.5 Stable Oxygen ($\delta^{18}$O) and Hydrogen ($\delta^2$H) Analyses

The stable oxygen isotope ($\delta^{18}$O) values for dilute waters are determined by the widely used and established technique of isotopically equilibrating water with pure CO$_2$ in a constant temperature environment (Epstein and Mayeda, 1953). In this procedure, 2 ml of water sample is equilibrated with 0.5 atmospheres of CO$_2$ for 25 hours at 25°C. The
δ¹⁸O of the water is measured from the equilibrated CO₂ using a mass spectrometer. The above method for analyzing δ¹⁸O is not adequate for brines. δ¹⁸O measurements done on concentrated aqueous solutions need to be corrected for salinity effects before comparison with δD. Sofer and Gat (1972) developed the following empirical equation to correct δ¹⁸O measurements for salinity due to high Mg²⁺, Ca²⁺ and K⁺:

\[ \delta^{18}O_{\text{corr}} = \frac{(1.11m_{\text{Mg}} + 0.47m_{\text{Ca}} + 0.16m_{\text{K}})}{1000} \times (\delta^{18}O_{\text{meas}} + 1000) + \delta^{18}O_{\text{meas}} \]

\(*\) (12)

\(m\) is the molality of ion concentration. After this correction, δ¹⁸O data can be used in the δD vs. δ¹⁸O plot with the GMWL or local meteoric water lines (Rozanski et al., 1993) to infer the origins of water and processes that might have affected the water in continental environments (Gat, 1996). In this study, concentrated brine samples were spiked with 100% H₃PO₄ to lower the pH before the equilibration procedure could be adopted. This step had to be added because the brine absorbed all the CO₂ used in the equilibration process. δ¹⁸O measurements obtained after the equilibration procedure still need to be corrected for salt effects.

δD measurements in fresh water samples are obtained by reacting the water with a metal (Friedman, 1953; Coleman et al., 1982; Shouakar-Stash et al., 2000) to produce H₂ gas. For samples with high concentrations of salts, (>35000 mg/L), various techniques have been described (O’Neil et al., 1986; Knaught and Beeunas, 1986; Horita and Matsuo, 1986; Lazar and Holland, 1988; Horita, 1989; Koehler and Kyser, 1991; Yang et al., 1996; Shouakar-Stash et al., 2000). Some of these analytical techniques entail distillation of brines at very high temperatures under vacuum; in which case, salt effect
corrections to δD (Gat, 1984; Horita and Gat, 1989) are unnecessary (Yang, 1996). δD analyses are completed on the hydrogen gas obtained through high-temperature reduction of water on zinc (Coleman et al., 1982). In this method, 2μL of water are injected into an evacuated 6 mm Pyrex tube that contains 150 mg of zinc shavings (Indiana zinc). The zinc and water are then heated to 500°C in an oven for 60 minutes to produce H₂ gas by the following equation:

\[
\text{H}_2\text{O (liquid)} + \text{Zn (solid)} \rightarrow \text{H}_2\text{(gas)} + \text{ZnO (solid)}
\]

In this study, all groundwater samples are concentrated chloride brines. Chlorides have been shown to poison metal surfaces and inhibit the metal-water reaction (Yang et al., 1996).

3.6 Procedure for the Distillation of Micro-liter Quantities of Water From Brine Samples

A distillation cell consisting of a vapor transfer vessel shown on Figure 6, and the procedure thereon were developed to distil the brine samples by heating 2μL of brine to ≥900°C under vacuum conditions. The cell is made from quartz glass to withstand high heating temperatures and the transfer vessel is Pyrex glass. The released water is transferred into the 6 mm Pyrex tube containing zinc using liquid nitrogen and then cryogenically purified using a slush of dry ice and alcohol.
After loading 150 mg of Indiana zinc into a 12-inch long Pyrex tube (Figure 6, Tube A), the system is set up by connecting tubes A, B and C to an external transfer arm as shown in the diagram of Figure 6. The system is attached to a vacuum line, using Cajon connectors, initially with all the valves (stopcocks 1, 2, and 3) open to the vacuum. After reaching vacuum conditions i.e. $10^{-1}$ mBar or better, stopcock 1 is closed and a liquid nitrogen (LN) trap (-180°C) is inserted around tube A. Using a micro-liter syringe, a 2µL of brine sample is injected through a septum in the cap of the distillation cell. The inside of the cap is sealed with a heat resistant septum. The brine is allowed 5 minutes to transfer from the needle to the LN trap. Meanwhile, with valves 2 and 3 open, the bottom part of the tube containing zinc is heated to about 340°C using a hot air gun (Master Heat Gun, Omega Engineering Inc.) until a gray halo forms on the inside walls of the tube, just above the zinc. The heat is removed when the halo forms and it takes approximately 3 to 5 minutes. The trapped brine is then cleaned of any air by opening Stopcock 1 to vacuum (stopcock 2 has to be closed).

The entire system is then separated from vacuum by closing stopcock 3 and keeping stopcock 1 and 2 open. The system is ready to distil. The LN trap is removed from Tube A and replaced with a heating sleeve (~900°C). The LN trap is inserted around Tube C to collect the distillate. This step is allowed 20 minutes to continuously distil and collect water from the brine. It has been demonstrated using laboratory standards that heating the brine with stopcock 1 closed causes a large error in the δD measurements (see table 1) due to fractionation. After 20 minutes, the heat is cut off and stopcock 1 closed down. The LN in Tube C is replaced with a slush of dry ice and alcohol (~79°C) and stopcock 3 is opened to purify the water of other gases.
The purification is completed when all the gases, especially CO₂, are removed and vacuum conditions recovered. The zinc and water are then sealed in Tube B by a flame. Both the zinc and water are then reacted at 500°C for one hour in an oven. The evolved H₂ gas is then analyzed for δ²H in a mass spectrometer. The δD values of the H₂ gas and δ¹⁸O measurements in the CO₂ gas were measured using the Micromass Optima dual-inlet gas source isotope ratio mass spectrometer (IRMS) at the Institute of Water Sciences, Western Michigan University in Kalamazoo, Michigan.

Figure 6: Schematic of the Vacuum Cell Used for Brine Distillation.
The results for $\delta D$ and $\delta^{18}O$ isotope ratios are reported on the V-SMOW scale. The analytical precision for $\delta^{18}O$ measurements is 0.2% and for $\delta D$ is $\pm 2\%$.

<table>
<thead>
<tr>
<th>Lab Standard</th>
<th>Closed Valve %</th>
<th>Open Valve %</th>
<th>Expected %</th>
</tr>
</thead>
<tbody>
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<tr>
<td></td>
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<tr>
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</tr>
<tr>
<td></td>
<td>-35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Measurements error: $\pm 2\%$

Table 1: Experimental Test Data on the Efficiency of the Brine Distillation Cell.
CHAPTER IV

RESULTS AND DISCUSSION

All field measurements are listed in Appendix 1. Analyses of the dissolved inorganic carbon, stable carbon, hydrogen and oxygen isotopes, and the major element chemistry of the Makgadikgadi brine are listed in Appendix 2.

4.1 DIC and Stable Carbon Isotope

DIC values range from 3.2 to 5.0 gC/L which is orders of magnitude higher than DIC from soil CO$_2$(gas) (see section 3.1). Based on soil P$_{CO2}$ conditions ($10^{-1}$ to $10^{-2}$ ppm) and thermodynamic equilibria between CO$_2$(gas) and water, the calculated DIC concentrations in infiltrating water would range from 0.06 to 0.1 gC/L. Models that describe the chemical evolution of dilute waters as they concentrate demonstrate the importance of solute fractionation processes which commonly result in brines dominated by just a few chemical species. The final brine composition is determined by the composition of the precursor solution (Hardie and Eugster, 1970) and in-lake geochemical processes (Herczeg and Lyons, 1991) that enrich the water in certain ions relative to others. Most salt-lake brines derive a large fraction of their solutes from groundwater inflow (Herczeg and Lyons, 1991).

Herczeg and Lyons (1991) showed that by increasing the P$_{CO2}$ in water from 1 to 50 atmospheres delays calcite saturation, which could lead to instances of supersaturation with respect to gypsum (CaSO$_4$). Precipitation of gypsum will suppress the calcium
concentrations to low levels and cause the DIC to invariably increase on evaporation before calcite saturation could be reached. This raises the pH to 8 and more. Considering the low $P_{CO_2}$ of the atmosphere, it is difficult to account for high DIC in the Makgadikgadi brine using a single-stage mechanism of evaporative concentration of rain or surface water alone. A combination of occasional flooding of the pans followed by fast evaporation prior to infiltration, and contacting with a high $P_{CO_2}$ emanating from the subsurface is a more likely scenario to generate the chemical composition of the Makgadikgadi brine. This combination model might explain residual calcium concentrations (0 to 100 mg/L) that are detected in some of the samples. Table 2 compares DIC concentration for several saline-alkaline lakes from around the world to the water chemistry of the Makgadikgadi system.

Active magmatic CO$_2$ build-up in lakes is known to occur in very few places in the world. In the volcanic lakes of Cameroon, West Africa, DIC concentrations ranged from 0.85 to 3.8 gC/L increasing with increasing water depths from 76 to 210 meters (Evans et al., 1993 and Kling et al., 1994). The DIC concentrations measured for the brine from Sua Pan are similar to values from the volcanic lakes of Cameroon, Mono Lake in USA, Lake Magadi in Kenya, Lake Woods and Werowrap in Australia and may share a similar mode of production to one or more of these lakes. Other saline lakes show relatively very low DIC, e.g. groundwater discharge lakes of Central Australia; HCO$_3^-$ concentrations range from 7 to 595 mg/L (Jankowski and Jacobson, 1989), and the Great Salt Lake, USA (HCO$_3^-$ + CO$_3^{2-}$ = 285 mg/L). The difference in DIC concentrations likely indicates a difference in the source water.
Mono Lake\(^1\) L. Magadi\(^2\) (Kenya) L. Woods\(^3\) (Australia) L. Werowrap\(^4\) (Australia) Makgadikgadi\(^4\) Pans

<table>
<thead>
<tr>
<th></th>
<th>Mono Lake (USA)</th>
<th>L. Magadi (Kenya)</th>
<th>L. Woods (Australia)</th>
<th>L. Werowrap (Australia)</th>
<th>Makgadikgadi Pans</th>
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<tbody>
<tr>
<td>HCO(_3)/CO(_3)</td>
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<td>44000-105720</td>
<td>28100</td>
<td>10527</td>
<td>20000</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>9.6</td>
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<tr>
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<td>4</td>
<td>9900-15000</td>
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<td>Na(K)-CO(_3)-Cl-SO(_4)</td>
<td>Na-Cl-HCO(_3)</td>
<td>Na(K)-Cl-CO(_3)-HCO(_3)(SO(_4))</td>
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</tbody>
</table>

Table 2: Comparisons of DIC Concentrations and Water Chemistries from Other Alkaline Saline Lakes and the Makgadikgadi System. All Concentrations are in mg/L. 1=Jones et al. (1977), 2=Jankowski and Jacobson (1989), 3=Gould (1986) and Current Study.

The water compositions of the low DIC lakes is dominated by Na(Mg)Cl or Na(Mg)Cl(SO\(_4\)) and this shows that not all saline lakes show high DIC concentrations. Saline lakes that are similarly enriched in DIC as the Makgadikgadi brine (Table 2 above) have associated volcanic bedrocks, suggesting the importance of source water to lake chemistry. Excess alkalinity may also result due to evaporative enrichment of solutes at or near the surface. This would require relatively high initial concentration of DIC in the inflow water, e.g. rainfall. Such high concentrations may therefore be unique to particular areas. The remains of high DIC in the Makgadikgadi brine may indicate evidence for near surface accumulations of carbon of magmatic origin. Excess alkalinity from high P\(_{CO_2}\) may strip calcium from the brine, enhance silicate weathering, production of silicic acid, and precipitation of magnesium as sepiolite.

The \(\delta^{13}C\) values of the brines range from -2.28 to -0.82\%; average -1.6±0.2\%. The values are similar to those measured for DIC in water that has equilibrated with geothermal CO\(_2(gas)\) (Evans et al., 1993; Kling et al., 1989; Rose and Davisson, 1996;
Calculation of the possible sources of DIC requires the use of equilibrium mass balances for the systems CO$_2$(gas) - HCO$_3$^- (aq) and CO$_2$(gas) - CO$_3^{2-}$(aq). The mass balance equations (14) and (15) (Clark and Fritz, 1997), used to calculate sources, assume that DIC is a result of hydration of CO$_2$(gas) to HCO$_3$^- (aq) and CO$_3^{2-}$(aq). The balance equations are pH and temperature dependent. For the Makgadikgadi brines, average pH = 9.6, T = 25°C, it is assumed that the DIC is controlled by equilibrium between CO$_2$(gas) and water to form HCO$_3$^- and CO$_3^{2-}$:

\[
\delta^{13}\text{C}_{\text{DIC}} = 0.77(\delta^{13}\text{C}_{\text{CO}_2\text{ (g)}} + \epsilon^{13}\text{C}_{\text{HCO}_3^-\text{CO}_2\text{ (g)}}) + 0.23(\delta^{13}\text{C}_{\text{CO}_2\text{ (g)}} + \epsilon^{13}\text{C}_{\text{CO}_3^{2-}\text{CO}_2\text{ (g)}}) \tag{14}
\]

\[
\delta^{13}\text{C}_{\text{DIC}} = 0.10(\delta^{13}\text{C}_{\text{CO}_2\text{ (g)}} + \epsilon^{13}\text{C}_{\text{CO}_2\text{ (aq)}} - \epsilon^{13}\text{C}_{\text{CO}_3^-\text{CO}_2\text{ (g)}}) + 0.90(\delta^{13}\text{C}_{\text{CO}_2\text{ (g)}} + \epsilon^{13}\text{C}_{\text{HCO}_3^-\text{CO}_2\text{ (g)}}) \tag{15}
\]

\[
\epsilon^{13}\text{C}_{\text{HCO}_3^-\text{CO}_2\text{ (g)}} = 7.9\%\text{ at } 25^\circ\text{C} \tag{16}
\]

\[
\epsilon^{13}\text{C}_{\text{CO}_3^{2-}\text{CO}_2\text{ (g)}} = 7.6\%\text{ at } 25^\circ\text{C} \tag{17}
\]

\(\epsilon^{13}\text{C}\) denotes fractionation factor between two species of carbon at equilibrium with one another; +7.9% between CO$_2$(gas) and HCO$_3$^- (aq) and +7.6% for CO$_2$(gas) to CO$_3^{2-}$(aq) at 25°C. \(\delta^{13}\text{C}_{\text{DIC}}\) are the measured isotopic compositions of the samples (-1.6±0.2‰). The results from the above equations indicate that the \(\delta^{13}\text{C}\) values of the source CO$_2$ for the Sua Pan brine would be about -9.5‰. This value falls within the range expected for mantle sources (\(\delta^{13}\text{C}\approx -7\) to -10.5‰) (Pineau and Javoy, 1983; DesMarais, 1986; DesMarais and Moore, 1984). The value of -9.5‰ is also very close to atmospheric CO$_2$(gas) (\(\delta^{13}\text{C}\approx -7\) to -8‰) (Clark and Fritz, 1997). Therefore, \(\delta^{13}\text{C}\) values in the Makgadikgadi brine do not definitively exclude crustal reservoirs as possible sources of
carbon. However, when this δ¹³C value is viewed in the light of the DIC concentrations, it is not likely from atmospheric carbon sources, which have relatively low P_{CO₂} values.

The production of carbon via biogenic pathways produces lighter values (≈ -14 to -30‰) (Whiticar et al., 1986; Deuser et al., 1973). Therefore, the δ¹³C values in the Makgadikgadi brine do not favor a biogenic CO₂(gas) source. The combination of relatively high DIC and heavy δ¹³C values are unusual for continental sources of CO₂, and strongly suggests that the carbon has a magmatic imprint. Therefore, the carbon composition in the Makgadikgadi brine approximates that of magmatic systems; hence, the DIC is likely of magmatic origin and potentially, the underlying basalt is the source.

4.2 DIC and Fluid Conductivity Measurements

The spatial distribution of DIC (Figure 7) and specific conductance (Figure 8) in the Makgadikgadi brine show a general trend of decreasing DIC and salinity from the northeast westward. A distinct anomaly of higher concentration in both figures is noticeable in the northeast. The linearity in this anomaly is unique because it shows little influence from the general groundwater flow direction, and may correlate with variation in the bedrock structure and discharge of highly saline water from fracture zones. Isolated areas of higher concentrations of DIC and salinity to the south may represent point-source contributions from small fractures. Away from these concentration anomalies, both DIC and fluid conductivity gradually decreases toward the edges of the pan. The decrease in the salinity is likely due to ingress and dilution by meteoric water at the pan margins.
Figure 7: A Contour Map Showing Spatial Patterns in DIC and the Location of a Zone of High DIC in the Northern Part of Sua Pan. The Linearity in the Anomaly May Indicate Faults in the Basement. Lower DIC Concentrations in the West are Related to Fresh Water Input.

Figure 8: A Contour Map of the Spatial Distribution of Fluid Conductivity in the Northern Part of Sua Pan Showing Anomalous Values in the Northeast That Show High Specific Conductance. In Addition, the Linearity in the Anomaly is Distinct and May Show a Variation in the Bedrock Where Saline Fluid Discharge Along Fractures. Low Salinity in the West Indicates Fresh Water Inputs.
4.3 Cl-Br-Na Systematics

The investigation of the sources of Cl and Br in the brine is based on selected brine samples (PW2, PW9, PW18, PW19, PW27, PW36, PW39, PW52, PW105 and PW124) that span the whole range of chloride concentration (59520 to 84805 mg/L). The samples have Cl/Br ratios that range from 470 to 695. Apparently, the high Cl/Br ratios samples (PW36, PW39, and PW52) are located in designated areas of recharge (Figures 7 and 8). Therefore, samples with high Cl/Br ratio might represent recharge waters that are still evolving toward equilibrium values shown by samples with lower ratios. These high Cl/Br samples could not be tied to borehole depth, lithological variation or pumping rate. The ratios for all the samples suggest that the brine does not possess the main characteristics of seawater (Cl/Br ratio = 288) or dissolution of pure halite (Cl/Br ratio >1000) (Kolak et al., 1999). Instead, for high bromide samples the Cl/Br ratios in the Makgadikgadi brine show a range that is similar to values reported for fluid-inclusion brines from magmatic rocks (390 to 714; average 552±162) (Banks et al., 2000; Davis et al., 1998).

There is poor correlation ($r^2=0.52$) in the bromide samples with increasing chloride concentration (Figure 9). The relationship between Cl and Br shows addition of both ions into solution and it is likely that evaporation plays a significant role.
Figure 9: Cross-Plot of Br vs. Cl for the Makgadikgadi Brines Showing a Co-varying Relationship Between the Ions.

4.4 Na/Cl Ratios

The Na/Cl molar ratio in the brine ranges from 1.23 in the northeast to 1.64 in the west. The higher Na/Cl ratio in the west might represent dilution of chloride by recharging water from the surface and production of sodium from weathering processes, most likely by leaching of alkali-rich silicate rock via the following reaction:

$$(\text{Na},\text{K})\text{AlSi}_3\text{O}_8 + 11/2\text{H}_2\text{O} + \text{CO}_2 \rightarrow (\text{Na}^+\text{,K}^+) + \text{HCO}_3^- + 2\text{H}_4\text{SiO}_4^0 + 1/2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4... (18)$$

The Na/Cl ratios provide evidence for excess Na from rock weathering compared to Cl and the amount of Na determined using the chloride dilution factor of ~30%, from chloride concentrations in the brine, suggests that up to 24% of the total Na budget might
have come from silicate hydrolysis. The DIC and Na that are produced from this process should be well correlated only if albite weathering is the only process, which is very unlikely. The relationships Na versus DIC (Figure 10) and K versus Na (Figure 11) are positive and not so well correlated ($r^2=0.5$). The correlation indicates the possibility of other overriding processes. This relationship also holds for dilution of groundwater and does not necessarily predict that there are additions of Na and DIC from weathering. It may also be expected from evaporating systems. The presence of volcanic lava beneath the pans (Figure 12) provides a geological understanding for silicate weathering.

![Graph](image.png)

Figure 10: Cross-Plot of Na and DIC for the Makgadikgadi Brine. The Relation is Positively Correlated Indicating Both might be Derived From Same Processes.
Figure 11: Na vs. K Relationship Showing Evolution of Water to Higher Ionic Strength.

Figure 12: Aeromagnetic Map of Northern Botswana Showing Various Geological Units, the Basalt Intrusion and the Location of the Makgadikgadi Pans. The Linear Feature in Dark Color is a Swarm of Very Shallow Regional Basalt Intrusion. The Area Marked With a Rectangular Shape is the Location of the Makgadikgadi Pans. Map Not to Scale.
4.5 Stable Oxygen and Hydrogen Isotopes

The $\delta^{18}O$ and $\delta^2H$ are a measure of concentrations of the stable isotopes of oxygen and hydrogen found in water molecules. Brine samples from Sua Pan are compared with the long-term (1962 to 2000) meteoric water line (Figure 13) constructed from weighted mean precipitation values for the IAEA station located in Pretoria, South Africa. The meteoric water line is defined by the relationship $\delta^2H = 6.2\delta^{18}O + 5.3$ and brine isotopic compositions form a group below this line. The observed deviation of the brine compositions from the meteoric water line shows that evaporation has occurred between rainwater and groundwater. When water evaporates from an open lake, the amount of evaporation that has taken place can be estimated from water balances using $\delta^{18}O$ and $\delta^2H$ isotopes. The evolution of $\delta^{18}O$ and $\delta^2H$ toward heavier compositions during evaporation of lakes can be described by a Rayleigh-type equation (Clark and Fritz, 1997). Gonfiantini (1986) presents the calculations for such mass balances and shows that the amount of water evaporated is a function of the humidity;

$$\delta^{18}O_{gw} - \delta^{18}O_{prec} = \varepsilon^{18}O_{total} \cdot \ln f$$

$$\delta^{18}O_{gw}$$ is oxygen isotopic composition for groundwater
$$\delta^{18}O_{prec}$$ is oxygen isotopic ratio for rainfall
$$\varepsilon^{18}O_{total} = 14.2(1-h)\% + 10^3 \ln a^{18}O$$

$\varepsilon^{18}O_{total}$ is the sum of the kinetic enrichment factor $(14.2(1-h)\%)$, where $h$ is the humidity, and the temperature dependent equilibrium fractionation factor $10^3 \ln a^{18}O$
(tabulated experimental data; see Clark and Fritz, 1997) between the evaporating liquid and vapor phase, \( f \) is the fraction of water that remains after evaporation. By using the average \( \delta^{18}O_{\text{prec}} \) value for the Pretoria meteoric water (-3%), average \( \delta^{18}O_{\text{GW}} \) of +3% (see Figure 14) and humidity of 50%, the amount of water \( f \), that remains is 69%. This suggests that about 31% evaporation has taken place to cause the shift in the brine compositions.

![Graph](image)

**Figure 13**: Relationship \( \delta^2H \) versus \( \delta^{18}O \) for the Meteoric Water Line (filled circles) and the Sua Pan Brine (filled triangles).

It does not seem realistic to conclude that the salinities in the brine are a result of evaporating surface water by only 31%. If equation 19 is considered and a concentration factor of 1000 (\( f = 0.001 \)) is applied to surface waters to produce the salinities, the isotopic values for the remaining water can be calculated to determine if isotopic values in the brine could be produced. The \( \delta^{18}O_{\text{GW}} \) in this case would be;
\[ \delta^{18}O_{GW} = \epsilon^{18}O_{total} \times \ln(f) + \delta^{18}O_{prec} \]
\[ \delta^{18}O_{prec} = -3; \; \epsilon^{18}O_{total} @30^\circ C = 16; \; f = 0.001 \]
\[ \delta^{18}O_{GW} = -19 \times \ln(0.001) = +113\% \]

Figure 14: $\delta^2H$ versus $\delta^{18}O$ Relationship for the Sua Pan Brine. Filled Circle is the Average Rainwater Composition, Filled Diamond is the Average Brine Composition and Filled Triangles are Individual Brine Compositions.

This calculated value of 113\% is quite different from the isotopic value of the brine (+3\%). Therefore, another source might be contributing water that is more saline and isotopically light. In Figure 15, applying the meteoric water equation on the actual brine compositions provides a reconstruction of the expected isotopic composition of the brine. The expected values fall along a line, and indicate heavier compositions compared to the measured values. Assuming the brine represents evaporated meteoric water, the isotopic compositions should range from +17 to +32\% for $\delta^2H$. It is clear from Figure 15 that the $\delta^2H$ values have drifted to lighter compositions. Since exchange of hydrogen with the
rocks is a less common phenomenon, mixing with an isotopically lighter and more saline end-member in the subsurface becomes a more realistic process. Magmatic waters are usually depleted in hydrogen. Estimated isotopic compositions for magmatic systems fall between $\delta^2H = -40$ to $-80\permil$ ($+6$ to $+9\permil$ for $\delta^{18}O$) (White, 1974; Campbell and Larson, 1998). It is therefore likely that the observed compositions in the Makgadikgadi brine could have resulted from mixing of evaporated and therefore isotopically heavier meteoric water from the surface with a lighter magmatic end-member from the subsurface.

![Graph](image)

**Figure 15:** Expected Isotopic Compositions of the Brine (filled circles) Reconstructed by Superimposing the Actual Values (filled triangles) on the Meteoric Water Equation.

### 4.6 Stable Oxygen and Chloride Concentration

The relationship between $\delta^{18}O$ and chloride for all samples (Figure 16) shows two groupings; one falls along a line of $\delta^{18}O$-chloride enrichment and the other samples form
a group that shows mostly isotopically enriched samples with diluted chloride concentration. The isotopically more enriched samples may represent recharged water from the surface. The $\delta^{18}$O-chloride relationship for the enriched samples (Figure 17) shows a weak trend but still with increasing chloride salinity and isotopic concentration. The increasing salinity with isotopic enrichment is expected for evaporating systems and therefore shows that evaporation is taking place. All the heavier samples are located close to the edges of the pan and other areas where groundwater recharge is presumed to take place. For these samples, a 0.5% increase in $\delta^{18}$O corresponds to an increase in chloride concentration of 11,000mg/L. It has been indicated in the preceding section that evaporation alone cannot cause this concentration. The good correlation ($r^2 = 0.75$) is obtained between $\delta^{18}$O and chloride (Figure 18) after eliminating samples that form a grouping. The trend likely indicates mixing of evaporated samples with more saline groundwater. Therefore, evaporation is a likely process by which salts are concentrated at the surface before the water infiltrates to become part of the groundwater environment then mixing in the subsurface. The infiltration may not necessarily come from recent flood events but might have taken place over geologic timescales. The compositions of the incoming water that is isotopically heavier due to evaporation but relatively dilute with respect to the solute load in the groundwater system might have changed in response to interactions with the subsurface. The fact that the heavier values of hydrogen and oxygen from the surface are not maintained in the aquifer is a sign that there is more than just evaporative concentration controlling the chemistry of the brine.
Figure 16: $\delta^{18}$O versus Cl Relationship for the Sua Pan Brine. Labeled Wells Represents Recharge From the Surface.

Figure 17: $\delta^{18}$O-Cl Relationship for the Isotopically Heavier Water From the Surface.
Figure 18: $\delta^{18}O$ versus Chloride for Samples That Fall Along a Line of Mixing.
CHAPTER V

SYNTHESIS AND CONCLUSIONS

The geo-chemical and isotopic studies of the hyper-alkaline Na-Cl-(CO₃⁺HCO₃) brine from the northern part of Sua Pan in the Makgadikgadi area have indicated that the brine has likely undergone various stages of in-lake modifications via a sequence of surface and subsurface processes. The study demonstrated the need for a multiple-stage process to account for the high salinities. Isotopic data have indicated that the of DIC concentrations, δ¹³C values in the brine indicate that of the DIC has imprints of a magmatic source while the chemical data indicated that surface evaporative processes have played some role in concentrating salts in the brine.

The first step in a three-stage process model is to evaporate surface water and concentrate salts. Based on the humidity value of 50%, it was demonstrated that surface waters undergo evaporation and lose 31% of the moisture before infiltrating. This amount of evaporation was shown to be too small to account for the high salinity in the brine. Most of the alkaline earth elements (Ca²⁺ and Mg²⁺) though are removed by precipitating as carbonate and silicate salts during the evaporation stage. The alkalis (Na⁺ and K⁺) and other anions acquire higher concentrations. After infiltration, the water from the surface encounters a large source of CO₂, presumably of magmatic nature. This enhances weathering of feldspars (albite), which releases Na into solution and fixes DIC leading to high pH conditions. The δ²H isotope showed depletions relative to parent evaporated rainwater and it was concluded that such depletions might be a result of mixing with an
isotopically very light source, which could only be of magmatic origin. This model indicates that the brine aquifer in the Makgadikgadi Pans is partially fed by underground discharge and partially by meteoric recharge.
## Appendix A

Summary of Field Data for Northern Part of Sua Pan

<table>
<thead>
<tr>
<th>Well I.D.</th>
<th>Southing</th>
<th>Easting</th>
<th>Elevation (ft)</th>
<th>W.L. (mbgl)</th>
<th>pH</th>
<th>Temp (°C)</th>
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