A Conceptual Overview of Surface and Near-Surface Brines and Evaporite Minerals

Warren W. Wood

THE GROUNDWATER PROJECT

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Warren W. Wood
Emeritus Scientist
Research Hydrologist, Visiting Professor Hydrogeology,
Department of Earth and Environmental Sciences,
Michigan State University
East Lansing, Michigan, USA

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The Groundwater Project
Guelph, Ontario, Canada

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Published by the Groundwater Project, Guelph, Ontario, Canada, 2021.

Wood, Warren W.
A Conceptual Overview of Surface and Near-Surface Brines and Evaporite Minerals / Warren W. Wood - Guelph, Ontario, Canada, 2021.
37 pages

ISBN: 978-1-77470-021-1

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Citation: Wood, Warren W., 2021, A Conceptual Overview of Surface and Near-Surface Brines and Evaporite Minerals↗. The Groundwater Project, Guelph, Ontario, Canada.

Domain Editors: Eileen Poeter and John Cherry
Board: John Cherry, Paul Hsieh, Ineke Kalwij, Stephen Moran, Everton de Oliveira and Eileen Poeter
Steering Committee: John Cherry, Allan Freeze, Paul Hsieh, Ineke Kalwij, Douglas Mackay, Stephen Moran, Everton de Oliveira, Beth Parker, Eileen Poeter, Ying Fan, Warren Wood, and Yan Zheng.

Cover Image: Salt flat, United Arab Emirates at a surface temperature of 65 °C and an air temperature of 51 °C (Wood et al., 2002).

Table of Contents

List of Figures

List of Tables

The Groundwater Project Foreword

The United Nations Water Members and Partners establish their annual theme a few years in advance. The theme for World Water Day of March 22, 2022, is "Groundwater: making the invisible visible." This is most appropriate for the debut of the first Groundwater Project (GW-Project) books in 2020, which have the goal of making groundwater visible.

The GW-Project, a non-profit organization registered in Canada in 2019, is committed to contribute to advancement in education and brings a new approach to the creation and dissemination of knowledge for understanding and problem solving. The GW-Project operates the website https://gw-project.org↗ as a global platform for the democratization of groundwater knowledge and is founded on the principle that:

"Knowledge should be free and the best knowledge should be free knowledge." Anonymous

The mission of the GW-Project is to provide accessible, engaging, high-quality, educational materials, free-of-charge online in many languages, to all who want to learn about groundwater and understand how groundwater relates to and sustains ecological systems and humanity. This is a new type of global educational endeavor in that it is based on volunteerism of professionals from different disciplines and includes academics, consultants and retirees. The GW-Project involves many hundreds of volunteers associated with more than 200 hundred organizations from over 14 countries and six continents, with growing participation.

The GW-Project is an on-going endeavor and will continue with hundreds of books being published online over the coming years, first in English and then in other languages, for downloading wherever the Internet is available. The GW-Project publications also include supporting materials such as videos, lectures, laboratory demonstrations, and learning tools in addition to providing, or linking to, public domain software for various groundwater applications supporting the educational process.

The GW-Project is a living entity, so subsequent editions of the books will be published from time to time. Users are invited to propose revisions.

We thank you for being part of the GW-Project Community. We hope to hear from you about your experience with using the books and related material. We welcome ideas and volunteers!

The GW-Project Steering Committee

December 2021

Foreword

Few who read this book live on the landscapes described in this book, which are inhospitable due to large accumulations of salt. This gives visitors the impression of being on another planet. Although few of us will personally experience this arid environment, it covers nearly 20% of the continental surface of the Earth and hence is an important terrain. It forms in response to a combination of arid or semi-arid climate and a topography that results in the pervasive formation of brine and associated mineral deposits. In closed basins, water from rainfall cannot escape by streamflow so the only way out is by evaporation, including evapotranspiration from a few salt-tolerant plants. When the water molecules evaporate, the dissolved salts are left behind to form brine with a salt concentration much higher than sea water. Accumulations of mineral deposits precipitate from the brines. These are referred to by different terms depending on the language of the region including sabkha (Arabic); salinas, salares, saladas, salars, and playas (Spanish); or salt pans, saline lakes, alkali flats, salt plains, dry lakes, and salt flats (English). The salts originate as dissolved solids in the rainfall and from the weathering of minerals in the geologic framework that makes up the terrain. The rain infiltrates in the uplands and flows as groundwater to discharge in the lowlands where salt accumulates. The story sounds simple but understanding the formation of the mineral species and solutes within the hydrologic landscape is complex.

There are more than a dozen different minerals, that form from the brines, often rich in chloride, sulphate or carbonate that are exquisitely beautiful when viewed under a microscope. Which mineral develops is a function of both the input of dissolved constituents (solutes) and, surprisingly to a large extent, the leakage of solutes from the basin. The process of increasing brine concentration depends on the thermodynamic state of the brine, the water vapor content of the atmosphere, and the dynamic interplay between hydrology and thermodynamics with varying temperature driving the mineral outcome. Although the book is written from a conceptual viewpoint, to fully appreciate the explanations provided in this book, the reader will need some prior understanding of groundwater flow systems, density dependent flow and introductory level thermodynamics. The scientific puzzles represented by brines and the minerals they produce are amongst the most sophisticated offered by multidisciplinary geoscience.

Dr. Warren Wood is one of the few scientists who has studied this complex interplay of factors governing brines and their minerals in surface and near surface conditions in several parts of the world. He has walked these barren landscapes with an eye to the evidence needed to unravel the mysteries.

John Cherry, The Groundwater Project Leader
Guelph, Ontario, Canada, December 2021

Acknowledgements

I appreciate the comments, corrections, editorial and technical improvements, and insight into the topic of this book by the following individuals:

- Tim Lowenstein, Binghamton University (State University of New York), United States of America;
- Craig Simmons, Flinders University, Australia; and,
- Hugh Whiteley, University of Guelph, Canada.

I am grateful for Amanda Sills, Daniel Noble, Nithya Mani, and Juliana Apolonio of the Groundwater Project for their oversight and copyediting of this book. I thank Eileen Poeter (Colorado School of Mines, USA) for reviewing, editing, and producing this book.

1 Introduction

Waters with elevated concentrations of solutes occur on all continents in both deep geologic basins and at or near the surface. This book focuses on the conceptual understanding of the hydrogeology and geochemistry of surface and near-surface (less than 100 m depth) environments of elevated solute environments. These environments are important because they have significant impact on ecology, economics, and water resources and provide important clues and proxies to the paleogeomorphology, paleohydrology, and paleoclimate of the area.

In general, permeant-elevated solute conditions in shallow systems occur because of groundwater and/or river water discharged to topographically closed depressions in arid or semi-arid areas where the water is removed only by evaporation. Topographically closed basins cover approximately 18 percent of the continental surface (Hammer, 1986). Examples of such basins are the Caspian Sea in Eurasia, Great Salt Lake in North America, Lake Eyre in Australia, Lake Titicaca in South America, and Lake Chad in Africa, as well as hundreds of smaller closed basins. The obvious exceptions to this origin are salt seeps generated by the discharge of deep geologic brines to the surface; these can occur in any climatic environment.

Shallow saline environments have been given a variety of names including: sabkhat (plural for sabkha, and its variant spellings, in the Arabic-speaking world); salinas, salares, saladas, salars, and playas (in the Spanish-speaking world); and pans, saline lakes, alkali flats, salt plains, dry lakes, and salt flats (in the English-speaking world). Brine, saline, and brackish water are different expressions for water with solute concentrations greater than 1,000 mg/L. For the purposes of this book, water is classified as:

- slightly saline, where solute concentrations range from 1,000 to 3,000 mg/L;
- moderately saline, where solute concentrations range from 3,000 to 10,000 mg/L;
- highly saline, where solute concentrations range from 10,000 to 35,000 mg/L; and,
- brine, where solute concentrations are greater than seawater (35,000 mg/L).

Rainfall/evaporation ratio maps that identify extremely arid, arid, and semi-arid areas are a good first approximation of areas where shallow saline environments typically form (Figure 1).

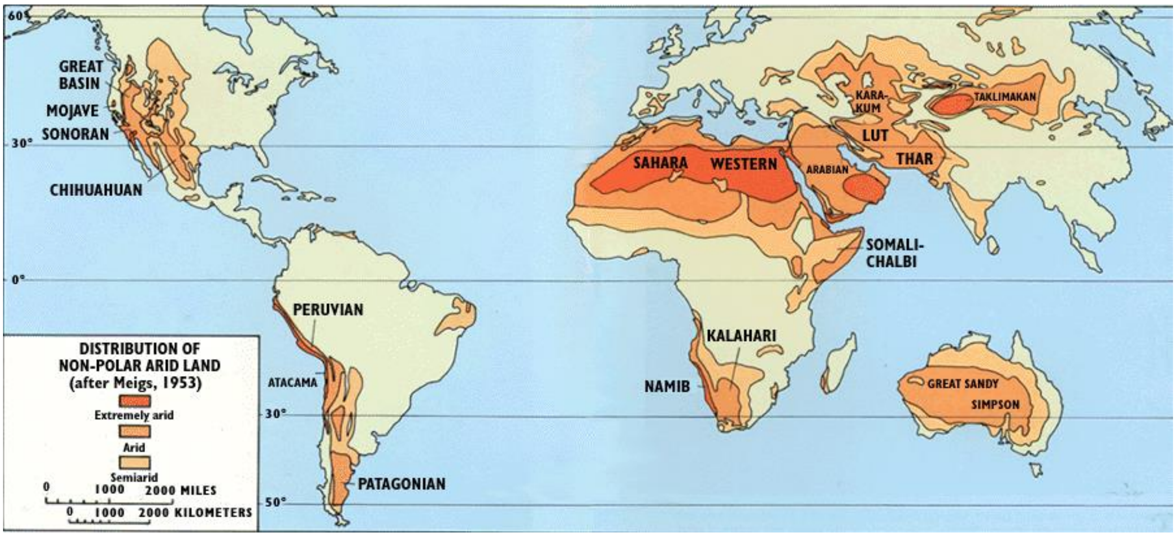


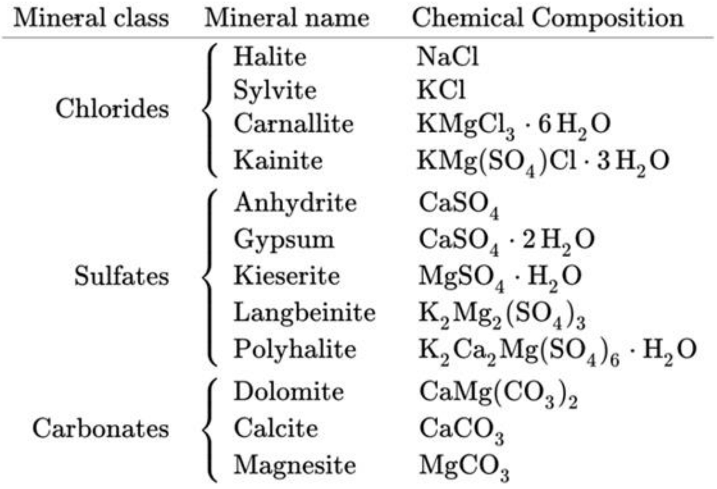
Figure 1 - Location of extremely arid, arid, and semiarid areas on Earth where contemporary near-surface brines typically develop (USGS, 1997).

The source of solutes in most shallow saline waters is largely the result of rock weathering, atmospheric input and relic solutes. Small accumulations of saline waters occur in various, more geographically restricted environments as described in Frape and Fritz (1987), Bottomley (1996) and Lowenstein and Risacher (2008).

The groundwater solute flux of surface and near surface features that are currently developing or developed in recent geologic time is relatively easy to measure. The boundary and initial conditions of the chemical and flow processes that control their development can generally be measured or reasonably inferred, as can the mass of *evaporites* in the deposits.

In contrast, deep basin brines, and evaporites and brines in igneous rocks, are difficult to sample. These brines formed tens of millions of years ago under unknown or poorly constrained boundary conditions and may be slowly evolving today. They require proxies to facilitate understanding of their origin. Additionally, the extended time, dependence on surrounding lithology, elevated temperatures, and pressures of deeper systems promote processes and reactions not commonly relevant in surface or near-surface features. The solutes of deep geologic brines have in general had their origins in a marine environment with a distinct set of minerals (Table 1). There are approximately 80 different marine evaporite minerals (Stewart, 1963), however, only 12 are common enough to form significant deposits and of those only six are uniquely marine (Table 1). Similarly, there are only eight unique minerals from the terrestrial saline environment (Table 2). The minerals halite, sylvite, carnallite, gypsum, anhydrite, calcite, and dolomite are common in both marine and terrestrial environments.

Table 1 - Common marine evaporite minerals and their composition (Stewart, 1963).



Mineral class	Mineral name	Chemical Composition
Chlorides	Halite	$NaCl$
	Sylvite	KCl
	Carnallite	$KMgCl_3 \cdot 6\,H_2O$
	Kainite	$KMg(SO_4)Cl \cdot 3\,H_2O$
Sulfates	Anhydrite	$CaSO_4$
	Gypsum	$CaSO_4 \cdot 2\,H_2O$
	Kieserite	$MgSO_4 \cdot H_2O$
	Langbeinite	$K_2Mg_2(SO_4)_3$
	Polyhalite	$K_2Ca_2Mg(SO_4)_6 \cdot H_2O$
Carbonates	Dolomite	$CaMg(CO_3)_2$
	Calcite	$CaCO_3$
	Magnesite	$MgCO_3$

Table 2 - Common terrestrial minerals and their composition.

Minerals	**Composition**
Epsomite	$MgSO_4 \cdot 7H_2O$
Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
Mirabilite	$Na_2SO_4 \cdot 10H_2O$.
Nahcolite	$NaHCO_3$
Thernadite	Na_2SO_4
Trona	$Na_3(CO_3)(HCO_3) \cdot 2H_2O$
Gaylussite	$Na_2Ca(CO_3)_2 \cdot 5H_2O$
Borax	$Na_2B_4O_7$

Approximately 8,000 to 10,000 years BCE (before the current era), the human diet shifted from salt-rich wild game to agricultural cereals and domesticated animals. More salt (halite or NaCl) was desired to preserve meat and to enhance flavor. Underground deposits were beyond reach, ocean salt was difficult to transport far inland, and salt springs were rare. Scarcity kept the mineral precious and salt became one of the world’s principal trading commodities with expressions like “salt of the Earth” becoming part of our language. A soldier’s pay, consisting in part of salt, was known as *solarium argentum*, from which we derive the word salary. A soldier’s salary was cut if he was “not worth his salt,” a phrase that came into being because the Greeks and Romans often purchased slaves with salt. During the Middle Ages, the spilling of salt was considered an omen of doom. After spilling salt, the spiller had to cast a pinch of it over his left shoulder to placate the evil spirts because the left side was thought to be sinister, a place where evil spirits tended to congregate. In Leonardo da Vinci’s painting The Last Supper, Judas is shown with an overturned saltcellar in front of him. Salt taxes were common and for centuries the French people were forced to buy all their salt from royal deposits. The salt tax (gabelle) was so high during the reign of Louis XVI that it became a major grievance and helped inflame the French Revolution. In protest against the high British tax on salt in India, Mahatma Gandhi led a pilgrimage of his followers to make their own salt. Some of the earliest known deep wells were drilled to find brines. Thus, salt has had a significant cultural impact.

2 Evaporation

Evaporation is critical to shallow brine formation and is driven by the gradient between the *thermodynamic activity* (effective concentration) of the water in the atmosphere and that of the water undergoing evaporation. As we know, water molecules move from high activity to low activity. The thermodynamic activity of the atmosphere is expressed as relative humidity such that a relative humidity of 65 percent has a thermodynamic activity of 0.65. Thermodynamic activity of groundwater at a given temperature is largely a function of the mole fraction of water relative to the total moles of dissolved material, ionic charge of the solutes, and size of the ions.

In the simple conceptual model, one can envision a water molecule with only a few dissolved solutes in solution. This water molecule can easily reach the surface and evaporate whereas a water molecule in a solution with many solutes will be blocked from a path to the surface and thus, not evaporated as rapidly Figure 2.

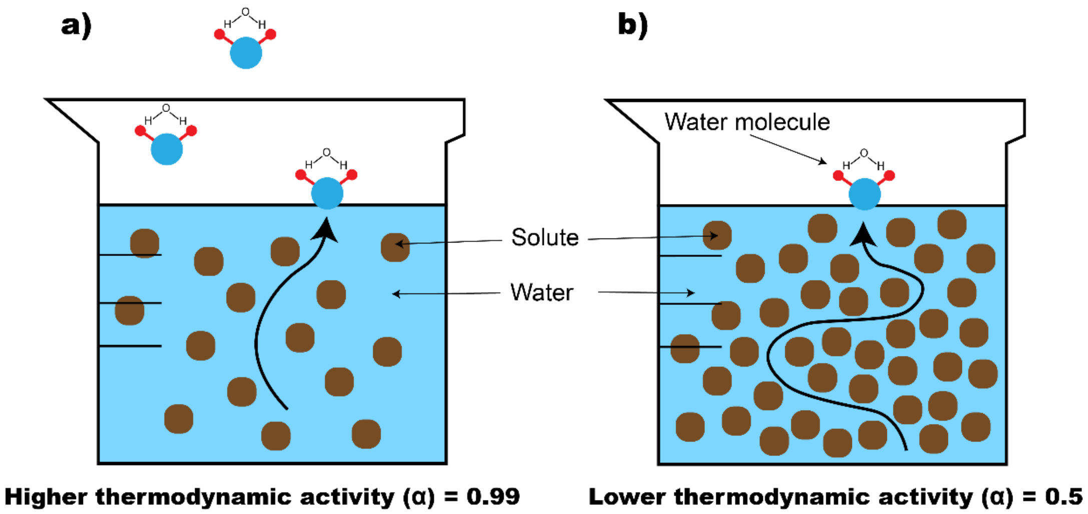


Figure 2 - Illustration of the effect of dissolved solids on evaporation. The more solutes present (lower thermodynamic activity) the lower the evaporation rate.

Thermodynamic activity is also impacted by the size and charge of ions in the water. For example, an NaCl dominated brine with a concentration of 100,000 mg/L will have a different ionic size and charge and therefore a higher thermodynamic activity than a 100,000 mg/L $MgCl_2$ brine (Figure 3). The formation of complex ions, ion pairs, and temperature are also factors in calculating the thermodynamic activity of a brine and these factors are included in various models for calculating the numerical value of thermodynamic activity. The most commonly used equations for highly saline and brine environments are those of Pitzer (Plummer et al., 1988). The thermodynamic activity of H_2O is usually provided in most geochemical computer codes such as PHREEQC (Parkhurst and Apollo, 2013). A detailed review of the activity calculation process is given by Blandamer and others (2005).

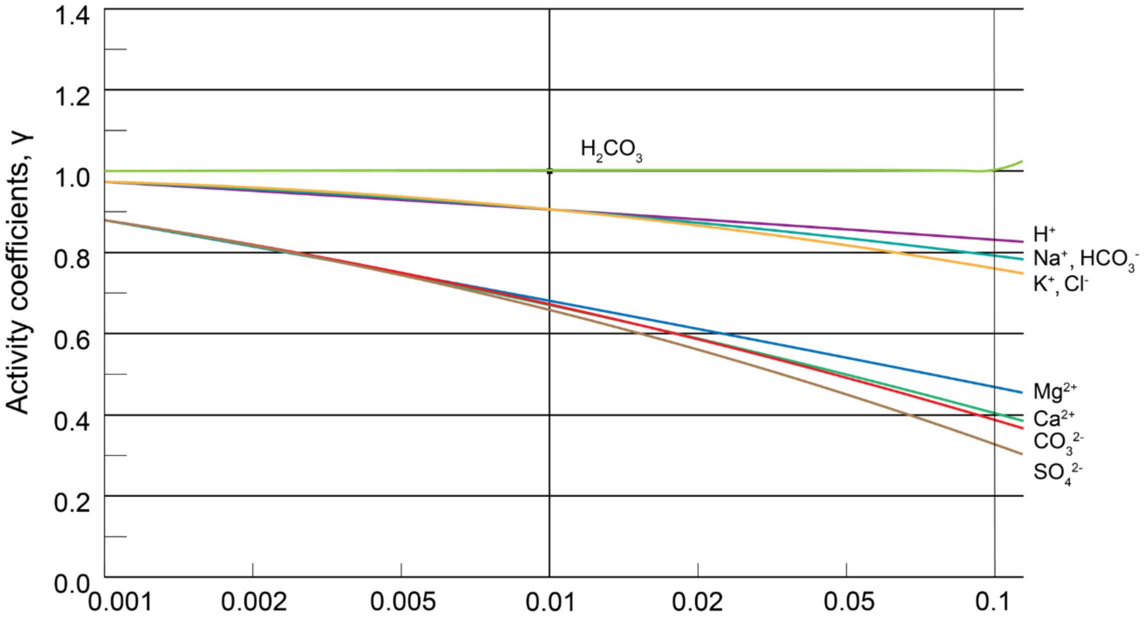


Figure 3 - Example of thermodynamic activity of solutes declining with increasing molality (horizontal axis) and charge and weight (modified from Freeze and Cherry, 1979).

The thermodynamic activity of average potable groundwater with less than 500 mg/L solutes is typically around 0.95 or greater. Any time the relative humidity of the atmosphere is less than 95 percent, evaporation of water can occur. In brine, the thermodynamic activity of water is commonly 0.5 to 0.6 thus, evaporation can occur only if relative humidity is less than 50 percent or 60 percent. In fact, if the relative humidity is greater than this value water will move from the atmosphere into the brine (Figure 4). Owing to the limited amount of water in a liter of atmosphere the amount of water transferred is usually small.

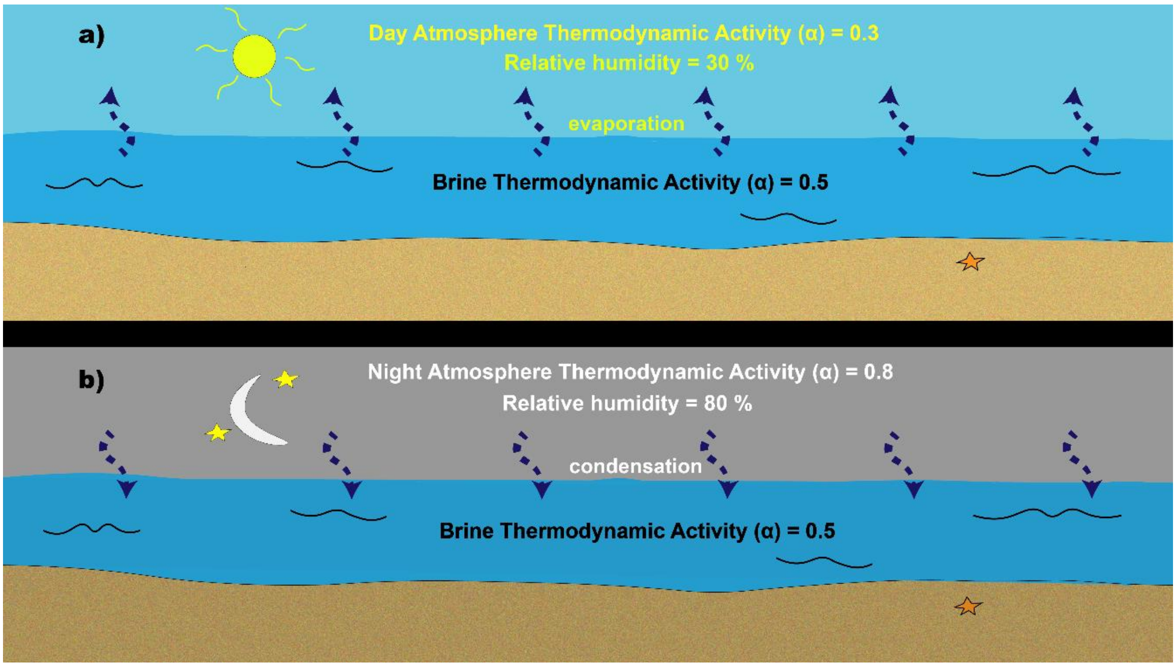


Figure 4 - Illustration of the change in water transfer from a) transport of water from the brine to the atmosphere during the day (low relative humidity) to b) transport of water from the atmosphere to the brine (high relative humidity).

The rate of evaporation is a linear difference between activity of water in the atmosphere and activity of water in the brine. Consequently, the rate of evaporation declines as the relative humidity approaches that of the brine; when they are equal, no evaporation of water occurs. As humidity increases, water from the atmosphere will move to the brine. As a result, evaporation from surface brine systems usually occurs only under limited daily or seasonal conditions.

An instructive example is from the coastal sabkhas of the Emirate of Abu Dhabi, United Arab Emirates, where sabkha brine has an activity of approximately 0.5 and thus, net evaporation occurs largely during the day in March through August (Figure 5). During much of the year and at night there is little, if any, evaporation. In fact, one commonly sees small shallow puddles of rainwater (that have acquired high salinity by dissolving surficial salts) remaining on the sabkha for weeks or months after a December rainfall event. Even though these pools contain water that is denser than the aquifer water they are shallow and do not have sufficient hydraulic head to cause recharge.

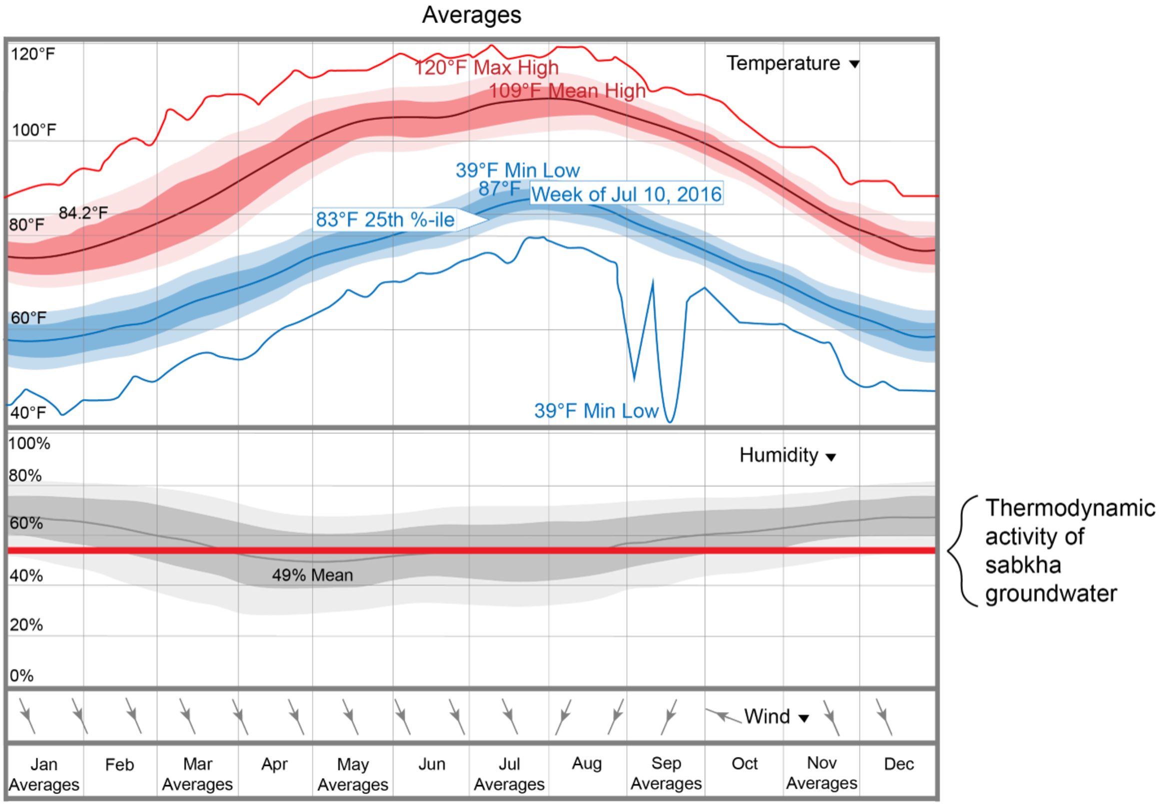


Figure 5 - Relative humidity (thermodynamic activity) for a typical year (2016) at Abu Dhabi airport located on the coastal sabkhas. Higher relative humidity generally occurs at night such that most net evaporation must occur during the day between March and August. Maximum and minimum daily temperature are shown for reference. Thermodynamic activity of sabkha brine (0.5) is shown for reference (modified from Weather Spark).

The role of humidity in controlling evaporation is also illustrated in Figure 6. Here, the change in weight of pans containing 1) water with less than 100 mg/L total dissolved solids (TDS) which is labeled Fresh in Figure 6, and 2) coastal sabkha brine with ~250,000 mg/L TDS which is labeled Saline in Figure 6. are shown with respect to the relativity humidity over 24 hours. In this example, the saline brine with a thermodynamic activity of 0.5 loses weight (water) throughout the day. In the early evening, when the relative humidity increases beyond 50 percent, the saline pan starts to gain weight via a net water transfer from the atmosphere to the pan. The fresh water pan, with a thermodynamic activity of 0.95, continues to lose weight past 50 percent relative humidity. The evaporation rate slows owing to a decrease in the activity gradient as well as solar radiation, which controls wind in the coastal area of Abu Dhabi where this experiment was conducted. Wind is a factor in evaporation rate as it aids in mixing and removing the recently added water molecules above the evaporating surface thus maintaining the thermodynamic gradient.

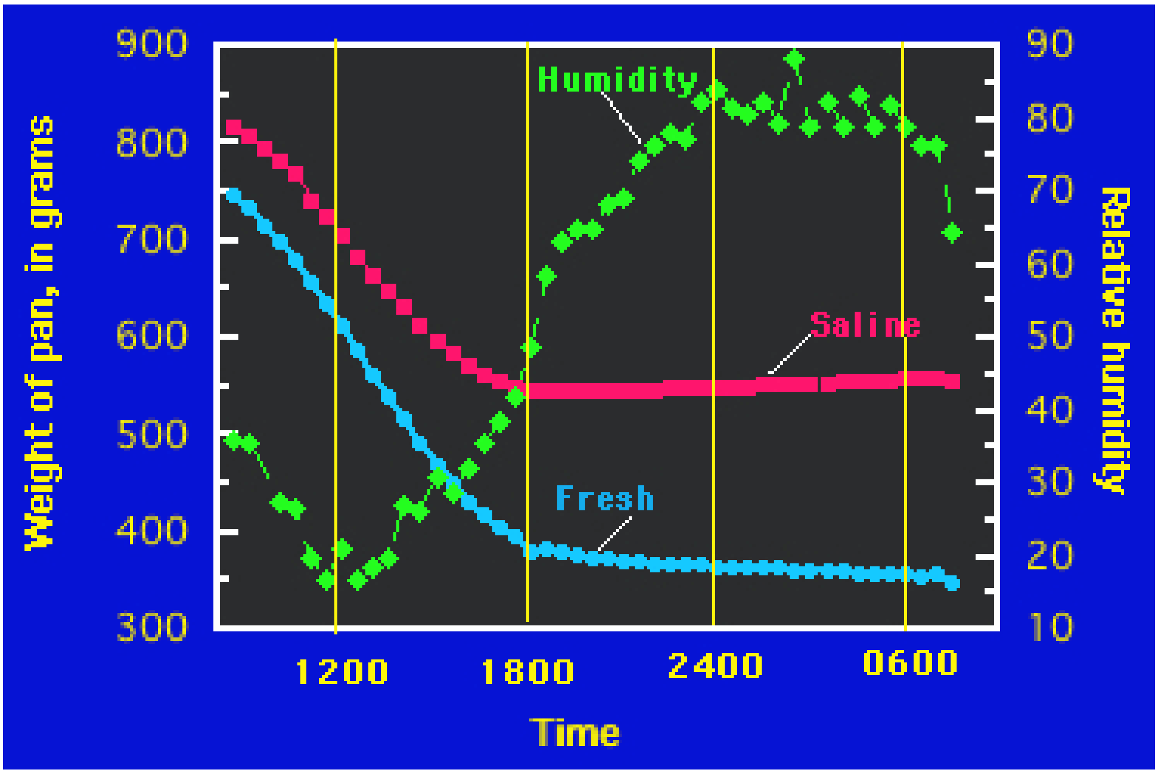


Figure 6 - Graph showing weight (left vertical axis) of two pans of evaporating Saline (red line) and Fresh (light blue line) water with respect to relative humidity (right vertical axis, green line) as a function of time (horizontal axis). Notice that the saline pan begins to gain weight (water) as the humidity exceeds 50 percent while fresh water, with an activity of 0.95, continues to lose water with increasing relative humidity. The flux of water from atmosphere to brine is low, even though the thermodynamic activity gradient is high, because of the low water content of the atmosphere.

The isotopes of ^{2}H and ^{18}O in water molecules are also impacted by evaporation. The more humid the environment, the lower the δ^{2}H/δ^{18}O ratio. That is, it is easier for the lighter hydrogen to escape by evaporation in a high humidity environment than for the heavier oxygen to escape. Consider the case of Sabkha Matti in the Emirate of Abu Dhabi. There are two areas of interest here: a low humidity environment (~100 km inland from the coast) and a high humidity (coastal) environment. Both areas receive precipitation from the same source that has a δ^{2}H/δ^{18}O ratio of 5.3. Surface water in the high humidity coastal environment loses more ^{2}H relative to ^{18}O reducing the ratio and resulting in a lower δ^{2}H/δ^{18}O ratio of 1.60, while the inland area maintains a higher δ^{2}H/δ^{18}O ratio of 2.25. This difference results in a different δ^{2}H/δ^{18}O ratio as shown by the slopes on the graph of Figure 7.

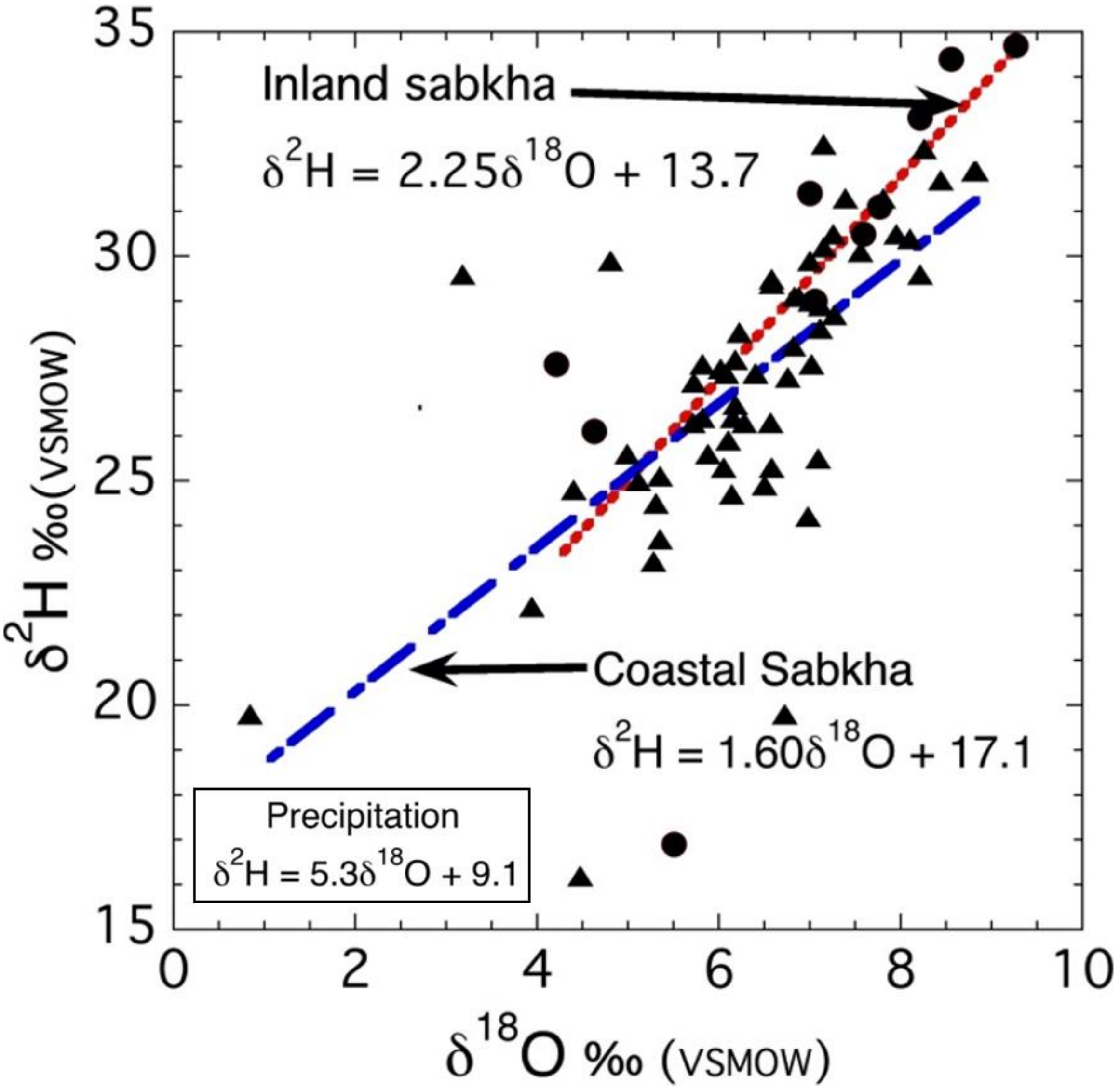


Figure 7 - Water isotopes of inland sabkha (lower humidity, circle data points) versus coastal sabkha (higher humidity, triangle data points) in Sabkha Matti, Abu Dhabi. Both areas receive rainfall from the same source. Humidity impacts oxygen and hydrogen isotopes differently resulting in a lower slope of 1.60 for the higher humidity coastal environment versus a slope of 2.25 for the lower humidity inland environment. The input precipitation has a slope of 5.3.

Isotope analysis of elements such as carbon, sulfate, nitrate, chloride, bromide, and others can provide insight into the origin and evolution of the solutes in these environments and this subject is covered by Peter Cook in another Groundwater Project book.

3 Source of Solutes

In general, most terrestrial evaporative environments are the result of regional discharges of groundwater and surface water that transport solutes and water to where the water is removed by evaporation, thus concentrating the solutes. In some cases, deep geologic brines are discharged directly to the surface. These brines originate in a variety of ways (Figure 8) including dissolution of relic salt minerals left from evaporating seas (e.g.,

$CaSO_4$, Figure 8a), release of fluid inclusions (Figure 8b) and water-rock interactions along mineral crystal boundaries (Figure 8c) (Roedder, 1984; Kamineni, 1987, Nordstrom et al., 1989; Frape and Fritz, 1987; Lowenstein and Risacher, 2009). Fluid inclusions are often abundant in granitic rocks. The fluid can range from 0 to 70 percent NaCl (Roedder, 1984) with an average composition of perhaps 10 percent NaCl (Nordstrom and Olsson, 1987). Sulfuric acid generated by pyrite oxidation dissolves the host rock generating a source of solutes (Edmunds et al., 1987) as shown in Figure 8c. The acid dissolves oligoclase, plagioclase, and biotite in density-driven convective hydrothermal-flow systems where hot, less dense water, is transported to the cooler oxygenated surface where its density increases and it sinks to repeat the cycle of dissolution and transport.

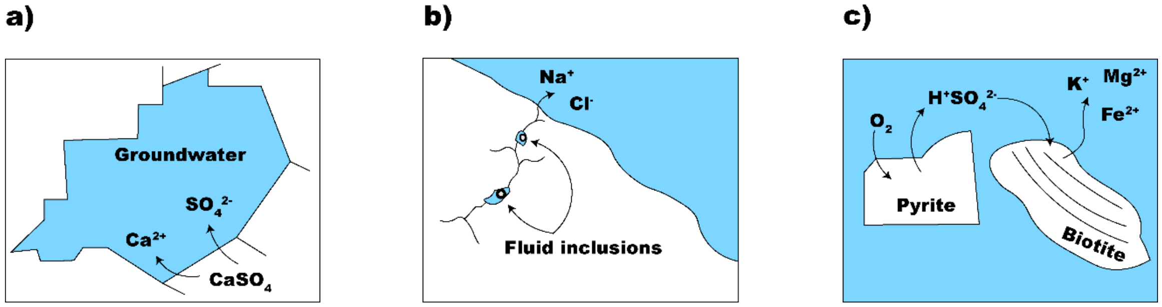


Figure 8 - Illustration of processes that add solutes to groundwater and form brine when the water evaporates: a) mineral dissolution; b) release of fluid inclusions; and, c) water-rock interactions.

In polar environments, water freezes and excludes most of the solutes so that ice is essentially free of solutes. If there is a topographic depression where the excluded solutes collect, brines can form through multiple freezing and thawing events (Frank and Gui, 2010; Starinsky and Katz, 2003). The process is analogous to the increase of solute concentration resulting from evaporation.

Radiolysis has been proposed as a source of brines in crystalline rocks. It is the process by which water is decomposed by alpha, beta and gamma rays from radioactive material thus concentrating the solutes (Vovk, 1981). More recent work, however, suggests that this is an unlikely source of most brines (Frape and Fritz, 1987).

4 Hydrological Systems

Hydrologically, a chemically closed system is one in which both solutes and water enter but only water can leave because the only outflow is evaporation which leaves solutes behind. There is no solute output thus solutes increase over time. In contrast, an open system is one that solutes and water both enter and leave so solutes do not accumulate. In reality most systems are “leaky.” In a “leaky” system selected solutes escape along with the water outflow (Figure 9).

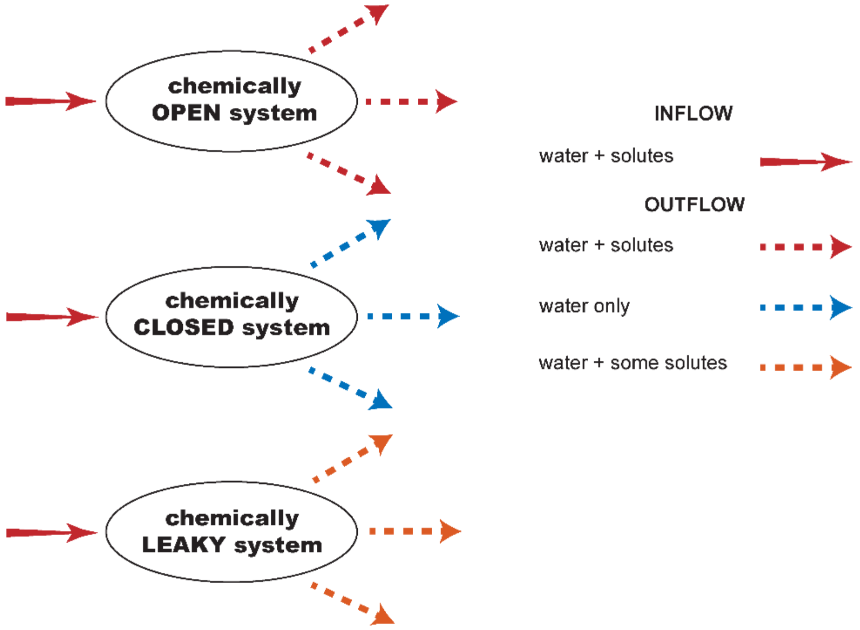


Figure 9 – Conceptual illustration of chemically open, closed and leaky groundwater systems.

This "leaky" condition changes the amount and type of mineral deposits as well as the solute ratios in the water (Figure 10). Closed and partly open "leaky" systems are discussed in Sections 4.1 and 4.2.

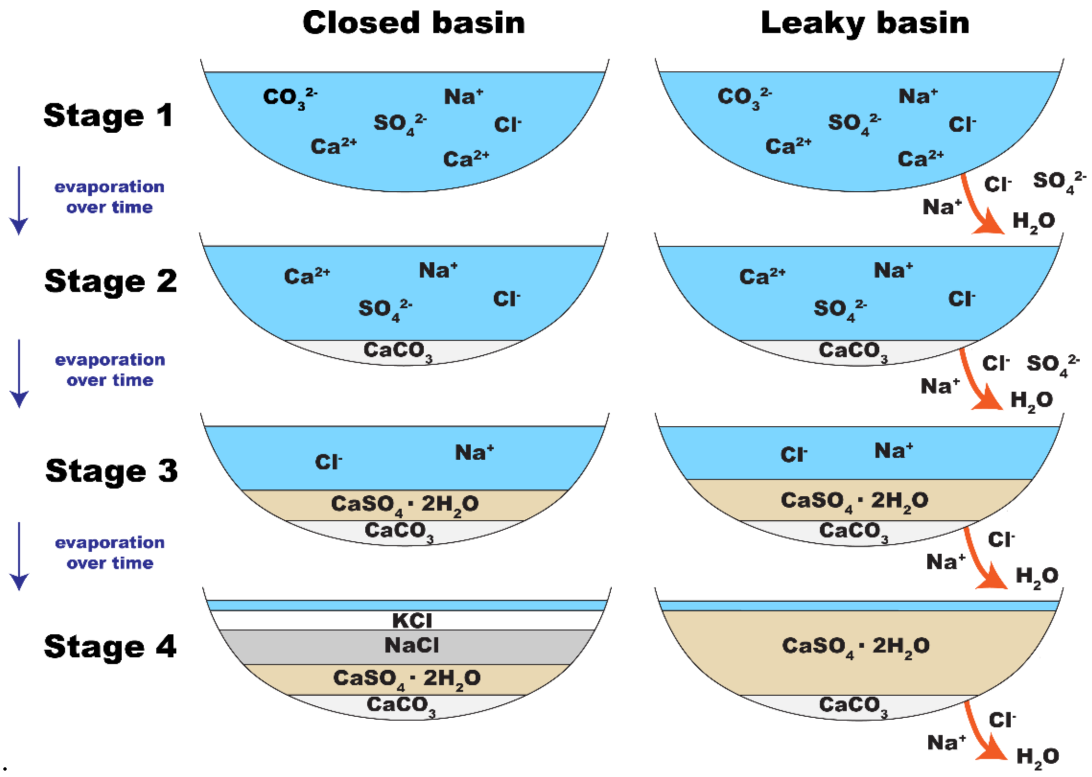


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Figure 10 - Illustration of the contrast in mineral development between a closed basin and a "leaky" basin. The type of minerals deposited and the relative amount of individual minerals are different.

4.1 Chemically Closed Systems

In a closed system, the solute concentration increases with evaporation eventually exceeding the K_{iap}/K_{eq} ratio of the lowest solubility minerals (K_{iap} is the ion activity product of the solutes; K_{eq} is the equilibrium constant of the minerals in the water). Those minerals precipitate, changing the remaining solute concentration and ionic ratios controlling the next mineral that will precipitate. This process is conceptually analogous to the well-studied process of solidus and liquidus in a cooling igneous magma. For a closed system at a given temperature, the evolution of solutes and minerals can be predicted for any known solute input ratio. This results in a set order of mineral deposits as was first demonstrated for sea water by Usiglio in 1849. Hardie and Eugster (1970) stated this concept in a modern thermodynamic paradigm.

Consider the evolution of calcium (Ca^{+2}) in seawater in a closed system at 25 °C and atmospheric CO_2 pressure. As evaporation proceeds, the least soluble mineral calcite ($CaCO_3$) precipitates from solution removing Ca^{+2} ions. As evaporation proceeds further, calcite continues to precipitate removing Ca^{+2} and CO_3^{-2} ions until either all the Ca^{+2} ions or the CO_3^{-2} ions are exhausted. In the case of seawater, the carbonate ion is completely consumed before the Ca^{+2} ion. Then, as evaporation proceeds the next least soluble mineral gypsum ($CaSO_4 \cdot 2H_2O$) will precipitate. Gypsum continues to precipitate until either Ca^{+2} or SO_4^{-2} is completely consumed. In the case of seawater at 25 °C there is more SO_4^{-2} than Ca^{+2} thus, all calcium is consumed marking the end of precipitation of calcium bearing minerals. Evaporation proceeds to the next least soluble common mineral, halite (NaCl), and it precipitates until all of the Na^{+1} or Cl^{-1} ions are consumed. This process yields the evolution of minerals and solutes during the evaporation of seawater observed by Usiglio (1849). That is, the specific and characteristic assemblage of mineral deposits is controlled by mineral solubility. If the temperature is cooler than the 25 °C used in the example above, the mineral mirabilite will form rather than gypsum as gypsum exhibits *retrograde solubility*, meaning it becomes more soluble with decreasing temperature.

Several problems are commonly encountered with this closed system model when brines or evaporate sediments are examined in detail. The first is the lack of *mass balance* (Eugster and Jones, 1979). The mass balance of a closed system requires that the sum of any dissolved solutes entering a basin must equal the amount of precipitated mineral phase in the basin plus the amount remaining in solution. Observations of lacustrine systems suggest there is almost always missing mass (Alderman, 1985; Spencer et al., 1985). That is, the mass of some constituents in the evaporite deposits is significantly less than that calculated using reasonable input fluxes. This problem is frequently addressed in the literature by changing the input solute with time to match the observed chemistry. This, however, is scientifically unacceptable unless there is independent evidence for the changing input.

The second problem is the lack of an equilibrium mineral assemblage. If a volume of water of known solute chemistry evaporates, a definite sequence and amount of evaporite deposition can be predicted based upon thermodynamic considerations. The predicted relative abundances of the evaporites, however, are seldom observed (King, 1947). In fact, one factor that makes many of these evaporite deposits economically interesting is the accumulation of thick deposits of one or a few selected minerals, rather than the collection of the many different minerals that would be expected from repeated basin fillings and subsequent evaporations. This is an enigma for a closed system but is resolved if one considers a partially open "leaky" system.

4.2 Chemically Open Leaky Systems

If a system is completely open to solutes, there will be no accumulation of solutes or evaporite minerals. In many systems some, but not all groundwater solutes leak from the system so that it is partly open or "leaky." Surprisingly, the leakage ratio (mass out/mass in) is in most cases more important in solute/evaporite evolution than the input solute ratios (Wood and Sanford, 1990; Sanford and Wood, 1991). As a result, it is possible to develop a large thickness of one or two minerals instead of the many minerals observed in a totally closed system. In a steady-state water flux condition, a leaky system permits a certain solute flux as the evolved solution escapes. This is referred to as the *leaky ratio* (Q_o/Q_i) where Q_o is total outflow flux and Q_i is total inflow flux (Figure 11).

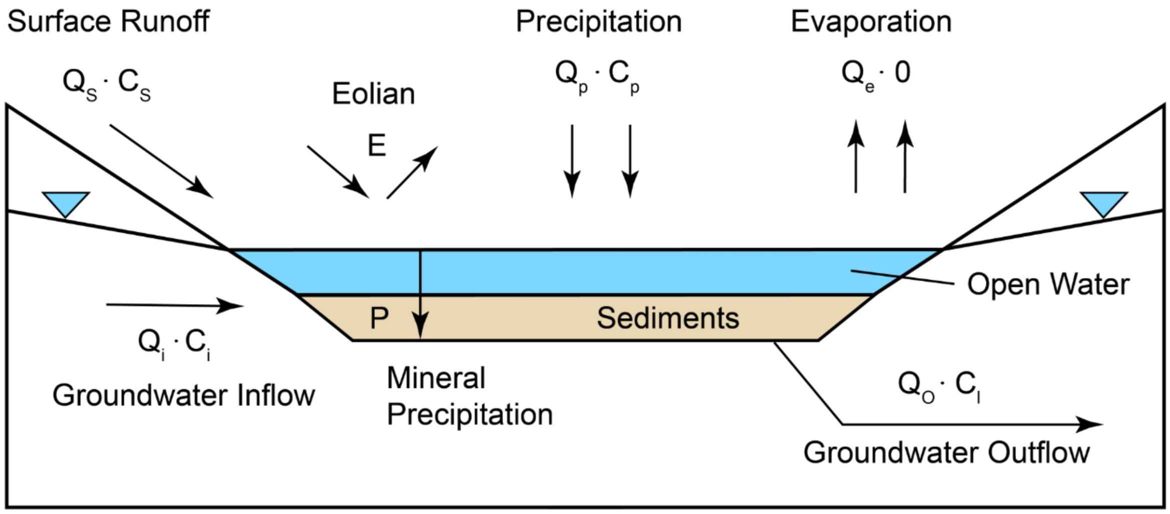

Figure 11 - Conceptual mass-balance model for a steady state leaky basin where the leakage ratio (Q_o/Q_i) has a significant control on the solute chemistry and the mineral development in the basin (Wood and Sanford, 1990).

The solute loss from a leaky system has profound control over the suite and thicknesses of evaporite minerals formed in the basin and the remaining solutes. For a conservative constituent (i.e., one that does not react), the relationship between leakage ratio (Q_o/Q_i) and *concentration ratios* (C_o/C_i) for different basin volumes evaporated (where volumes evaporated essentially represent time) is illustrated in Figure 12. The concentration ratio C_o/C_i is the concentration of output solutes to the concentration of input solutes. As shown in Figure 12, the C_o/C_i ratio reaches a constant maximum at different numbers of basin volumes for different leakage ratios Q_o/Q_i. Importantly, after the C_o/C_i becomes constant, the minerals generated are constant and this results in large deposits of a few minerals.

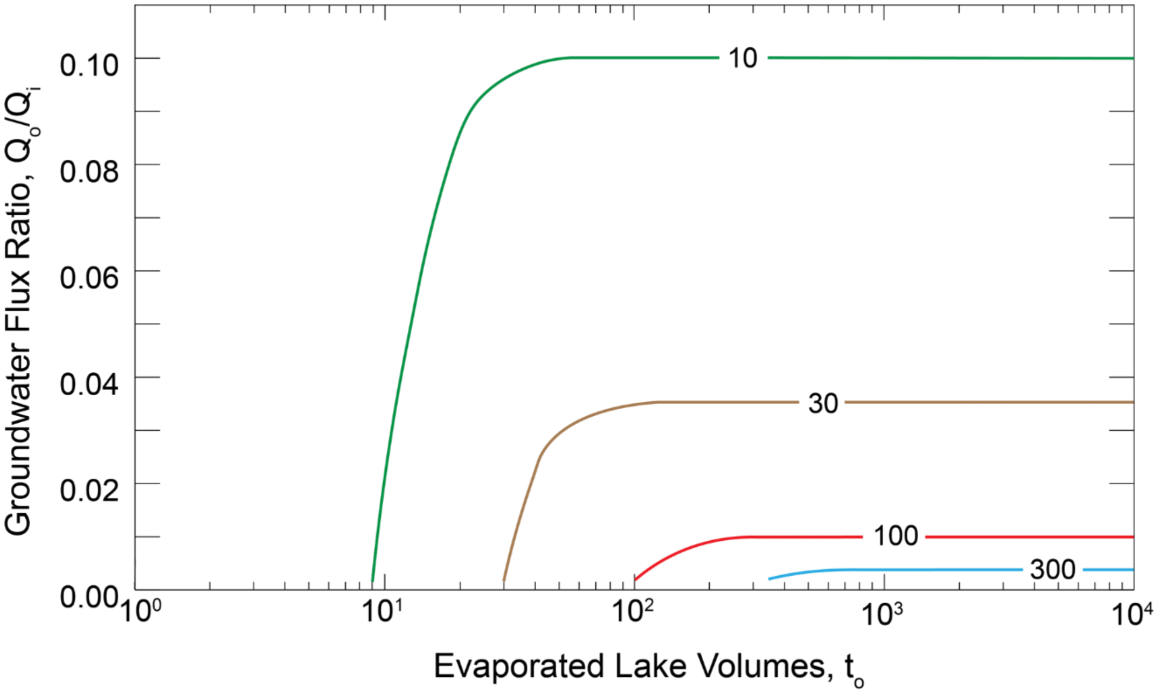

Figure 12 - The steady state C_o/C_i ratio for a conservative constituent as a function of the number of evaporated basin volumes t_o for leakage ratios (Q_o/Q_i) of 10, 30,100, and 300. C_o is solute concentration of the groundwater outflow and C_i is the input concentration. (modified from Sandford and Wood, 1991).

The impact of leakage ratio is illustrated by the difference between Figure 13a and Figure 13b which have the same input solute chemistry but different leakage ratios. In Figure 13a, the leakage ratio is 0.001 indicating it leaks more than the system shown in Figure 13b with a leakage ratio of 0.0001. Systems with a smaller the leakage ratio have mineral development that is more similar to a closed basin.

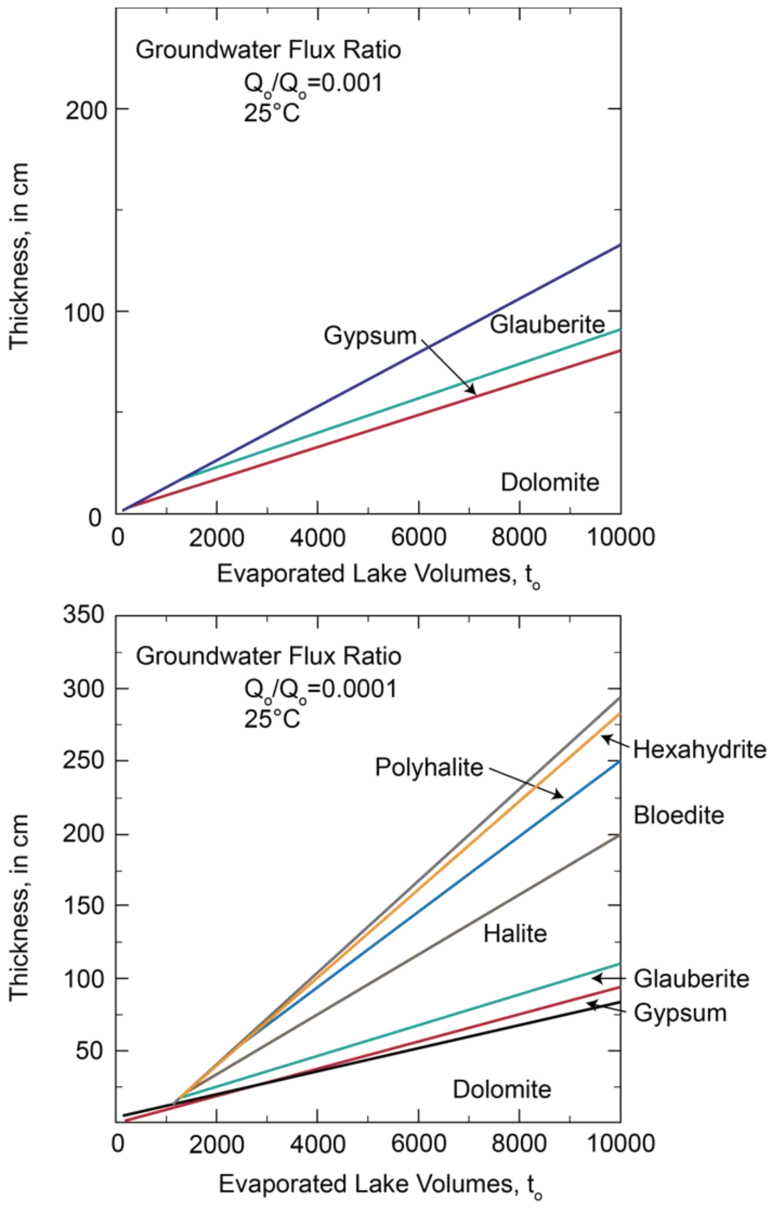

Figure 13 – Comparison of simulated minerology and thickness of deposits in systems with the same input water but different leakage ratios. a) An example of the mineralogy and thickness associated with a leakage ratio of 0.001. b) The different mineralogy and thickness developed in a system with less leakage, represented by a ratio of 0.0001. The water input to both systems has the same Southern High Plains groundwater solute chemistry. The solute changes follow a similar pattern, but the lower leakage ratio results in formation of layers comprised of minerals that form later in the precipitation process (from Wood and Sanford, 1990).

In the more open system (Figure 13a) with a leakage ratio of 0.001, only three minerals develop. In the less leaky basin (Figure 13b) with a leakage ratio of 0.0001, eight minerals form including halite, hexahydrite, and polyhalite, which are not present in the leakier system. The smaller the leakage ratio, the closer the system is to being a closed basin and the more similar the mineral development is to minerals formed in a closed system. In contrast, a very leaky basin might form only low solubility calcite or gypsum.

Solute evolution as a function of the number of basin volumes evaporated (which is a measure of the length of evolution time) with the input water chemistry (that of sea water) is illustrated in Figure 14 for two different leakage ratios, 0.001 and 0.01.

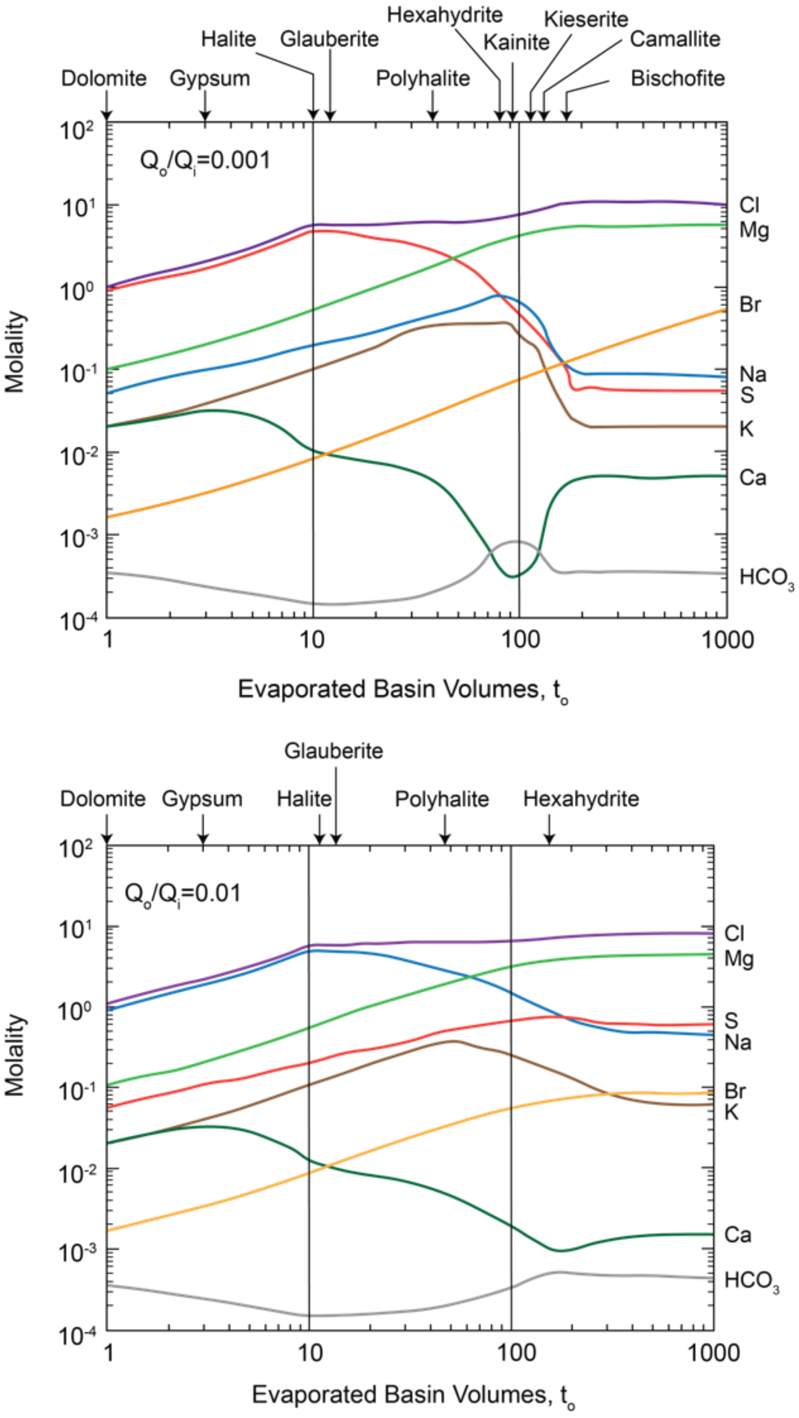

Figure 14 - Graphs showing the difference in solute evolution resulting from different leakage ratios: a) solute evolution as driven by evaporation from a basin with less leakage, Q_o/Q_i = 0.001 as compared to a system with more leakage as shown in b) where Q_o/Q_i = 0.01. Modified from Sanford and Wood (1991).

Inclusion of a leaky system conceptual model, in contrast to only an open or closed system, resolves many of the problems encountered when using a closed system model to explain mineral development observed in field settings.

5 Temperature Control of Mineral Deposition

Groundwater in an unconfined aquifer is separated into the saturated zone, capillary fringe, and unsaturated zone (Figure 15). In both the saturated and capillary zone, the pore spaces are completely filled with water; in the unsaturated zone, both gas and water fill the pore spaces. Relative humidity is 100 percent in the portion of the unsaturated zone that is more than a few centimeters below land surface, so evaporation seldom occurs from the unsaturated zone. The flux of water evaporated from the unsaturated zone declines exponentially with depth from the surface to the top of the capillary zone (Ripple et al., 1970). If depth to the top of the capillary zone is more than a few meters, then there is almost no upward flux of water. There is, however, some direct water vapor removed from the unsaturated zone by diurnal barometric pumping that moves air and water vapor into and out of the subsurface.

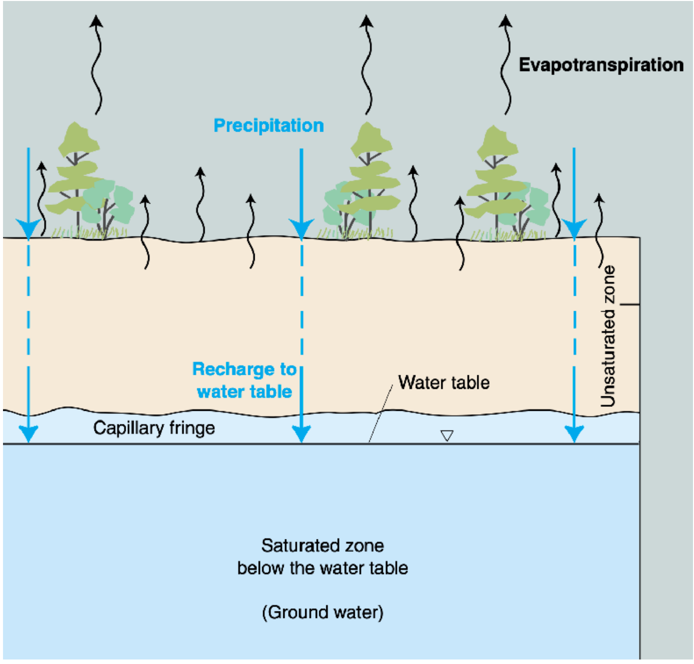

Figure 15 - Illustration of relative position of water table, capillary fringe, and unsaturated zone (modified from Alley et al., 1999).

The capillary fringe is typically on the order of 0.01 m thick in gravel, up to 1 m thick in fine sand, and 3 m or more in clay-sized material. Evaporation of water occurs at a much greater rate from the water table or capillary zone where they intersect the surface. The area of water surface exposed to the atmosphere is a function of porosity. As a first approximation, we can say that evaporation rate from the soil will be on the order of porosity time the evaporation rate from a Class A evaporation pan in the area. That is, where the saturated or capillary zone intersect the surface in a material with 25 percent porosity, evaporation will be approximately 25 percent of the amount evaporated from a Class A evaporation pan.

Authigenic minerals such as calcite, dolomite, gypsum and anhydrite that commonly occur in the capillary zone (Figure 16) are referred to as evaporites. This suggests that they reach thermodynamic supersaturation by removal of water that concentrates the solutes. However, the pore spaces in the capillary zone are filled with water so evaporation only occurs at the top of the capillary fringe. Thus, mineral precipitation a meter or so below the capillary surface is likely not a result of concentration due to evaporation. It is proposed that mineral precipitation in the capillary zone is controlled by seasonal temperature and solute flux variation, not evaporation.

Figure 16 - Authigenic gypsum, anhydrite and minor carbonate minerals forming in the capillary zone of a coastal sabkha in the Emirates of Abu Dhabi, United Arab Emirates. This nearly homogeneous aeolian sediment (with grain sizes ranging from 0.16 to 22 mm) comprised of 65 percent detrital carbonate and 35 percent quartz that was deposited between 8000 and 9000 years ago, has been receiving an upward brine flux of 4 mm/year from underlying deep geologic formations. Conservative solutes have been concentrated over geologic time by evaporation (Wood, et al., 2002) and recycled by density driven convection (Van Dam et al., 2009 and 2014; Wood and Böhlke, 2017).

The conceptual model for this thermal induced precipitation in the Abu Dhabi sabkha is as follows:

- solutes and water are transported upward toward the surface from deeper formations in response to the low topographic position of the sabkha on the ocean edge;
- evaporation from the surface concentrates the solutes by removing the water; and,
- during transport through the capillary zone, the solutes experience large changes in both seasonal temperature and transport rates. Transport rate varies as a function of varying evaporation rates. Temperature variation changes their solubility resulting in precipitation or solution depending on the current conditions.

Thus, the interplay between changing temperature and changing solute flux, determines the type of mineral precipitation and its spatial distribution. There is a net mineral accumulation in the capillary zone, but it is a dynamic system with both mineral precipitation and solution occurring at different times. The sabkha of Abu Dhabi experience a seasonal variation of at least 20 °C (Figure 17) and evaporation is limited to summer months (Figure 5) leading to time-dependent mineral deposition and brine formation. Figure 17 illustrates the annual temperature variation at different depths that control the dissolution/precipitation of minerals and are particularly important to the behavior of *retrograde minerals* (minerals that become less soluble with increasing temperature). Mineral equilibrium values are a function of temperature (Figure 18) so the rate of precipitation and dissolution varies with depth from season to season as the surface temperature propagates downward in the system. In a warmer phase of the annual heat fluctuation, retrograde minerals precipitate; in a cooler phase, they dissolve. Mineral equilibrium coefficients do not vary linearly with temperature. When annual temperature variations combine with a seasonal water flux that is greater during warm periods (when thermodynamic activity of atmosphere is lower), a net accumulation of retrograde minerals can occur (e.g., deposition of minerals such as calcite, aragonite, dolomite, gypsum, and anhydrite).

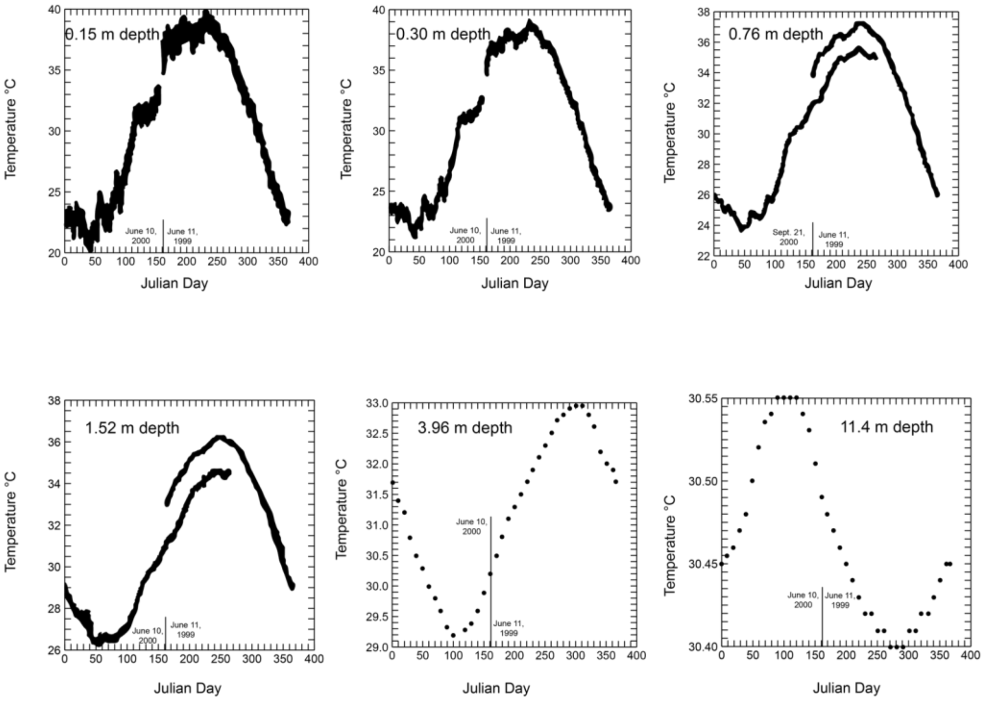

Figure 17 - Annual temperature variation for six depths in the sabkha of the Emirate of Abu Dhabi illustrating the potential for thermal control of retrograde minerals.

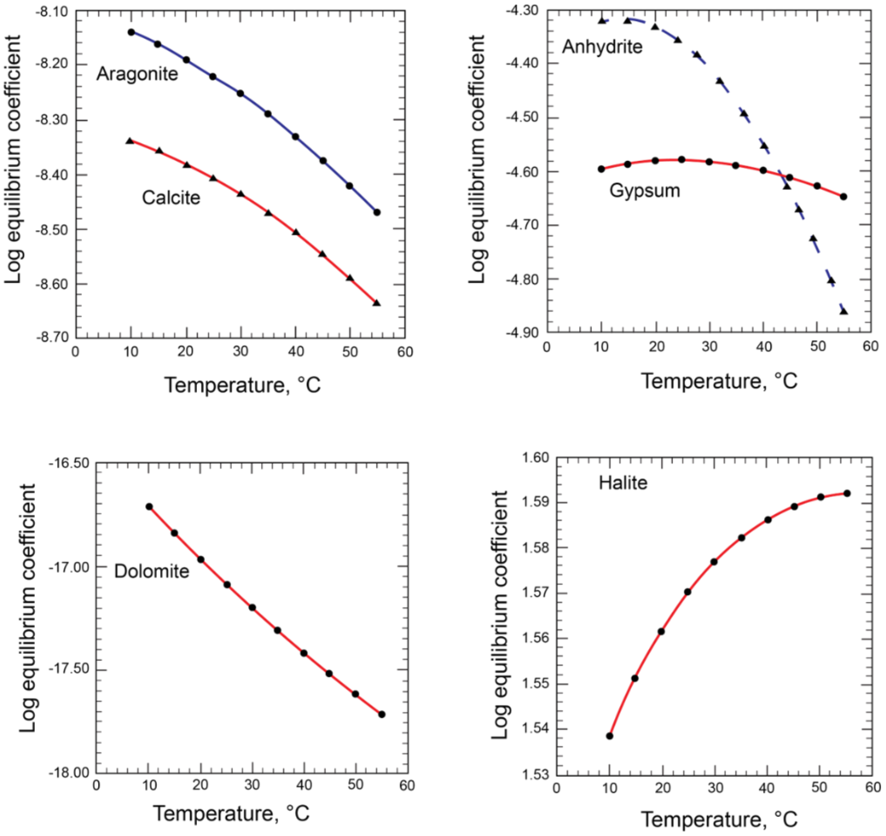

Figure 18 - The equilibrium constants as a function of temperature illustrate the retrograde solubility of calcite, aragonite, dolomite, gypsum, and anhydrite compared to normal solubility of halite with increasing concentration with temperature (data from PHREEQC as reported in Parkhurst and Appelo, 2013).

Retrograde mineral formation is controlled by temperature, *not* by concentration due to evaporation, as is commonly assumed. Thus, calcite, aragonite, dolomite, gypsum, and anhydrite should be called *thermalites* not evaporites. Normally soluble minerals such as halite and sylvite are concentrated on the surface as true evaporites (Figure 19). Correct thermodynamic interpretation of the origin of these deposits is important for understanding the millions of hectares of land around the world that are currently undergoing salinization and for accurate reconstruction of the tectonic, sedimentological, geochemical, and paleo-climatic conditions of the geologic past.

Figure 19 - Sabkha surface showing halite (NaCl) forming in large polygonal features on the surface as a result of evaporation from a coastal sabkha in the Emirate of Abu Dhabi (Wood et al., 2002).

6 Fluid Dynamics of Saline Systems

Natural *density-driven free convection* is important in meteorology and oceanography and has been studied for over a century in theoretical and laboratory settings. However only recently has density-driven free convection been identified as an active process in groundwater hydrogeology (Van Dam et al., 2009; Van Dam et al., 2014; Stevens et al., 2009). Studies have shown the critical importance of this process for contaminant transport (Mao et al., 2006; Liu and Dane, 1996; Zhang and Schwartz, 1995; Koch and Zhang, 1992; Schincariol and Schwartz, 1990), hydrothermal ore deposition (Coumou et al., 2008; Garven et al., 1999), carbon sequestration (Riaz et al., 2006), nuclear waste disposal (Yang and Edwards, 2000), and brine reflux beneath saline lakes (Holzbecker, 2005; Wooding et al., 1997; Rogers and Dreiss, 1995).

Electrical resistivity tomography (ERT) was used to document the density-driven free convection of convective fingers following a significant rainfall event on a sabkha

60 km northwest of the city of Abu Dhabi, United Arab Emirates. The convective fingers are visible in Figure 20a (Van Dam et al., 2009). In this sabkha system, free convection occurs when high-density surface water, generated by dissolution of surface salt by rainfall, recharges the aquifer. This observation is supported by analysis of the same system a year after the rain event. It revealed that the convection fingers had dissipated leading to the decay of the convective instabilities with time (Figure 20b).

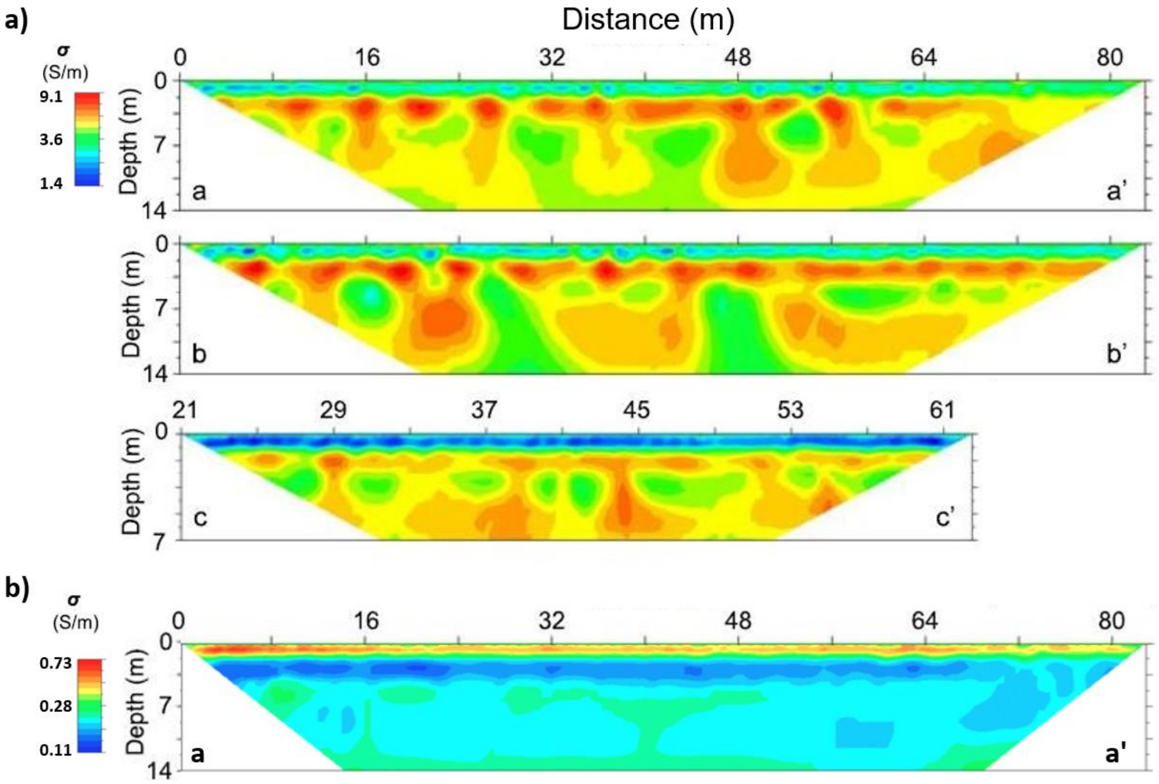

Figure 20 - Density driven free convection in the United Arab Emirates sabkha illustrated by inverted resistivity images from dipole-dipole ERT (electrical resistivity tomography) surveys. a) Rainwater dissolved salts on the surface creating a dense solution that recharged the sabkha aquifer as revealed by fingering of dense salt water which is indicated by high (red) conductivity (S/m, Siemens per meter) observed along three different compass azimuths shown as profiles a-a', b-b', and c-c' (modified from Van Dam et al., 2009). b) Using the same electrode position, resistivity meter, and analysis method; data collected a year later on profile a-a' revealed that the unstable convective flow had dissipated such that the high conductivity fingering had largely disappeared along profile a-a' (modified from Van Dam et al., 2014).

This interpretation of the dissipation of the convective fingers is consistent with the ubiquitous presence of tritium throughout the aquifer, additional analysis of the aquifer halite budget, and hydrodynamic modeling of the transient character of the fingering instabilities (Van Dam et al., 2014). Numerical modeling results show that the transient dynamics of the gravitational instabilities (their initial development, infiltration into the underlying lower-density groundwater, and subsequent decay) agree with the timing observed in time-lapse ERT measurements. Experimental observations and modeling results are consistent with the hypothesis that density-driven free convection is occurring in this system (Van Dam et al., 2014). This is further supported by evaluation of the isotopes of nitrogen (Wood and Böhlke, 2017).

7 Gas Losses

In addition to mineral precipitation altering the solute chemistry, there is a loss of CO_2 gas from precipitation of $CaCO_3$ (calcite). As groundwater which has 10 to 70 times greater partial pressure of CO_2 reaches the surface it degasses CO_2 and precipitates $CaCO_3$ (calcite). Nitrogen (N_2) gas is also lost from shallow surface environments (Wood and Bohlke, 2017). Mass balance of the Abu Dhabi sabkha solutes suggests that the dominant source of nitrogen is atmospheric precipitation. However, the nitrogen isotopes of the sabkha suggest an isotopically heavier deep basin source. This apparent paradox is resolved when it is recognized that density-driven convection within the sabkha aquifer transports nitrate (NO_3^{-1}) with isotopically light atmospheric nitrogen from the oxygenated surface to a reducing environment at the base of the aquifer. Here, some nitrate is reduced to nitrogen gas N_2, which is isotopically lighter. The light N_2 is then carried back to the surface by the convective flow where it escapes to the atmosphere, leaving isotopically heavier nitrogen behind (Figure 21). This process is repeated each time density-driven free convection occurs and gradually changes the remaining nitrogen to an isotopically heavier form (Wood and Böhlke, 2017).

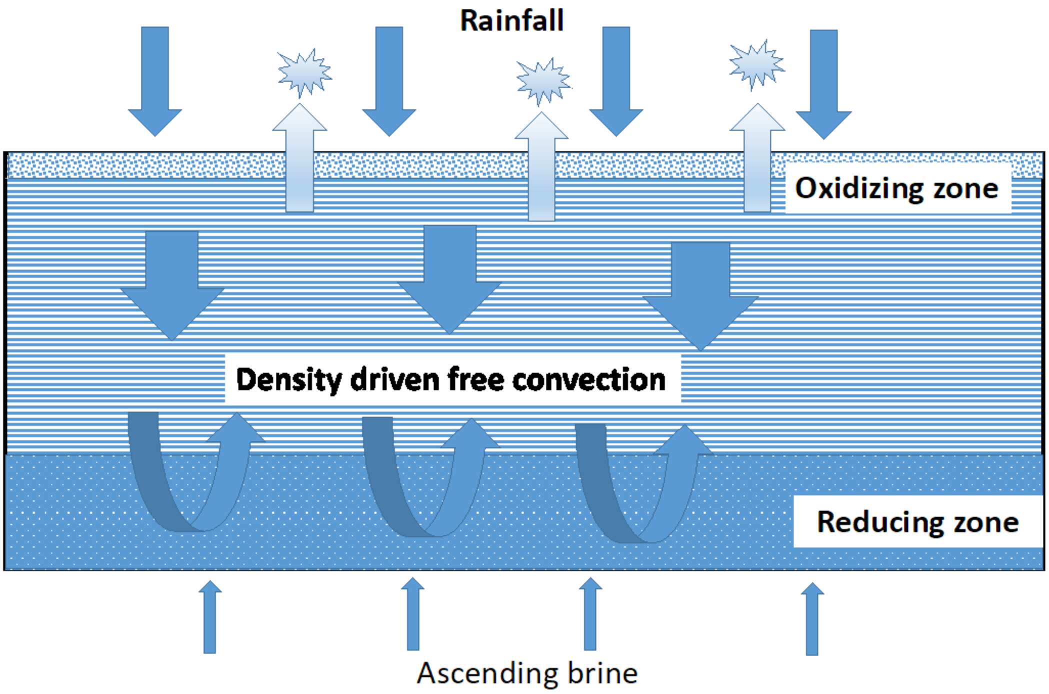

Figure 21 - Schematic depiction of a density-driven free-convection model that carries isotopically light atmospheric nitrogen from the oxygenated surface down to a reducing environment at the base of the aquifer where some nitrate is reduced to nitrogen gas N^2, which is isotopically lighter. Light N^2 then escapes to the atmosphere, leaving isotopically heavier nitrogen results in reduction of NO_3^{-1} to N^2 which is carried back to the surface and lost to the atmosphere as a gas (modified from Wood and Böhlke, 2017).

In addition to nitrogen gas loss, bromide is lost as a gas from both saline lakes and salt flats including the Dead Sea (Hebestreit et al., 1999; Matveev et al., 2001), Great Salt Lake (Stutz et al., 2002), and Salar de Uyuni in Bolivia (Honninger et al., 2004). This is measured using differential optical absorption spectroscopy (DOAS). Utilizing a mass balance approach on the sabkha from Abu Dhabi suggests an annual bromide flux loss of 85 kg/km^2 (Wood and Sanford, 2007).

8 Summary and Conclusion

This book provides an introductory conceptual overview of the most common processes of shallow brine and evaporite mineral formation, not a thorough scholarly review of the literature. Each of the processes has been discussed in excellent research papers and the cited references lead the reader to a more complete body of literature. Whereas the field examples presented herein are of limited geographical distribution, the principles are applicable worldwide and illustrate the subtleties of shallow saline systems. Although evaporation is critical to water removal, the degree of leakage of a system and the solubility of minerals control the evolution of solute concentrations and mineral precipitation. The loss of mass in the gas phase is also important for several elements and needs to be included in mass balance calculations.

Science involves a thought process that allows us to anticipate future conditions thus, it is useful to ask how understanding of near surface brine/evaporite systems helps in predicting the future of these and similar systems. As climate is rapidly changing, Earth’s arid and semi-arid areas are expanding. By studying current and paleo examples of near surface brine/evaporite systems, we can predict how water that is discharged to the surface will behave in these expanded arid areas and how changes in water use (e.g., due to changes in vegetation or groundwater development) will impact brine evolution. Such study also facilitates exploration for economically valuable evaporite deposits when coupled with our expanding knowledge of paleo regional-flow systems and paleoclimate. Understanding how a deposit forms aids in estimating the economic reserves and evaluating how active systems will respond to development of groundwater resources, as well as changes in precipitation and evaporation. In short, knowledge of the origin and evolution of current systems improves our confidence in predicting the development and evolution of similar systems in the future.

9 Concepts to Consider

Conceptual Consideration 1

You have been asked to make a presentation to university class in geochemistry studying brine evolution. Describe and compare the brine and mineral evolution in a shallow system that has evolved in a closed system to a system that has solute leakage.

Click for response to conceptual consideration 1⤵

Conceptual Consideration 2

Brines in subsurface evaporating environments are potentially subject to density driven convective flow (dense surface brines descending to the bottom of formation). These events mix the solutes and thus, change the solute chemistry by changing the temperature, pH, Eh or other critical parameters that control the thermodynamic state. How does this process work and how would you measure, evaluate, or document density driven convective flow in a shallow brine system?

Click for response to conceptual consideration 2⤵

Conceptual Consideration 3

Many near surface brine areas exhibit authigenic deposits of calcite, dolomite, gypsum, anhydrite, and halite. Describe the fundamental thermodynamic "equations of state" that control mineral precipitation and dissolution in this environment.

Click for response to conceptual consideration 3⤵

Conceptual Consideration 4

In evaluating solute mass balance of shallow saline systems, one might wish to record the gas phase loss as well as loss to solid phase mineral precipitation. Whereas mineral precipitation is readily visible and mass estimates can be reasonably made, gas losses are invisible and not commonly measured. How would you estimate, or measure, gas losses from a shallow saline system?

Click for response to conceptual consideration 4⤵

Conceptual Consideration 5

As a consulting hydrogeologist you have been hired to evaluate the economic potential of lithium brine on a playa lake property in Nevada, USA. What parameters would you measure and how would you design the data collection work?

Click for response to conceptual consideration 5⤵

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11 Possible Responses for Concepts to Consider

Response to Concept 1, One of Many Possible Responses

The process of solute concentration by evaporation is a function of mineral precipitation that removes the solutes associated with the precipitating mineral. That is, as water evaporates the solutes become more concentrated until thermodynamic saturation occurs and minerals begin to precipitate. Consider for example a closed system (no escape of solutes) undergoing evaporation in which the precipitation of calcite ($CaCO_3$) proceeds until either all the calcium (Ca^{+2}) or all the carbonate (CO_3^{-2}) is removed from the solution. As evaporation continues, the next insoluble mineral that uses the remaining Ca^{+2} or CO_3^{-2} in its structure will precipitate. For example, precipitation of anhydrite ($CaSO_4$) will use any remaining Ca^{+2} as long as there is sufficient SO_4^{-2} in solution. This process continues until the next insoluble mineral starts to precipitate and so on until the thermodynamic activity of the water is the same as the atmosphere and evaporation can no longer occur. In a completely closed system this precipitation process is conceptually analogous to the evolution of minerals in a cooling magma (but with different thermodynamic controls, heat for cooling magma versus thermodynamic activity of each solute for the brine system). The end point of the concentration by evaporation process is the equalization of the thermodynamic activity coefficient of the air with that of the evaporating solution, which is analogous to a cooling magma reaching the point where at least one of the constituents required to form the most thermodynamically favorable mineral has been depleted and the next mineral in the sequence begins to form from the cooling magma.

In an open system the hydrogeology is a major factor in the evolution of brine. The evolutional sequence in a closed system is a function only of the initial concentration and ratio of the individual solutes in the water entering the system. In a chemically open or “leaky” system, the solute evolution depends largely on the ratio of mass-flux discharge to mass-flux recharge. If the system is open or “leaky”, some of the solutes continually escape from the system and thus, are not available for mineral precipitation. This leakage persistently alters the solute/mineral precipitation evolution sequence. In this way the same input water may evolve to a NaCl brine, a $NaHCO_3$ brine, a $CaCl_2$ brine, $MgCl_2$ brine, or another type of brine depending on the leakage ratio. The smaller the leakage ratio the more the solutes will evolve like those in a closed basin.

Return to Conceptual Consideration 1↥

Response to Concept 2, One of Many Possible Responses

It is likely that the density driven convection in a shallow brine system is generated by an unusual event, such as an infrequent, long, intense rainfall, in contrast to continuous or periodic events as might be expected in a large geothermal system. Consequently, it is challenging to capture and record an overturn event while it is in progress. In the Abu Dhabi sabkha system discussed in this book, halite and other extremely soluble salts that accumulated on the surface over 10 to 20 years were dissolved in a rainfall event lasting nearly a week, creating a dense solution on the surface with sufficient head to initiate recharge. The surface brine was denser than the aquifer brine because dissolution of minerals is not controlled by humidity, so brines created by dissolution can have a higher total solute concentration (thus higher density) than brines created by evaporation.

The most direct method of capturing a density driven convection event is by repeated geophysical measurements that can sense the change in electrical conductivity with both time and depth. That is, by establishing a network of fixed measurement locations that can be revisited after potential overturn events to measure any change from background conditions. This typically results in many uneventful recordings because an overturn event (where the surface solutes are transported to the bottom of the aquifer) may occur once per decade or less frequently. After a triggering event, several days or weeks may pass before an event reaches the stage at which it can be measured and it can disappear in a few months. The time between the triggering event and when it can be measured is dependent on many factors including hydraulic conductivity, the magnitude of the recharge event and other factors. If it is important to gain information about an event, it might be worth the significant cost of automating the system to capture readings after potential triggering events if the site is remote and difficult to access.

Owing to the difficulty of capturing an event by direct geophysical measurements, it is possible to capture the long-term chemical and isotopic effects of overturn events if the system has different oxidation-reduction conditions between its top and bottom, perhaps due to influx of a reducing underlying deep-basin brine. If oxidation-reduction conditions differ with depth, an overturn event may significantly alter isotopes and concentrations of redox-sensitive major elements such as carbon, sulfate, and nitrogen. That is, on reduction the new condition may cause them to change phase to either solid or gas and be lost as a solute. The change of phase is always accompanied by an isotopic change, and this might be detected by isotopic analysis of groundwater samples. Whereas capturing the effects of density driven convection may not be as intellectually satisfying as direct measurement, it may be sufficient to provide data consistent with a density driven convection that are difficult to explain by other processes. Furthermore, the capture of long-term chemical and isotopic effects might be useful in selecting a site for direct measurement because it is an indication that density driven convection is likely to be occurring at that location.

Return to Conceptual Consideration 2↑

Response to Concept 3, One of Many Possible Responses

These ubiquitous minerals are often referred to as "evaporites" because the flow system transporting the solutes forming minerals is driven by the combination of an upward hydraulic gradient and the removal of water by evaporation. Evaporites, however, may not be an appropriate term as calcite, dolomite, gypsum, and anhydrite commonly form in the fully saturated capillary zone a few tens of centimeters below the surface thus, are not directly impacted by evaporation. That is, the capillary zone is fully saturated so it is not clear how evaporation at the surface would impact their development without some kind of density driven convection on a local scale transporting solutes from the surface downward a few centimeters and the physics of such a process is very murky! Given Occam's Razor, it is believed that in many systems the presence of these common minerals is a result of the annual thermal pulse from solar heating propagating downward. These four minerals are unusual in exhibiting retrograde solubility, that is, they become less soluble with increasing temperature in contrast to nearly all other 4000 naturally occurring minerals that are more soluble with increasing temperature. In summer the propagation of the annual solar pulse causes precipitation of theses minerals. In winter, the propagation of cooler temperatures causes solution of these same retrograde minerals thus, net accumulation over time is a delicate balance of greater groundwater flux at times of mineral precipitation (when the summer solar pulse arrives at that depth) and less at times of mineral dissolution (when the winter low temperatures prevail). Temperature is also a factor in precipitation of normal soluble minerals on the surface because they precipitate as the daily or annual temperature cools. Thus, both temperature variation and the solute flux control mineral accumulation in this environment.

Return to Conceptual Consideration 3⮥

Response to Concept 4, One of Many Possible Responses

There is both a direct and indirect approach to measurement of solute loss as a gas phase. In the direct method a flux box is placed over a representative portion of the system and concentration of the gas of interest is measured at regular intervals over a 24-hour period at several locations during different seasons. Those data are used along with the area of the system to calculate the annual flux of the gas out of the system. A less direct, but perhaps better-integrated value might be obtained by using the geochemistry or isotopes to identify changes that reflect gas loss. For example, of the major ions in groundwater carbon, nitrogen, and sulfur have gases phases and their phase change would generate an isotope change in the remaining solute. We know that most groundwater has a CO_2 concentration that is tens of times greater than the atmospheric concentration of CO_2 and CO_2 degases when the groundwater reaches the atmosphere. Thus, changes in pH, calcium, and bicarbonate concentration relative to the recharge values would suggest the loss of both CO_2 to gas and carbon loss to mineral precipitation. This would be reflected in the isotopes as well as in the solute balance. The relative amount of carbon in each phase would need to be determined by a thermodynamic speciation model. The loss of N_2 gas by reduction of nitrate (NO_3^{-1}) might be estimated by the change in nitrogen isotopes relative to the recharge concentration to the system. Similarly, the loss of sulfate to H_2S gas might be evaluated by sulfur isotopes.

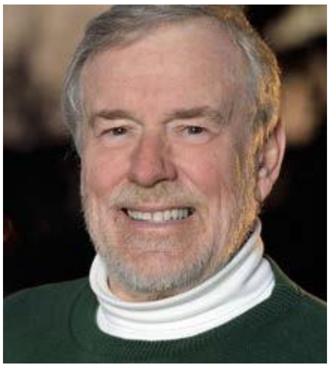
Return to Conceptual Consideration 4↥

Response to Concept 5, One of Many Possible Responses

The first parameter to measure might be the mass of recoverable lithium in the deposit using measurements of the concentration of lithium in the brine and accounting for variable specific yield. The second might be to analyze for secondary ions such as bromide, magnesium, or actinide and lanthanide elements that might be valuable if extracted along with the lithium. One might also evaluate whether it is feasible to use an evaporation pond to further concentrate the brine before processing. That is, to determine the thermodynamic activity of the brine relative to local relative humidity and also evaluate whether the pond would present a hazard to migrating waterfowl. One then might ask how difficult it would be to extract the brine, that is, what is the hydraulic conductivity and specific yield of the aquifer and how many wells would be needed for the optimum rate of withdrawal. The optimum rate is controlled by the size of the processing plant that, in turn, is determined by market factors. To manage the deposit, you might want to know the origin of the lithium. For example, is it concentrated from rainfall and surface runoff over the surrounding rock that reaches the basin, or is it from an ascending deep basin brine, or is it local groundwater discharging to the basin and evaporating; and is it a fossil or an active system? Another concern would be whether there are any restrictions on the rate and volume of water withdrawal from the aquifer system. That is, would extracting the brine impact local agricultural activities or endangered species? One might also construct a hydrologic flow model of the system to account for water flux and a solute transport model to evaluate different development schemes depending on sources of solutes.

Return to Conceptual Consideration 5⮥

12 About the Author



Dr. Warren W. Wood is currently a Visiting Professor of Hydrogeology in the Department of Earth and Environmental Sciences, Michigan State University and formerly the Christiansen Fellow, St. Catherin's College, Oxford University, U.K. and Research Hydrologist U.S. Geological Survey. Warren has published more than 120 research articles on hydrogeology of arid areas and lectured at over 100 universities in North America, China, Botswana, Japan, Oman, UAE, Saudi Arabia, Israel, Jordon, Qatar, U.K., Germany, and France. Warren was awarded the Meritorious Service Award by the U. S. Department of Interior; M. King Hubbert Medal by the National Ground Water Association; Distinguished Service Award, Geological Society of America and Elected Fellow of the Geological Society of America. Warren served at Editor-in-Chief of the Journal Ground Water and testified before U.S. congress, briefed the Secretary of Interior, and Chairman of the Nuclear Regulatory Commission on role of hydrogeology in nuclear waste disposal.

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Modifications to Original Release

page iii, revised citation link to go to the specific book page rather than the book overview page

page 11, changed "Section 4.1" to "Sections 4.1 and 4.2"

page 12, added definitions to the end of the first sentence as follows: (K_{iap} is the ion activity product of the solutes; K_{eq} is the equilibrium constant of the minerals in the water).

page 26, Edmunds et al, reference corrected

page 26, Frape and Fritz reference corrected

page 27, Kamineni reference corrected

page 27, Nordstrom, 1987 reference corrected

page 27, Liu and Dane, 1996, hyperlink corrected

page 27, Mao et al., 2006, hyperlink corrected

page 28, Nordstrom et al., 1989, hyperlink corrected

page 36, changed "formally" to "formerly"