PROPERTIES OF GEOLOGIC FLUIDS

4.1. OCCURRENCE AND COMPOSITION.

Geologic fluids are present in virtually all crustal rocks (Bodnar and Costain, 1991). About 20% of the volume of most sedimentary basins consists of geologic fluids. The composition of geologic fluids has the potential to provide important information on the geochemical, hydrological, thermal, and tectonic evolution of the Earth's crust (Hanor, 1994a, p. 151).

Most geologic fluids are aqueous brines, a mixture of water and NaCl. In water, NaCl dissociates into positively charged Na^+ ions and negatively charged Cl^- ions. An **ion** is a molecule with a net electrical charge. Positively charged ions are termed **cations** and negatively charged ions are **anions**. Besides Na, other important cations found in subsurface brines include Mg, K, Ca, and Sr.

Not all geologic fluids are water based. Examples of economically important geologic fluids that are not aqueous are oil and gas. Magma or liquid rock is another geologic fluid, however, 99% or more of all geologic fluids found in the Earth's crust are water-based, and our discussion is thus focused almost entirely on groundwater.

4.2. TERMINOLOGY AND UNITS.

The salinity of aqueous geologic fluids ranges from *fresh* to *brine* (Table 4.1). In this text, the term **salinity** is used to denote the total concentration of dissolved solids (**TDS**), not just the concentration of NaCl. The salinity of geologic fluids is controlled by solubility and availability of **solute**. The symbol ‰ denotes *parts per thousand,* or total mass of solute per 1000 mass units of **solution.** Seawater is about 35‰ TDS.

Example: If 100 g of salt is mixed with 900 g of water we have 1000 g of solution with a total dissolved solids (TDS) of 100‰. The solution is 10% salt by weight, or has a **weight percent** of 10.

TABLE 4.1	Salinity Terminology[*]
Description	**TDS (‰)**
Fresh	< 1
Brackish	1–10
Saline	10–100
Brine	> 100 (up to ~400)

[*]Seawater is 35 ‰

TABLE 4.2	Comparison of Salinity Units		
Weight Percent Solute		**‰**	**NaCl Molality**
1		10	0.17
5		50	0.90
10		100	1.9
20		200	4.3
30		300	7.3
40		400	11.4

The **molality** (m) of a solution is the moles of solute per kilogram of *solvent*. Molality should not be confused with molarity (M). **Molarity** is the moles of solute per liter of *solution*. A **mole** is the amount of a substance that contains 6.02×10^{23} molecules (**Avogadro's number**). The **molecular weight** of a substance is a number equal to what a mole of a particular substance would weigh in grams. The molecular weight of any substance is the sum of the **atomic weights** of a molecule's constituent atoms and may thus be found from the **periodic table**. A comparison of salinity units is given in Table 4.2.

Example: From the periodic table we find that the atomic weight of Na is 22.99; the atomic weight of Cl is 35.45. Thus, the atomic weight of NaCl is 58.44, meaning that 58.44 g of NaCl constitutes one mole of NaCl. Mixing 58.44 g of NaCl with enough water to produce a liter of solution results in a solution with a molarity of one. If we mix 58.44 g of NaCl with 941.56 g of water, we would have a solution with a molality of 1/0.94156 = 1.06. This salt solution would be 58.44‰ NaCl or have a weight percent of 5.844.

Problem:

a. Find a general expression for conversion of weight percent solute to molality. (b) Apply the expression derived in part (a) to find the molality of a NaCl solution that is 10% solute by weight.

Molality is defined as moles of solute per kilogram of solvent.

1. Find the moles of solute in one kilogram of *solution*.

    The number of moles of solute can be found by dividing the mass of the solute (in grams) by the molecular weight (which is moles per gram). In a kilogram of solution, the mass of solute (in grams) is 1000 (g) $\times$ (W/100) = 10W, where W is the weight percent solute. The number of moles of solute is then the total mass of solute in grams divided by its molecular weight (MW). Thus, the moles of solute per kilogram of solution is 10W/MW.

2. Find the moles of solute in one kilogram of *solvent*.

    The mass of the *solvent* (in grams) is the mass of the solution minus the mass of the solute = 1000 − 10W. Thus, for every 10W/MW moles of solute we have (1000 − 10W)/1000 kilograms of solvent. The molality then is

$$\text{molality} = \frac{\dfrac{10W}{MW}}{\dfrac{(1000 - 10W)}{1000}} \qquad (4.1)$$

$$\text{molality} = \frac{1000W}{MW(100 - W)} \qquad (4.2)$$

where W is the weight percent solute in a solution and MW is the molecular weight of the solute.

b. The atomic weight of Na is 22.99, the atomic weight of Cl is 35.45. The molecular weight of NaCl is thus 22.99 + 35.45 = 58.44. If a solution is 10% NaCl by weight (W = 10), then substituting into equation (4.2) we find

$$\text{molality} = \frac{(1000)(10)}{(58.44)(100 - 10)} \qquad (4.3)$$

$$\text{molality} = 1.90 \qquad (4.4)$$

4.3. Composition and Origin of Solutes.

The discussion that follows is largely focused on solutes in fluids from sedimentary basins as opposed to basement or crystalline rocks. Although the bulk of the continental and oceanic crusts are composed of crystalline rock, our knowledge of the fluids in these rocks is limited. Most samples of crustal fluids have been obtained as a byproduct of petroleum exploration. Nearly all oil and gas are found in sedimentary basins, and the total number of boreholes drilled (and fluid samples collected) in such settings far exceeds similar studies in crystalline or basement rocks. Some notable exceptions are a study of fluids from basement rocks in the Canadian Shield (Frape and Fritz, 1987), and analysis of the brines found in the 9-km-deep borehole drilled by the German Continental Deep Drilling Project (Lodemann et al., 1997).

The salinity of aqueous fluids in sedimentary basins ranges from fresh, close to the surface, to over 400‰ in evaporite-rich basins such as the Michigan Basin (Figure 4.1). An **evaporite** is a sediment or a rock deposited by evaporation of a solution such as seawater. The highest known salinity (643 g-liter^{-1}) is for a $CaCl_2$-brine from the Saline Formation in the Michigan Basin (Case, 1945; Hanor, 1994a, p. 154). Although some exceptions are known, in general salinity tends to increase with depth (Hanor, 1979). Dickey (1969) noted that the increase of total salinity with depth in many oil fields tends to be linear (Figure 4.2).

Chloride makes up over 95% by mass of the anions in most sedimentary basin fluids with salinities greater than 10‰. Brackish and freshwater fluids more commonly have bicarbonate, sulfate, or acetate as their dominant anion (Hanor, 1994a, p. 155). There is a **cationic shift** in high-salinity waters. Sodium is the dominant cation by mass in fluids of moderate to low salinities (Figure 4.3), however, as salinity increases, the relative proportion of Na decreases while the proportions of K, Mg, and Ca increase. The most notable increase is in Ca, which typically becomes the dominant cation by mass in fluids whose salinities exceed 300‰.
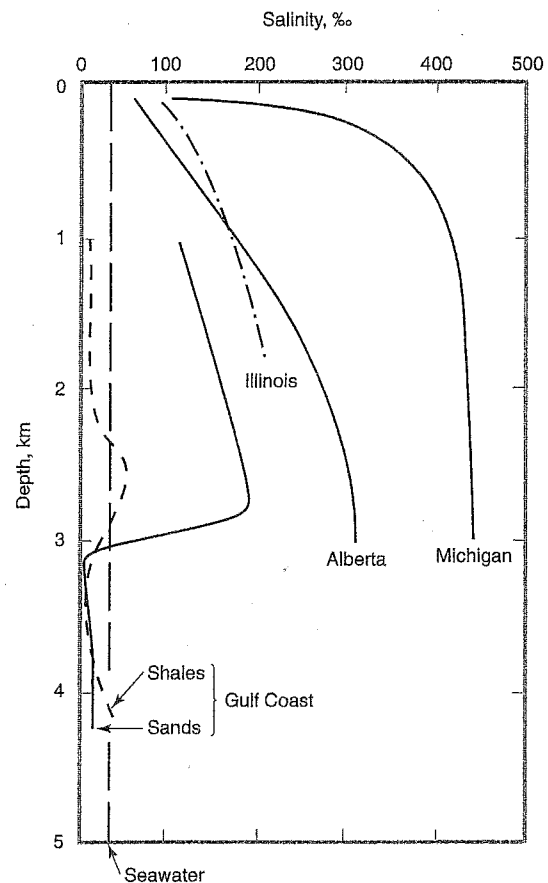

Figure 4.1 Maximum salinities versus depth for the Illinois, Alberta, Michigan, and Gulf Coast sedimentary basins. Note reversal of usual trend of increasing salinity with increasing depth for sands from the Gulf Coast basin.
(From Hanor, 1987, p. 82.)

At the present time, we do not have a definitive understanding of what mechanisms control the composition of solutes in the aqueous pore-fluids found in sedimentary basins, nor do we necessarily understand what geologic factors may affect the relative importance of different processes under different circumstances. The following mechanisms have all been proposed to account for the origin and composition of solutes: (1) subaerial evaporation of seawater or continental waters, (2) subsurface dissolution of evaporites, (3) membrane filtration, and (4) fluid-matrix interactions.
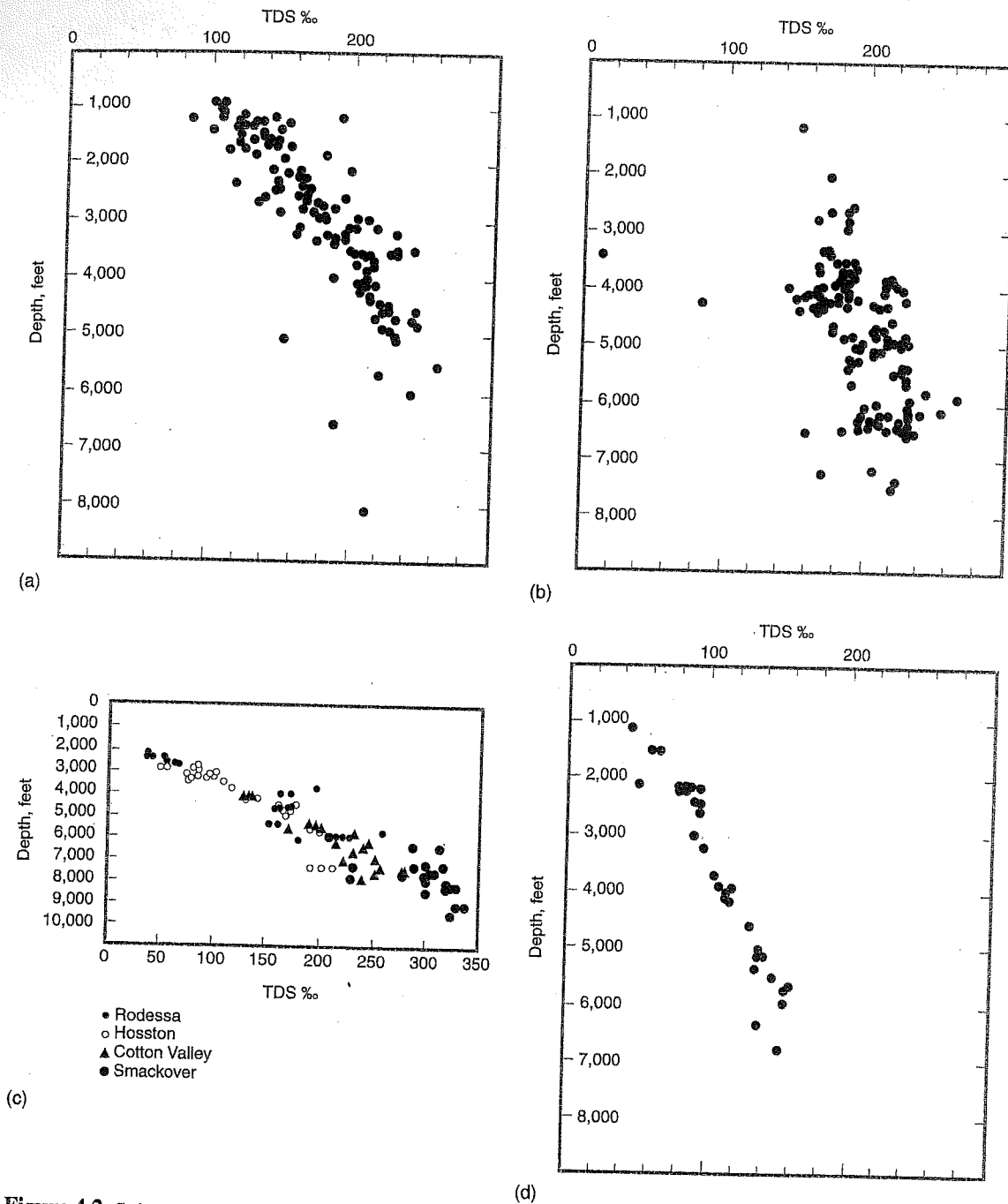
Figure 4.2 Solute concentration versus depth for oil field brines from (a) oil producing sands of the Pennsylvanian Cherokee Group in Oklahoma, (b) Ordovician Wilcox and Simpson sands of Oklahoma, (c) randomly selected waters from different horizons ranging from Jurassic to Cretaceous in southern Arkansas and northern Louisiana, (d) Eocene Wilcox sands of central Louisiana.
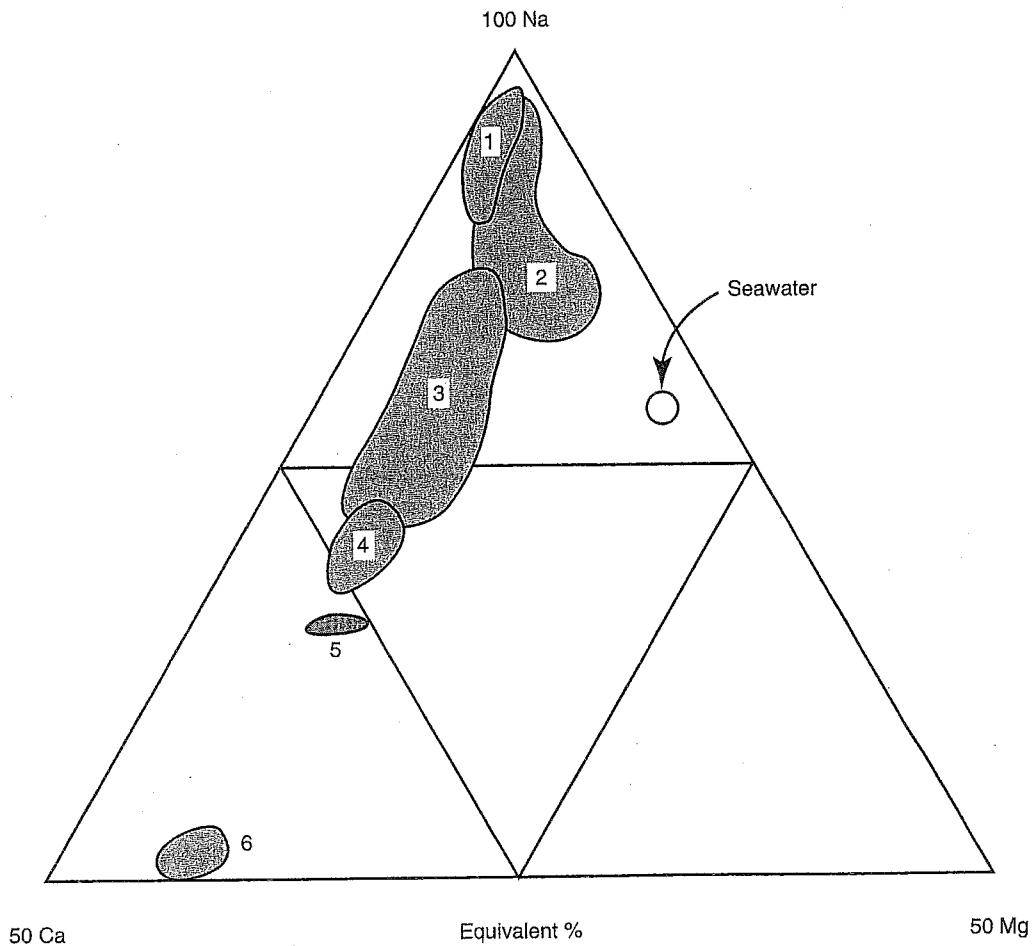(From Dickey, 1969, p. 363–365.)

Figure 4.3 Variations in proportions of dissolved Na, Ca, and Mg in brines from (1) Texas, (2) California, (3) Kansas and Oklahoma, (4, 5) Appalachia, and (6) Arkansas
(From Hanor, 1987, p. 82; after DeSitter, 1947.)

Evaporation of seawater by itself cannot account for the major anion and cation composition of subsurface brines. One reason is that subaerially evaporated seawater has sulphate as a major solute over all stages of evaporation, yet sulphate is a minor constituent of most subsurface brines. Hanor (1994a, p. 156) concluded that "While it is probable that some subsurface brines have had evaporated marine waters as their ultimate precursors, it is obvious that other processes have been at work to account for their major solute composition." Some brines derived from continental waters (e.g.,

lakes, rivers, etc.) may resemble subsurface brines in overall chemical composition and salinity, but there can be significant differences, especially in anionic composition and the relative abundance of dissolved Mg.

The subsurface dissolution of evaporites has been documented to contribute to the solute composition of some aqueous brines in sedimentary basins. In the Gulf Coast Basin of the southeast US (Figure 4.4), the spatial variations in pore water salinity around some salt domes provide clear evidence for the dissolution of salt diapirs as the source
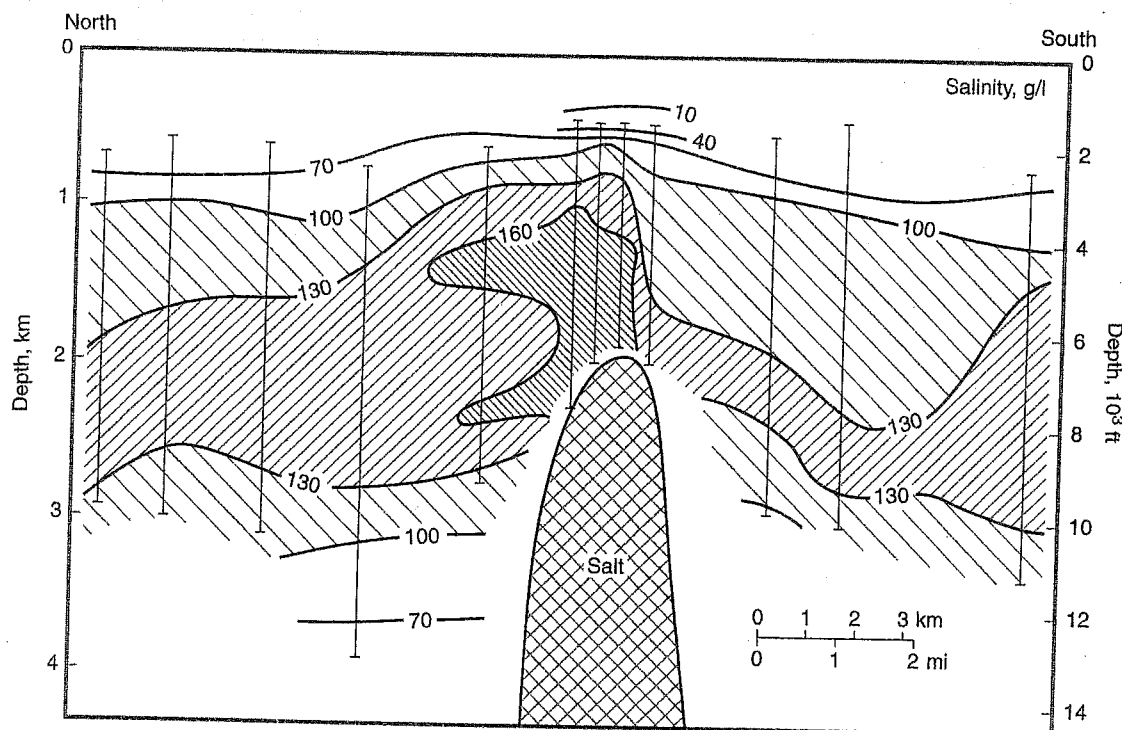
Figure 4.4 Variation in pore water salinity in the vicinity of the Welsh salt dome, Louisiana Gulf Coast. (From Hanor, 1994b, p. 41; after Hanor 1988.)

of the brines (Bennett and Hanor, 1987; Hanor, 1994a). Field mapping of salinity variations in the Gulf Coast Basin suggests that salts dissolved from halite domes have moved many kilometers vertically and tens of kilometers laterally throughout the surrounding sedimentary sequence (Bray and Hanor, 1990; Hanor and Sassen, 1990).

Membrane filtration has been proposed as a mechanism that could explain the existence of brines in evaporite-poor sedimentary basins. **Membrane filtration** refers to the filtering out of cations and anions by electrically polar clay molecules. Neutral water molecules pass through clay layers without difficulty, but charged anions and cations are electrostatically repulsed by the uneven distribution of charges on the surface of clay minerals. In theory, pore fluids on the influent side of a shale membrane will become progressively more saline due to membrane filtration.

Although membrane filtration has been demonstrated in the laboratory, there is *no known*

example of subsurface brines having been produced by this mechanism. Hanor (1994a) pointed out that the Gulf Coast Basin of the southeast US is exemplary of the type of setting where membrane filtration should be producing brines. Upward flow through overpressured shale sections into overlying hydrostatically pressured sand layers should have produced higher salinities below the clay-rich shales. But, the opposite is observed: salinity actually decreases below the top of the shale sequence. Hanor (1994a, p. 159) speculated that the upward flow of fluids from the Gulf Coast overpressured zone takes place by way of fractures, bypassing the filtration that would be expected for flow through the porosity of the clay-rich shales.

Although both subaerial evaporation of marine and continental waters and subsurface dissolution of evaporites have the potential for producing brines with the range of salinities and dissolved chlorine concentrations of most subsurface brines

Nelson Horatio Darton: Master of Field Geology

Nelson Horatio Darton (1865–1948) was born on December 17, 1865, in Brooklyn, New York. At the age of 14, Darton quit public school to become an apprentice in his uncle's pharmacy. The young Darton showed an enormous aptitude for chemistry, supplementing the practical experience obtained in his uncle's pharmacy with supplemental readings. By the age of 15, Darton had acquired a reputation as a practical chemist and had developed his own consulting business. During his teenage years, Darton contributed several scientific papers to the chemical literature and was asked by the editor of *Scientific American* to take charge of the chemical and mineralogical part of the "notes and queries" column. Just before his sixteenth birthday, Darton was elected a member of the American Chemical Society.

Darton became interested in geology, and in 1882 (at the age of 17) published three papers on the occurrence of minerals in the vicinity of New York City. Darton spent more and more time on geologic collecting trips and field studies, and eventually his work caught the attention of G. K. Gilbert of the U.S. Geological Survey. Gilbert offered Darton a position with the USGS that he started in 1886 and kept for 50 years. At the USGS, Darton's exceptional aptitude for field geology was recognized, and he was assigned a series of geologic mapping duties. During his investigation of the geology of the Atlantic Coastal Plain, Darton became interested in the geology of artesian wells and underground water. In 1896, Darton published USGS Bulletin 138, *Artesian Well Prospects in the Atlantic Coastal Plain Region*, and became recognized as the Survey's leading expert on artesian wells.

Darton's accomplishments, especially in the field of geologic mapping, seem almost superhuman in retrospect. In the field seasons of 1893 and 1894, Darton mapped 9,350 square miles in New York State at the rate of 100 to 150 square miles per day, much of this being covered by horse and buggy, or on foot. In

Nelson Horatio Darton (1865–1948)

1905, Darton published what he considered to be his finest work, USGS Professional Paper 32, *Preliminary Report on the Geology and Underground Water Resources of the Central Great Plains*. This report consisted of 433 pages and contained 72 plates as well as many photographs and geologic maps. Although Darton did have the assistance of a team of coworkers, it is nevertheless remarkable that this monograph was one of eleven publications he authored that year. In the citation for the Geological Society of America Penrose Medal that Darton received in 1940, Douglas Johnson (Johnson, 1940, p. 82)

in sedimentary basins, these processes *cannot* explain their major cation composition. Thermodynamic buffering by silicate-carbonate mineral assemblages (i.e., matrix-fluid chemical reactions) has a first-order control on subsurface fluid compositions. The chemical potential of chloride, or the aqueous concentration of anionic charge, is a master variable in driving fluid-matrix interchanges and controlling fluid composition. Chloride composition, in turn, is controlled largely by

testified not only to the enormous quantity of Darton's work, but also to its quality:

> I testify to our astonishment that one man could do so much and do it so uniformly well. Tonight we pay tribute to the fact that in the wealth of Darton's productive work there is so much that has withstood the acid test of time, so little of major importance that has required correction or revision.

Darton reputedly took a sturdy pride in his work. The story is told (King, 1949, p. 161) that one day Darton came upon a fellow geologist who was examining an outcrop. The other man said, half-humorously, *"I have made my guess as to what this formation this is, what is your guess?"* Darton replied, *"I never guess, I find the facts and I know."* Co-workers at the USGS would later relate that they considered Darton to have a big ego, without much of a sense of humor. A story illustrates Darton's view of himself. In the early days, the method of operation of the USGS was for many people to spend a season in the field and then return to Washington, DC in the winter. The Geologic Society of Washington (DC) was a prestigious group with many of the USGS scientists as members; as of the year 2000, the GSW still meet at the Cosmos Club in Washington. At one meeting, the Chairman was commenting on members in the audience, and said "the father of groundwater is here tonight" (or some such words) presumably intending to introduce Meinzer, at which point Darton stood up. In the opinion of some, Darton was entirely justified in his presumption.

Although Darton's interests and contributions to the science of geology were spread across many subdisciplines, he is especially remembered for his hydrogeological studies of the Dakota Aquifer in South Dakota. In 1900, Darton and his assistants began a study of the geology and underground waters of the central Great Plains. They collected data from thousands of wells, documenting the geologic controls on

groundwater occurrence and flow. It was Darton who emphasized that *"underground water is a geologic problem that requires a study of the formations carrying it"* (Darton, 1941, p. 86).

During his career Darton received a long list of honors and awards. An abbreviated list includes the Daly Gold Medal of the American Geographical Society (1930), the Penrose Medal of the Geological Society of America (1940), and the Legion of Honor of the American Institute of Mining and Metallurgical Engineers (1944).

At age 70, Darton characterized his imminent forced retirement as "facing a terrible period of inactivity." He was granted a year's extension by US President Franklin D. Roosevelt, and arrangements were made for him to continue to use USGS facilities for another 12 years as an emeritus scientist. On February 28, 1948, Darton quietly passed in his sleep. During his lifetime, he published more than 220 contributions to the geologic sciences. Darton was one of the giant figures of the heroic age of American geology; he was the acknowledged master of field technique and the greatest reconnaissance geologist of all time.

FOR ADDITIONAL READING

Johnson, D., and Darton, N. H. 1941. Presentation of the Penrose Medal to Nelson Horatio Darton, Medalist, Address by Douglas Johnson and Response by Doctor Darton. *Proceedings of the Geological Society of America for 1940*, 81–88.

King, P. B. 1949. Memorial to Nelson Horatio Darton. *Proceedings Volume of the Geological Society of America*, April: 145–170.

Monroe, W. H. 1949. Memorial, Nelson Horatio Darton (1865–1948). *AAPG Bulletin*, 33: 116–124.

physical processes of fluid flow. The extensive fluid-matrix interactions that control the cation composition of subsurface brines in sedimentary basins may make it difficult to infer the ultimate origin of pore fluids from their present-day composition alone (Hanor, 1994a, p. 171–72). Studies of subsurface brines from basement rocks in the Canadian Shield led Frape and Fritz (1987) to a similar conclusion: solute composition is controlled by fluid-matrix interactions.

4.4. ISOTOPES.

Isotopic analysis is a valuable tool in the study of how fluids originated and evolved. An **isotope** is a variation of an **element** that has the same number of **protons** in the **nucleus**, but a different number of **neutrons**. The higher the atomic weight of an isotope, the heavier it is. For example, the heavy oxygen isotope is O^{18}, the light oxygen isotope is O^{16}. In this notation, O denotes oxygen, and the superscripted number is the total number of protons and neutrons in the oxygen atom. Thus O^{18} has two more neutrons in each atom compared to O^{16}.

Isotopes have the same gross chemical properties but different weights. There are subtle differences in the behavior of different isotopes of the same element, and these differences may be exploited to learn about natural systems.

Isotopic ratios are measured using **a mass spectrometer.** A mass spectrometer is "an instrument designed to separate charged atoms and molecules on the basis of their masses based on their motions in electrical and/or magnetic fields" (Faure, 1977, p. 65). In a mass spectrometer, a sample is first ionized by subjecting it to a stream of high-speed electrons. The collision of these electrons with a sample molecule strips that molecule of an electron, and the sample molecule acquires a positive charge. The positively charged ion is then accelerated through an electric field while simultaneously being subjected to a magnetic field. The magnitude of the deflection of the ion in the magnetic field gives a measure of the ratio of its charge to its mass. Thus isotopes with identical charges but slightly different masses can be separated and their relative proportions in a sample measured.

Isotopes are either radioactive or stable. Radioactive isotopes decay through nuclear reactions; their primary hydrogeologic use is in dating groundwater. Stable isotopes are not subject to radioactive decay and are largely used to understand the source and evolution of groundwater.

4.4.1. Stable Isotopes.

Stable isotopes are those that are not radioactive. The most common stable isotopes studied in connection with geologic fluids are the isotopes of oxygen and hydrogen. Oxygen has three naturally-occurring isotopes. These are O^{18} (0.2%), O^{17} (0.04%), and O^{16} (99.76%). Hydrogen has two stable isotopes, H^1 (99.99%) and H^2 (0.01%). H^2 is also known as deuterium and is denoted by the capital letter D.

The process that makes it possible to use stable isotopes in groundwater studies is fractionation. **Fractionation** is the separation of a mixture into parts that possess different properties. The oxygen and hydrogen isotopes found in water can undergo fractionation due to chemical and biological changes, or physical changes such as evaporation, condensation, freezing, and melting. Studies of the resulting isotopic ratios can then be used to infer the nature of the process that caused the fractionation or the source of the original water that underwent fractionation.

Fractionation is expressed as a ratio relative to a standard composition,

$$\delta_{heavy} = \frac{(heavy/light)_{sample} - (heavy/light)_{standard}}{(heavy/light)_{standard}} \times 1000‰ \tag{4.5}$$

The isotopic ratio may alternatively be defined with respect to the light isotope as δ_{light}. The standard commonly used in studies of oxygen and hydrogen isotopes is **standard mean ocean water (SMOW)** (Craig, 1961). The present-day composition of ocean water is "exceedingly uniform" (Taylor, 1974, p. 850), and this is why it can be used as an isotopic standard. Exceptions are the areas subject to high rates of evaporation (e.g., the Red Sea) or dilution from freshwater (e.g., near the mouth of a large river).

Evaporation and condensation are both important fractionation processes for the hydrogen and oxygen isotopes found in water. The lighter isotopes of both hydrogen and oxygen tend to evaporate more easily than the heavier isotopes. Thus atmospheric water has a lighter isotopic composition than seawater, however, the opposite is true for condensation. Heavier isotopes tend to condense more easily. Most atmospheric water comes from evaporation of seawater, and this evaporation is disproportionately concentrated at low latitudes where
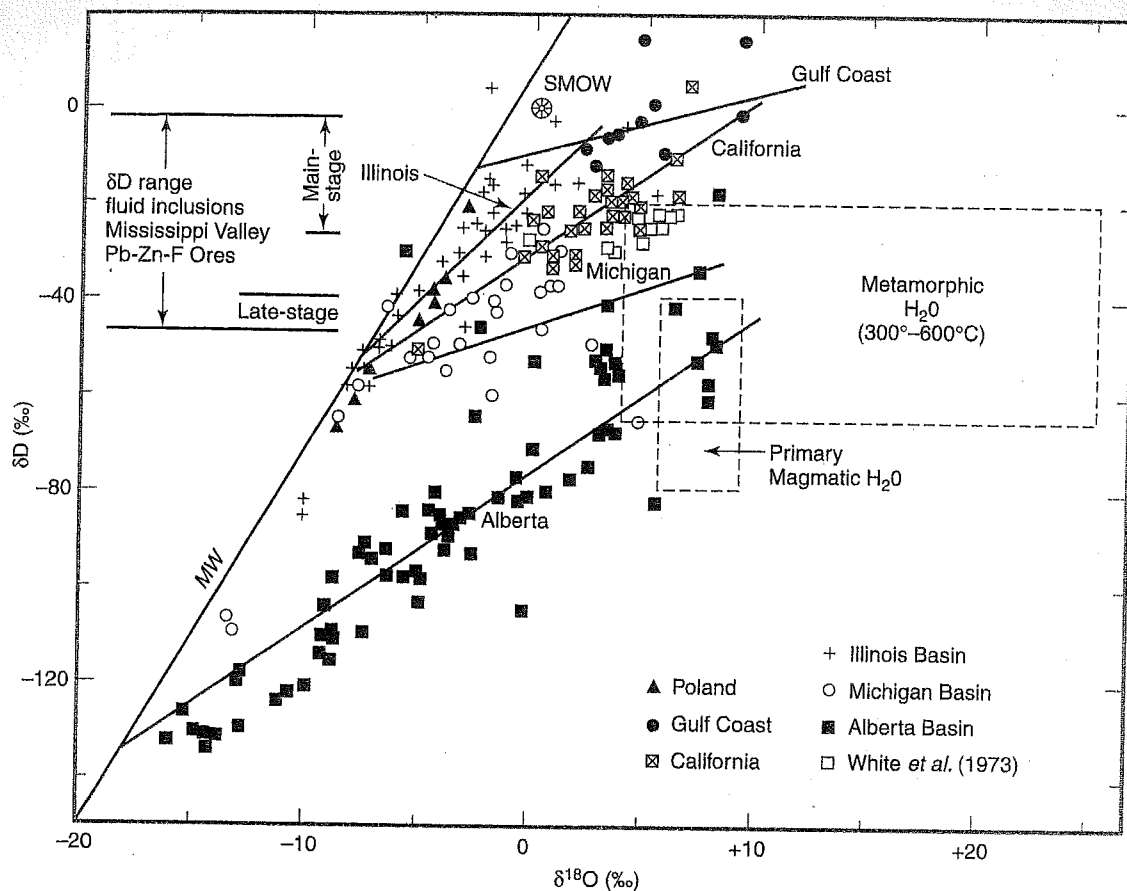
Figure 4.5 Values of δD and $\delta^{18}O$ for standard mean ocean water (SMOW), meteoric water (MW line), magmatic water, metamorphic water, and brines from several sedimentary basins. Also shown is the range of isotopic compositions, which characterize water found in fluid inclusions associated with Mississippi Valley-type lead–zinc deposits.

(From Taylor, 1974, p. 852.)

temperatures are higher. As atmospheric water vapor travels from the equator to the poles, it tends to progressively lose heavier oxygen and hydrogen isotopes through condensation. Thus atmospheric water and precipitation are increasingly depleted in the heavier isotopes with higher latitudes. This trend is known as the **meteoric water line** (Figure 4.5). Meteoric water is that which occurs in, or originates from, the atmosphere.

Oxygen isotopes can also be used to estimate the paleotemperature of seawater. The precipitation of $CaCO_3$ from seawater into the shells of marine organisms is affected by temperature, and thus the ratio O^{18}/O^{16} in carbonate skeletons is diagnostic of temperature at the time the shell was formed. But, interpretation of such ratios is not straightforward, because the mean isotopic composition of seawater has changed over time. During the last million years or so, Earth has been subjected to cyclic climatic variations known as ice ages. Ice ages tend to last about 100,000 years, and are separated by relatively brief interglacial periods about 10,000 years long. During an ice age, the mean planetary surface temperature typically falls about 5°C and continental ice sheets accumulate at high and middle latitudes. The accumulation of vast

amounts of isotopically depleted ice in the form of great ice sheets enriches remaining seawater in the heavier isotopes. Thus the isotopic composition of ocean water was not constant in the geologic past. Paleotemperatures can also be inferred by direct analysis of the isotopic composition of ancient ice layers that have accumulated at the poles.

One way in which fractionation occurs in groundwater in the solid Earth is through the exchange of oxygen isotopes. Oxygen is the most abundant element in the Earth's crust, constituting 46% of the crust by weight (Press and Siever, 1986, p. 13). In contrast, hydrogen makes up only 0.14% of the crust by weight (Press and Siever, 1986, p. 595). As meteoric water enters the crust through infiltration, it tends to exchange the lighter O^{16} isotope for the heavier O^{18} isotope (Figure 4.5).

4.4.2. Radioactive Isotopes.

Radioactive isotopes are those that undergo nuclear decay and change from one element into another; they are used in geologic dating. Examples of radioactive isotopes that are employed in dating rocks include Uranium, Thorium, Rubidium-Strontium, and Potassium-Argon. Radioactive isotopes used to date groundwater include Carbon-14 (C^{14}), Tritium (H^3), Chlorine-36 (Cl^{36}), Helium-3 (He^3), and Helium-4 (He^4).

The rate at which radioactive isotopes decay is proportional to the number of atoms present,

$$\frac{dN}{dt} = -\lambda N \qquad (4.6)$$

where N (dimensionless) is the number of atoms remaining at any time, t (s) is time, and λ (s^{-1}) is the **decay constant**. Each radioactive isotope has a unique decay constant (λ). The negative sign in equation 4.6 indicates that the rate at which N is changing is negative. That is, the total number of atoms (N) is decreasing with increasing time. Equation 4.6 can be re-arranged and integrated,

$$\frac{dN}{N} = -\lambda dt \qquad (4.7)$$

$$\int \frac{dN}{N} = -\int \lambda dt \qquad (4.8)$$

$$\log_e (N) = -\lambda t + c \qquad (4.9)$$

where c is a dimensionless constant of integration. If at $t = 0$, there are N_0 atoms present, then

$$c = \log_e (N_0) \qquad (4.10)$$

or

$$\log_e (N) = -\lambda t + \log_e (N_0) \qquad (4.11)$$

Exponentiating both sides and keeping in mind that $e^{(a+b)} = e^a e^b$,

$$N = N_0 e^{-\lambda t} \qquad (4.12)$$

The **half-life** of a radioactive isotope is the time it takes for half of an initial amount of atoms of one element or isotope (the **parent isotope**) to change to atoms of another element or isotope (the **daughter isotope**). Let the half-life be denoted by $\tau_{1/2}$ (s). When one half-life has passed ($t = \tau_{1/2}$), $N = N_0/2$, thus

$$\frac{N_0}{2} = N_0 e^{-\lambda \tau_{1/2}} \qquad (4.13)$$

Suppose that we have a radioactive parent isotope that decays into a stable daughter isotope. At time $t = 0$, we have N_0 parent atoms. At time $t > 0$, we have (from equation 4.12) $N_0 e^{-\lambda t}$ parent atoms left. The number of daughter atoms (D, dimensionless) generated must be equal to the number of decayed parent atoms. Thus

$$D = N_0 - N_0 e^{-\lambda t} = N_0 (1 - e^{-\lambda t}) \qquad (4.14)$$

It is more convenient to express D in terms of N, because we cannot measure N_0, we can only measure D and N. From equation 4.12,

$$N_0 = \frac{N}{e^{-\lambda t}} \qquad (4.15)$$

Substituting equation 4.15 into equation 4.14,

$$D = N(e^{\lambda t} - 1) \qquad (4.16)$$

because $1/e^{-\lambda t} = e^{\lambda t}$. Equation 4.16 can be solved for time (t),

$$t = \frac{1}{\lambda} \log_e \left[1 + \frac{D}{N} \right] \qquad (4.17)$$

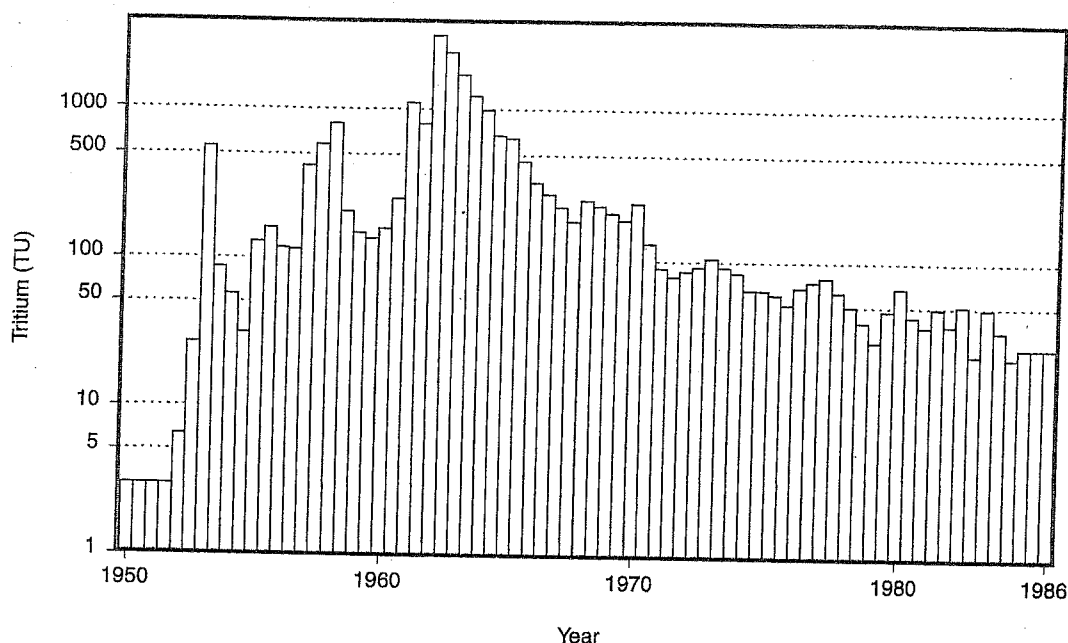

Figure 4.6 Tritium concentration in precipitation near Ottawa, Canada. Note logarithmic scale. (From Robertson and Cherry, 1989, p. 1103.)

Thus, if the decay constant (λ) is known, and the ratio of parent and daughter atoms can be measured, the time since decay started (t) can be estimated. If the number of daughter atoms was zero at time $t = 0$, the estimated time (t) represents the age of a rock or groundwater sample.

Carbon-14 (C^{14}) is produced in the atmosphere by the interaction of cosmic-ray produced neutrons and nitrogen (N^{14}). The concentration of C^{14} in the atmosphere is in a dynamic equilibrium, with new C^{14} being produced at the rate necessary to replace that which decays. Radioactive C^{14} is incorporated into carbon dioxide, which is readily dissolved in surface waters. Once surface water has infiltrated into the subsurface, no further addition of radioactive C^{14} occurs. If no contamination occurs, C^{14} activity should therefore be a direct measure of the time elapsed since a water molecule has entered the subsurface through recharge. C^{14} has a half-life of 5,730 years and is generally useful for dating groundwater less than 50,000 years old. The accuracy of C^{14} dating may be problematical due to several sources of contamination. Groundwater exchanges carbon atoms with the solid Earth. Phillips et al. (1989) list possible sources of contamination that include dissolution of soil and aquifer carbonate, as well as exchange of groundwater calcium for matrix sodium.

Tritium (H^3) is a short-lived isotope of hydrogen; it has a half-life of 12.3 years. Tritium is produced naturally in the upper atmosphere by the reactions of protons and neutrons with nitrogen and oxygen. After oxidation, tritium is incorporated into atmospheric water and the hydrologic cycle. Tritium can also be produced by the detonation of nuclear bombs in the atmosphere. During the most active phase of nuclear above-ground testing, from 1952 through 1963, the concentration of tritium in the atmosphere rose by three orders of magnitude (Figure 4.6). The rapid rise in tritium concentration that occurred during this period of time is a useful tracer in shallow groundwater studies.

Tritium levels are expressed in units of tritium units. One **tritium unit (TU)** is equal to a natural or pre-bomb level of one tritium atom per 10^{18} hydrogen atoms. The utility of tritium studies is increased by simultaneous measurement of its decay product, Helium-3 (He^3). A typical application of tritium analyses is to estimate infiltration rates by modeling the migration of the tritium spike caused by nuclear testing. The interpretation of tritium measurements can be condensed into three rules of thumb (Mazor, 1991):

1. Groundwater with tritium levels below 0.5 TU predates 1952.
2. Groundwater with a tritium concentration above 10 TU postdates 1952.
3. Groundwater with a tritium concentration between 0.5 and 10 TU is a mixture of pre- and post-1952 water.

Chlorine-36 (Cl^{36}) is a radioactive isotope of chlorine with a half-life of 301,000 years. Cl^{36} is produced in the atmosphere by the interaction of cosmic rays with Argon-40. Argon is the third most abundant gas in the atmosphere; it constitutes about 1% of the atmosphere's volume. Cl^{36} can also be produced in the near-surface environment by interaction of cosmic rays with minerals in surface rocks. In the subsurface, the radioactive decay of Uranium and Thorium produces some Cl^{36}. In comparison to atmospheric production, surface and subsurface production of Cl^{36} are relatively small, and the Cl^{36} that is produced tends to be mineralogically bound and immobile. It is therefore usually safe to assume that most of the Cl^{36} found in groundwater originates from meteoric recharge. Two exceptions are geologic settings where evaporite dissolution is occurring or geothermal waters are circulating (Phillips et al., 1986).

Cl^{36} has two advantages in groundwater dating. First, it has (compared to tritium and carbon-14) a relatively long half-life. Secondly, chlorine usually undergoes few interactions with solid phases. Thus, it is much less subject to contamination. Cl^{36} dating was not possible prior to 1979 when advances in mass spectrometry techniques first made it possible to reliably measure Cl^{36} concentrations at the low levels at which it typically occurs ($Cl^{36}/Cl < 10^{-14}$). One of the first studies that demonstrated the utility of Cl^{36} in dating groundwater was an analysis of fluids from the Great Artesian Basin of Australia by Bentley et al. (1986) (see Figure 1.4).

Helium has two isotopes: the lighter and rarer He^3, and the heavier and more common He^4. Terrestrial helium isotopes are from one of two sources: (1) primordial helium trapped inside the Earth at the time of its accretion, or (2) helium produced radiogenically in the solid Earth by the radioactive decay of Uranium and Thorium. Although some crustal He^3 is produced radiogenically by the breakdown of Lithium-6 (Li^6), most of the He^3 found in the crust is primordial. Primordial helium is believed to have an isotopic ratio He^3/He^4 of the order of 10^{-4}, the value that characterizes gas-rich meteorites (O'Nions and Oxburgh, 1983). Helium that outgasses from the mantle today has a ratio (He^3/He^4) near 10^{-5}. The dilution from the primordial He^3/He^4 ratio (10^{-4}) is believed to be due to ongoing radioactive generation of He^4. In "normal" crust and mantle rocks, the production ratio (He^3/He^4) is 1.0×10^{-8} (O'Nions and Oxburgh, 1983, p. 429). The relative abundances of He^3 and He^4 are normally expressed by comparing them to the atmospheric ratio R_A for which (He^3/He^4) = 1.4×10^{-6}. Thus the isotopic ratios due to radioactive production of He^4 in the crust would be $R/R_A = 1.0 \times 10^{-8}/1.4 \times 10^{-6} = 0.01$. In contrast, areas of the crust where mass and heat are being transferred from the mantle show enrichment in He^3 (Oxburgh et al., 1986). Elevated levels of primordial He^3 in groundwater are a clear indication of mantle outgassing. Mid-ocean spreading ridges are characterized by isotopic helium ratios (R/R_A) of about 10. Other areas that show evidence of mass/heat transfer from the mantle include continental rifts, hot spots, and geothermal springs (Figure 4.7) (Ballentine et al., 1991).

In theory, the accumulation of He^4 can be used to date groundwater (Torgersen, 1980; Torgersen and Clarke, 1985). The theory depends on the more-or-less constant generation of He^4 by the decay of thorium and uranium that are "ubiquitous"
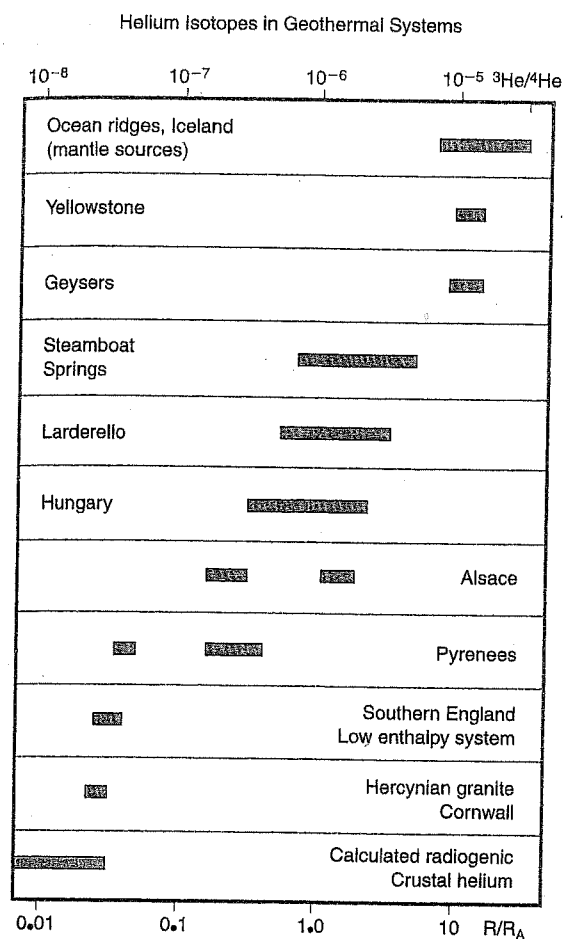
Helium Isotopes in Geothermal Systems

Figure 4.7 Characteristic distribution of helium isotopes in geothermal waters. Larger ratios of R/R_A indicate more mantle involvement.
(From Deak et al., 1988, p. 294.)

entrain not only locally produced He^4, but the entire crustal production. Torgersen and Clarke (1985) studied He^4 concentration in the Jurassic Aquifer of the Great Artesian Basin in Australia. They concluded that for relatively young groundwater (age less than 50,000 years) the concentration of He^4 was controlled by in situ radioactive decay of Uranium and Thorium. But, in the main part of the Great Artesian Basin they found that the rate of He^4 accumulation was 74 times the rate of production by radioactive decay in the aquifer. They concluded that the massive addition of He^4 to the Jurassic Aquifer was consistent with the production of nearly the entire production of crustal helium. The facilitation of He^4 release throughout the crust implies relatively high permeability in the lower crust.

4.5. ORIGIN OF PORE FLUIDS.

Water found in subsurface aqueous brines has traditionally been designated as meteoric, connate, or juvenile. **Meteoric water** is that which occurs in, or is derived from, the atmosphere. **Connate water** is water that was trapped in pore spaces at the time a rock was first formed; connate refers to pore fluid physically present at the time of sediment deposition. Hanor (1994b, p. 34) noted that connate means "born with," and thus should not be applied to pore water that has physically remained in its original pore spaces over geologic time but undergone chemical changes through fluid-matrix interactions. **Juvenile water** is water derived from the interior of the Earth that has not previously been present in the atmosphere or surface of the Earth.

Our present understanding suggests that the above three definitions are outdated and should be replaced by a new classification scheme. For example, the word "connate" strictly interpreted implies that a fluid has not evolved or interacted with a rock matrix. Today we understand that such a situation is rare to nonexistent. Furthermore, the word connate tells us nothing regarding the origin of the water. Rather, it refers to a condition of stagnation that usually does not exist in nature.

in nearly all crustal rocks (Torgersen and Clarke, 1985, p. 1211). In practice, uncertainties are introduced by the rate of release of He^4 from the solid to the liquid phase and the volume ratio of the solid phase (that releases He^4) to the liquid phase (that accumulates He^4). Torgersen and Clarke (1985, p. 1211) noted that the agreement between He^4 ages and ages calculated by C^{14} dating were often quite poor. He^4 dating usually yields an older age, often by factors up to 60 times. These discrepancies may reflect the fact that some aquifers can

A more useful classification scheme is to divide water into oceanic, meteoric, and evolved. **Oceanic water** is water that is found in the Earth's oceans, or water that is found elsewhere but has not significantly changed its composition from the time it left the oceans. **Evolved water** is water that originated as either meteoric or oceanic water, but has subsequently changed its composition through chemical and/or physical processes. In this classification scheme, the term juvenile is discarded. Juvenile water constitutes a negligible portion of geologic fluids in the crust, even in hydrothermal or deep geothermal systems (Kharaka, 1986, p. 174). The term once applied to water vapor emitted from volcanoes, however, with our present understanding of plate tectonics and subduction, it appears likely that most volcanic emissions may contain substantial amounts of recycled water that originated in the oceans or atmosphere and subsequently evolved.

The new classification scheme avoids much of the confusion inherent in the old terminology. Consider, for example, the pore water in a newly deposited layer of terrigenous sediment. By definition, this is connate water, but was derived immediately from meteoric water. If the pore fluid had been derived from oceanic water, it would also have been termed connate. The word "connate" does not help us understand the origin of the fluid.

Up to 1966, it was thought that the pore fluids in sedimentary rocks were largely connate. In that year, our understanding started to change when Clayton et al. (1966) studied brines from the Illinois, Michigan, and Alberta sedimentary basins. Plots of the isotopic composition of water from these basins (Figure 4.5) extrapolated back to the local meteoric water line in each case. The conclusion of Clayton et al. (1966) was that the connate pore fluids in each of these basins had been flushed out by meteoric water. Meteoric water in sedimentary basins commonly evolves isotopically by adding the heavier isotopes of both oxygen and hydrogen. A correlation between the amount of total dissolved solids and the degree of isotopic enrichment in O^{18} suggested to Clayton et al. (1966) that the isotopic evolution of meteoric water in sedimentary basins occurs mostly through fluid-matrix

interaction. Most of the O^{18} enrichment is due to exchange with O^{18}-rich calcite. Calcite is ubiquitous in sedimentary basins and is enriched in O^{18} at the time of its formation due to equilibrium partitioning. During burial at higher temperatures, calcite is dissolved, exchanges oxygen isotopes with the surrounding fluid, and precipitates again. During this process, calcite becomes isotopically lighter and pore fluid becomes isotopically heavier (Knauth and Beeunas, 1986). In the case of the hydrogen isotopes, subsurface water can become either enriched or depleted in deuterium through exchanges with hydrous minerals such as clays. The nature (heavier or lighter) and extent of the isotopic evolution depends upon the isotopic composition of the hydrous matrix minerals and the original meteoric water. Knauth and Beeunas (1986, p. 425) stated that there should be little hydrogen-isotope exchange between meteoric water and hydrous minerals at temperatures below 100°C.

Not all pore fluids originate as meteoric water. Kharaka (1986) showed that some pore fluids from the Gulf Coast Basin in the southeast United States originated as ocean water. Extrapolation of the oxygen and hydrogen isotopic ratios of these fluids leads back to SMOW, not the meteoric water line (Figure 4.8). The deuterium depletion seen in pore fluids from the Gulf Coast Basin was attributed by Kharaka (1986) to isotopic exchanges with clay minerals possessing a very light original δD value. The Gulf Coast basin is undergoing active subsidence, and the younger sediments have not yet had the opportunity to be uplifted and flushed with meteoritic water.

Kharaka (1986) characterized formation waters in sedimentary basins as generally "highly mobile." In support of this assertion, Kharaka (1986) cited studies of fluids from the Western Canadian Sedimentary Basin, the Dniepor-Donets Basin and Ukrainian Shield, the Upper Silesian Coal Basin in Poland, and the Sacramento Valley in California. There is evidence at all of these sites that fluids of different ages and origins have mixed. Thus, in general, isotopic analyses suggest that the fluid regime in sedimentary basins usually involves the active circulation of meteoric water.
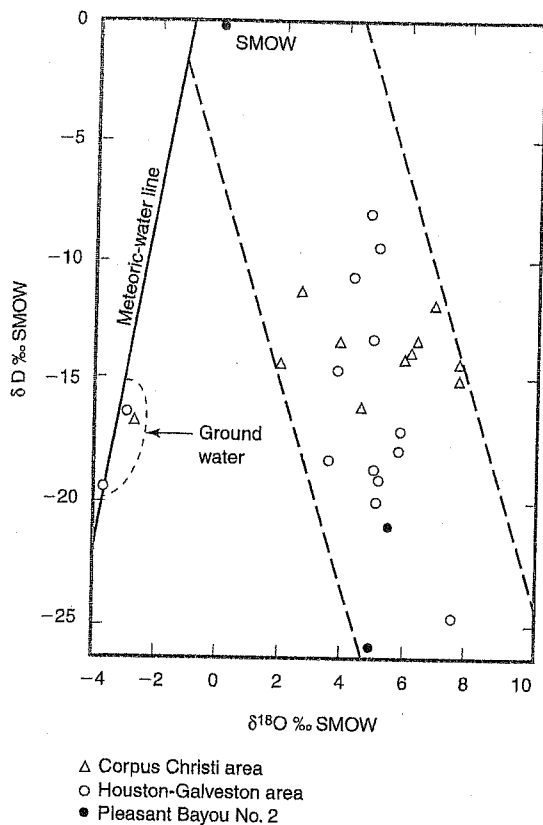
△ Corpus Christi area
○ Houston-Galveston area
● Pleasant Bayou No. 2

Figure 4.8 Isotopic composition of formation waters from northern Gulf of Mexico Basin. Trend of decreased δD values with increasing $\delta^{18}O$ values goes through SMOW and away from the meteoric water line. (From Kharaka, 1986, p. 176.)

In contrast to conclusions drawn from stable isotope analyses, some recent studies of Br-Cl-Na systematics (Figure 4.9) suggest that at least some brines in sedimentary basin originated from seawater evaporation, and that the original ocean water has not been completely replaced by meteoric water, although it may have been diluted. **Br-Cl-Na systematics** is the study of similarities and differences amongst the composition and concentration of these ions (Bromine, Chlorine, and Sodium) in geologic fluids. The main utility of Br-Cl-Na systematics is that the method can be used to discriminate between brines formed from

evaporation of seawater, and those formed by dissolution of evaporites. As seawater begins to evaporate, the ratios Cl/Br and Na/Br remain constant (Figure 4.9). When the brine concentration reaches about 162 g/liter, halite (NaCl) begins to precipitate and the ratios Cl/Br and Na/Br begin to decrease as both Na and Cl are removed by halite precipitation while Br remains dissolved. Thus brines formed by evaporation of seawater tend to have high concentrations of bromine. In contrast, brines formed through the dissolution of halite by freshwater tend to have low concentrations of bromine. Walter et al. (1990) and Stueber and Walter (1994) studied pore fluids from the Illinois Basin (Figure 4.10) and concluded on the basis of Br-Cl-Na systematics that remnant marine fluids had contributed substantially to overall pore fluid composition, especially in older rocks. These data indicate that stable isotope plots, which extrapolate back to the meteoric water line are evidence of dilution by meteoric waters, not complete replacement.

4.6. PHYSICAL PROPERTIES OF WATER.

4.6.1. Phase Diagram for Water.

Water phase is determined by pressure and temperature (Figure 4.11). The point at which all three phases may coexist is the **triple point**. Under the high fluid pressures that may be characteristic of the subsurface, water may be liquid at temperatures well exceeding its boiling point ($\sim$100°C) at standard pressure. Below the **critical point** (Figure 4.11), liquid water and water vapor exist as distinct and separate phases. Above the critical point, a single supercritical fluid exists at all temperature and pressure conditions, and all physical, chemical and transport properties of water vary in a continuous manner with changing pressure or temperature—there are no discontinuities in these properties. The properties of water gradually become more liquid-like or more gas-like as temperature and/or pressure changes in the supercritical fluid (Bodnar and Costain, 1991, p. 983).
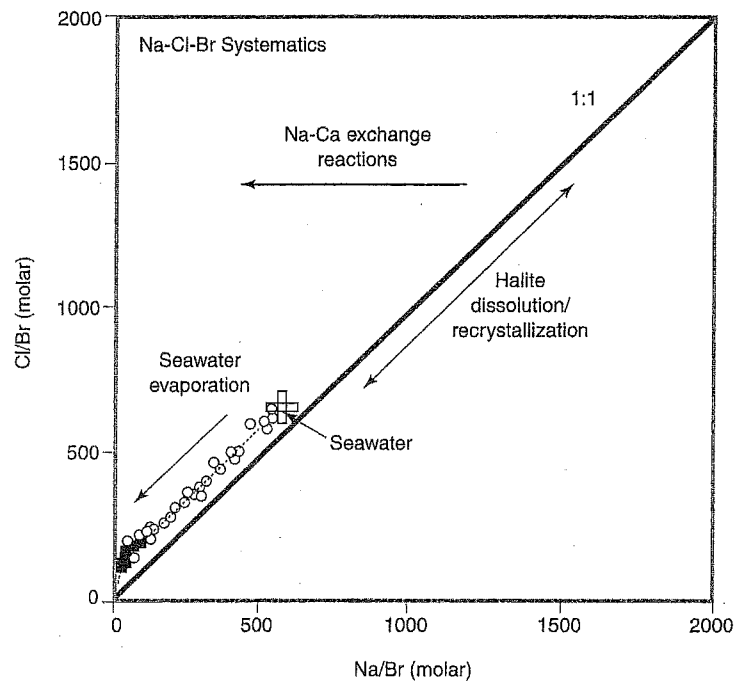
Figure 4.9 Na-Cl-Br (Sodium-Chlorine-Bromine) systematics.
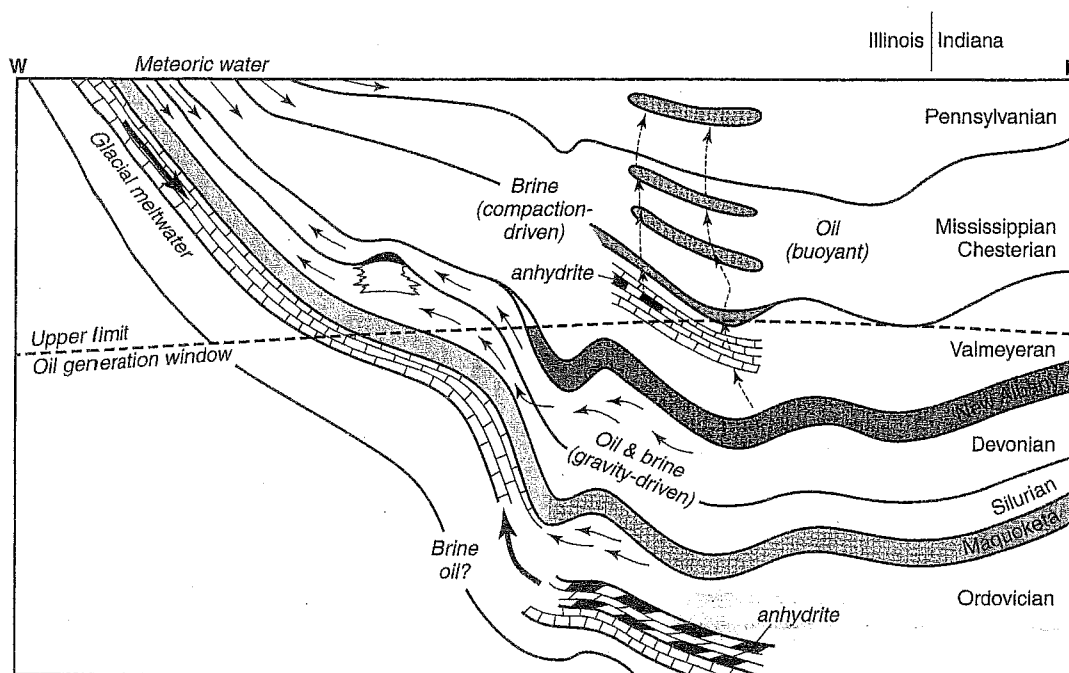(From Kesler et al., 1995, p. 641.)

Figure 4.10 Schematic cross-section through the Illinois Basin showing distribution of meteoric water and brine derived from seawater evaporation. Also shown are driving forces that include sediment compaction, topographic gradients, and buoyancy forces.
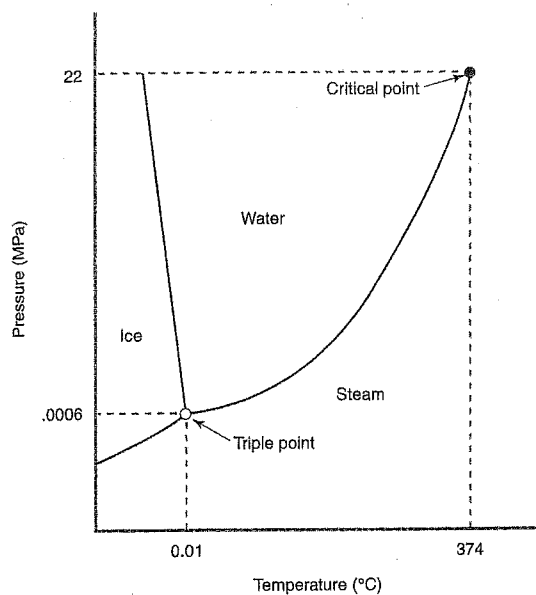(From Stueber and Walter, 1994, p. 1438.)

Figure 4.11 Phase diagram for water.

Near the critical point, the physical and thermodynamic properties of water reach maxima or minima and change rapidly with small changes in either temperature or pressure. As a consequence, small changes in pressure or temperature near the critical point may have large influences on a fluid's capacity for heat and mass transport. Buoyancy forces and fluid heat capacity become large, and the viscosity of the fluid is reduced. An increase in heat capacity and decrease in viscosity near the critical point imply that a fluid's capacity for heat and mass transport is at a maximum at or near the critical point.

Phase diagrams for the aqueous brines found in the Earth's crust may differ significantly from that for pure water (Figure 4.11). In many crustal environments, the physical properties and phases of aqueous brines in the crust are adequately represented by those of the H_2O-CO_2-$NaCl$ system (Bodnar and Costain, 1991, p. 983). Addition of $NaCl$ to H_2O causes the critical point to shift to higher temperatures and pressures, while addition of CO_2 causes the critical point to migrate to slightly lower temperatures but much higher pressures. The shift of the critical point due to the pres-

ence of dissolved solutes such as $NaCl$ or dissolved gasses like CO_2 may have important consequences for understanding geologic processes such as ore formation that rely upon heat and mass transport by moving fluids. For example, the region of optimum heat and mass transport for a 20% $NaCl$ solution by weight is in the neighborhood of ~560–620°C and 700–1100 bars, compared to ~400°C and 300 bars for pure water (Bodnar and Costain, 1991, p. 985).

4.6.2. Specific Heat Capacity, Heats of Fusion and Vaporization.

The **specific heat capacity** of a substance is the amount of energy or heat necessary to raise the temperature of a specified mass of that substance by a specified amount. The specific heat capacity (C, J-kg^{-1}-$°K^{-1}$) of pure water at 0°C and 1 atm pressure is

$$C = 4184 \ (J\text{-}kg^{-1}\text{-}°K^{-1}) \qquad (4.18)$$

Specific heat capacity may also be expressed in units of calories per gram per degree Celsius (cal-g^{-1}-$°C^{-1}$). To convert from cal-g^{-1}-$°C^{-1}$ to J-kg^{-1}-$°K^{-1}$, multiply by

$$1 \frac{cal}{g\text{-}°C} \times 4.184 \frac{J}{cal}$$
$$\times 1000 \frac{g}{kg} \times 1 \frac{°K}{°C} = 4184 \frac{J}{kg\text{-}°K} \qquad (4.19)$$

The **heat of fusion** is the amount of heat or energy necessary to change a specified mass of a substance from a solid to a liquid while maintaining a constant temperature and pressure. The heat of fusion of pure water is about 80 cal-g^{-1}. To convert to J-kg^{-1}, multiply by

$$80 \frac{cal}{g} \times 4.184 \frac{J}{cal} \times 1000 \frac{g}{kg} = 3.35 \times 10^5 \frac{J}{kg} \qquad (4.20)$$

The **heat of vaporization** is the amount of heat or energy necessary to change a specified mass of a substance from a liquid to a vapor while maintaining a constant temperature and pressure. The heat of vaporization of pure water is about 540 cal-g^{-1}. To convert to J-kg^{-1},

$$540 \frac{cal}{g} \times 4.184 \frac{J}{cal} \times 1000 \frac{g}{kg} = 2.26 \times 10^6 \frac{J}{kg}$$

(4.21)

4.6.3. Density.

The density of pure water at STP is about 1000 kg-m^{-3}. To convert kg-m^{-3} to g-cm^{-3}, multiply by

$$1000 \frac{kg}{m^3} \times 1000 \frac{g}{kg} \times \frac{1m^3}{10^6 cm^3} = 1 \frac{g}{cm^3} \quad (4.22)$$

Water density is affected by temperature, pressure, and salinity. Water density tends to *decrease* with *increasing* temperature, but *increase* with *increasing* pressure and salinity. In the Earth's crust, salinity and temperature tend to be more important in controlling fluid density than pressure (Phillips et al., 1981).

Temperature in the Earth's crust is controlled by the geothermal gradient and the ground surface temperature. The **geothermal gradient** is the rate at which temperature increases with depth. The geothermal gradient is largely determined by the thermal conductivity of crustal rocks and heat flow from the Earth's interior. Surface ground temperature is controlled by climate, and ranges from about 25°C near the equator to as low as −22°C at polar extremes. The mean annual air temperature for Earth is about 15°C, however, ground temperatures tend to be 2–3°C warmer than air temperatures, so the average ground surface temperature on Earth is about 17 to 18°C. The average geothermal gradient ranges from about 10°C-km^{-1} to as high as 60°C-km^{-1}. A nominal estimate of the average geothermal gradient on the continents is 25°C-km^{-1} (see Kappelmeyer and Haenel, 1974; Jessop, 1990).

As long as we are not in an unusual geologic situation, fluid pressure in the upper continental crust is determined simply by the weight of the overlying fluid as given by equation 2.23. Consider a fluid with a constant salinity of 5 molal that is about 22–23% TDS by weight. How does its density change with increasing depth in an area characterized by a typical ground surface temperature of 17°C and average geothermal gradient of

TABLE 4.3 Effect of Pressure and Temperature on Fluid Density

Depth (km)	Fluid Pressure (MPa)	Temperature (°C)	Fluid Density (kg-m^{-3})
1	10	42	1146
2	20	67	1125
3	30	92	1113
4	40	117	—
5	50	142	1092

25°C-km^{-1}? Using data given by Phillips et al. (1981), water density can be calculated as a function of pressure and temperature (Table 4.3). The tendency of *increasing* temperature to *decrease* fluid density is usually greater than the tendency of *increasing* pressure to *increase* fluid density. In other words, temperature is usually a more important determinant of fluid density in the Earth than pressure.

The above calculations show that a constant-salinity fluid would usually decrease in density with increasing depth and temperature in the Earth's crust. This situation could be gravitationally unstable; a buoyancy force would tend to promote the overturn of the less dense fluid. Whether or not the fluid in a given area overturns would depend on the geothermal gradient and the permeability of the rocks in that area, however, the situation illustrated above usually does not occur because salinity usually increases with depth. The increase of salinity with depth is sufficient to counteract the decrease of fluid density associated with temperature increases, and fluid density usually increases with increasing depth. The fluids found in the upper continental crust are thus usually stable, and should not spontaneously overturn. There are some exceptional circumstances where this generalization is violated. One example might be near an igneous intrusion where the thermal gradients and buoyancy forces due to thermal expansion would be unusually high.
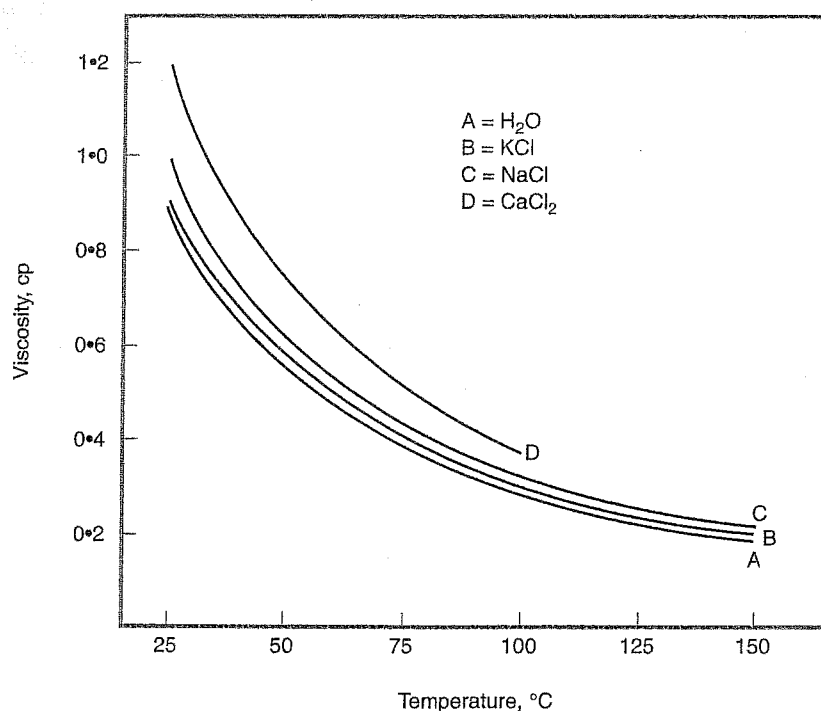
Figure 4.12 Viscosity of water and 1 molal solutions of NaCl, KCl, and CaCl, as a function of temperature.
(From Phillips et al., 1981, p. 24.)

4.6.4. Viscosity.

Viscosity is the property of a fluid that offers resistance to flow. More formally, viscosity (μ, kg-m^{-1}-s^{-1}) is defined as the constant of proportionality between the shear stress applied to a fluid and its deformation rate. In this text, the term viscosity means absolute or **dynamic viscosity**. **Kinematic viscosity** is the dynamic viscosity (μ) divided by fluid density (ρ).

The viscosity of pure water is strongly dependent on temperature (Figure 4.12). Empirically, we find that (Touloukian et al., 1975)

$$\mu = 2.4 \times 10^{-5} \times 10^{[248/(T+133)]} \quad \textbf{(4.23)}$$

where μ is viscosity in kg-m^{-1}-s^{-1} and T is temperature in °C.

Note that water viscosity decreases by a factor of ten from 0 to 150°C (Table 4.4). For an average geothermal gradient of 25°C-km^{-1}, 150°C corre-sponds to depths of about 5–6 km. The decrease of fluid viscosity with increasing temperature (and thus increasing depth) implies that, all other factors being equal, deep flow is promoted. Of course, all other factors are never equal, and the decrease of permeability with depth usually overshadows the decrease of fluid viscosity. But, a viscosity decrease of an order of magnitude or more is large enough to potentially have important implications for fluid flow in the upper crust. Salinity also has an effect on viscosity, but the effect of temperature is usually much greater (Figure 4.12). An alternative viscosity unit is the **poise**. One poise = 0.1 kg-m^{-1}-s^{-1}.

4.6.5. Surface Tension.

The water molecule (H_2O) is dipolar. While the overall electrical charge is zero, one end of the water molecule has a net negative charge, and the

TABLE 4.4	Effect of Temperature on Water Viscosity	
Temperature (°C)	Water Viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)
0	1.8×10^{-3}
50	5.4×10^{-4}
100	2.8×10^{-4}
150	1.8×10^{-4}

other end has a net positive charge. As a result, water molecules tend to stick together, with the positive end of one attracted to the negative end of another. **Surface tension** is the strength of the attractive force between liquid molecules. The surface tension of water causes it to form a film on its surface strong enough to support a steel needle. Surface tension also causes water to form drops, instead of spreading out evenly and smoothly. Amongst common liquids, only mercury has a greater surface tension. In addition to sticking to

each other, water molecules also tend to adhere to certain substances, such as glass. The combination of surface tension and adherence is responsible for the important phenomenon of capillarity that is discussed in chapter 6.

The surface tension of water can be decreased through the addition of a class of chemicals known as surfactants. Detergent and soap are common surfactants. The decreased surface tension that is produced by adding surfactants increases the cleaning ability of water by increasing its ability to spread, wet surfaces, and enter small spaces. The human body produces a natural surfactant in the lungs that aids respiration. Surface tension also decreases with increasing temperature. Thus hot water is a better cleanser than cold. The manufacture of lead shot takes advantage of the phenomenon of surface tension by pouring molten lead through a screen mesh at the top of a tower. By the time the lead drops have fallen to the bottom of the tower, surface tension has pulled them into a spherical shape.

REVIEW QUESTIONS

1. Define the following terms in the context of hydrogeology:
   a. ion
   b. cation
   c. anion
   d. salinity
   e. solute
   f. solution
   g. TDS
   h. weight percent
   i. ‰
   j. fresh
   k. brackish
   l. saline
   m. brine
   n. molality
   o. molarity
   p. mole
   q. Avogadro's number
   r. molecular weight
   s. atomic weight
   t. periodic table
   u. evaporite
   v. cationic shift
   w. membrane filtration
   x. isotope
   y. element
   z. proton
   aa. nucleus
   bb. neutron
   cc. mass spectrometer
   dd. stable isotope
   ee. fractionation
   ff. SMOW
   gg. meteoric water line
   hh. meteoric
   ii. radioactive isotope
   jj. decay constant

    kk. half-life
    ll. parent isotope
  mm. daughter isotope
   nn. TU
   oo. connate
   pp. juvenile
   qq. oceanic water
   rr. evolved water
   ss. Br-Cl-Na systematics
   tt. triple point
   uu. critical point
   vv. specific heat capacity
  ww. joule
   xx. Kelvin
   yy. heat of fusion
   zz. heat of vaporization
  aaa. geothermal gradient
  bbb. dynamic viscosity
  ccc. kinematic viscosity
  ddd. poise
  eee. surface tension

2. What percent of the volume of sedimentary basins consists of fluids?

3. What are the most important cations in the aqueous brines found in the Earth's crust? What is the most important anion?

4. What three factors control the composition of solutes in the aqueous brines found in the Earth's crust?

5. What is the level of TDS in seawater?

6. What is the molecular weight of H_2O? of $CaCl_2$? of $CaCO_3$?

7. A solution is 5% NaCl by weight. What is its molality?

8. A solution is 10% $CaSO_4$ by weight. What is its molality?

9. An NaCl solution has a molality of 3.0. What is its weight percent?

10. How does salinity change with increasing depth in sedimentary basins?

11. How many known examples are there of subsurface brines being produced by membrane filtration?

12. What process explains the major cation composition of aqueous brines in sedimentary basins?

13. What is the "master variable" that drives fluid-matrix interchanges and controls fluid composition?

14. What stable isotopes are most commonly analyzed in groundwater studies?

15. Why is meteoric water increasingly depleted in heavy isotopes with increasing latitude?

16. How has the isotopic composition of the oceans changed over the last million years?

17. A sample of groundwater from a well has a C^{14} concentration that is 1/8 that of local meteoric water. How much time has passed since this water entered the subsurface? What are likely sources of error in your estimate?

18. A sample of groundwater from a well has a Cl^{36} concentration that is 1/4 that of local meteoric water. How much time has passed since this water entered the subsurface?

19. What areas show enrichment in the He^3 isotope? What is the significance of He^3 enrichment?

20. A classification scheme divides terrestrial water into what three categories?

21. Why is the water found in sedimentary brines commonly enriched in O^{18}? Where does the O^{18} come from?

22. Do most of the aqueous brines found in sedimentary basins originate as meteoric or oceanic water? Summarize the evidence and arguments for each possibility.

23. Where is a fluid's capacity for heat and mass transport at a maximum?

24. What is the specific heat capacity of pure water at STP?

25. How much energy does it take to vaporize 100 g of ice at 0°C? (assume STP).

26. What is the average geothermal gradient on the continents? What is the range? What is

the average ground surface temperature on Earth?

27. What three factors affect fluid density in the crust? Which two factors are the most important?

28. Calculate the viscosity of water at 75, 100, and 125°C.

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Notation Used in Chapter Four

Symbol	Quantity Represented	Physical Units
C	specific heat capacity	$J\text{-}kg^{-1}\text{-}°K^{-1}$
c	constant of integration	dimensionless
D	number of daughter atoms	dimensionless
$\delta_{heavy}, \delta_{light}$	isotopic fractionation ratio	dimensionless
λ	radioactive decay constant	s^{-1}
M	molarity	$mole\text{-}m^{-3}$
m	molality	$mole\text{-}kg^{-1}$
μ	water viscosity	$Pa\text{-}s = kg\text{-}m^{-1}\text{-}s^{-1}$
MW	molecular weight	$kg\text{-}mole^{-1}$
N, N_o	number of atoms, number of atoms present at time zero	dimensionless
‰	parts per thousand	dimensionless
T	temperature in degrees Celsius	°C
t	time	s
$\tau_{1/2}$	half-life	s
TDS	total dissolved solids	dimensionless
W	weight percent solute	dimensionless