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Deep Fluids in the Continents: I. Sedimentary Basins

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NOMENCLATURE

Oil-field brine, basinal brine, basinal water, and formation water. A number of descriptive terms have been used in the literature to describe deep aqueous fluids in sedimentary basins. No satisfactory overall classification system exists, due to the fact that these waters can be assessed by several different criteria. These include: the salinity of the water, the concentration and origin of various dissolved constituents, and the origin of the H₂O, which is commonly different from that of the solutes. The following terminology has been extracted mainly from Hanor (1987) and from Kharaka and Thordsen (1992). The interested reader should also consult White *et al.* (1963) and Sheppard (1986).

Salinity. Synonymous with total dissolved solids (TDS), generally reported in milligrams per liter (mg l⁻¹) as determined either (1) directly by summing measured dissolved constituents or by weighing solid residues after evaporation, or (2) indirectly from electrical conductivity or spontaneous potential response.

Chlorinity. The dissolved chloride concentration, generally reported in mg l⁻¹.

Formation water. Water present in the pores and fractures of rocks immediately before drilling (Case, 1955). This term is used extensively in the petroleum industry, but has no genetic or age significance.

Brine. Water of salinity higher than that of average seawater, that is, more than 3.5 × 10⁴ mg l⁻¹ TDS. The majority of oil-field waters

are brines according to this definition, whereas only a small fraction could be classified as brines based on the definitions of Davis (1964) and Carpenter *et al.* (1974), which place the lower salinity limit of brines at 1 × 10⁵ mg l⁻¹.

Saline water. Water of salinity (1–3.5) × 10⁴ mg l⁻¹.

Brackish water. Water of salinity (0.1–1) × 10⁴ mg l⁻¹.

Freshwater. Water of salinity less than 1,000 mg l⁻¹.

Na–Ca–Cl-type water. In this classification scheme, the cations followed by the anions are listed in order of decreasing concentrations. The concentration, commonly in mg l⁻¹, of any ion listed must be ≥5% of the concentration of TDS. This is equivalent to ≥10% of the total of cations or anions (Kharaka and Thordsen, 1992).

Meteoric water. Water derived from rain, snow, streams, and other bodies of surface water that percolates in rocks and displaces interstitial water that may have been connate, meteoric, or of any other origin. Meteoric water in sedimentary basins is generally recharged at higher elevations along the margins of the basin. The time of last contact with the atmosphere is intentionally omitted from this definition, but may be specified to further define meteoric water. Thus, “Recent meteoric water,” “Pleistocene meteoric water,” or “Tertiary meteoric water,” would indicate the time of last contact with the atmosphere (Kharaka and Carothers, 1986).

Connate water. The word *connate* (Latin for “born-with”) was introduced by Lane (1908) to describe what he presumed to be seawater of unaltered chemical composition trapped in the pore spaces of a Proterozoic pillow basalt since the time of extrusion onto the seafloor. The term has since taken on a variety of meanings. While some authors prefer to use connate in its original sense (e.g., Hanor, 1987), others have used it to refer to waters that have been modified chemically and isotopically, but have been out of contact with the atmosphere since their deposition, although they need not be present in the rocks with which they were deposited (e.g., White *et al.*, 1963; Kharaka and Thordsen, 1992). Connate water may be specified as marine connate, if it was deposited with marine sediments.

5.16.1 INTRODUCTION

Pore water with salinities commonly ranging from 5,000 to $3 \times 10^5 \text{ mg l}^{-1}$ TDS (total dissolved solids) comprises ~20% (v/v) of most sedimentary basins (e.g., Hanor, 1987; Kharaka and Thordsen, 1992). This water, which is generally sampled while drilling for petroleum or is co-produced with oil and gas, has *in situ* temperatures of ~20 to >150 °C and fluid pressures of ~100 to >1,000 bar. The chemical and isotopic compositions of this water provide important information on the geochemical, hydrologic, thermal, and tectonic evolution of the Earth’s crust. Deep basinal water is an important crustal reservoir of mobile elements, such as the halogens, and fluid and solute fluxes between this water and surface continental water and the oceans are an integral part of the hydrologic and exogenic cycles. Water in sedimentary basins also acts as an intermediate reservoir for volatiles degassing from the lower crust and mantle and as such can be used to study deep-seated processes (Ballentine and O’Nions, 1991; Kennedy *et al.*, 1997).

The geochemistry of basinal waters provides insight into a number of important processes that occur within sedimentary basins, especially the (1) generation, transport, accumulation, and production of petroleum; (2) chemical aspects of mineral diagenesis, including dissolution, precipitation, and the alteration of sediment porosity and permeability; (3) transport and precipitation of copper, uranium, and especially lead and zinc in sediment-hosted Mississippi-Valley-type ore deposits; (4) tectonic deformation; (5) transport of thermal energy for geothermal and geopressured-geothermal systems; and (6) interaction, movement, and ultimate fate of large quantities

of liquid hazardous wastes injected into the subsurface (Hanor *et al.*, 1988; Kharaka and Thordsen, 1992; Tuncay *et al.*, 2000).

Interest in the geochemistry of formation waters has risen in the last 10 years for two main reasons. First, depleted petroleum fields and saline aquifers in sedimentary basins are being investigated as possible repositories for the storage of large amounts of anthropogenic CO₂ in the subsurface for thousands of years, thus moderating the anticipated future increases in the concentrations of atmospheric CO₂ and mitigating global warming, arguably the most important environmental issue facing the world today (Herzog and Drake, 1998; White *et al.*, 2003; Kharaka *et al.*, 2006a). The success of such operations will depend largely on understanding water–mineral–CO₂ interactions in the subsurface (Hitchon, 1996b; Gunter *et al.*, 2000). Second, petroleum production, drilling operations, and improperly sealed abandoned wells have caused major contamination of surface and groundwaters and soils in energy-producing states in United States, and probably throughout the world (Richter and Kreitler, 1993; Kharaka *et al.*, 1995; Kharaka and Dorsey, 2005). Contamination results mainly from the improper disposal of saline water produced with oil and gas (as of early 2000 in USA, 20–30 billion barrels per year) and from hydrocarbons, and produced water releases caused by equipment failures, vandalism, and accidents. Prior to the institution of federal regulations in the 1970s, produced waters in the USA were often discharged into streams, creeks, and unlined evaporation ponds. Because these waters are highly saline and may contain toxic metals, organic and inorganic components, and naturally occurring radioactive material (NORM), including ²²⁶Ra and ²²⁸Ra, they have caused salt scars and surface and groundwater pollution (Stephenson, 1992; Otton *et al.*, 1997, 2005; Kharaka *et al.*, 1999a, 2005).

The history of thought on the origin of saline subsurface water dates back to ancient times (White *et al.*, 1963; Hanor, 1983, 1987). The first comprehensive chemical analyses of basinal water only appeared in the late 1800s (e.g., Hunt, 1879). With the rapid development of the oil and gas industry in the early twentieth century, a large database for the composition of formation waters co-produced with hydrocarbons became available. This led to further development of hypotheses regarding the origin of basinal waters (Warren and Smalley, 1994; Gas Research Institute, 1995; Breit *et al.*, 2001).

Since the early 1970s there has been a significant expansion in our knowledge and understanding of the properties, interactions, and origin of water in sedimentary basins. This

has come about as a result of (1) improved sampling tools, including downhole samplers and the U-tube, and improved analytical methodologies that require only a small sample volume for the determination of multielements at very low concentrations of $\mu\text{g l}^{-1}$ or lower (Freifeld *et al.*, 2005; Harmon and Vannucci, 2006); (2) increased availability and utilization of data for a variety of stable and radioactive isotopes (Fritz and Fontes, 1980, 1986; Faure, 1986; Clark and Fritz, 1997; Cook and Herczeg, 2000; Chapter 5.15); (3) major improvements in the chemical thermodynamic data and procedures for applying them to brines and minerals (Johnson *et al.*, 1992; Shock, 1995; Helgeson *et al.*, 1998); and (4) development and application of detailed geochemical, hydrological, and solute transport codes (Kharaka *et al.*, 1988; Bethke, 1994; Wolery, 1992; Hanor, 2001; Birkle *et al.*, 2002; Thorstenson and Parkhurst, 2004). We now know that these fluids are much more mobile and that their interactions with rocks are much more complex than previously realized. Also, the discovery of high concentrations (up to $1 \times 10^4 \text{ mg l}^{-1}$) of reactive organic species in these waters has led to a new field of organic-inorganic interactions and has developed bridges between the fields of aqueous fluids, organic matter, and petroleum (Willey *et al.*, 1975; Crossey *et al.*, 1986; Hanor and Workman, 1986; Kharaka *et al.*, 2000).

In this chapter, we review what is known about the geochemistry of water in sedimentary basins in the continental and transitional continental oceanic crust. The emphasis is on water below the zone of shallow meteoric groundwater circulation, and on the main processes that are responsible for the modification of the chemical and isotopic composition of these waters including (1) mixing; (2) dissolution of evaporites, especially halite; (3) reflux and incorporation of bitterns, the residual water remaining after the precipitation of evaporites; (4) dissolution and precipitation of minerals other than evaporites; (5) interaction with rocks, principally clays, siltstone, and shale that behave as geological membranes; (6) activity of bacteria that can survive in sedimentary rocks at temperatures up to $\sim 80^\circ\text{C}$ (Carothers and Kharaka, 1978); (7) interactions with organics, including petroleum and solid organic matter; and (8) diffusion, especially in and near salt domes.

5.16.2 FIELD AND LABORATORY METHODS

Much of the detailed information that has been generated on the composition of deep

waters in sedimentary basins has come from the analysis of aqueous fluids co-produced with crude oil and natural gas. A total of ~ 3.5 million oil and gas wells has been drilled in United States alone since 1859; fewer than 1 million wells are, as of early 2000s, producers (Kharaka and Thordsen, 1992; Breit *et al.*, 2001).

Most sampling takes place at the wellhead rather than downhole. The fluids are therefore subjected to major reductions in temperature and pressure, to gas loss and to exposure to oxidizing conditions during sampling. The special methods that must be used in sample collection, preservation, and field and laboratory determinations of chemical components and isotopes in formation waters are detailed in Lico *et al.* (1982) and Kharaka *et al.* (1985).

Because of the importance of understanding water-rock-gas interactions in field experiments to investigate the potential for geologic storage of CO_2 in depleted petroleum fields and saline aquifers in sedimentary basins (Hovorka *et al.*, 2001, 2006), a more rigorous sampling protocol was carried out using evacuated and/or syringe-like downhole samplers (500–1,000 ml volume) that provided accurate data on water and gas compositions of the subsurface fluids (Kharaka *et al.*, 2006a). During the CO_2 injection, intensive fluid sampling was obtained from an observation well using a novel downhole U-tube system designed for this experiment to track the arrival of CO_2 (Freifeld *et al.*, 2005). The drilling and circulation fluids used were tagged with rhodamine WT (fluorescence is another good tracer) to allow for identification of uncontaminated formation water (Kharaka *et al.*, 2006b).

Wells selected for sampling in a petroleum field must meet the following criteria: they (1) have not been affected by water and CO_2 flooding or chemical treatment, including acidification; (2) have a single and narrow perforation zone; (3) produce large amounts of water relative to oil; (4) produce $>0.16 \text{ m}^3$ of water per $\sim 3 \times 10^4 \text{ m}^3$ of gas (10 barrels per million ft^3); and (5) have ports for sampling before the fluid enters a separator. In cases where the objective of the study is to determine disposal options for produced water, sampling from water disposal tanks may be appropriate to determine the physical and chemical properties of the mixture.

The fluids from petroleum wells are collected in prewashed and prerinsed 8 or 20 l carboys with a bottom spigot. Water and oil require from 5 min to several hours to separate, depending on the temperature, proportion of water, and the composition of oil and water. Immediately after separation of water from oil, the water is passed through glass wool to

remove solids and oil droplets before the samples are collected in separate 125 ml flint-glass bottles with polyseal caps for the field determination of conductance, pH, Eh, alkalinity, and H₂S, and for laboratory determination of the carbon isotopes (Lico *et al.*, 1982).

Filtration and preservation of water samples immediately after collection is important to prevent loss of constituents through precipitation and sorption. Filtration through a 0.45 µm filter, using either compressed nitrogen or compressed air as the pressure source, is adequate for determination of the major cations and all of the anions. Filtration through a 0.1 µm filter, however, is required for aluminum, mercury, and other trace metals, because colloidal oxyhydroxides of iron and manganese and clay particles can pass through larger pores; these particles would then dissolve upon acidification, increasing the concentration of these trace metals (Kennedy *et al.*, 1974; Kharaka *et al.*, 1987). Filtration and field chemical determinations are better performed in a mobile laboratory equipped with pH meters, a spectrophotometer, and filtration, titration, and other field equipment. Because of the presence of oil, the measurement of Eh is difficult for oil-field waters, even using flow-through cells (Kharaka *et al.*, 1987).

Samples collected for heavy and trace metals (iron, manganese, lead, zinc, and mercury) analyses require additional care to minimize contact of the samples with air during collection and filtration. This is required to prevent oxidation of metals (e.g., Fe²⁺) and their precipitation as oxyhydroxides leading to co-precipitation and adsorption of other metals. Contact with air is minimized by (1) flushing the air in the carboy with nitrogen or argon or even natural gas; (2) inserting the tubing from the wellhead as far down in the carboy as possible through a hole drilled through the cap; (3) filling the carboy completely with the fluids; (4) plugging the hole in the cap with a rubber stopper after the carboy is filled; (5) minimizing the length of the tygon tubing connecting the filtration unit to the carboy and filling it with formation water prior to filtration; (6) discarding the first 250 ml of the filtered sample; and (7) using the next liter of filtered water to rinse the collection bottles (Kharaka *et al.*, 1987).

Samples for the analysis of dissolved organic compounds are filtered through a 0.45 µm Teflon or silver filter and stored in amber bottles fitted with Teflon inserts in the caps. Stainless-steel filtration units and copper or metal tubing are used for collection and filtration of these samples. Mercuric chloride (40 mg l⁻¹ mercury) is added as a bactericide and the filtered samples are stored at ~4 °C until analysis.

New methodologies for the laboratory analysis of cations and metals include the use of inductively coupled plasma emission spectrometry (ICP/ES) or the combination of ICP with mass spectrometry (ICP/MS) (e.g., Ivahnenko *et al.*, 2001; Harmon and Vannucci, 2006). The advantages of plasma techniques include (1) a wide and linear dynamic concentration range; (2) multielement capability; and (3) relatively free of matrix interferences. The use of ion chromatography (IC), gas chromatography (GC), and GC/MS has increased for the analysis of anions and dissolved organics (Barth, 1987; Kharaka and Thordsen, 1992; Ivahnenko *et al.*, 2001).

Chemical data from drill-stem and wire-line tests are always suspect, because of likely contamination with drilling fluids and of mixing with water from different production zones. Chemical analyses of water from carbonate reservoirs should be carefully examined for signs of contamination. These reservoirs are often stimulated by acid injection, and the contaminating effects of the acid are noticeable for months after treatment. Properly evaluated, chemical data from producing wells may provide concentration values for a limited number of major cations and anions (Hitchon, 1996a; Breit *et al.*, 2001). However, the concentrations of many of the dissolved constituents needed for evaluating mineral diagenesis, including field pH, dissolved silica, aluminum, and inorganic alkalinity, are not generally available (Kharaka and Thordsen, 1992).

5.16.2.1 Water from Gas Wells

Chemical analyses from gas wells, especially those from higher-temperature reservoirs, may not represent the true chemical composition of formation waters from the production zone because of dilution by condensed water vapor produced with natural gas. Water vapor condenses because of the drop in temperature and pressure as the gases expand on entering the well. This problem is not generally recognized and is probably responsible for many of the reports of fresh or brackish water in petroleum reservoirs (Kharaka *et al.*, 1985).

5.16.2.2 Information from Wire-Line Logs

The salinity of formation waters is often calculated using electrical resistivity and spontaneous-potential (SP) logs, and the values obtained are reasonable, except in geopressed zones with high shale content (Hearst and

Nelson, 1985; Rider, 1996). An alternative technique for calculating salinities of waters in geopressed shaly sediments makes combined use of γ ray, conductivity, and porosity logs (Revil *et al.*, 1998). It is often possible to determine vertical variations in salinity over a distance of several kilometers from a single log.

5.16.3 CHEMICAL COMPOSITION OF SUBSURFACE WATERS

5.16.3.1 Water Salinity

The salinity of pore waters in sedimentary basins varies by approximately five orders of magnitude from a few milligrams per liter in shallow meteoric flow regimes to over $4 \times 10^5 \text{ mg l}^{-1}$ in evaporite-rich basins such as the Michigan Basin, USA, and the Williston Basin, USA–Canada. The most saline formation water reported in the literature is a $6.43 \times 10^5 \text{ mg l}^{-1}$ Ca–Na–Cl-type brine from the Salina formation of the Michigan Basin (Case, 1945). However, not all sedimentary basins contain brines. Well-known examples include the evaporite-free Central Valley, CA, USA (Kharaka and Berry, 1974; Fisher and Boles, 1990), and the Pattani (Lundegard and Trevena, 1990) and Mahakam (Bazin *et al.*, 1997a) Basins, Indonesia, where salinities are in general that of seawater or lower.

Salinities in sedimentary basins generally increase with depth, but the rate of increase is highly variable (Table 1 and Figure 1). The variations can be large in waters from different areas of the same basin (Table 2) and even in waters from the same petroleum field (Figure 2). Salinities in some basins, such as the Central Valley, California, and the southern Louisiana and southeastern Texas Gulf Coast, show salinity reversals with depth. Nearly constant water salinities ($(1.9\text{--}2.4) \times 10^4 \text{ mg l}^{-1}$) have been documented over a depth interval of 700–2,800 m in widely varying lithologies in the North Slope, Alaska (Kharaka and Carothers, 1988).

5.16.3.1.1 Controls on salinity

Spatial variations in salinity put important constraints on the interpretation of the origin of basinal brines and on the quantification of diffusion, advection, and dispersion, which are responsible for subsurface solute transport. For example, lateral salinity plumes have been mapped around a number of shallow Gulf Coast salt domes (e.g., Bennett and Hanor, 1987), providing direct evidence for the dissolution

of halite as the source of salinity in these areas. Salinities often increase with depth in basins where there is deep bedded salt and/or deep brines derived from the subaerial evaporation of seawater (Posey and Kyle, 1988; Kharaka and Thordsen, 1992). Diffusive transport (Manheim and Bischoff, 1969; Kharaka, 1986) and dispersive mixing of halite-saturated waters and bittern brines with ambient formation waters and the near-surface recharge of low-TDS meteoric waters into basins (e.g., McIntosh *et al.*, 2002) produce formation waters with a wide range in salinity. These field observations have led to studies involving numerical modeling to investigate the mechanisms and rates of solute transport driven by salt dissolution (e.g., Kharaka, 1986; Ranganathan and Hanor, 1987).

There is also field evidence that halite-derived brines can be transported over long distances in sedimentary basins. For example, the chemical compositions of waters from the Houston–Galveston area, Texas, and several other areas in the northern Gulf of Mexico basin indicate dissolution of halite (Kharaka *et al.*, 1985; Macpherson, 1992). However, in a number of these areas, there are no known salt domes within 50 km of the sampled sites. Large-scale fluid advection is probably the main mechanism for the transport of dissolved species there, because large fluid potential differences are present in the formations, and numerous faults can act as fluid conduits. Recent advances in quantitative basin modeling (e.g., Ortoleva *et al.*, 1995; Garven, 1995; Person *et al.*, 1996; Wilson *et al.*, 1999) have shown that fluid flow and solute transport can take place on the scale of hundreds of kilometers.

5.16.3.2 Major Cations

Sodium is the dominant cation in oil-field waters. It generally constitutes 70% to >90% of the total cations by mass (Tables 1–3). Calcium is generally the second most abundant cation. Its concentration can rise, especially in Na–Ca–Cl-type waters, to values of up to $\sim 5 \times 10^4 \text{ mg l}^{-1}$ (Table 1). This increase in its concentration with salinity can, however, be different for different parts of the same basin or different basins. The concentrations and proportions of magnesium are generally much lower than those in ocean water and decrease with increasing subsurface temperatures. The concentrations and proportions of strontium, barium, and iron are generally higher than those in ocean water and increase with increasing calcium concentration and chlorinity. The

Table 1 Chemical composition (mg l⁻¹) of formation waters from Sacramento and San Joaquin Valleys, California; North Slope, Alaska; and the central Mississippi Salt Dome Basin, Mississippi.

	<i>Sacramento</i>			<i>San Joaquin</i>		<i>North Slope</i>		<i>Central Mississippi</i>	
	<i>Grimes</i>	<i>Malton-Black Butte</i>	<i>San Emidio Nose</i>	<i>Wheeler Ridge</i>	<i>Kettleman North Dome</i>	<i>Barrow</i>	<i>Prudhoe Bay</i>	<i>Reedy Creek</i>	<i>West Nancy</i>
Sample no.	81-NSV-15	81-NSV-1	74-SEN-3	75-WR-5	912-1	78-AX-52	78-AX-54	84-MS-11	84-MS-1
Well name	GOU4#2	19-1	21-15	21-28	323-21	S. Barrow 5	Arco 13	W. M. Geiger	W. L. West
Production zone ^a	Forbes	Forbes	Reef Ridge	Tejon	Lower McAdams	Barrow Sandstone	Sadlerochit Group	Rodessa	Smackover
Depth (m) ^b	2,074	1,524	3,337	2,691	3,520	728	2,820	3,486	4,428
Temperature (°C)	65	58	149	117	141	16	94	102	118
TDS ^c	18,600	21,400	10,900	44,300	10,000	22,100	21,900	320,000	275,000
Li	0.32	0.35	1.95	1.95	3.05	2.1	4.0	35	74
Na	6,830	7,510	4,000	7,450	3,760	7,980	7,600	61,700	54,800
K	35.5	28.4	620	135	92.4	3.0	86	990	6,500
Mg	72	148	7.0	27	3.4	67	20	3,050	3,350
Ca	182	331	67	5,550	30.7	119	182	46,600	33,900
Sr	14.3	18.8	8.0	187	4.4	16.1	20.2	1,920	1,670
Ba	6.4	4.6	4.2	12	3.98	175	3.8	60	48
Fe	0.58	54	0.36	2.8	0.31	5.5	63	465	0.47
NH ₃	34	30	73	32	8.9	19	17	34	119
F			3.0	2.0	0.3	1.6	1.5	1.5	11.5
Cl	11,000	12,700	3,460	21,450	4,680	11,800	10,600	198,000	170,000
Br	44	74	57	80	45	62	54	2,020	2,080
I	30	66	14	46	27	28	19	17	80
HCO ₃ ^d	359	417	2,870	2,210	1,190	1,710	2,930	206	197
SO ₄	<0.5	0.9	38	50	0.5	n.d.	69	64	161
H ₂ S	0.07	<0.1	0.02	0.11	3.02	<0.1	<0.1	<0.02	57.4
SiO ₂	31	18	109	46	128	11	62	28	34
B			92	600	43	42	158	59	342
pH	7.6	7.6	7.7	6.9	7.4	7.2	6.5	5.08	5.48

Source: Kharaka and Thordsen (1992).

^aProduction zones are those used by oil companies. ^bDepth is depth below ground level of midpoint of perforation. ^cTDS is calculated total dissolved solids. ^dHCO₃ is field-titrated alkalinity and includes organic and inorganic species.

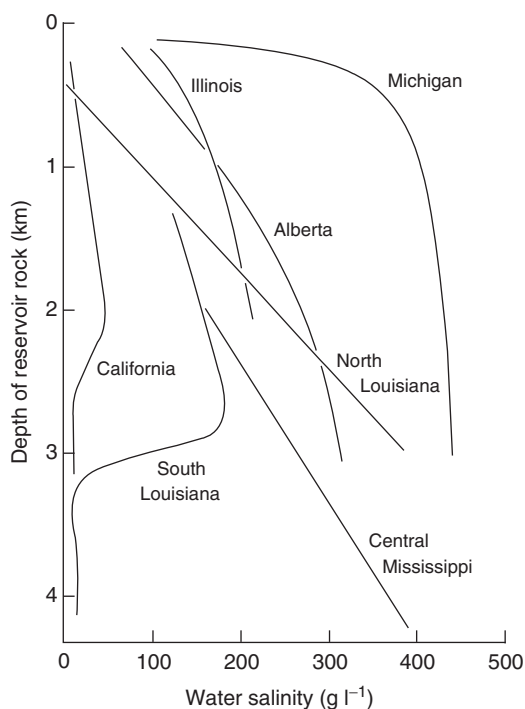


Figure 1 Salinity distribution with depth of the reservoir rocks from several basins in North America. Note the different trends and the reversal of salinity in California and south Louisiana. Source: [Kharaka and Thordsen \(1992\)](#).

ratios of lithium, potassium, rubidium, and cesium to sodium generally increase with increasing subsurface temperatures, but again, there is a great deal of scatter in the data and their proportions vary from basin to basin ([Kharaka and Thordsen, 1992](#); [Hanor, 2001](#)).

Plots of cation concentrations versus chloride differ in slope between the monovalent and divalent cations ([Hanor, 1996a, 2001](#)). Both sodium ([Figure 3](#)) and potassium show an approximately 1:1 slope on log-log plots, but the divalent cations, magnesium, calcium ([Figure 4](#)), and strontium, show approximately 2:1 slopes. This difference in the rate of increase of sodium and calcium with salinity gives rise to the observed progression from Na-Cl to Na-Ca-Cl to Ca-Na-Cl waters with increasing salinity in basinal waters ([Hanor, 1987](#); [Wilson and Long, 1993](#); [Davisson and Criss, 1996](#)).

It is generally agreed that most of the chloride in basinal brines has been derived from some combination of the subsurface dissolution of evaporites (e.g., [Kharaka et al., 1985](#); [Land, 1997](#)) and the entrapment and/or infiltration of evaporated seawater (e.g., [Carpenter, 1978](#); [Kharaka et al., 1987](#); [Moldovanyi and Walter, 1992](#)). Dissolution of halite produces waters dominated by sodium chloride. Evaporation of seawater produces waters having the general

trends shown for ion-Br ([Figure 5](#)), Na-Cl ([Figure 3](#)) and Ca-Cl ([Figure 4](#)), but most formation waters have neither the cation (nor anion) composition of an NaCl solution or of evaporated modern seawater ([Stueber and Walter, 1991](#); [Hanor, 2001](#)). During the diagenetic evolution of formation water, there is up to an order of magnitude gain in calcium and strontium (not shown) and up to an order of magnitude loss in magnesium and potassium relative to evaporated modern seawater ([Figure 6](#)). As brines derived from the dissolution of halite begin to evolve diagenetically, dissolved sodium is lost and dissolved potassium, magnesium, calcium, and strontium are gained. The observed approximately 1:1 and 2:1 variations in the concentrations of cations versus chloride can be accounted for largely by rock buffering ([Hanor, 2001](#)).

Unlike magnesium, calcium, and strontium, there is no significant trend between dissolved barium and chlorinity or salinity. There is, however, a general inverse correlation between barium and SO_4^{2-} ([Figure 7](#)), which is consistent with the hypothesis that equilibrium with respect to barite (BaSO_4) may be the factor controlling barium concentrations ([Kharaka and Berry, 1974](#); [Hanor, 2001](#)).

5.16.3.2.1 Dissolved aluminum

Dissolved aluminum concentrations in subsurface waters are generally less than 0.5 mg l^{-1} ; reported higher values are probably due to improper sample treatment in the field ([Kharaka et al., 1985, 1987](#)). Determination of dissolved monomeric aluminum requires field filtration through a $0.1 \mu\text{m}$ or smaller-size filter to prevent contamination with fine clay particles, followed by field solvent extraction as detailed in [Lico et al. \(1982\)](#). There are insufficient data of high quality at present to establish the systematics of dissolved aluminum in most deep sedimentary basins. An alternative approach has been to calculate values for dissolved aluminum using geochemical modeling, assuming fluid equilibrium with respect to muscovite, microcline, albite, or other aluminosilicate minerals that are known to be present in the reservoir rocks. For example, [Palandri and Reed \(2001\)](#) have calculated total dissolved aluminum values from 1×10^{-4} to $1 \times 10^{-2} \text{ mg l}^{-1}$ for waters from a number of sedimentary basins based on the assumption of equilibrium. Similar calculations by [Bazin et al. \(1997a, b\)](#) for the North Sea and the Mahakam Basin, Indonesia, yield total aluminum concentrations on the order of $3 \times 10^{-3} \text{ mg l}^{-1}$.

The solubility of aluminum in natural waters is commonly treated in terms of $\text{Al}_{(\text{aq})}^{3+}$, the

Table 2 Chemical composition (mg l⁻¹) and production data of formation waters in the geopressed zones from coastal Texas and Louisiana.

	<i>Lafayette, LA</i>		<i>Houston-Galveston, TX</i>		<i>Corpus Christi, TX</i>		<i>McAllen-Pharr, TX</i>	
	<i>Weeks Island</i>	<i>Tigre Lagoon</i>	<i>Chocolate Bayou</i>	<i>Halls Bayou</i>	<i>Portland</i>	<i>East Midway</i>	<i>Pharr</i>	<i>La Blanca</i>
Sample no.	77-GG-19	77-GG-55	76-GG-7	76-GG-24	76-GG-63	77-GG-73	77-GG-73	77-GG-117
Well name	St.Un. A#9	Edna Delcambre #1	Angle #3	Houston “FF”#1	Portland A-3	Taylor E-2 Lower Frio	Kelly A-1	La Blanca #12
Production Zone ^a	S-Sand	Sand #3	Upper Weiting	Schenck	Morris		Marks	7,150 Sand
Depth (m) ^b	4,275	3,928	3,444	4,161	3,514	3,662	3,018	2,903
Temperature (°C) ^c	117	114	118	150	123	128	127	148
Pressure ^d	43.1	75.8	52.4	80.0	58.0	62.2	52.4	56.6
Fluid production ^e								
Oil/condensate	21.9	0	0.5	3.8	4.8	2.7	0	0.3
Water	56.0	633	6.7	57.9	7.5	0.2	7.1	51.0
Gas	6.1	7.9	5.1	70.8	25.1	4.9	3.2	17.1
TDS ^f	235,700	112,200	73,300	58,100	17,800	36,000	36,600	7,500
Na	78,000	40,000	26,500	20,500	6,500	13,250	9,420	2,680
Li	16	7.1	9.9	15	3.6	4.2	7.5	1.2
K	1,065	265	400	180	68	72	240	46
Rb	3.4	0.8	0.4	0.9	0.3	0.5	0.8	0.1
Cs	11.8	3.5					2.9	0.3
Mg	1,140	270	220	170	15	48	18	3.3
Ca	10,250	1,860	2,000	800	89	330	4,225	150
Sr	920	320	365	170	7.0	23	256	9.6
Ba	185	8.2	290	59	1.4	13	27	1.5
Fe	84	0.4	10.2	22	2.3	1.6	4.1	<0.1
Cl	143,000	67,900	42,700	34,500	9,270	21,000	22,000	3,950
F	0.8	0.8	0.8		1.5	7.3	3.9	5.7
Br	419	63	52	32	19	45	78	15
I	18	26	16	11	25	45	22	16
B	44	57	35	91	62	35	105	117
NH ₃	100	69	29	13	5.8	13.5	21.5	4.2
H ₂ S	0.4	0.5	1.2	1.4	<0.1	0.04	<0.1	<0.1
HCO ₃ ^g	450	1,050	455	409	1,600	1,180	114	400
SO ₄	6.4	220	2.7	16	110	42	7.0	57
SiO ₂	48	57	87	110	93	132	90	88
pH	6.2	6.3	5.9	6.8	6.8	6.4	6.8	7.3

Source: [Kharaka and Thordsen \(1992\)](#).^a Production zones are names used by oil companies. ^b Depth is depth below ground level of midpoint of perforation. ^c Temperature is measured subsurface temperature. ^d Pressure is original bottom-hole pressure in MPa (1 psi = 6.9 kPa). ^e Fluid production is in m³ d⁻¹. ^f TDS is calculated total dissolved solids. ^g HCO₃ is the field titrated alkalinity and includes organic and inorganic species.

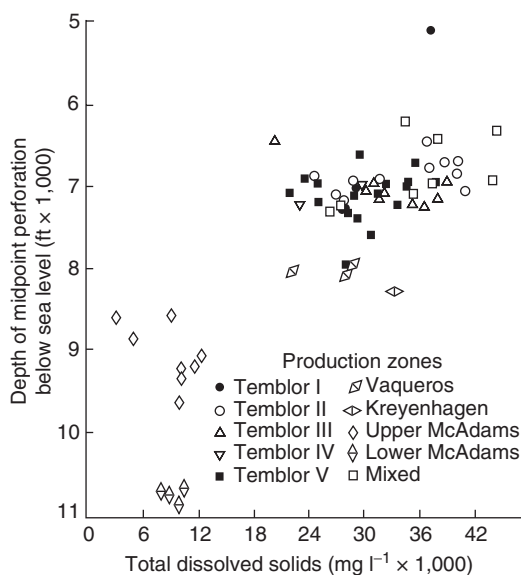


Figure 2 Distribution of salinity of formation waters from Kettleman North Dome oil field, California. Note the much lower salinity of water in the deeper McAdams Formation compared to Temblor Formation. Source: [Kharaka and Berry \(1974\)](#).

aluminum fluoride $\text{AlF}_{n(\text{aq})}^{3-n}$ and hydroxide complexes $(\text{Al}(\text{OH})_{n(\text{aq})})^{3-n}$. However, thermodynamic calculations by [Kharaka et al. \(2000\)](#) show that organic acid anions, especially dicarboxylic acid anions, form strong complexes with aluminum. Thermodynamic calculations by [Tagirov and Schott \(2001\)](#) show that in neutral to acidic fluids that contain dissolved fluoride in excess of 1 mg l^{-1} , the Al–F complexes $\text{AlF}_{n(\text{aq})}^{3-n}$ should dominate aluminum speciation at temperatures below 100°C and that hydroxy–fluoride complexes of aluminum, especially $\text{Al}(\text{OH})_2\text{F}_{(\text{aq})}^0$ and $\text{AlOHF}_{2(\text{aq})}^0$, should be dominant at temperatures of 100 – 400°C . Calculations by these authors show that fluoride concentrations of 2 mg l^{-1} , which are common in basinal waters ([Kharaka and Thordsen, 1992](#); [Worden et al., 1999](#)), could be enough to increase total aluminum concentrations as much as two orders of magnitude. Such an increase would adjust calculated aluminum concentrations in the above studies to values on the order of 0.01 – 1.0 mg l^{-1} . These values are similar to the range of aluminum values of 0.04 – 0.37 mg l^{-1} determined by direct chemical analysis by [Kharaka et al. \(1987\)](#) in the brines from Mississippi Salt Dome Basin, USA.

5.16.3.2.2 Water pH

There is a general decrease in reported pH values with increasing chlorinity, and formation

waters become progressively more acidic. It should be noted that the reported pH values were made in the field or in the laboratory on fluids at Earth surface conditions and are uncorrected for *in situ* pressure–temperature (P – T) conditions and the possible loss of volatiles, especially CO_2 . The true *in situ* pH values of deep subsurface fluids are largely unknown, but can be computed from field measurements of pH that have been corrected by titration with the lost CO_2 ([Kharaka et al., 1985](#)) or on the basis of assumed equilibrium relations with calcite under subsurface conditions ([Merino, 1975, 1979](#); [Palandri and Reed, 2001](#)). The loss of acid volatiles, such as CO_2 , generally increases pH by 1–2 pH units ([Kharaka et al., 1985](#)). However, many of the values for the *in situ* pH of highly saline waters of the Smackover formation, Arkansas, calculated on the assumption of fluid equilibrium with respect to calcite, are substantially higher than field pH values ([Moldovanyi and Walter, 1992](#)).

5.16.3.2.3 Dissolved silica

Silica concentrations in formation waters range from ~ 10 to 200 mg l^{-1} as SiO_2 and are controlled primarily by the solubilities of quartz, chalcedony, or cristobalite, which are dependent on subsurface temperature and, to a lesser extent, on pressure ([Kharaka and Mariner, 1989](#)). Many authors have noted that although quartz is a nearly ubiquitous phase in sedimentary basins, many basinal waters are not in thermodynamic equilibrium with quartz ([Land and Macpherson, 1992b](#)). The slow precipitation kinetics of quartz at low to moderate basinal temperatures results in fluid equilibration with metastable polymorphs of silica such as Opal-A and Opal-CT ([Bjørlykke and Egeberg, 1993](#)) or with ultramicrocrystalline ($< 0.02 \text{ mm}$) quartz ([Azaroual et al., 1997](#)). Pore waters can become greatly supersaturated with respect to quartz ([Hutcheon, 2000](#)). According to [Kharaka and Mariner \(1989\)](#) and [Bjørlykke et al. \(1995\)](#) quartz equilibrium is achieved when temperatures exceed $\sim 70^\circ\text{C}$. In the Mahakam Basin, Indonesia, quartz equilibrium temperatures are on the order of 100 – 120°C ([Bazin et al., 1997a](#)).

5.16.3.2.4 Boron

The boron cation, B^{3+} , exists in aqueous solution as undissociated boric acid $\text{B}(\text{OH})_3$ and as the borate ion $\text{B}(\text{OH})_3^-$. Formation waters with pH values < 9 favor $\text{B}(\text{OH})_3$ as the predominant species, because the pK values for

Table 3 Chemical composition (mg l⁻¹) of formation waters from High Island Field, offshore Texas.

Sample # ^a	83-TX-1	83-TX-2	83-TX-3	83-TX-5	83-TX-6	83-TX-7	83-TX-8	83-TX-9	83-TX-10	83-TX-11	83-TX-12
Well name	A-11A	A-11B	A-10A	A-9A	C-8A	C-14A	B-14A	B-2A	A-14B	A-12A	A-45-1
Depth (m) ^b	2,045	1,876	2,184	2,140	1,849	1,838	1,789	1,741	2,216	2,052	3,719
Temperature (°C) ^c	70	55	66	67	53	52	50	49	77	64	98
TDS ^d	74,000	80,000	61,000	159,000	44,000	39,000	138,000	92,000	63,000	88,000	91,000
Li	1.79	1.97	1.74	5.03	0.63	0.58	4.89	2.21	1.79	2.25	5.50
Na	26,300	28,400	19,800	53,700	15,400	13,300	47,700	31,800	22,300	30,400	30,900
K	160	172	139	244	110	103	250	167	143	183	271
Rb	0.15	0.16	0.12	0.24	0.08	0.10	0.19	0.14	0.17	0.16	0.39
Cs	0.09	0.07	0.07	0.29	0.03	0.04	0.24	0.15	0.07	0.14	0.21
Mg	788	869	287	1,270	499	349	1,040	1,010	363	873	482
Ca	1,320	1,370	1,030	3,810	679	850	2,840	2,250	1,130	2,010	2,690
Sr	97	119	59	346	36	27	238	147	66	129	146
Ba	77	102	75	316	40	52	256	171	90	113	200
Mn	0.28	0.19	0.16	0.60	0.09	0.23	0.25	0.43	0.29	0.43	2.63
Fe	7.4	5.8	1.7	17.2	4.3	3.4	11.3	4.4	13.9	5.0	6.5
NH ₃	140	152	97	206	73	83	182	170	112	182	121
B	23	25	31	33	16	16	40	18	37	24	42
Al (µg l ⁻¹)				<1	15				<1	<1	3
H ₂ S titration	0.25	0.68	0.85	0.08	0.00	0.51	0.68	0.51	0.85	0.93	0.76
H ₂ S electrode	0.04	0.02	0.06	<0.01	0.05	0.04	0.08	0.09	<0.01	0.08	<0.01
Organic (C)	54	60	162	78	73	82		36	209	47	933
Inorganic (C)	89	94	71	34	84	76		64	44	75	38
F	2.3	2.9	1.9	0.53	2.0	5.9	0.81	0.50	13.1	0.81	0.51
Cl	44,400	48,400	33,400	99,000	26,200	23,000	84,600	56,200	37,700	53,800	53,300
Br	143	88.9	102	177	102	287	90.9	108	185	113	118
I	4.0	4.7	4.5	3.1	5.1	4.3	4.6	4.4	5.6	4.3	6.2
SO ₄	12.4	9.9	16.0	7.4	9.9	9.9	0.5	0.4	14.8	15.3	11.5
SiO ₂	40.1	38.8	45.4	30.0	40.8	60.0	31.6	32.9	162	41.2	65.8
Alk ^e (HCO ₃)	494	546	568	308	480	443	293	350	460	402	2,140
pH	7.51	7.39	7.34	7.25	7.59	7.54	7.09	7.11	7.60	6.97	6.83

Source: Kharaka and Thordsen (1992).

^aSamples from Sigh Island 573 field (Mobil Oil) except sample 83-TX-12, which is from High Island 571 field (Columbia Gas). ^bDepth is that of midpoint of perforation below sea level (depth of water column is ~75 m). ^cTemperature is the measured subsurface temperature. ^dTDS = mg l⁻¹ total dissolved solids. ^eAlk is field-titrated alkalinity as HCO₃, and comprises organic as well as inorganic species.

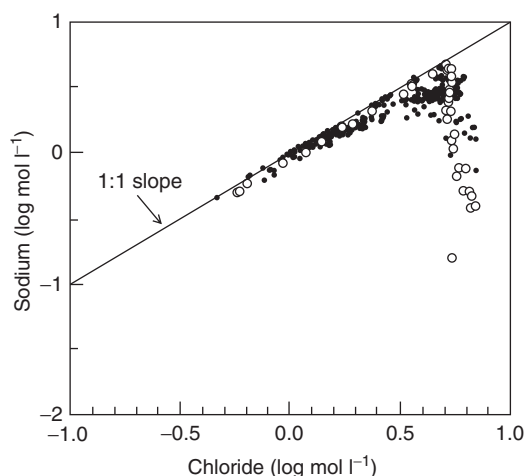


Figure 3 Concentrations of Na in basinal brines as a function of Cl (solid dots). Open circles represent Na-Cl variations in evaporated seawater. Source: Hanor (2001).

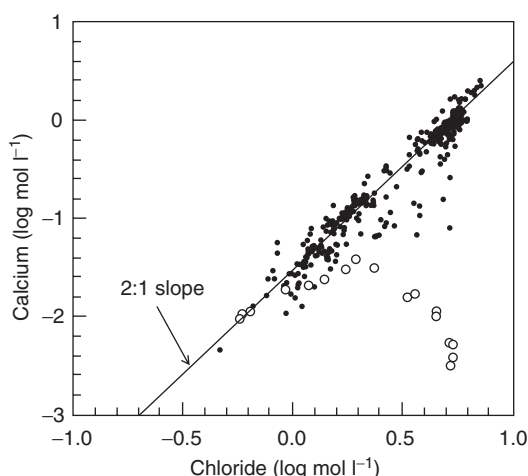
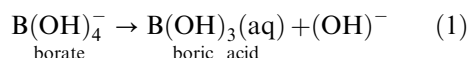


Figure 4 Concentrations of Ca in basinal brines as a function of Cl (solid dots). Open circles represent Ca-Cl variations in evaporated seawater. Source: Hanor (2001).

following reaction



are 4.77 at 25 °C, and 3.42 at 100 °C (Kharaka *et al.*, 1988). Bassett (1977) presented evidence for the existence of polynuclear boron species when boron concentrations are high. Organic-boron complexes may also exist, and organically bound boron has the potential to be used to trace hydrocarbon migration paths in subsurface waters (Mackin, 1987).

Boron is leached from rocks and organic matter, especially at high temperatures. Removal mechanisms for boron include adsorption on clay mineral surfaces at low temperatures

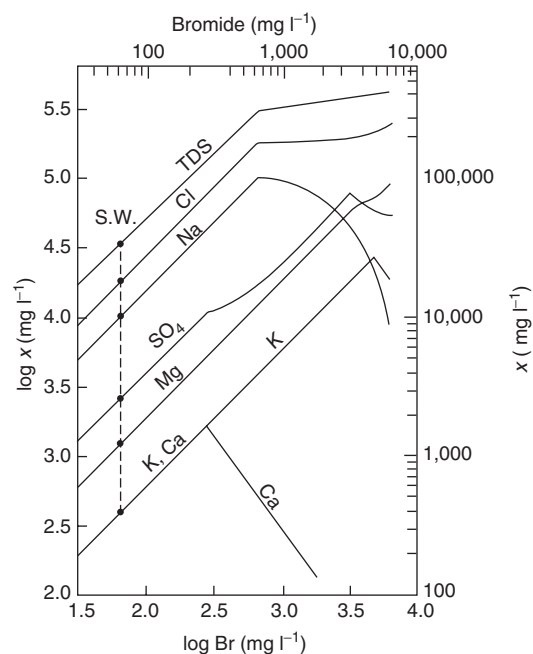


Figure 5 Concentration trends of salinity and several cations and anions in evaporating seawater. After Carpenter (1978) and Kharaka and Thordsen (1992).

(< 120 °C) (You *et al.*, 1996) and the incorporation of boron in exchange for tetrahedral silicon during higher-temperature silicate diagenesis (Spivack *et al.*, 1987). Clay minerals play a key role in the boron budget. The clay mineral group illite/smectite (Harder, 1970) contains an order of magnitude more boron than quartz, carbonate, and feldspar. Some types of organic matter contain several hundred parts per million boron. Because metasedimentary graphite contains little boron, boron is probably released together with hydrogen and oxygen during the thermal degradation of organic compounds (Williams *et al.*, 2001a).

The reported boron concentrations in Gulf Coast (USA) brines range from a few to ~700 mg l⁻¹ (Kharaka *et al.*, 1987; Land and Macpherson, 1992a). Dissolved boron shows no correlation with chloride concentration but does show some increase with depth and temperature (Kharaka *et al.*, 1985). The B/Br ratios are highly elevated relative to the seawater evaporation trend for boron and bromide, reflecting derivation of almost all of the boron from rock and/or organic sources.

5.16.3.3 Water-Rock Reactions Controlling Cation Concentrations

Dissolution of halite, as noted earlier, is probably the most important mechanism

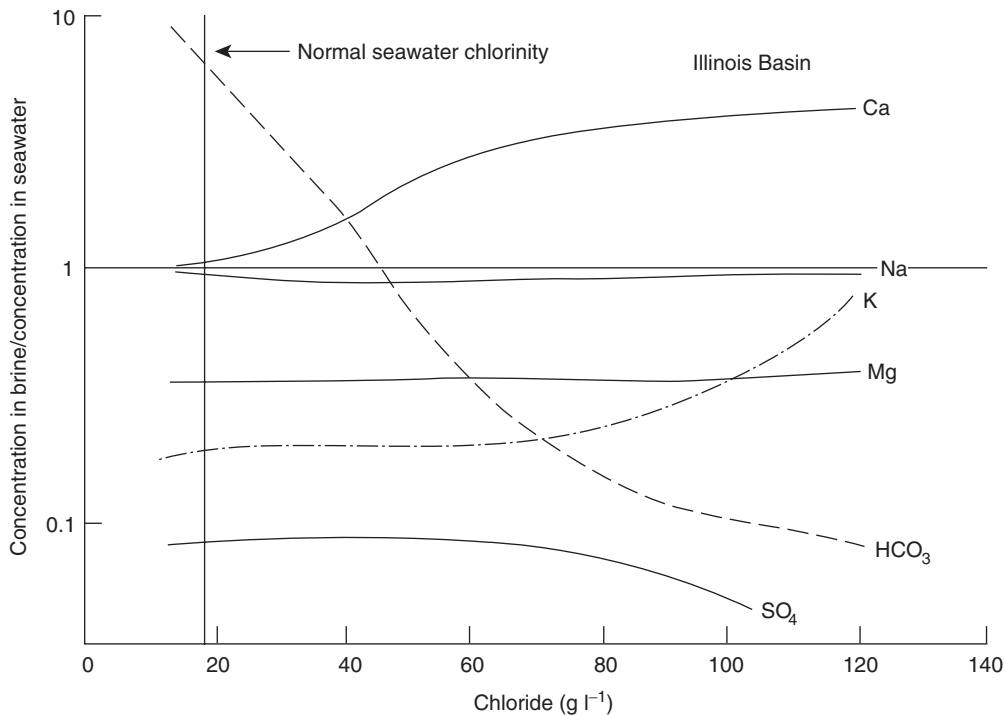


Figure 6 Generalized relative variations in the composition of major ions in formation waters from the Illinois Basin. The normalized ratios indicate that relative to seawater, the formation waters are always depleted in SO_4^{2-} , Mg, and K, but that they become progressively enriched in Ca and K and depleted in HCO_3 with increasing chlorinity. After Hanor (1987).

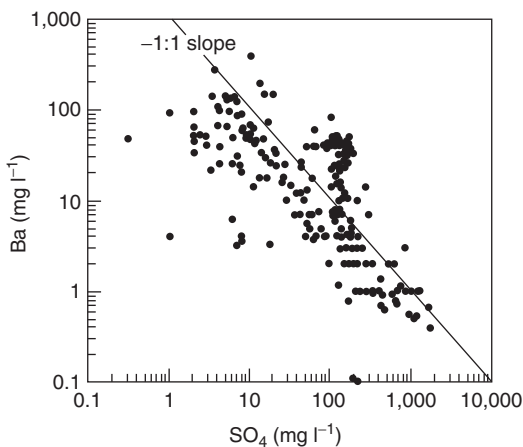


Figure 7 Variation in dissolved Ba with SO_4^{2-} for basinal waters worldwide. Inverse relation suggests buffering by barite. Source: Hanor (2001).

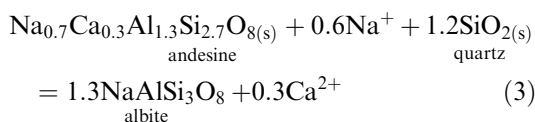
responsible for the increased sodium (and chloride) concentration in the very high salinity ($>1 \times 10^5 \text{ mg l}^{-1}$ dissolved solids) brines present in many sedimentary basins where evaporites are, or were present. The concentrations of cations, especially multivalent

species, are determined by the origin of the water and by the many chemical, physical, and biological processes that modify the original composition of the water. These processes generally act together to increase or decrease the concentrations of the solutes. The ultimate control on the concentration of a given solute is usually the solubility of the least soluble mineral of the solute. For example, the concentration of calcium in water from a given reservoir may increase because of membrane filtration, albitization of plagioclase feldspar, and/or dolomitization of limestone. Eventually, the water will attain saturation with respect to calcite, the usual ultimate control on the calcium (and carbonate) concentrations.

Congruent and incongruent dissolution and precipitation reactions, other than for halite, which probably control the major cation compositions of formation waters include dolomitization of limestone, resulting in a major increase of calcium and a major decrease of magnesium, as in the following reaction:



Albitization of plagioclase feldspar, as in the reaction below, also increases calcium concentrations, but lowers the concentration of sodium:

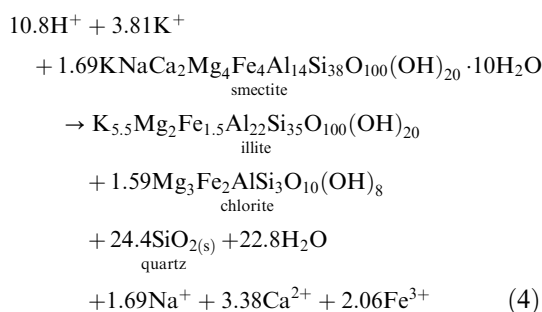


The concentrations of potassium in the samples obtained from the Norphlet Formation in the central Mississippi Salt Dome Basin are those expected from the Louann Salt bittern; potassium values in other samples obtained from reservoirs of Jurassic age are lower by a factor of ~ 2 (Kharaka *et al.*, 1987). The decrease in the dissolved potassium in these samples is attributed to the formation of authigenic illite and potassium feldspar (Carpenter *et al.*, 1974; Kharaka *et al.*, 1987).

The generally lower magnesium concentrations in formation water, in comparison to that of evaporated seawater, could result from diagenetic formation of chlorite, dolomite, and ankerite (Hower *et al.*, 1976; Boles, 1978). Formation of ankerite becomes important at subsurface temperatures higher than $\sim 120^\circ\text{C}$ (Boles, 1978). The concentrations of alkali metals, in the absence of evaporites, are strongly affected by temperature-dependent reactions with clays (transformation of smectite to mixed layer illite/smectite, then with increasing temperature to illite) and feldspar (e.g., Kharaka and Thordsen, 1992). The concentrations of potassium and sodium may be higher or lower than in seawater; the concentrations of lithium and rubidium are generally higher.

The transformation of smectite to mixed layer smectite–illite, and ultimately to illite, with increasing temperature is an extremely important reaction in many sedimentary basins, including the northern Gulf of Mexico Basin (Hower *et al.*, 1976; Boles and Franks, 1979; Kharaka and Thordsen, 1992). The water and solutes released and consumed by this transformation are major factors in the hydrogeochemistry of these basins, because of the enormous quantities of clays involved. Several reactions conserving aluminum or maintaining a constant volume have been proposed for this transformation (Hower *et al.*, 1976; Boles and Franks, 1979). The reaction proposed below (Equation (4)) conserves aluminum and magnesium, and is probably a closer approximation based on the composition of formation waters

in these systems:



The Fe^{3+} in the above reaction will be reduced to Fe^{2+} by organics and some may precipitate as pyrite or ankerite. At any rate, the overall reaction consumes large amounts of potassium and hydrogen and adds important amounts of calcium, sodium, and some Fe^{2+} to the formation water.

5.16.3.3.1 Cation geothermometry

The Li/Na, K/Na, and Rb/Na ratios generally increase with increasing depth (increasing temperatures). The proportions of alkali metals alone or combined with those of alkaline-earth metals (magnesium and calcium in particular), and the concentrations of SiO_2 are so strongly dependent on subsurface temperatures that they have been combined into several chemical geothermometers (Table 4) that can be used to estimate these temperatures (Fournier *et al.*, 1974; Kharaka and Mariner, 1989, 2005; Pang and Reed, 1998). The most useful “chemical markers” for increasing subsurface temperatures are the concentrations of silica, boron, and ammonia, and the Li/Mg, Li/Na, and K/Na ratios.

5.16.3.4 Major Anions

At salinities of less than $\sim 1 \times 10^4 \text{ mg l}^{-1}$ and relatively shallow depths, the anionic composition of subsurface water is highly variable and can be dominated by sulfate, bicarbonate, chloride, or even acetate (Hem, 1985; Drever, 1997). Shallow groundwater generally is dominated by sulfate, which is replaced by bicarbonate as the dominant species in deeper meteoric groundwater. Acetate may comprise a large portion of total anions, especially in the Na–Cl– CH_3COO -type waters that are present mainly in Cenozoic reservoir rocks at temperatures of 80 – 120°C . In these waters, acetate and other organic acid anions (see Section 5.16.3.5) can reach

Table 4 Equations for the general chemical geothermometers and their applicability for use in formation waters from sedimentary basins.

<i>Geothermometer</i>	<i>Equation^a</i>	<i>Recommendations</i>
Quartz	$t = \frac{1,309}{0.41 - \log(kpf)} - 273$ $k = \frac{a_{\text{H}_2\text{SiO}_4}}{a_{\text{H}_2\text{O}}^2}; \quad pf = (1 - 7.862 \times 10^{-5} e^{3.61 \times 10^{-3} t} p)$	70–250 °C
Chalcedony	$t = \frac{1,032}{-0.09 - \log(kpf)} - 273$	30–70 °C
Mg–Li	$t = \frac{2,200}{\log(\sqrt{\text{Mg/Li}}) + 5.47} - 273$	0–350 °C
Na–K	$t = \frac{1,180}{\log(\text{Na/K}) + 1.31} - 273$	Do not use in oil-field waters
Na–K–Ca	$t = \frac{1,647}{\log(\text{Na/K}) + \beta [\log(\sqrt{\text{Ca/Na}}) + 2.06] + 2.47} - 273$ $\beta = 4/3 \text{ for } t < 100; = 1/3 \text{ for } t > 100$	Do not use in oil-field waters
Mg-corrected, Na–K–Ca	<p>Same as Na–K–Ca (above) with Mg-corrections</p> $t = t_{\text{Na–K–Ca}} - \Delta t_{\text{Mg}}$ <p>For $0.5 < R < 5$</p> $\Delta t_{\text{Mg}} = 1.03 + 59.97 \log R + 145.05(\log R)^2 - 36,711(\log R)^2/T - 1.67 \times 10^7 \log(R/T^2)$ <p>For $5 < R < 50$</p> $\Delta t_{\text{Mg}} = 10.66 - 47,415R + 325.87(\log R)^2 - 1.032 \times 10^5 \left((\log R)^2/T - 1.968 \times 10^7 (\log R)^2/T^2 \right) + 1.605 \times 10^7 (\log R)^3/T^2$ <p>No correction should be attempted if $R > 50$</p> $R = \frac{\text{Mg}}{\text{Mg} + 0.61 \text{ Ca} + 0.31 \text{ K}} \times 100$	0–350 °C
Na/Li	$t = \frac{1590}{\log(\text{Na/Li}) + 0.779} - 273$	0–350 °C

Source: Kharaka *et al.* (1988).^aConcentrations in mg l⁻¹; *t*, temperature in °C; *T* in K; *p*, pressure in bar; *a*, activity of the subscripted species; Na–K–Ca equation and Mg corrections from Fournier and Potter (1979) (for details see Kharaka and Mariner, 1989).

concentrations of up to $1 \times 10^4 \text{ mg l}^{-1}$ and contribute up to 99% of the measured alkalinities (Willey *et al.*, 1975; Kharaka *et al.*, 2000).

Chloride is by far the dominant anion in nearly all formation waters having salinities in excess of $3 \times 10^4 \text{ mg l}^{-1}$ (Tables 1 and 2). Explaining the origin of saline waters in

sedimentary basins is, to some degree, the problem of explaining the origin of the dissolved chloride. Chloride and bromide are fairly closely coupled in their subsurface geochemistry, but the other dissolved halogens, fluoride and iodide, have distinctly different systematics in basinal waters. Sulfate, bicarbonate, and the

organic acids provide valuable information on the effects of reactions involving organic matter on formation water chemistry. Other anionic species and weak acids, such as borate and boric acid, may provide information on the degree of water–rock interaction.

5.16.3.4.1 Chloride and bromide

The principal sources of dissolved chloride in the more saline fluids of sedimentary basins include dissolved chloride buried at the time of sediment deposition, chloride derived by refluxing of subaerially evaporated surface brines, chloride derived from subsurface mineral dissolution, principally halite, and marine aerosols. The Cl–Br systematics of sedimentary brines provide useful constraints on interpreting the origin of chloride in these waters (Carpenter, 1978; Kharaka *et al.*, 1987; Kesler *et al.*, 1996).

Although bromide and chloride are both monovalent anions of similar ionic radii ($\text{Br}^- = 1.96 \text{ \AA}$, $\text{Cl}^- = 1.81 \text{ \AA}$), Cl^- is strongly preferentially partitioned over Br^- into sodium, potassium, and magnesium halogen salts during precipitation (Hanor, 1987; Siemann and Schramm, 2000). During the initial

evaporation of seawater, both bromide and chloride increase in concentration in the residual hypersaline waters, and the Br/Cl ratio of these waters does not vary (Figure 8). When halite saturation is reached, chloride is preferentially precipitated as a constituent of halite. Because only a small fraction of the bromide is incorporated in the halite lattice as $\text{Na}(\text{Cl}, \text{Br})$, the Br/Cl ratio of the residual brine increases with progressive evaporation (Figure 8). As saturation with respect to K–Mg–Cl salts is reached, the slope of the Br–Cl curve begins to flatten out, because these minerals discriminate against bromide somewhat less than halite. The upper limit to bromide concentrations produced by evaporating seawater is $\sim 0.6 \times 10^4 \text{ mg l}^{-1}$; the upper limit for chloride is $\sim 2.5 \times 10^5 \text{ mg l}^{-1}$.

Brines formed by subaerial evaporation of seawater should, in theory, have elevated Br/Cl ratios. Brines formed by the dissolution of halite should have low Br/TDS (Rittenhouse, 1967) and Br/Cl ratios (Carpenter, 1978; Kharaka *et al.*, 1987). Brines representing these end members and mixtures of these and/or meteoric and/or connate marine waters have been identified in sedimentary basins on the basis of their Br/Cl and Br/TDS ratios (Kharaka *et al.*, 1987; Hanor, 1987; Worden, 1996).

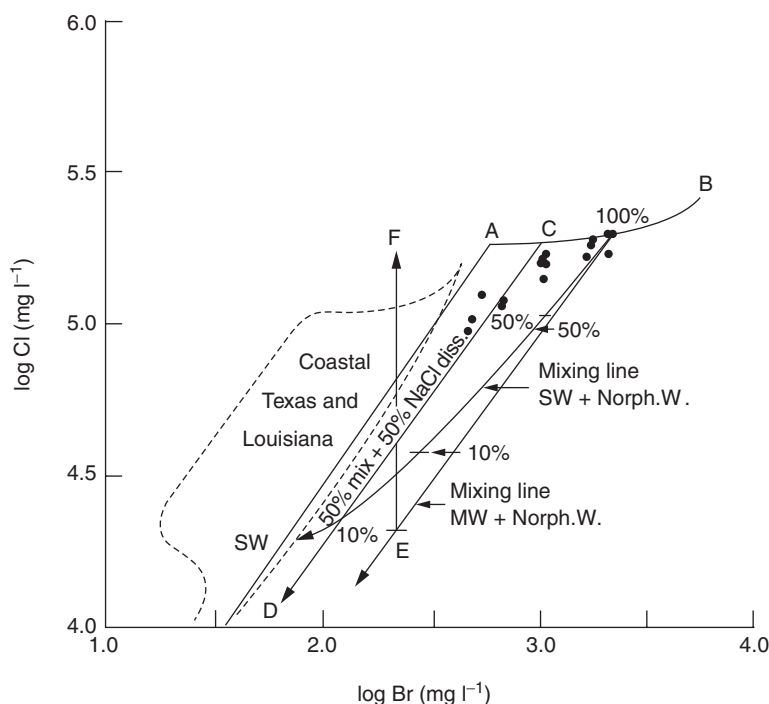


Figure 8 Distribution of Cl and Br in formation waters from the central Mississippi Salt Dome Basin relative to the evaporation line for seawater (SW, A–B) and mixing lines between Norphlet water (Norph. W) and meteoric (MW) and sea (SW) waters. Line E–F gives the trend when the mixture of meteoric and Norphlet waters dissolves halite with 70 ppm Br. Line C–D gives the trend where 50% of the Cl concentration in the mixture of meteoric and Norphlet waters is from dissolution of halite. Note that the samples from Coastal

Texas and Louisiana (dashed field) plot in a different field. Source: Kharaka and Thordsen (1992).

The high Br/Cl ratios of waters in the Smackover Formation, USA, for example, support the hypothesis that bromide-rich, subaerially produced brines are important saline end members in this system (Kharaka *et al.*, 1987; Moldovanyi and Walter, 1992). The central Mississippi Salt Dome Basin provides an excellent example of a system where bittern (residual) water is an important component of the formation water (Table 3). The very high salinities of the brines (up to $3.5 \times 10^5 \text{ mg l}^{-1}$ dissolved solids) and their major ion concentrations are directly or indirectly related to their origin as bitters in the Louann Salt. This conclusion is based on the relation between the “chemical markers” bromide and chloride, sodium and total cations, as well as on the isotopic composition of the water (Carpenter *et al.*, 1974; Stoessell and Carpenter, 1986; Kharaka *et al.*, 1987). The bromide and chloride concentrations are much higher than those expected from dissolution of halite and the values (Figure 8) plot on or below the seawater evaporation line. Kharaka *et al.* (1987) indicate that the samples that plot on or below the seawater evaporation line result from mixing of bitters with meteoric waters (Figure 8).

The low Br/Cl values of waters in South Louisiana, USA, in contrast, indicate that their high salinity is derived from the dissolution of halite-dominated salt domes (Kharaka *et al.*, 1978, 1985; Hanor, 1987). Other examples include brines in the Paradox Basin (Hanshaw and Hill, 1969) and fluids in Devonian sediments of the Alberta Basin, Canada (Hitchon *et al.*, 1971). The waters of the Norwegian Shelf have an intermediate Br/Cl signature. This supports the conclusion of Egeberg and Aagaard (1989) that they contain at least some contribution from subaerially produced brines in addition to brines generated by the dissolution of halite.

There are several other processes that modify the Cl–Br systematics in formation waters. These include the incongruent dissolution of halite, the incongruent dissolution of chloride salts other than halite, differential rates of molecular diffusion, and the introduction of bromide from organic compounds (Land and Prezbindowski, 1981). Br/Cl ratios in excess of those normally associated with subaerial evaporation may result from the incongruent dissolution of Na–K–Mg–Cl mineral assemblages during progressive burial (Hanor, 1987; Land *et al.*, 1995).

5.16.3.4.2 Iodide

The concentration of dissolved iodide typically ranges from <0.01 to $>100 \text{ mg l}^{-1}$ in

basinal waters (Collins, 1975; Worden *et al.*, 1999). An exceptional value of $1,560 \text{ mg l}^{-1}$ has been reported for a brine sample from Mississippian limestone of the Anadarko Basin, OK, where iodide is extracted from the brine commercially (Johnson and Gerber, 1998). There is no correlation between the iodide and chloride concentrations, and the occurrence of iodide appears to be unrelated either to evaporative concentration or to salt dissolution. The probable source of iodide in basinal waters is organic matter. Iodide is an essential trace element in the biological cycle, and it is estimated that $\sim 70\%$ of crustal iodide resides in organic matter in marine sediments (Muramatsu *et al.*, 2001). Iodide is released during the progressive thermal degradation of organic material, and is preferentially partitioned into the aqueous phase as I^- (Collins, 1975; Kharaka and Thordsen, 1992; Muramatsu *et al.*, 2001).

5.16.3.4.3 Fluoride

Fluoride exists in formation waters primarily as fluoride, F^- , and cation–fluoride complexes, such as NaF^0 , CaF^+ , and MgF^+ (Richardson and Holland, 1979). Concentrations of fluoride in formation waters vary from <1 to $>30 \text{ mg l}^{-1}$ (Worden *et al.*, 1999). There appears to be a threshold value, $\sim 1 \times 10^5 \text{ mg l}^{-1}$, for chloride below which fluoride concentrations are typically below 5 mg l^{-1} and above which they are in the range of $10\text{--}20 \text{ mg l}^{-1}$. Occasionally they are even higher. Sources of fluoride and controls on the concentrations of fluoride have not been extensively studied. Biogenic fluorapatite, bentonite, and smectitic shales are potential sources (Hitchon, 1995).

The control of fluoride concentration by fluorite (CaF_2) saturation is possible in some waters. Fluorite solubility has been shown to be a complex function of temperature, salinity, and major ion chemistry (Holland and Malinin, 1979; Richardson and Holland, 1979). Hitchon (1995) found that lower salinity waters of the Alberta Basin are generally undersaturated with respect to fluorite, and that there is a gradual increase in fluoride to CaF_2 saturation as temperature and salinity increase.

5.16.3.4.4 Inorganic carbon species

The alkalinity of most formation waters, operationally defined by titration of a given volume of water with H_2SO_4 to an inflection pH, is contributed predominantly by bicarbonate and organic acid anions (Figure 9). The inflection pH for inorganic alkalinity is close to 4.5. For organic acid anions it is at a pH value

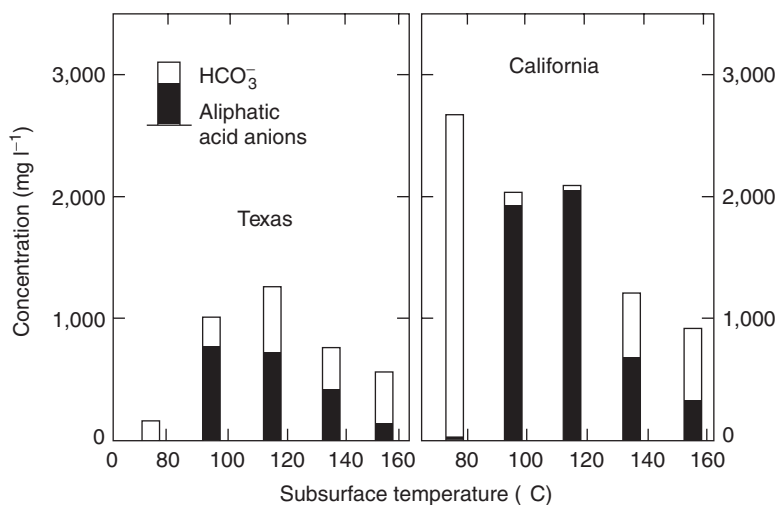
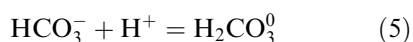


Figure 9 Average concentrations of aliphatic acid anions and bicarbonate alkalinity (as HCO_3^-) in oil-field waters from Texas and California. Note that organic acid anions contribute most of the total alkalinity at temperatures of 80–140 °C. After Carothers and Kharaka (1978).

of 2–3 (Willey *et al.*, 1975; Carothers and Kharaka, 1978). Total inorganic (organic anions are discussed in more detail below) alkalinity, comprised mainly of HCO_3^- and CO_3^{2-} species, is generally less than a few hundred milligrams per liter in waters having salinities in excess of $3 \times 10^4 \text{ mg l}^{-1}$. Alkalinity generally decreases with increasing salinity. There are two main reasons for this decrease. Both are related to the solubility of carbonate minerals, primarily calcite. First, in a calcium carbonate-buffered system, carbonate alkalinity should decrease with the marked increase in dissolved calcium that occurs with increasing salinity. Second, the increase in H^+ (lower pH) with increasing salinity shifts dissolved carbonate and bicarbonate toward carbonic acid:



5.16.3.4.5 Sulfate

Sulfur can exist in aqueous solution in at least five oxidation states, but data on sulfur species in basinal fluids are limited primarily to sulfate, $\text{S}(\text{VI})$, and sulfide, $\text{S}(\text{-II})$. Sulfate (SO_4^{2-}) will be discussed here, and hydrogen sulfide (H_2S) and bisulfide (HS^-) will be discussed in Section 5.16.7.

The concentration of SO_4^{2-} in formation waters rarely exceeds $1,000 \text{ mg l}^{-1}$ even though it is present in high concentration in seawater ($2,700 \text{ mg l}^{-1}$) and in even higher concentrations in residual brines formed by seawater evaporation (Figure 5). Unlike major cations

and alkalinity, there is no significant correlation between the concentration of SO_4^{2-} and chloride or salinity, but the solubility of anhydrite decreases rapidly with increasing temperature and provides the ultimate control on SO_4^{2-} concentrations (Kharaka and Thordsen, 1992). The wide variations in sulfate concentrations that exist on the basinal and even the oil-field scale may also reflect rate-controlled processes involving (1) release of sulfate by the dissolution of sulfate minerals, such as gypsum and anhydrite (Land *et al.*, 1995; Hitchon, 1996a) and the oxidation of pyrite (Dworkin and Land, 1996); (2) dispersive fluid mixing; (3) precipitation as barite (BaSO_4); (4) removal by bacterial sulfate reduction (BSR) at shallow and deeper zones, particularly in the presence of hydrocarbons (Gavrieli *et al.*, 1995); and (5) removal by thermochemical sulfate reduction (TSR) that becomes important at temperatures $>100^\circ\text{C}$ (Machel, 2001).

5.16.3.5 Reactive Organic Species

Since the beginning of the last quarter of the twentieth century there has been considerable interest in the origin and interactions of dissolved reactive organic species in subsurface waters (Willey *et al.*, 1975; MacGowan and Surdam, 1990; Drever and Vance, 1994; Bennett and Larter, 1997; Kharaka *et al.*, 2000; Franks *et al.*, 2001). Geochemical interest in organic species stems from their important role in mineral diagenesis (Surdam *et al.*, 1989; Seewald, 2001). They act as proton donors for a variety of pH-dependent reactions, as pH and Eh buffering agents, and they form complexes

with metals such as aluminum, iron, lead, and zinc. They can be used as proximity indicators in petroleum exploration (Kartsev, 1974; Carothers and Kharaka, 1978) and they may serve as possible precursors for natural gas (Kharaka *et al.*, 1983; Drummond and Palmer, 1986).

5.16.3.5.1 Monocarboxylic acid anions

The concentrations of dissolved organic species in oil-field waters (20–200 °C) are much higher than in groundwater. Acetate concentrations may reach values as high as 1×10^4 mg l⁻¹ (Kharaka *et al.*, 1986, 2000; MacGowan and Surdam, 1990). Acetate, propionate, butyrate, and valerate were identified as the dominant organic species in these waters (Willey *et al.*, 1975; Carothers and Kharaka, 1978). Prior to the identification of these aliphatic acid anions by Willey *et al.* (1975), these organics were generally grouped with and recorded as

bicarbonate alkalinity, because they are titrated with H₂SO₄ that is used to measure field alkalinities. Willey *et al.* (1975) and Carothers and Kharaka (1978) showed (Figure 9) that these organic acid anions contribute up to 99% of the measured alkalinities.

Their concentration is controlled primarily by subsurface temperature and the age of the reservoir rocks. The distribution of aliphatic acid anions in oil-field waters from several basins shows (Figure 10) three distinct temperature zones (Kharaka *et al.*, 2000). Zone 1 is characterized by concentrations of acid anions <500 mg l⁻¹ and temperatures <80 °C. The concentration of acetate in this zone is generally low, and propionate generally predominates. Bacterial degradation is believed to be responsible for the low concentration of organic species in zone 1 (Carothers and Kharaka, 1978). The highest concentrations of aliphatic acid anions are present in the youngest (Tertiary age) and shallowest reservoir rocks of zone 2

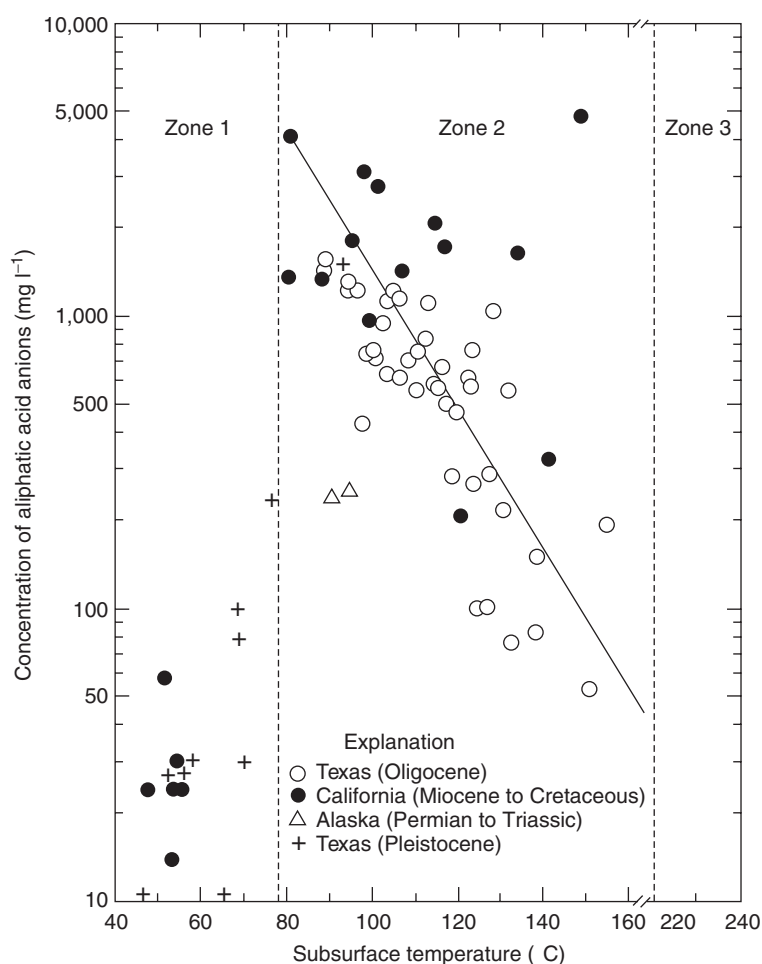


Figure 10 Concentrations of aliphatic acid anions (C₂–C₅) in formation waters from three sedimentary basins. Note that the highest concentrations are at ~80 °C and that they thereafter decrease with increasing temperatures. Source: Kharaka *et al.* (1988).

(temperatures 80–120 °C). Their concentration generally decreases with increasing subsurface temperatures (Figure 10) and with the age of the zone 2 reservoir rocks. Acetate constitutes more than 90% of acid anions; propionate comprises ~5% of these anions (Carothers and Kharaka, 1978; Lundegard and Kharaka, 1994). The boundary of zone 3, where no measurable acid anions are present, is placed at ~220 °C. This temperature is obtained by extrapolating the points of zone 2 (Kharaka *et al.*, 1986).

The decrease in the concentrations of acid anions with increasing temperature (Figure 10) and the age of the reservoir rocks (Carothers and Kharaka, 1978; Kharaka *et al.*, 2000) indicates that thermal decarboxylation is responsible for the conversion of acid anions into CO₂ and hydrocarbon gases. Further evidence for the importance of thermal decarboxylation in the destruction of acid anions is obtained from the $\delta^{13}\text{C}$ values of dissolved bicarbonate, CO₂ and CH₄ in natural gas, and diagenetic calcite and ankerite from Gulf Coast and California basins (Boles, 1978; Carothers and Kharaka, 1980; Lundegard and Land, 1986; Lundegard and Kharaka, 1994). These $\delta^{13}\text{C}$ values indicate that the carbon in CO₂ gas, dissolved carbonate, and carbonate cements was derived largely from an organic source.

Experimental studies show that decarboxylation rates for acetic acid are extremely sensitive to temperature and the types of available catalytic surfaces. Rate constants for acetic acid decarboxylation at 100 °C differ by more than 14 orders of magnitude between experiments conducted in stainless steel and in catalytically less active titanium (Kharaka *et al.*, 1983; Drummond and Palmer, 1986). Naturally occurring mineral surfaces provide rather weak catalysts (Bell, 1991). Decarboxylation rates calculated from field data indicate half-life values of 10–60 Myr at 100 °C (Kharaka, 1986; Lundegard and Kharaka, 1994).

5.16.3.5.2 Dicarboxylic acid anions

Data for the concentrations of dicarboxylic acid anions in formation waters from sedimentary basins are much more limited than for monocarboxylic anions. Some of the reported values are controversial (Hanor *et al.*, 1993; Kharaka *et al.*, 1993a). The total reported range is 0–2,640 mg l⁻¹ (for discussion and references see Kharaka *et al.*, 2000). The highest concentrations of dicarboxylic acid anions are those reported by MacGowan and Surdam (1988, 1990) for water samples from ~40 petroleum wells located mainly in the San Joaquin and Santa Maria Basins, California, and in

northern Gulf of Mexico Basins. They reported values of up to 494 mg l⁻¹ oxalate, 2,540 mg l⁻¹ malonate, and 66 mg l⁻¹ maleate from wells in the North Coles Levee field, San Joaquin Valley Basin, California. Several wells in the North Coles Levee and the nearby Paloma field were resampled by several other investigators (MacGowan and Surdam, 1990; Fisher and Boles, 1990; Kharaka *et al.*, 1993b). These authors found much lower and more typical concentrations of dicarboxylic acid anions (total of ~200 mg l⁻¹). Their concentration is probably limited by a rapid rate of thermal decomposition (MacGowan and Surdam, 1988; Crossey, 1991) and by the low solubility of calcium oxalate and calcium malonate (Kharaka *et al.*, 1986; Harrison and Thyne, 1992).

It is clear from the above discussion that there are large variations and some uncertainty in the reported maximum concentrations of mono- and dicarboxylic acid anions in formation waters. The use of these maximum values leads to erroneous results and conclusions. Maximum reported values together with more reasonable and likely maximum values are listed in Table 5. Only measured concentrations of organic and inorganic species from petroleum wells should be used in rigorous geochemical simulations (Kharaka *et al.*, 1987). If field data are not available, then more reasonable conclusions are obtained by using the probable maximum values of Table 5.

5.16.3.5.3 Other reactive organic species

Data for the concentration of organic species other than the mono- and dicarboxylic acid anions are few. Degens *et al.* (1964) and Rapp (1976) identified several amino acids, including serine, glycine, alanine, and aspartic acid, but their concentrations were <0.3 mg l⁻¹. In formation waters of the High Island field, offshore Texas, Kharaka *et al.* (1986) identified a number of species, including phenol, 2-, 3-, and 4-methylphenol, 2-ethylphenol, 3-, 4-, and 3-, 5-dimethylphenol, cyclohexanone, and 1- and 4-dimethylbenzene. Fisher and Boles (1990) identified various polar aliphatics (fatty acids to C₉ with various methyl and ethyl substituents), cyclics (phenols and benzoic acids), and heterocyclics (quinolines). They were able to quantify, at the parts per million or sub-parts per million level, the concentrations of phenol, methyl-substituted phenols, and benzoic acid. Lundegard and Kharaka (1994) reported data that waters from oil and gas wells in the Sacramento Valley, CA, contained the following organic species: phenols (up to 20 mg l⁻¹), 4-methylphenol (up to 2 mg l⁻¹),

Table 5 Maximum reported and likely concentrations of mono- and dicarboxylic acid anions in oil-field waters.

<i>Acid anion</i>		<i>Concentration (mg l⁻¹)</i>		<i>References (maximum reported)^a</i>
<i>IUPAC</i>	<i>Common</i>	<i>Reported</i>	<i>Likely</i>	
<i>Monocarboxylic anions</i>				
Methanoate	Formate	174	10	1
Ethanoate	Acetate	10,000	5,000	2
Propanoate	Propionate	4,400	2,000	1
Butanoate	Butyrate	682	500	3
Pentanoate	Valerate	371	200	3
Hexanoate	Caprolate	107	100	4
Heptanoate	Enanthate	99	100	1
Octanoate	Caprylate	42	100	1
<i>Dicarboxylic anions</i>				
Ethanedioate	Oxalate	494	10	1
Propandioate	Malonate	2,540	100	1
Butandioate	Succinate	63	100	4
Pentandioate	Glutarate	95	100	5
Hexandioate	Adipate	0.5	10	4
Heptanedioate	Pimelate	0.6	10	4
Octanedioate	Suberate	5.0	10	4
cis-Butenedioate	Maleic	26	50	1

Source: Kharaka *et al.* (2000).^a1, MacGowan and Surdam (1988); 2, Surdam *et al.* (1984); 3, MacGowan and Surdam (1990); 4, Kharaka *et al.* (1985); 5, Kharaka *et al.* (2000).

benzoic acid (up to 5 mg l⁻¹), 4-methylbenzoic acid (up to 4 mg l⁻¹), 2-hydroxybenzoic acid (up to 0.2 mg l⁻¹), 3-hydroxybenzoic acid (up to 1.2 mg l⁻¹), 4-hydroxybenzoic acid (up to 0.2 mg l⁻¹), and citric acid (up to 4 mg l⁻¹). Additional dissolved organic species, including organosulfur compounds, will probably be discovered as analytical procedures improve (Kharaka *et al.*, 1999a, 2000).

Significant concentrations of nonpolar, but toxic dissolved organic compounds, including benzene, toluene (up to 60 mg l⁻¹ for BTEX), phenols (20 mg l⁻¹), and polyaromatic hydrocarbons (upto 10 mg l⁻¹ for PAHs), may be present in oil-field waters.

5.16.3.5.4 Origin of major reactive species

Hydrous pyrolysis experiments of crude oils generated relatively large concentrations of mono- and dicarboxylic acid anions with relative abundances generally similar to those observed in sedimentary basin waters. But analysis of all of the pertinent data indicates that the major part of the organic acid anions in formation waters is probably generated by the thermal alteration of kerogen in source rocks (Kharaka *et al.*, 1993b; Lewan and Fisher, 1994). This conclusion is based on several observations:

1. The oxygen content of oil (0–1 wt.%) is ~20 times lower than that of kerogen (Tissot and Welte, 1984).

2. The yields of organic acid anions per unit weight are approximately two orders of magnitude lower in experiments with oil than in kerogen experiments (Lundegard and Senftle, 1987; Barth *et al.*, 1989; Kharaka *et al.*, 1993b).
3. Oil is much less abundant than kerogen in sedimentary basins.
4. High concentrations of organic acid anions have been reported from gas fields (e.g., the Sacramento Valley Basin, CA), where liquid petroleum has probably never existed (Lundegard and Kharaka, 1994).

5.16.4 ISOTOPIC COMPOSITION OF WATER

The oxygen and hydrogen isotopes of H₂O have become the most useful tools in the study of the origin and evolution of subsurface waters (for detailed reviews, see Sheppard, 1986; Kharaka and Thordsen, 1992). Prior to the use of isotopes, it was generally assumed that most of the formation waters in marine sedimentary rocks were connate marine in origin (White *et al.*, 1963). Clayton *et al.* (1966) were the first to use the isotopic composition of H₂O to show that waters in several sedimentary basins are predominantly of local meteoric origin. The connate water was lost by compaction and flushing. The extensive use of isotopes of water, solutes, and associated minerals coupled with studies of the regional

geology and paleohydrology have shown that subsurface waters generally have a complicated history and that they are commonly mixtures of waters of different origins (Graf *et al.*, 1966; Connolly *et al.*, 1990; Kharaka and Thordsen, 1992; Birkle *et al.*, 2002).

The distribution and controls on the isotopic composition of present-day precipitation and surface waters, especially in mountainous terrains, are complex (e.g., Kharaka *et al.*, 2002); this topic is covered in detail in Chapter 5.11. This isotopic composition together with data for paleoclimates and regional paleogeography can be used to deduce the isotopic composition of old surface waters, including ocean water. An understanding of these parameters is needed to interpret the origin of deep basin brines (Kharaka and Thordsen, 1992). Reactions between water and minerals, dissolved species, associated gases, and other liquids with which they come into contact can modify the isotopic composition of water, especially the value of $\delta^{18}\text{O}$. In addition to mixing of waters of different isotopic composition, the following are the main processes that modify the isotopic composition of formation waters in sedimentary basins: (1) isotopic exchange between water and minerals; (2) evaporation and condensation; (3) fractionation caused by the membrane properties of rocks; and (4) isotopic exchange between water and other fluids, especially petroleum.

5.16.4.1 Formation Waters Derived from Holocene Meteoric Water

The isotopic compositions of waters in some basins indicate that formation waters are related principally to recent local meteoric waters (Clayton *et al.*, 1966; Hitchon and Friedman, 1969; Kharaka and Thordsen, 1992). The δD values of these waters (Figure 11) show a “hydrogen isotope shift” in addition to the generally observed “oxygen isotope shift.” The origins of these shifts vary, but the lines fitted to the δD and $\delta^{18}\text{O}$ plots (Figure 11) in each case intersect the global meteoric waterline (Craig, 1961) at values that approximate those of present-day meteoric water in the area of recharge (Clayton *et al.*, 1966; Kharaka and Thordsen, 1992).

Oxygen and hydrogen isotopes of water are sometimes not sufficient by themselves to indicate the origin of water. Kharaka *et al.* (1973) showed that plots of δD values and TDS indicated a connate marine origin for the waters from the McAdams Formation (Eocene) of California and a meteoric origin for those from the overlying formations; the isotope data alone (Figure 11) could indicate a meteoric

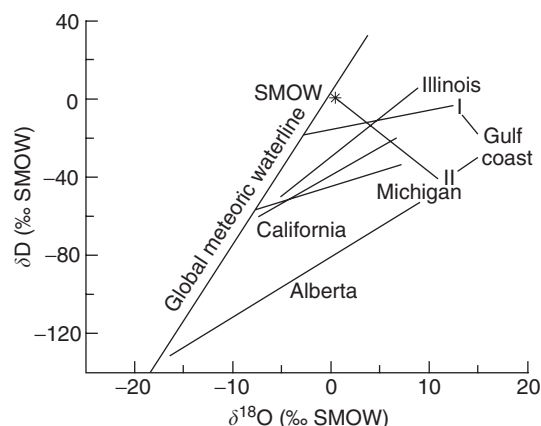


Figure 11 Isotopic compositions of oil-field waters from several basins in North America. Original lines from Clayton *et al.* (1966), Hitchon and Friedman (1969), and Kharaka *et al.* (1973, 1979). Note that except for Gulf Coast II, the isotope lines intersect the Global Meteoric Line (Craig, 1961) at points with isotopic values of present-day meteoric water (Kharaka and Thordsen, 1992).

origin for all the waters as they plot on the same trend. Also, a detailed study (Connolly *et al.*, 1990) of δD and $\delta^{18}\text{O}$ values of water and minerals, combined with chloride and strontium concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ values, suggests that the waters in the Alberta Basin, Canada, are not all meteoric (Figure 11), but that they define three hydrochemical groups. The upper group is dominated by modern meteoric water; the other two groups are a mixture of old (Laramide age) meteoric water and original bittern or residual brine.

5.16.4.2 Formation Waters from “Old” Meteoric Water

Stable isotopes of water in addition to age determinations based on ^{14}C have shown that the waters in many petroleum fields are “old” meteoric water, that is, older than Holocene and probably Pleistocene in age (Bath *et al.*, 1978; Kharaka and Thordsen, 1992; Clark and Fritz, 1997). Clayton *et al.* (1966) were the first to show that a number of formation-water samples from the Michigan and Illinois Basins were probably recharged during the Pleistocene Epoch, because their $\delta^{18}\text{O}$ values are much lower than those for present-day meteoric water.

Kharaka *et al.* (1979) and Kharaka and Carothers (1988) were probably the first to present evidence for meteoric water older than Pleistocene in sedimentary basins. These authors presented isotopic and chemical data for

formation waters from exploration and producing oil and gas wells from the North Slope of Alaska. The water samples were obtained from reservoir rocks between 700 and 2,800 m in depth and in age from Triassic to Mississippian. The waters from all formations, however, are remarkably similar in TDS ($(1.9\text{--}2.4) \times 10^4 \text{ mg l}^{-1}$) and in the concentration of the major cations and anions. The least-squares line through the δD and $\delta^{18}\text{O}$ values for these waters (Figure 12) intersects the meteoric waterline at δD and $\delta^{18}\text{O}$ values of -65‰ and -7‰ , respectively. This line does not pass through the values for standard mean ocean water (SMOW) or for the present-day meteoric water of the region.

The conclusion drawn by Kharaka and colleagues was that these formation waters were meteoric in origin, but that the recharge occurred when the North Slope had an entirely different climate. The relationship between mean annual temperature and the isotopic composition of meteoric water (Dansgaard, 1964) suggests that the mean annual temperature at the Brooks Range, the most likely recharge area, was $15\text{--}20^\circ\text{C}$ higher at the time of

recharge than today. Paleoclimatic indicators show that annual temperatures in northern Alaska were as high as this during the Miocene, as well as throughout most of the Early Cenozoic and the Mesozoic (Wolfe, 1980; Bryant, 1997).

5.16.4.3 Formation Waters of Connate Marine Origin

In several sedimentary basins, geological and hydrodynamic considerations indicate that formation waters were originally connate marine in origin. The Gulf of Mexico is a prime example of such a basin. The extensive drilling for petroleum, especially in the northern half of this basin, has documented a very thick sequence (up to $1.5 \times 10^4 \text{ m}$) of Cenozoic terrigenous shales, siltstones, and sandstones; there are no major unconformities. Fine-grained sediments contain the largest percentage of connate water at the time of deposition (initial porosity up to 80%); most of this water is squeezed out into the interbedded sandstones during compaction (Kharaka and Thordsen, 1992).

Abnormally high fluid pressures (geopressed zones) are another important characteristic of these basins. In the northern Gulf of Mexico Basin, geopressed zones with hydraulic pressure gradients higher than hydrostatic (10.5 kPa m^{-1} ($0.465 \text{ psi ft}^{-1}$)) are encountered at depths that range from $\sim 2,000 \text{ m}$ in south Texas to more than $4,000 \text{ m}$ in parts of coastal Louisiana (Kharaka *et al.*, 1985). Calculated fluid potentials indicate hydraulic heads that are higher than any recharge areas in the basin, indicating water flow upward and updip. The geologic and paleogeographic history of the northern Gulf of Mexico Basin suggest that the flow has always been updip and toward the recharge areas to the north and northwest, indicating that much of the water is connate water squeezed from the marine shales and siltstones of the basin (Kharaka and Carothers, 1986; Land and Fisher, 1987).

The isotopic composition of formation waters from many fields in the northern Gulf of Mexico Basin (Figure 13) fall on a general trend that passes through SMOW and away from the meteoric water of the area. The isotopic data show that the formation waters in the geopressed and normally pressured zones are neither meteoric in origin nor the result of mixing of meteoric with ocean water. Kharaka and Carothers (1986) used mass balance equations to show that isotopic interaction between connate marine water and clay minerals having very light original δD value (-70‰) is responsible for this unusual isotopic trend.

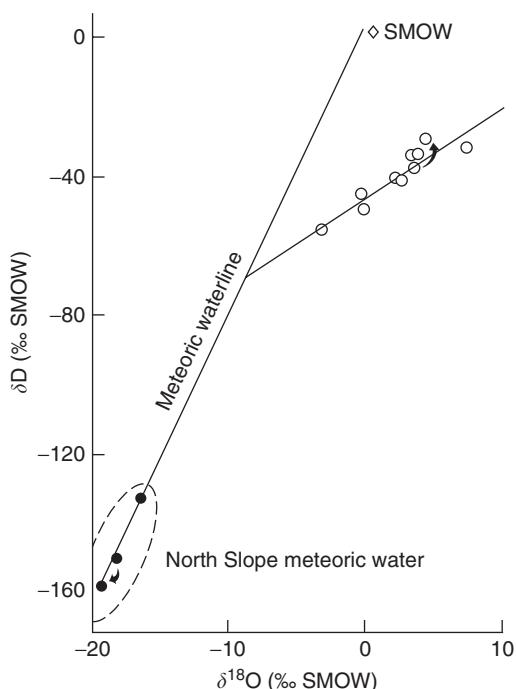


Figure 12 Isotopic composition of formation waters from the North Slope, Alaska. The solid line is the least-squares line drawn through the data. Also shown are values for SMOW, meteoric water in the area, and the GMWL. Note that the line through the data does not pass through SMOW or the local meteoric water. Arrows indicate corrected values as described in Kharaka and Carothers (1988).

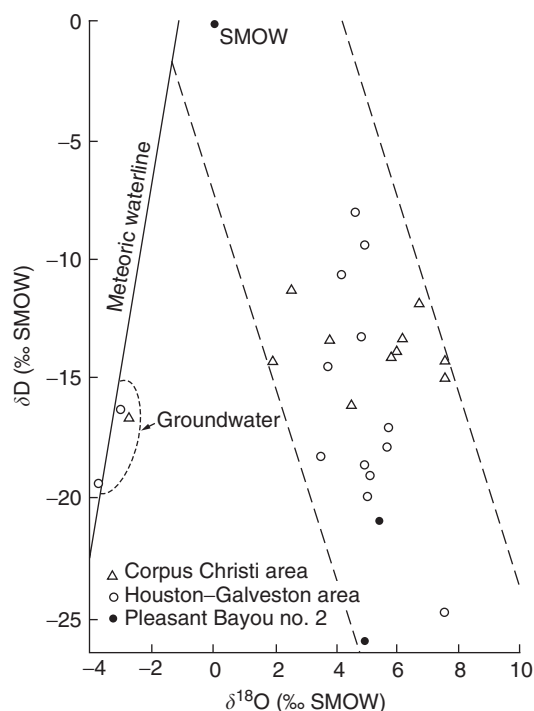


Figure 13 Isotopic composition of formation waters from northern Gulf of Mexico Basin. Note that the trend shows decreased δD values with increasing $\delta^{18}O$ values and that the trend goes through SMOW and away from the local groundwater (Kharaka *et al.*, 1979).

The concentration and isotopic composition of noble gases in natural gas produced from wells in the Gulf of Mexico Basin also support the conclusion that the formation water is marine connate in origin (Mazor and Kharaka, 1981). Finally, age determinations using $^{129}I/I$ ratios for 60 formation water samples from several oil fields in Texas and Louisiana gave ages of 53–55 Ma, pointing to the Wilcox Group shale as the main source of iodide. Moran *et al.* (1995) point out that even older (Mesozoic age) shale could not be ruled out, because of uncertainties in estimating the composition of the fissiogenic component.

5.16.4.4 Bittern Connate Water in Evaporites

Evaporated seawater trapped in precipitated salt and associated sediments and adjacent rocks (bittern water) is probably an important component of formation waters in several sedimentary basins (Carpenter *et al.*, 1974; Kharaka *et al.*, 1987; Moldovanyi and Walter, 1992). The central Mississippi Salt Dome Basin is such a basin. The isotopic composition of its formation waters (Figure 14) belongs to three main

groups. Samples from rocks of Jurassic age (Smackover and Norphlet Formations) have δD values (-1‰ to -3‰), that is, approximately equal to that of SMOW; they have $\delta^{18}O$ values ($5.1\text{--}0.3\text{‰}$) that are highly enriched in ^{18}O . Samples obtained from rocks of Cretaceous age have δD values (-9‰ to -13‰) that are depleted in deuterium relative to both SMOW and the samples from rocks of Jurassic age. Finally, samples obtained from shallow groundwaters in the area have δD and $\delta^{18}O$ values that plot close to the global meteoric waterline (GMWL). The δ^3D values (Figure 14) give the D/H measurements in terms of the activities of deuterium in solutions calculated using a correction factor from Sofer and Gat (1972).

The isotopic composition of the waters supports the conclusion, based on plots of bromide versus chloride and combinations of other chemical constituents (Carpenter *et al.*, 1974; Stoessell and Carpenter, 1986; Kharaka *et al.*, 1987), that the formation waters in rocks of Jurassic age are evaporated seawater. The δD and $\delta^{18}O$ values of evaporating seawater initially increase with increasing evaporation, but at higher degrees of evaporation the trend reverses and (Figure 14) describes a loop on the δ -diagram (Holser, 1979). Knauth and Beeunas (1986) have shown that line B in Figure 14 is the most likely trajectory for evaporating seawater in the Gulf Coast. This line passes very close to the point giving the δ -values for the water in the Norphlet formation, which is that expected from evaporating seawater at the point of halite precipitation. The δ -values of the samples from the Smackover formation were initially close to those from the Norphlet formation; the $1\text{--}2\text{‰}$ shifts in $\delta^{18}O$ values are probably related to isotopic exchange with the enclosing carbonate minerals (Heydari and Moore, 1989).

5.16.4.5 Brines from Mixing of Different Waters

Formation waters in sedimentary basins are highly mobile; this leads to mixing of waters of different age or of different origin and age (Kharaka and Carothers, 1986; Worden *et al.*, 1999; Ziegler and Coleman, 2001). Hitchon and Friedman (1969) made a very detailed isotopic and chemical study of the surface and formation waters of the Western Canada sedimentary basin. Using mass balance calculations for deuterium and TDS, they concluded that the observed distribution of deuterium in the formation waters could best be explained by mixing of diagenetically modified seawater

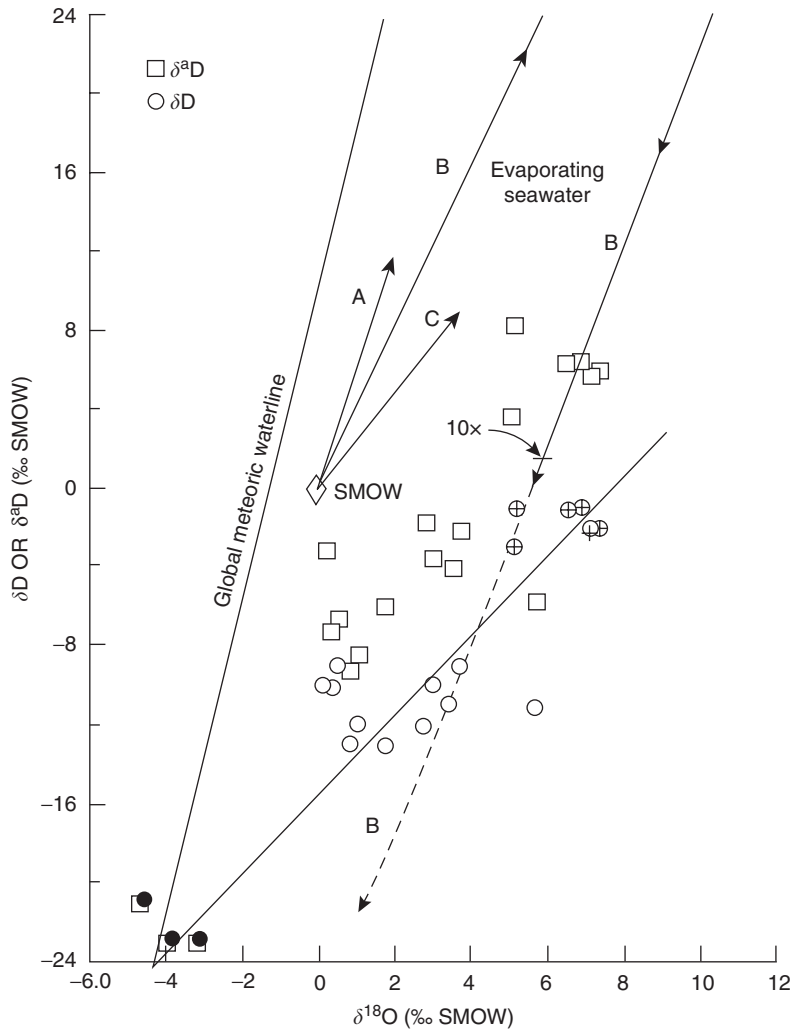


Figure 14 Isotopic composition of shallow groundwater (solid circles) and formation waters from Jurassic (open circles with +) and Cretaceous (open circles) rocks from the central Mississippi Salt Dome Basin. δ^aD values (squares) were computed from δD values and a correction factor $\Delta\delta$ from Sofer and Gat (1972). Lines originating from SMOW are the range of trajectories for seawater undergoing evaporation, with line B being from Holser's (1979) estimate of evaporating seawater in the Gulf Coast. The least-squares line for the δD and $\delta^{18}O$ values is also indicated. After Kharaka *et al.* (1987).

with ~ 2.9 times its volume of fresh meteoric water. They attributed the ^{18}O enrichment of formation waters to extensive exchange with carbonate rocks (see also Connolly *et al.*, 1990).

Other examples of deep-basin waters related to simple mixing of meteoric water with marine connate waters have been documented in the Dnepr–Donets Basin, Ukraine (Vetshteyn *et al.*, 1981) and the Sacramento Valley, California (Berry, 1973; Kharaka *et al.*, 1985). Knauth (1988) used water isotopes and chemical data for waters in the Palo Duro Basin, Texas, to indicate extensive mixing between bittern brines and two pulses of meteoric water with different isotopic compositions. Mixing between waters of the same origin but affected

by different processes is probably common in sedimentary basins. Kharaka *et al.* (1985) used δD and $\delta^{18}O$ values and the chemical composition of formation waters from High Island field, offshore Texas, to show (Figure 15) that the formation waters in Pleistocene reservoir rocks involved mixing of two marine connate waters. One end member is an essentially unmodified marine connate water of Pleistocene age (samples 6 and 7 in Figure 15); the other (sample 5) is a highly chemically and isotopically modified marine connate water possibly of Miocene age. Approximately the same mixing proportions were obtained using stable isotope values (Figure 15) and concentrations of sodium, chloride, calcium, and lithium.

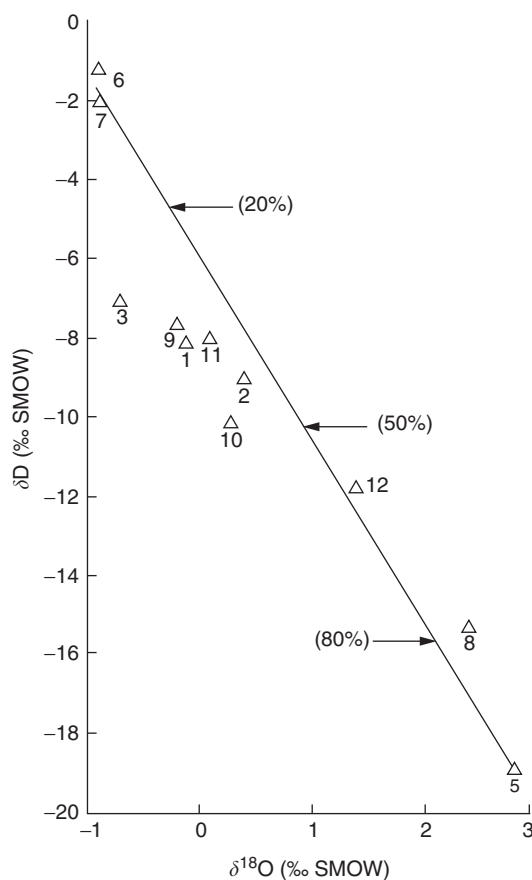


Figure 15 Isotopic composition of formation waters from High Island field, offshore Texas. Percentages represent mixing proportions of the deep brine with Pleistocene connate (sea) water. Source: Kharaka *et al.* (1985).

5.16.4.6 Do the Compositions of Basinal Brines Reflect Secular Variations in Seawater Chemistry?

Studies of the composition of fluid inclusions in ancient evaporites suggest that there have been significant secular variations in seawater chemistry (Horita *et al.*, 2002; Lowenstein *et al.*, 2003). Modern seawater is SO_4 -rich and relatively Ca-poor. As a consequence, when modern seawater is evaporated to gypsum saturation, Ca^{2+} is effectively precipitated nearly entirely from solution, leaving behind a Ca-depleted and SO_4 -enriched brine. However, fluid-inclusion evidence developed to date suggests that during much of the early to middle Paleozoic and the Cretaceous the oceans were SO_4 -poor and Ca-rich. Evaporation of these waters would have produced brines depleted in sulfate, enriched in Ca^{2+} , and having elevated Ca/Na ratios.

Based on this fluid-inclusion evidence and on their calculated compositions of evaporated

Ca-rich ocean waters, Lowenstein *et al.* (2003) proposed that "...basinal brines, which are present in most Phanerozoic sedimentary basins, inherited their chemistries and salinities from evaporated paleoseawaters when the world oceans were Ca-rich and SO_4 -poor (CaCl_2 seas)." Lowenstein *et al.* further proposed that "Typical basinal brines in Silurian–Devonian formations of the interior Illinois Basin, United States, show the same compositional trends as those of progressively evaporated CaCl_2 -rich Silurian seawater." They also noted that basinal brines from the US Gulf Coast vary in major ion chemistry with age of the host sediment. Brines from Jurassic and Cretaceous sediments have high Ca/Na ratios, and brines from Cenozoic sediments have lower Ca/Na ratios.

Hanor and McIntosh (2006) reviewed the above proposals of Lowenstein *et al.* (2003) and the following discussion is based, in part, on that review. Hanor and McIntosh showed that brines in Silurian and Devonian host rocks of the Illinois and Michigan Basins are significantly enriched in Ca^{2+} and depleted in Mg^{2+} relative to the calculated Silurian seawater evaporation values of Lowenstein *et al.* (2003) and that significant diagenetic alteration is thus required to explain their composition. In addition, Das *et al.* (1990) analyzed fluid inclusions in Silurian halite and brines in Silurian host sediments in the Michigan Basin. The brines are significantly depleted in K^+ and Mg^{2+} and highly enriched in Ca^{2+} relative to the fluids in the halite inclusions. The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios of the brines in Silurian sediments are thus significantly less than that of evaporated Silurian seawater. Potassium and SO_4^{2-} are also depleted. The high K^+ concentrations in some of the higher salinity brines may reflect the dissolution of K-salts, such as sylvite, which are present in the Michigan Basin. The low Na^+ concentrations at high salinity may have been inherited from evaporated marine waters, but they are closer to modern evaporated seawater than to calculated evaporated Silurian seawater.

The Mississippian, Permian, and Middle Jurassic were not periods of pronounced Ca-enrichment in seawater, yet evaporated marine waters formed during these times yielded brines that subsequently became enriched in Ca^{2+} (Moldovanyi and Walter, 1992; Stueber *et al.*, 1993, 1998). In addition, brines in many basins show evidence for the dissolution of halite being an important source of salinity in addition to, or instead of, evaporated seawater. As long as there is halite present, the generation of salinity could continue to occur long after the deposition of

evaporites and the possible reflux of evaporated seawater. An excellent example is provided by the Cenozoic section of the Gulf of Mexico Basin where a large volume of saline water has been generated by the dissolution of Jurassic salt (Kharaka and Thordsen, 1992; Land and Macpherson, 1992a; Hanor, 2004). An alternative explanation for the observation that Gulf Coast brines in Mesozoic sediments have higher Ca/Na ratios than brines in these Cenozoic sediments is simply that the latter brines are typically much less saline than the former (Hanor, 2004) and should have lower Ca/Na ratios (see Section 5.16.3.2) rather than the fact they have host sediments of different ages. Even the concept of assigning an age to a basinal brine is problematic given the dynamics of fluid flow and solute transport, which can occur in sedimentary sequences. For example, what aspects of the composition of Silurian-hosted brines in the Illinois and Michigan Basins were actually fixed during the Silurian?

5.16.5 ISOTOPIC COMPOSITION OF SOLUTES

Significant advances in isotope analytical techniques over the last several decades have greatly expanded our knowledge of the isotopic composition of natural waters (Bullen *et al.*, 2001). Highly precise data are now available for isotopic compositions of hydrogen, oxygen, carbon, and sulfur, and a large body of data is available for the strontium, boron, and noble gas isotopes. More recently, data for isotope systematics of lithium, chloride, bromide, and iodide in basinal waters have been accumulating. Applications of isotope geochemistry in studies of sedimentary basins have included identifying the sources of solutes and of H₂O, quantifying the degree of rock–water exchange, tracing fluid flow paths, determining paleotemperatures, and calculating the age and residence time of basinal fluids. The systematics of many isotopic systems, such as those of strontium, have been well worked out for formation waters. Some systems, such as that of bromide, are in their infancy, and others, such as the stable isotope geochemistry of chloride, are beset by unresolved questions regarding their interpretation.

This section covers the stable isotopes of boron, lithium, carbon, sulfur, chloride, bromide, and strontium and the radiogenic isotopes of chloride and iodide (see Chapter 5.15). The isotopes of noble gases are described in Section 5.16.7. Recent reviews of other isotopic systems, which have been used in subsurface

hydrogeology, are given in the volume edited by Cook and Herczeg (2000).

5.16.5.1 Boron Isotopes

Boron has stable isotopes with atomic mass of 10 and 11. These have natural abundances of ~19.82% and 80.18%, respectively (Palmer and Swihart, 1996; Aggarwal *et al.*, 2000). The analyses of ¹¹B/¹⁰B isotopic ratios are reported in the standard $\delta^{11}\text{B}$ notation: $\delta^{11}\text{B}\text{‰}$.

Natural waters range in $\delta^{11}\text{B}$ from –16‰ to +60‰ relative to the SRM NBS 951 standard. This exceptionally wide range reflects the large variability in the isotopic composition of boron sources and the large fractionation factors attendant to the partitioning of boron between aqueous and solid phases (Barth, 1998). The major factor in the isotopic fractionation of boron is the preference of ¹⁰B for tetrahedral coordination with oxygen, either in the borate ion, $\text{B}(\text{OH})_4^-$ (aq), or in silicate mineral surface and lattice sites, and the preference of ¹¹B for trigonal coordination with oxygen as in dissolved boric acid, $\text{B}(\text{OH})_3$ (aq). Under diagenetic conditions, boron is present largely in trigonal coordination in fluids but in tetrahedral coordination in silicates. Fractionation is less mineral specific than coordination specific (Williams *et al.*, 2001b). Lighter isotopes are generally concentrated in the more volatile phase because of their higher vibrational frequency, but boron is an important exception because of the importance of coordination state in the fractionation of its isotopes.

The value of $\delta^{11}\text{B}$ in seawater is 40‰, in marine carbonates it is 10–30‰, and in continental rocks and siliciclastic sediments –15‰ to 5‰ (Palmer and Swihart, 1996; Aggarwal *et al.*, 2000). Boron isotopic values for Gulf Coast waters range from +10‰ to +50‰; (Land and Macpherson, 1992a). There is a general decrease in $\delta^{11}\text{B}$ and an increase in boron with increasing depth and temperature, reflecting the release of light boron during silicate mineral diagenesis. During deep burial diagenesis some boron is reincorporated into crystal lattices. The $\delta^{11}\text{B}$ of diagenetic mineral phases should therefore reflect the $\delta^{11}\text{B}$ of the ambient fluid. Since boron substitution for silicon involves the breaking of Si–O bonds, there should be a coincident change in the $\delta^{18}\text{O}$ of mineral phases. However, boron fractionation is so large that the value of $\delta^{11}\text{B}$ may be more sensitive than $\delta^{18}\text{O}$ to fluid rock exchange under diagenetic conditions. Williams *et al.* (2001b) have developed a boron-fractionation equation based on this concept that can possibly be used to determine paleotemperatures.

5.16.5.2 Lithium Isotopes

Lithium has two stable isotopes, ${}^6\text{Li}$ and ${}^7\text{Li}$, which have abundances of 7.5% and 92.5%, respectively. Lithium is a soluble alkali element. Because its ionic radius is small (0.78 Å), it behaves more like magnesium (0.72 Å than the alkalis). Li^+ tends to substitute for Al^{3+} , Fe^{2+} , and especially for Mg^{2+} . Because of their large relative mass difference, lithium isotopes have the potential to exhibit sizable fractionation, as has been demonstrated by high-precision isotopic analysis.

Lithium isotopic compositions are now reported in terms of $\delta^7\text{Li}$ (Tomascak, 2004) but until recently reported in terms of $\delta^6\text{Li}$, an unusual formulation because the abundance of the heavier isotope is in the denominator (Chan *et al.*, 2002); $\delta^6\text{Li}$ is defined by

$$\delta^6\text{Li}(\text{‰}) = \left[\frac{({}^6\text{Li}/{}^7\text{Li})_{\text{sample}}}{({}^6\text{Li}/{}^7\text{Li})_{\text{std}}} - 1 \right] \times 1,000$$

Lithium in seawater, with an average $\delta^6\text{Li}$ value of -32‰ , is therefore isotopically heavy. Marine sediments, with $\delta^6\text{Li}$ values of $+1$ – 15‰ , are much lighter. Other reported ranges in $\delta^6\text{Li}$ values for geological materials include those of mid-ocean ridge basalts, -8‰ to -21‰ ; hemipelagic clays, -9‰ to -15‰ ; and continental crustal rocks, -8‰ to -21‰ (Huh *et al.*, 1998). All lithium isotopes are referenced to the NBSL-SVEC Li_2CO_3 standard (Clark and Fritz, 1997).

Chan *et al.* (2002) studied the isotopic composition of lithium in oil-field brines in the Heletz-Kokhav oil field in the southern coastal plain of Israel. The formation waters have chloride concentrations of $(1.8\text{--}4.7) \times 10^4 \text{ mg l}^{-1}$ and are thought to represent seawater evaporated into the gypsum stability field and subsequently altered by the dissolution of halite. Lithium concentrations range from 0.97 to 2.3 mg l^{-1} and increase with increasing chloride. The $\delta^6\text{Li}$ values range from -198‰ to -30‰ and are thus lighter than seawater (32‰), reflecting a rock-dominated source for lithium rather than an evaporated seawater source.

5.16.5.3 Carbon Isotopes

The origin of inorganic and organic carbon in sedimentary basins and the systematics of its isotopes have received a great deal of attention (e.g., Clark and Fritz, 1997). The stable carbon isotopic composition of dissolved carbon species, such as HCO_3^- , $\text{CO}_2(\text{aq})$, $\text{CH}_4(\text{aq})$, and the

organic acids, is normally reported as $\delta^{13}\text{C}\text{‰}$ Pee Dee belemnite (PDB) standard. There are two major reservoirs of carbon in sedimentary basins, marine carbonate having $\delta^{13}\text{C}$ values of $\pm 4\text{‰}$ and organic carbon with values between -10‰ and -35‰ . Bacterial and thermogenic reduction of organic matter to methane produces two isotopically distinct CH_4 reservoirs: biogenic CH_4 with $\delta^{13}\text{C}$ of -50‰ to -90‰ , and thermogenic CH_4 with $\delta^{13}\text{C}$ between -20‰ and -50‰ .

Carothers and Kharaka (1980) reported $\delta^{13}\text{C}$ values of inorganic carbon dissolved in oil-field waters from California and Texas, and discussed the sources and reactions that yield $\delta^{13}\text{C}$ of -20‰ to 28‰ . Dissolution of carbonate minerals and the oxidation of reduced carbon both produce bicarbonate as a by-product. Emery and Robinson (1993) reported a range from -60‰ to 10‰ , depending on the source of the carbon and the fractionation factors accompanying the production of HCO_3^- .

An increasing body of evidence indicates that the large volumes of CO_2 , which have been observed in basins such as the Pannonian Basin, Hungary, the Cooper-Eromanga Basin, Australia, and the South Viking Graben, North Sea, may have deep-seated sources (Wycherley *et al.*, 1999). The isotopic composition of CO_2 released by mantle, deep crustal, and shallow high-temperature processes is estimated to be intermediate between values for inorganic marine carbonate and organic carbon. Wycherley *et al.* (1999) cite the following values: magmatic origin/mantle degassing, -4‰ to -7‰ ; regional metamorphism, 0‰ to -10‰ ; contact metamorphism of carbonates, -2‰ to -12‰ ; and contact metamorphism of coals -10‰ to -20‰ . It should be noted, however, that due to the number of sources for carbon of varying $\delta^{13}\text{C}$ values and especially due to the ease of isotopic exchange and re-equilibration as well as mixing, carbon isotopes are not highly diagnostic and cannot be used alone to identify carbon sources (Kharaka *et al.*, 1999b). Carbon isotopes in shallow groundwater are discussed by Kendall and Doctor (see Chapter 5.11).

5.16.5.4 Sulfur Isotopes

The isotopic composition of sulfur in geologic materials is reported in the usual δ notation as $\delta^{34}\text{S}\text{‰}$ Vienna Canon Diablo troilite (VCDT). The isotopic geochemistry of sulfur is complex, because it exists in several redox states, each with a wide variety of fractionation mechanisms (Seal *et al.*, 2000). The three principal redox states of concern here are sulfur as sulfate(vi), sulfide

(-II), and elemental sulfur. Below $\sim 200^\circ\text{C}$, the nonbiologic rate of isotopic exchange between dissolved sulfate and sulfide is slow and isotopic equilibrium between the species is rare (Ohmoto and Lasaga, 1982). Kinetic effects therefore dominate the isotopic systematics of sulfur in sedimentary basins. The principal kinetic effects are associated with the reduction of sulfate to elemental sulfur or sulfide S(-II). This can be achieved both microbially with large fractionation effects and thermochemically with minimal fractionation. Fractionation is usually minor during the oxidation of sulfide to sulfate (Seal *et al.*, 2000).

The principal sources of sulfate in formation waters are dissolved marine sulfate, sulfate derived from the dissolution of evaporites, and sulfate formed by the oxidation of sulfides. Sulfate is destroyed by reduction to hydrogen sulfide. The value of $\delta^{34}\text{S}$ in gypsum is only $\sim 1.6\text{‰}$ heavier than sulfate in solutions from which it precipitates. The isotopic composition of sulfur in gypsum in Phanerozoic deposits precipitated from seawater during evaporation thus tracks the secular changes in the isotopic composition of sulfur in seawater ($\sim 10\text{--}30\text{‰}$).

The lighter isotopes of sulfur are preferentially partitioned into sulfide during microbial SO_4^{2-} reduction. Hydrogen sulfide is much lighter than the precursor sulfate, and the residual sulfate is heavier. Sulfate reduction during early diagenesis therefore drives the $\delta^{34}\text{S}$ of residual pore-water sulfate toward higher values. Thermochemical reduction of sulfate at higher basinal temperatures, however, typically produces sulfide similar in isotopic composition to the parent sulfate (Machel, 2001).

Dworkin and Land (1996) found that the $\delta^{34}\text{S}$ values of sulfate in Frio (Oligocene) formation waters were modified by the addition of light sulfur derived from the oxidation of pyrite. The $\delta^{18}\text{O}$ values of dissolved sulfate in these waters fall within the range found in Mesozoic and Cenozoic seawater, and are interpreted by Dworkin and Land to reflect sulfate derived from deeper Jurassic evaporites. This conclusion, however, must be qualified because, at temperatures $>100^\circ\text{C}$, oxygen isotopes equilibrate between oxygen in water and in sulfate (e.g., Kharaka and Mariner, 1989). Gavrieli *et al.* (1995) document two stages in the evolution of the isotopic composition of sulfate-sulfur in oil fields in southwestern Israel. Early shallow bacterial reduction increased the $\delta^{34}\text{S}$ of residual dissolved Miocene sulfate from 20‰ to 26‰ . In the presence of crude oil, additional sulfate was reduced and increased the $\delta^{34}\text{S}$ values to a maximum of 54‰ .

5.16.5.5 Chlorine Isotopes

Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl , and one radioactive isotope, ^{36}Cl (half-life = 0.301 Myr). The stable isotopic composition of chloride in geologic materials is reported in the conventional δ notation as $\delta^{37}\text{Cl}$. Seawater, which is used as the isotopic standard, has a $\delta^{37}\text{Cl}$ of 0‰ . Most natural waters have $\delta^{37}\text{Cl}$ values between -1‰ and $+1\text{‰}$. However, values of -8‰ have been measured in marine pore waters. Minerals in which chloride substitutes for OH at high temperatures have $\delta^{37}\text{Cl}$ values as high as 7‰ (Banks *et al.*, 2000).

During halite precipitation from evaporated seawater, ^{37}Cl is preferentially partitioned into the solid phase. $\delta^{37}\text{Cl}$ of the residual brines and of subsequently precipitated halite become progressively lighter. However, during the last stages of evaporation, preferential incorporation of ^{35}Cl into potassium and magnesium salts reverses the fractionation trend, and the residual brine and the precipitated salts become isotopically heavier (Eastoe *et al.*, 1999; Banks *et al.*, 2000). The $\delta^{37}\text{Cl}$ of halite precipitating from evaporated seawater with a $\delta^{37}\text{Cl}$ value of 0‰ is $\sim 0.29\text{‰}$. Eastoe *et al.* (1999) found a minimum $\delta^{37}\text{Cl}$ value of -0.9‰ in brines produced during the laboratory evaporation of seawater at the beginning of the potash facies.

The mechanisms that fractionate chloride isotopes during diagenesis are still not well established (Eastoe *et al.*, 1999). Eggenkamp (1998) found a range from -0.27‰ to -4.96‰ in the $\delta^{37}\text{Cl}$ of formation waters from North Sea oil fields. In some fields $\delta^{37}\text{Cl}$ decreased with decreasing chloride concentration. Water from oil reservoirs had a much smaller range in $\delta^{37}\text{Cl}$, from 0‰ to -1.5‰ , over a wide range of chloride concentrations. Bedded salt in the Gulf of Mexico Basin has $\delta^{37}\text{Cl}$ values of -0.5‰ to $+0.3\text{‰}$ (Eastoe *et al.*, 2001), values consistent with a $\delta^{37}\text{Cl}$ value of 0.0‰ for Jurassic seawater. Eastoe *et al.* (2001) suggest that the slightly heavier values for diapiric salt ($0.0\text{--}0.5\text{‰}$) are the result of the incongruent dissolution of halite, which presumably releases lighter chloride preferentially. The $\delta^{37}\text{Cl}$ values of formation waters from the Gulf of Mexico Basin range from -1.9‰ to $+0.7\text{‰}$. Waters having $\delta^{37}\text{Cl}$ values $<0.6\text{‰}$ are found in siliciclastic strata of Eocene to Miocene age, but not in Plio-Pleistocene sediments or in Mesozoic carbonates, which contain waters of higher $\delta^{37}\text{Cl}$ composition. Eastoe *et al.* (2001) invoke differences in the rate of diffusion of ^{35}Cl and ^{37}Cl as a possible fractionation mechanism.

5.16.5.6 Bromine Isotopes

Bromine isotope geochemistry is in its beginning stages. Bromine has two stable isotopes, ^{79}Br and ^{81}Br , having relative mass abundances of 50.686% and 49.314%, respectively (Eggenkamp and Coleman, 2000). Variations in isotopic composition are reported as $\delta^{81}\text{Br}$ (SMOB), where SMOB is standard mean oceanic bromide. Several processes have the potential for causing significant fractionation of the bromide isotopes. These include concentration of bromide in bittern water during salt precipitation from evaporating seawater, oxidation of bromide to Br_2 , and the natural production of organobromide compounds. Eggenkamp and Coleman (2000) found a range of 0.08–1.27‰ in $\delta^{81}\text{Br}$ in formation waters of the Norwegian North Sea. There is a negative correlation between $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$, reflecting differences in fractionation mechanisms of the two isotopic systems.

5.16.5.7 Strontium Isotopes

The strontium isotopic composition of formation waters has shown great utility as a means of identifying sources of strontium in formation waters, the degree of water–rock exchange, and the degree of mixing along regional fluid flow paths (e.g., Armstrong *et al.*, 1998). The strontium isotopic composition of geological materials is expressed as the ratio of $^{87}\text{Sr}/^{86}\text{Sr}$, which can be measured with great analytical precision. Radiogenic ^{87}Sr is produced by the decay of ^{87}Rb (half-life = 4.88×10^{10} years). Rocks having high initial concentrations of rubidium, such as granites, are characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Rocks derived from materials having low rubidium concentrations, such as mantle-derived rocks, have correspondingly low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Since the Precambrian, the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater has fluctuated between ~ 0.7070 and 0.7092 as the result of variations in the relative rates of input of ^{87}Sr -enriched strontium from continental weathering and ^{87}Sr -depleted strontium from mantle sources. Fluids in sedimentary basins containing Paleozoic strata typically have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in excess of seawater values that are contemporaneous or coeval with the depositional age of the current host sediment. This is well illustrated by the data of Connolly *et al.* (1990) for the Alberta Basin, Canada. The enrichment is due to the release of strontium attending the alteration of silicates. Due to the significant increase of $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater since the Jurassic, some

formation waters in Cenozoic sedimentary basins actually have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than those of contemporaneous seawater due to the addition of strontium dissolved from older and deeper sedimentary sources (e.g., McManus and Hanor, 1993). Precipitates derived from such sources, such as barite in Holocene seafloor vents in the Gulf of Mexico, have lower $^{87}\text{Sr}/^{86}\text{Sr}$ values less than present-day seawater (Fu, 1998).

5.16.5.8 Radioactive Isotopes and Age Dating

A number of radioactive isotopes produced primarily by cosmic ray interactions in the upper atmosphere, especially ^{14}C (Clark and Fritz, 1997; Mazor, 1997), ^{36}Cl (Andrews *et al.*, 1994; Phillips, 2000), ^{129}I (Moran *et al.*, 1995; Fabryka-Martin, 2000), ^{39}Ar and ^{81}Kr (Porcelli *et al.*, 2002; Loosli and Purtschert, 2005), as well as total dissolved ^4He (Torgersen and Clarke, 1985; Solomon, 2000), have been used, in conjunction with data for the stable isotopes and calculated flow rates, for determining the age of natural waters, including fluids in sedimentary basins (Bethke *et al.*, 1999, 2000; Bethke and Johnson, 2002). The 5.73 kyr half-life of ^{14}C at 5.73 kyr is so short that it is useful only for dating basinal meteoric water younger than ~ 40 kyr. ^{36}Cl ($t_{1/2} = 0.301$ Myr) is useful for dating water of up to ~ 2 Myr in age. These isotopic systems are reviewed by Phillips and Castro (see Chapter 5.15).

The ratio of ^{129}I ($t_{1/2} = 15.7$ Myr) to total iodide can be used to estimate ages up to ~ 80 Myr. The determination of even greater ages is theoretically possible by using ^4He generated from the decay of uranium and thorium in rocks (Froehlich *et al.*, 1991). The ages obtained, however, carry large uncertainties, because the radiogenic isotopes can have several sources (e.g., Fabryka-Martin, 2000) and are often subject to fractionation due to isotopic exchange and partitioning. In addition, the origin and age of H_2O in formation waters is generally different from that of the radiogenic and other isotopes used for age determinations (Froehlich *et al.*, 1991; Kharaka and Thordsen, 1992; Clark and Fritz, 1997).

The ratio of ^{129}I to total I, at times in combination with $^{36}\text{Cl}/\text{Cl}$ ratios, has been successfully used to estimate the residence time of subsurface waters, to trace the migration of brines, and to identify hydrocarbon sources (e.g., Fabryka-Martin, 2000). However, this method can also be used to illustrate the difficulties of dating “very old” formation water,

and include: (1) the ratios of $^{129}\text{I}/\text{I}$ generally are between $1,500 \times 10^{-15}$ and 20×10^{-15} , requiring the use of accelerator mass spectrometry for their measurement; (2) there are major uncertainties in the correct value of the initial $^{129}\text{I}/\text{I}$ ratios; (3) errors in the estimation of the rate of subsurface release of ^{129}I by spontaneous fission of ^{238}U ; and (4) additional (diagenetic) release of ^{127}I from organic-rich sediments (Fabryka-Martin, 2000; Moran *et al.*, 1995). For several of these reasons, the $^{129}\text{I}/\text{I}$ and $^{36}\text{Cl}/\text{Cl}$ ratios could not be used to estimate the residence and travel time of water in the Milk River aquifer, Alberta, Canada (Fabryka-Martin, 2000).

The age of brine inclusions in Louisiana salt domes was estimated to be ~ 8 Myr by $^{129}\text{I}/\text{I}$ ratios that assumed no significant *in situ* production of ^{129}I , because of the low uranium concentration in salt (Fabryka-Martin *et al.*, 1985). Moran *et al.* (1995) found that the comparison between measured ratios and the decay curve for hydrospheric ^{129}I results in minimum source ages much older than present host formation ages, indicating migration of brine from older and deeper sources. Corrections for the fissiogenic component of ^{129}I gave Eocene ages (53–55 Myr) for brines residing in Miocene reservoirs. However, Mesozoic sources could not be ruled out, because of uncertainties in estimating the magnitude of the fissiogenic component. Some of the measured $^{129}\text{I}/\text{I}$ ratios showed that the brines had resided in formations with locally high uranium values (Moran *et al.*, 1995).

5.16.6 BASINAL BRINES AS ORE-FORMING FLUIDS

Sedimentary formation waters have long been invoked as ore-forming fluids in a number of distinctly different geologic settings. Although ore deposit classification schemes vary, the following have been genetically associated with basinal fluids: (1) Mississippi-Valley-type lead, zinc, copper, barium, and fluoride deposits; (2) shale-hosted lead, zinc, and barium deposits; (3) rift-basin and redbed copper deposits; (4) sandstone-hosted uranium deposits; and (5) carbonate-hosted celestine (SrSO_4) deposits.

Much of the information available on the nature of the fluids that were involved in the genesis of these deposits comes from physical and chemical measurements made on fluid inclusions in ore and gangue minerals. For example, chemical analyses of inclusions indicate that many of these fluids were Na–Ca–Cl-brines having salinities in the range of $(1\text{--}3) \times 10^5 \text{ mg l}^{-1}$ (Hanor, 1979; Sverjensky,

1986; Giordano and Kharaka, 1994). Mass balance considerations (Barnes, 1979) indicate that concentrations of base and ferrous metals in ore-forming solutions must be at least $1\text{--}10 \text{ mg l}^{-1}$ to form typical hydrothermal ore deposits. The discussion below emphasizes the mechanisms of solubilization of metals in formation waters. For a comprehensive treatment of the migration of ore-forming fluids and mechanisms of ore precipitation from single or mixed fluids, see Sverjensky (1986), Kharaka *et al.* (1987), and Giordano (2000).

5.16.6.1 Metal-Rich Brines

The concentration of heavy metals in oil-field waters, with the exception of iron and manganese, is generally low (Kharaka and Thordsen, 1992; Hitchon *et al.*, 2001). In the case of lead, zinc, and copper, and with the exception of fewer than half a dozen localities worldwide, the concentrations are $< 100 \text{ mg l}^{-1}$. The concentrations of rare metals (e.g., mercury, gold, and silver) are generally one to several orders of magnitude lower (e.g., Giordano, 2000).

The central Mississippi Salt Dome Basin is a metal-rich brine locality that has been studied extensively (Carpenter *et al.*, 1974; Kharaka *et al.*, 1987). The brines (Table 4) are Na–Ca–Cl-type waters of extremely high salinity (up to $\sim 3.5 \times 10^5 \text{ mg l}^{-1}$ TDS), but low concentrations of aliphatic acid anions. The metal concentrations in many samples are very high, reaching values $\geq 100 \text{ mg l}^{-1}$ for lead, 250 mg l^{-1} for zinc, 500 mg l^{-1} for iron, and 200 mg l^{-1} for manganese (Table 6).

The samples with high metal contents have extremely low concentrations ($< 0.02 \text{ mg l}^{-1}$) of H_2S . Samples that have high concentrations of H_2S have low metal contents that are typical of oil-field waters (Kharaka *et al.*, 1987). Exceptionally rich sources of metals such as redbeds may be needed to provide sufficient amounts of metals for the formation of ore deposits. Redbeds are attractive for this reason and because they contain so little reduced sulfur, and that leached metals will tend to remain in solution.

5.16.6.2 Solubilization of Heavy Metals

A major problem in explaining metal transport in basinal brines is the very low solubility of base metal sulfides, particularly at temperatures less than $\sim 150^\circ\text{C}$. For example, the calculated activity product $(a_{\text{Zn}^{2+}})(a_{\text{H}_2\text{S}^0})$ for solutions in equilibrium with sphalerite, $\text{ZnS} + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2\text{S}^0$, using SUPCRT92

Table 6 Selected metal concentrations (mg l^{-1}) of formation waters from central Mississippi Salt Dome Basin.

Sample ID	Fe	Mn	Pb	Zn	Al ^a	Cd	Cu ^a
84-MS-1	137	57.5	8.39	49.6		0.49	<20
84-MS-2	97.4	38.2	0.07	1.22	59	0.05	<20
84-MS-3	61.9	10.6	0.04	0.53	133	0.02	<20
84-MS-4	346	63.9	53.2	222	267	0.83	<20
84-MS-5	407	70.2	60.5	243	42	0.81	61
84-MS-6	284	21.0	26.8	95.1	67	0.63	21
84-MS-7	261	83.5	34.6	172	79	0.86	<20
84-KS-8	194	69.3	22.8	107	132	0.67	34
84-MS-9	0.54	15.5 ^a	<0.5 ^a	12.0 ^a		<0.2 ^a	<0.2
84-MS-10	84.9	44.8	0.08	0.31		0.02	<20
84-MS-11	465	212	70.2	243	367	0.99	21
84-MS-12	65.3	16.4	0.17	0.28		0.03	<20
84-MS-14	0.75	2.78	0.16	0.20		<0.02	<20
84-MS-15	223	53.2	2.28	4.10		0.02	<20
84-MS-16	0.53	9.98	0.02	0.07	142	<0.02	<20
84-MS-18	0.15	3.2 ^a	<0.5 ^a	13 ^a		0.08 ^a	0.61
84-MS-19	0.47	1.64	0.04	0.06		0.03	<20
84-MS-20	0.07	1.46	0.03	0.16		0.05	<20
Field blank ^a	10.6	1.05	1.04	12.6		0.08	<0.20

Source: Kharaka *et al.* (1987).^a $\mu\text{g l}^{-1}$.

(Johnson *et al.*, 1992), is only $10^{-15.1}$ at 100 °C, 500 bar, and at a neutral pH of 6.04. The activity product for lead and H_2S for a solution in equilibrium with galena under these conditions is only $10^{-17.7}$. Thus, aqueous complexes of base metals are required to account for the minimum concentrations of the ore-forming metals. Experimental work and thermodynamic calculations have focused primarily on metal–chloride, metal–bisulfide, and metal–organic complexes as possible solubilizing agents (Sverjensky, 1986; Hanor, 1996b; Giordano, 2000). There is still some disagreement on the relative importance of these complexing agents, although most authors today favor chloride complexing, as discussed below.

5.16.6.3 Bisulfide Complexing

Considerable attention has been paid to complexing of metals by reduced sulfur species. Some of the complexes of zinc and lead that have been considered include $\text{Zn}(\text{HS})_3^-$, $\text{Zn}(\text{HS})_4^{2-}$, $\text{Pb}(\text{HS})_3^-$, $\text{Pb}(\text{HS})_2^0$, and $\text{Pb}(\text{HS})_2^0$ (Barnes, 1979; Kharaka *et al.*, 1987). Giordano and Barnes (1981) concluded, on the basis of experimental studies, that ore-forming solutions at temperatures <200 °C with total dissolved sulfur contents of less than $\lesssim 1 \text{ m}$ (ca. $3.2 \times 10^4 \text{ mg l}^{-1}$) cannot transport significant quantities of lead as bisulfide complexes. Extensive metal complexing by the bisulfide complexes requires much higher pH values

than those found in saline formation waters (Kharaka *et al.*, 2000).

5.16.6.4 Organic Complexing

As discussed in Section 5.16.3.5.3, there has been considerable interest in recent years in the possible role of organic ligands as complexing agents of metals in basinal waters (e.g., Kharaka *et al.*, 1987, 2000). Aliphatic acid anions, such as acetate, which are generally the most abundant of the reactive organic species, have received the most attention (Giordano and Kharaka, 1994). There is, however, an inverse correlation between metal content and organic acid concentrations in basinal waters (Hanor, 1994). Concentrations of lead and/or zinc well above 1 mg l^{-1} have been reported only in low-acetate waters. At acetate concentrations $\gtrsim 50 \text{ mg l}^{-1}$, reported metal concentrations are low. Dicarboxylic acid anions form stronger metal–organic complexes, but field data and geochemical modeling indicate that the occurrence of high metal concentrations is not directly related to high concentrations of dissolved organic species (Hanor, 1996b; Kharaka *et al.*, 2000).

5.16.6.5 Chloride Complexing

The solubility of PbS and ZnS in waters containing dissolved chloride is enhanced by the formation of metal–chloro complexes: MeCl^+ , MeCl_2^0 , MeCl_2^- , and MeCl_4^{2-} . Most fluids that have concentrations of dissolved lead and

dissolved zinc exceeding 1 mg l^{-1} also have chloride concentrations in excess of $\sim 1 \times 10^5 \text{ mg l}^{-1}$ ($\text{TDS} = 1.7 \times 10^5 \text{ mg l}^{-1}$). A few waters from the Gulf Coast with a chloride concentration between $6 \times 10^4 \text{ mg l}^{-1}$ ($\text{TDS} = 1 \times 10^5 \text{ mg l}^{-1}$) and $1 \times 10^5 \text{ mg l}^{-1}$ have metal concentrations in excess of 1 mg l^{-1} . Thermodynamic calculations using Pitzer equations of state show that several properties of typical basinal fluids combine to increase the solubility of PbS and ZnS, at a fixed temperature and activity of dissolved H_2S , by as much as 15 orders of magnitude through an order of magnitude increase in salinity and chlorinity (Hanor, 1996b). These include:

1. the significant decrease in pH with increasing salinity;
2. the onset of the predominance of the tetrachloro complexes (MeCl_4^{2-}), whose activities increase by a factor of 10^4 with increasing chloride concentration; and
3. the strongly nonideal behavior of Cl^- , which results in activity coefficient terms that are significantly greater than unity in very saline waters.

5.16.6.6 Geochemical Modeling of Ore Fluids

Geochemical modeling is a valuable tool for assessing the importance of ligands, including chlorides, bisulfides, and organic acid anions in the transport of significant quantities of metals in ore solutions (Giordano and Kharaka, 1994; Kharaka *et al.*, 2000). The geochemical code used in such modeling must (1) have thermochemical data for the dominant inorganic and organic species present in formation waters and for the minerals of interest; (2) include temperature and pressure corrections for the thermochemical data; and (3) be able to treat high-salinity solutions using Pitzer or comparable ion-interaction formulations.

In geochemical modeling, there have been two approaches used to study the importance of organic ligands, bisulfides, and chlorides in the transport and deposition of metals. In the first approach, simulations are carried out using variable concentrations of known organic and other ligands that are added to model compositions for the ore fluids, especially fluids for Mississippi Valley type and redbed-related base metal deposits (Giordano and Kharaka, 1994; Hanor, 2000). In the second approach, Kharaka *et al.* (1987) used the measured chemical composition of metal-rich and metal-poor brines from the central Mississippi Salt Dome Basin to compute the concentrations of sodium, calcium, magnesium, aluminum, iron, lead, and zinc complexed with acetate and other measured

organic ligands as well as with chlorides and bisulfides under subsurface conditions.

Results from both approaches indicate that (1) high concentrations ($\sim 100 \text{ mg l}^{-1}$) of lead and zinc can be present in oil-field brines only if the concentration of total H_2S is at the microgram per liter level; in such fluids, significant quantities of dissolved lead and zinc can be transported as carboxylate complexes; (2) lead and zinc in Mississippi-Valley-type ore fluids appear to be transported dominantly as chloride complexes; and (3) the brines are close to equilibrium with galena and sphalerite under the likely subsurface temperatures, pressures, and pH (Kharaka *et al.*, 1987; Sicree and Barnes, 1996; Giordano, 2000).

5.16.6.7 Fluoride

Fluid inclusion studies have shown that basinal fluids responsible for depositing fluorite ore deposits typically have salinities of 20–26 wt.% NaCl equivalent and high calcium concentrations (Munoz *et al.*, 1991). As noted earlier, concentrations of fluoride typically exceed 10 mg l^{-1} in formation waters having chloride concentrations $>100 \text{ g l}^{-1}$; below this threshold, fluoride concentrations are typically $<5 \text{ mg l}^{-1}$. This threshold may be related to complexing of fluoride with calcium and magnesium at elevated salinities, which greatly increases the solubility of fluorite (Richardson and Holland, 1979; Munoz *et al.*, 1991; Hitchon, 1995).

5.16.6.8 Barium and Strontium

Although complete solid solution exists, at least metastably, between barite (BaSO_4) and celestine (SrSO_4), most (Ba, Sr) SO_4 ore deposits consist of one or the other end member. This fractionation probably reflects the buffering of strontium in basinal brines by silicate-carbonate mineral assemblages. The concentration of strontium in these brines increases roughly exponentially with increasing salinity. Barium concentrations, however, are controlled by saturation with respect to barite (Figure 7).

Basinal fluids with the highest Sr/Ba ratios, and therefore most likely to form celestine rather than barite, have high salinities and moderately high levels of sulfate, which suppress the concentrations of barium. The precursors to such waters can be produced in coastal marine settings by the evaporation of seawater. As these brines reflux through underlying sediments, they can leach substantial

amounts of strontium. If these diagenetically altered fluids are then discharged back up into overlying gypsum or anhydrite beds, celestine is apt to precipitate. Many barite deposits have formed where reduced, high-barium waters have mixed with oxidized waters high in sulfate (Hanor, 2000).

5.16.7 DISSOLVED GASES

Gases have measurable, but variable, solubilities in aqueous solutions. The aqueous concentration of a volatile species in equilibrium with a pure gas phase at a fixed temperature increases with increasing gas pressure, and decreases with increasing salinity due to the salting-out effect (Figure 16). Changes in solubility with temperature are more variable. At a fixed pressure, a volatile species such as CO₂ may display retrograde solubility at low temperatures, but an increase in solubility at higher temperatures (Figure 15). In general, however, the solubility of volatile species increases down a typical basinal depth gradient, in response to increasing temperature and pressure. While many volatile species exist in sedimentary basin waters, we will examine; only the systematics of dissolved methane, carbon dioxide, hydrogen sulfide, and the noble gases.

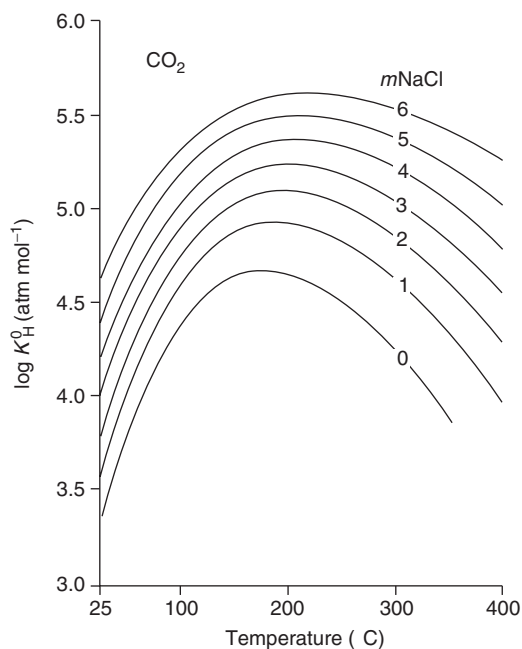


Figure 16 Solubility of CO₂, reported in terms of Henry's law constant K_H^0 (see text), as a function of temperature and salinity of water. After Drummond, (1981).

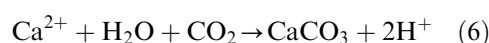
5.16.7.1 Methane

Extensive field testing was conducted during the oil crisis of the 1970s to assess the concentration of dissolved CH₄ and of other geopressured-geothermal resources in the northern Gulf of Mexico and in other basins in USA. The tests showed that saline pore fluids to depths exceeding 6 km are saturated with respect to CH₄ (Wallace *et al.*, 1979; Kharaka and Berry, 1980). The high content of dissolved CH₄ in basinal brines is due to the thermocatalytic destruction of kerogen and liquid hydrocarbons, especially in the deeper sections (high *T* and *P*) of the basins (Tissot and Welte, 1984).

Experimental work on the solubility of CH₄ (e.g., Haas, 1978; Price, 1979) permits estimation of the solubility of CH₄ over much of the range of pressures, temperatures, and salinities characteristic of sedimentary basins (Kharaka *et al.*, 1988; Spycher and Reed, 1988). High concentrations of CH₄ have been found in the two-phase fluid inclusions in sedimentary ore deposits and in diagenetic mineral overgrowths, and corrections for the presence of CH₄ have to be made to inclusion homogenization temperatures to derive accurate estimates of filling temperature and pressures (Hanor, 1980).

5.16.7.2 Carbon Dioxide

Dissolved CO₂ in formation waters originates primarily from kerogen and other organic sources, from calcite and other carbonate minerals, and/or from mantle sources (see Section 5.16.5.3). The solubility of CO₂ in water (Figure 16), as that of CH₄, shows a strong dependence on temperature and salinity (Drummond, 1981). CO₂ is much more reactive than CH₄, and plays a more important role in water-CO₂-mineral interactions in the subsurface, especially in the carbonate and pH-sensitive interactions (Kharaka *et al.*, 1985). The concentration of dissolved CO₂ in formation waters can be represented by the fugacity of CO₂ (*f*CO₂) in a real or fictive gas phase in equilibrium with that of water (Spycher and Pruess, 2005). The partial pressure and fugacity of CO₂ can be calculated after measuring the CO₂ concentration in a coexisting gas phase at known *P* and *T* (Smith and Ehrenberg, 1989; Spycher and Reed, 1988) or by calculating *f*CO₂ assuming equilibrium with respect to calcite (Hutcheon, 2000):



Several authors have noted an increase in $f\text{CO}_2$ with increasing temperature in some sedimentary basins, including the Texas Gulf Coast, USA, the Patani Basin, Thailand, and the North Sea (Smith and Ehrenberg, 1989; Lundegard and Trevena, 1990; Hutcheon, 2000). The CO_2 fugacities increase systematically from ~ 0.1 bar at 50°C to 100 bar at 175°C . The phase boundary for the reaction of kaolinite with dolomite to form chlorite, calcite, and CO_2 parallels the CO_2 –temperature trend observed in the field. This is indicative of CO_2 buffering, but the fugacities predicted are one to two orders of magnitude low (Hutcheon *et al.*, 1993; Hutcheon, 2000).

5.16.7.2.1 Storage of CO_2 in sedimentary basins

Global warming and the resulting climate change are arguably the most important environmental challenges facing the world in this century (White *et al.*, 2003). In 2005, the global average temperature was about 0.7°C higher than during preindustrial times, and model calculations show the temperature difference increasing to about $2\text{--}6^\circ\text{C}$ by year 2100 (Houghton, 2004). There is a broad scientific consensus that global warming results primarily from increased concentrations of atmospheric greenhouse gases (GHGs), especially CO_2 emitted largely from the burning of fossil fuels (Broecker, 2006). Increased anthropogenic emissions of CO_2 have increased its atmospheric concentrations from about 280 ppm during preindustrial times to about 380 ppm today, and based on several defined scenarios, atmospheric CO_2 concentrations were projected by Intergovernmental Panel on Climate Change (IPCC) to increase to a range of 450–1,100 ppm in year 2100 (Prentice *et al.*, 2001). Carbon sequestration, in addition to energy conservation, increased efficiency in electric power generation and utilization, increased use of lower carbon intensity fuels, and increased use of nuclear energy and renewable sources, is now considered necessary to stabilize atmospheric levels of GHGs and global temperatures at values that would not severely impact economic growth and the quality of life on Earth (White *et al.*, 2003). Sedimentary basins in general and depleted petroleum fields and deep saline aquifers in particular are being investigated as possible repositories for large amounts of anthropogenic CO_2 that must be sequestered to stabilize atmospheric CO_2 concentrations (Korboel and Kaddour, 1995; Durocher *et al.*, 2004; Hovorka *et al.*, 2006). These basins are attractive for CO_2 storage,

because they have huge potential capacity, estimated at 350–11,000 Gt of CO_2 worldwide, and advantageous locations close to major CO_2 sources (Holloway, 1997, 2001). In addition, a great deal of relevant geological, geochemical, and hydrologic information can be obtained from the large number of wells (~ 3.5 million in USA) drilled for oil and gas operations (Kharaka and Dorsey, 2005).

In geologic sequestration, CO_2 captured from fossil fuel–fired power plants and other sources may be stored in: (1) structural traps such as depleted petroleum reservoirs, primarily as supercritical immiscible fluid (hydrodynamic trapping); (2) saline formation water as H_2CO_3^0 , HCO_3^- and other dissolved C species (solution trapping); and/or (3) carbonate minerals, including calcite, magnesite, siderite, and/or ankerite (mineral trapping) (Gunter *et al.*, 1993; Palandri and Kharaka, 2005). Initially, the bulk of injected CO_2 will be stored as supercritical fluid because the target reservoirs are likely to have temperatures and pressures higher than 31°C and 74 bar, the critical values for CO_2 . The injected CO_2 will rapidly dissolve in formation water that contacts the fluid, but mineral trapping, which would depend on the availability of reactive Ca, Mg, Fe, and other divalent cations in formation water or the reservoir rocks, could be slower, yet more permanent, because many carbonate phases can remain stable for geologically significant time periods (Hitchon, 1996b; Palandri and Kharaka, 2005). Understanding gas–water–mineral interactions in sedimentary basins could facilitate the isolation of anthropogenic CO_2 in the subsurface for thousands of years, thus moderating rapid increases in concentrations of atmospheric CO_2 and mitigating global warming (White *et al.*, 2003; Kharaka *et al.*, 2006a). Because of economic benefits and more than 30 years of commercial application, it is expected that injection into depleted petroleum fields for enhanced oil recovery (EOR) will be the earliest method of CO_2 disposal. However, as the amounts of CO_2 to be sequestered increase, deep saline aquifers will likely become preferred storage sites, because of their huge potential capacity and advantageous locations close to CO_2 sources (Holloway, 1997; Hitchon, 1999). In addition to storage capacity, key environmental questions include CO_2 leakage related to the storage integrity, and the physical and chemical processes that are initiated by injecting CO_2 underground (Allis *et al.*, 2005; Hepple and Benson, 2005; Knauss *et al.*, 2005).

A multilaboratory field experiment to investigate the potential for geologic storage of CO_2 in saline aquifers in sedimentary basins was conducted by injecting approximately 1,600

metric tons of refinery CO₂ during October 2004 into a 24m sandstone zone of the Oligocene Frio Formation—an extensive regional petroleum and brine reservoir in the US Gulf Coast (Hovorka *et al.*, 2006). Downhole and surface samples of formation water and gas were obtained from the injection well and an observation well completed about 30m up-dip using a variety of sampling tools and methodologies (Kharaka *et al.*, 2006a). Samples were obtained from both wells before CO₂ injection for baseline data, during the injection to track its breakthrough and postinjection to investigate the “residual” CO₂ (Hovorka *et al.*, 2006) and its leakage into the overlying “B” sandstone zone, and temporal changes in fluid composition (Kharaka *et al.*, 2006a). Also, surface and wellbore geophysical logging using electrical, seismic, and the Schlumberger reservoir saturation tool (RST) was carried out to provide baseline characterization and to investigate changes in the composition and distribution of the CO₂ plume (Hovorka *et al.*, 2001, 2006).

Results from the Frio brine field test demonstrated the relatively straightforward method of CO₂ injection and its rapid transport to the observation well. Field geochemical methodologies, especially measurements of pH, alkalinity (Figure 17) and gas compositions (Freifeld *et al.*, 2005), proved highly effective for tracking the injected CO₂. The tracking of CO₂ was later confirmed by laboratory determinations of dissolved Fe, Mn, and Ca, and isotopes, especially $\delta^{18}\text{O}$ values of brine and CO₂, and $\delta^{13}\text{C}$ values of DIC (dissolved inorganic carbon) and CO₂ (Kharaka *et al.*, 2006a). Results of geochemical modeling, using

updated SOLMINEQ (Kharaka *et al.*, 1988), indicate that the Frio brine in contact with the supercritical CO₂ would have a pH of about 3 at subsurface conditions, and this low pH causes the brine to become highly undersaturated with respect to carbonate, aluminosilicate, and most other minerals present in the Frio formation. Because mineral dissolution rates are generally higher by orders of magnitude at such low pH values (Palandri and Kharaka, 2004), the observed increases in concentrations of HCO₃⁻ and Ca likely result from the rapid dissolution of calcite, and the observed large increases in concentrations of Fe, Mn, Zn, Pb, and other metals likely were caused by dissolution of the observed iron oxyhydroxides.

This rapid dissolution of minerals caused by low-pH brine could have important environmental implications with regard to creating pathways in the rock seals and well cements that could facilitate leakage of CO₂ and brine. Maintaining reservoir integrity that would limit CO₂ leakage into overlying formations, and ultimately into the atmosphere, to very low levels is essential to the success of injection operations (Hepple and Benson, 2005). Preventing brine migration into overlying drinking water supplies is equally important, because dissolution of minerals would mobilize Fe, Mn, and other toxic metals, in addition to the chemicals in the pristine brine. The observed mobilization of organics, including BTEX, phenols, and other toxic compounds, from this and other nonoil-bearing aquifer would further compound the environmental severity of CO₂ and brine leakage (Kharaka *et al.*, 2006b).

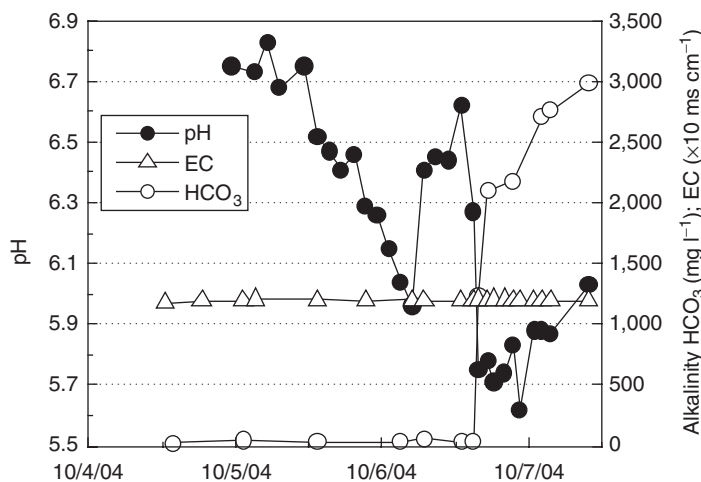


Figure 17 Electrical conductance (EC), pH, and alkalinity of Frio brine from the observation well determined on site during CO₂ injection. Note the sharp drop of pH and high alkalinity increase with the breakthrough of CO₂ (Kharaka *et al.*, 2006b).

5.16.7.3 Hydrogen Sulfide

Reservoirs of natural gas generally contain only small amounts of H_2S , but in some cases contain 2–30% (v/v) $\text{H}_2\text{S(g)}$ (Hitchon *et al.*, 2001; Worden and Smalley, 2001). Sources of this H_2S include (1) degradation of sulfur-rich kerogen, (2) breakdown of sulfur-rich crude oil, (3) BSR, and (4) TSR (Worden and Smalley, 2001; Machel, 2001). BSR is generally limited to temperatures below $\sim 80^\circ\text{C}$, leaving TSR as the only mechanism that contributes high concentrations of H_2S to natural gas (Worden and Smalley, 2001). Sources of sulfate include aqueous sulfate and sulfate derived from the dissolution of anhydrite.

In clastic sedimentary sequences, where iron-bearing mineral phases are abundant, most of the sulfide can be precipitated as iron sulfide, usually pyrite, and concentrations of H_2S in formation waters in such sequences are often below the limit of detection (Kharaka *et al.*, 1987). A pyrite–siderite or a pyrite–ankerite buffer may be controlling H_2S partial pressures in clastic hydrocarbon reservoirs in the Norwegian Shelf and Gulf Coast (Aagaard *et al.*, 2001). Predicted and measured H_2S partial pressures increase over several orders of magnitude with depth in these basins. In iron-poor carbonate sediments H_2S partial pressures are largely unbuffered, and concentrations of dissolved hydrogen sulfide can approach $1,000\text{ mg l}^{-1}$ (Wade *et al.*, 1989). Hitchon *et al.* (2001) found a linear relation between the concentration of HS^- in formation waters and the H_2S (vol.%) in associated natural gas in carbonate reservoirs of the Alberta Basin, Canada.

5.16.7.4 Noble Gases

The noble gas geochemistry of natural waters, including formation waters in sedimentary basins, has been used to determine paleotemperatures in the recharge areas, to determine the age of the waters (Torgersen and Clarke, 1985; Porcelli *et al.*, 2002; Loosli and Purtschert, 2005), to evaluate water washing of hydrocarbons, and to identify mantle-derived volatiles (Pinti and Marty, 2000). The dissolved noble gases, (helium, neon, argon, krypton, and xenon in sedimentary waters) have four principal sources: the atmosphere, *in situ* radiogenic production, the deep crust, and the mantle. These sources have characteristic chemical and isotopic compositions (Ozima and Podosek, 1983; Kennedy *et al.*, 1997).

The partitioning of atmospheric noble gases (ANGs) between air and surface water follows Henry's law, and noble gas solubility is usually

described in terms of the Henry's law coefficient, which varies with temperature and salinity: the concentration of the various noble gases in groundwaters derived from surface waters depends on (1) the mean annual temperature of recharge, (2) mean atmospheric pressure, and (3) the salinity of the recharge water. After correcting for salinity and the elevation of the recharge area, ANG abundances can be used to define the paleotemperature of recharge areas (Mazor and Bosch, 1987).

Dissolved radiogenic noble gases, which have been used in basinal studies, include ^3He , ^4He , $^{20-22}\text{Ne}$, ^{40}Ar , and $^{131-136}\text{Xe}$ (Ballentine *et al.*, 1996; Pinti and Marty, 2000). The isotope ^4He is produced by α decay of ^{235}U , ^{238}U , and ^{232}Th ; ^3He is produced by decay of tritium generated from the neutron activation of ^6Li ; and ^{40}Ar is produced by electron capture decay of ^{40}K . Of the xenon isotopes, ^{136}Xe is produced by the spontaneous fission of ^{238}U , and ^{129}Xe is produced by β decay of ^{129}I . Isotopes of neon and other isotopes of argon and xenon are produced by a variety of other nuclear reactions.

Much of the ^{40}Ar produced by decay of ^{40}K is retained within the mineral lattice at temperatures below $250\text{--}300^\circ\text{C}$. In contrast, the closure temperature of ^4He , produced by the decay of ^{235}U , ^{238}U , and ^{232}Th , is usually below 100°C . One would expect, therefore, that noble gases in water from the deeper regions of the crust would have higher $^4\text{He}/^{40}\text{Ar}$ ratios than noble gases in shallow parts of sedimentary basins.

Basinal fluids often contain significant amounts of mantle-derived noble gas isotopes, although these tend to be masked by high background levels of ANG (O'Nions and Oxburgh, 1988). The most prominent mantle signal is excess ^3He . R_a , the ($^3\text{He}/^4\text{He}$) ratio of air, is 1.38×10^{-6} . The $^3\text{He}/^4\text{He}$ ratio of crustal origin is typically <0.03 times R_a . In contrast, mantle-derived $^3\text{He}/^4\text{He}$ values relative to air are ≥ 8 (Kennedy *et al.*, 1997; Kharaka *et al.*, 1999b). The $^3\text{He}/^4\text{He}$ ratio in some basinal waters associated with oil fields can be enriched by an order of magnitude relative to the expected values from *in situ* radiogenic production; $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ ratios in basinal fluids in excess of their atmospheric values have been taken as evidence for the presence of mantle-derived helium and neon (Ballentine and O'Nions, 1991). Fluids in extensional basins, such as the Pannonian and Paris basins, or in continental rifts have clear mantle-derived noble gas signatures in the form of excess ^3He , ^{129}Xe , and ^{21}Ne (Ballentine and O'Nions, 1991). Basins in which there is active sediment loading, such as the Po Basin,

Italy, do not have a clearly defined mantle gas signature (Elliot *et al.*, 1993).

Noble gases exist in formation waters as uncharged, nonpolar species. They preferentially partition from aqueous solutions into nonpolar solvents such as crude oil and natural gas (Kharaka and Specht, 1988). The degree of partitioning depends on factors such as temperature, gas atomic radius, and the salinity of the aqueous phase. Distinct variations in $^{20}\text{Ne}/^{36}\text{Ar}$, $^{84}\text{Kr}/^{36}\text{Ar}$, and $^{130}\text{Xe}/^{36}\text{Ar}$ are produced by fractionation in multiphase fluid systems. These variations have been used as a tool in oil exploration and reservoir evaluation. Pinti and Marty (2000) give detailed examples of these applications in the Pannonian Basin, Hungary and in the Paris Basin, France.

5.16.8 THE INFLUENCE OF GEOLOGICAL MEMBRANES

The ability of soils, clays, and shale (the geological membranes) to serve as semipermeable membranes has been conclusively demonstrated by experimental data (McKelvey and Milne, 1962; Kharaka and Berry, 1973; Fritz and Marine, 1983; Demir, 1988; Whitworth and Fritz, 1994) and field evidence (Bredehoeft *et al.*, 1963; Hanshaw and Hill, 1969; Berry, 1973; Kharaka and Berry, 1974). The chemical composition of water in sedimentary basins can be significantly affected by interaction with geological membranes:

1. Compacted clays and shale serve as semipermeable membranes that retard or restrict the flow of dissolved chemical species with respect to water. Subsurface water that has flowed through a geological membrane (effluent water) is lower in TDS and has a chemical composition different from that of the original solution (input water) or to the solution remaining in the aquifer on the input side of the membrane (hyperfiltrated water).
2. Subsurface waters squeezed from massive shale and siltstones are present in large areas in many sedimentary basins such as the Gulf Coast (Kharaka *et al.*, 1980) and the Central Valley, California (Berry, 1973; Kharaka *et al.*, 1985); these also exhibit increasing "membrane effluent" characteristics with increasing depth (increased compaction). The lowest salinities of the waters in these two basins are in the range $\sim(0.5-1) \times 10^4 \text{ mg l}^{-1}$. These values are about a quarter of the salinities of formation waters at comparable depths in these basins that were not affected by this process. Laboratory

experiments (Kryukov *et al.*, 1962; Y. K. Kharaka, unpublished results, 1976) have shown that water squeezed from uncompacteds clays and shale has the same salinity and chemical composition as the initial solution. As compaction pressure is increased, the salinity of squeezed water decreases and shows other membrane filtration characteristics.

3. Clay minerals have cation exchange capacities that range from ~ 5 (kaolinite) to 150 (smectite) per 100 g. Exchange reactions are relatively fast and can modify the composition of subsurface waters.
4. Clay transformations, especially the conversion of smectites into illites, are important reactions in many sedimentary basins at temperatures higher than $\sim 80^\circ\text{C}$. The exchange capacity of illite is about half that of smectite. This transformation can therefore result in the uptake of potassium on clays and the release of quantitatively important amounts of adsorbed species to subsurface waters.

Kharaka (1986) reports detailed studies of "membrane effluent" effects in the Central Valley, California, in the northern Gulf of Mexico Basin, and in the North Slope, Alaska. In each basin, the compositions of effluent and hyperfiltrated waters were compared. The "membrane effluent" characteristics that were observed include the following "chemical markers": lower TDS and Ca/Na and Br/Cl ratios, and higher Li/Na, NH_3/Na , B/Cl, HCO_3/Cl , and F/Cl ratios. These "chemical markers" are similar to those predicted from laboratory studies when these are extrapolated to the temperature, pressure, and hydraulic pressure gradients in sedimentary basins (Kharaka and Smalley, 1976; Haydon and Graf, 1986; Demir, 1988).

Nevertheless, the importance of membrane filtration in modifying the chemical composition of subsurface waters is controversial (Hannor, 1987). Manheim and Horn (1968) discussed the difficulties of producing brines by shale membrane filtration, concluding that the pressure requirements for significant membrane filtration were not encountered in geologic environments. Fluid pressure or hydraulic potentials are needed to force water through shale. However, membrane filtration will lead to an increase in the concentration of solution on the input side of shale relative to the output side. Flow and membrane filtration will cease when the osmotic head thus generated equals the original hydraulic potential. The US Gulf Coast has sometimes been mentioned as an area where production of brine by membrane filtration should be occurring because high

fluid-pressure gradients exist across thick regional shale sequences (Graf, 1982; Kharaka, 1986). However, in many regions of the Gulf Coast formation waters of higher salinity are found on the effluent side of these over-pressured shales. Processes such as salt dome dissolution rather than membrane effects are the dominant controls on salinity in this area (Hanor, 1994).

Manheim and Horn (1968) are correct in stating that water must pass through shale to be concentrated and diluted by membrane filtration. Flow through shale in sedimentary basins is indeed prevalent (Bredehoeft *et al.*, 1963). Flow is particularly important in two common field situations. The first is encountered in geopressed systems, such as in the US Gulf Coast, in which fluid potentials much higher than hydrostatic values (thousands of meters) are encountered that force water through shale before the development of equal and counteracting osmotic potentials (Kharaka *et al.*, 1980; Graf, 1982). The second situation is encountered in recharging sedimentary basins. Kharaka and Berry (1974) showed that fresh meteoric water recharged at Reef Ridge in the San Joaquin Valley, California, USA, percolates through the Temblor Formation. A portion of this water passes through the overlying McClure Shale. This increases the salinity of water remaining in the Temblor Formation. The salinity of water as it reached the Kettleman North Dome oil field is up to $4 \times 10^4 \text{ mg l}^{-1}$. Of course, the chemical composition of water at Kettleman North Dome is also modified by the other water-rock interactions discussed by Kharaka and Berry (1974), Merino (1975), and in this chapter.

5.16.9 SUMMARY AND CONCLUSIONS

Formation waters with salinities ranging from $\sim 5,000$ to $>3.5 \times 10^5 \text{ mg l}^{-1}$ dissolved solids play a major role in the physical and chemical processes that occur in sedimentary basins. Detailed inorganic and organic chemical analyses, together with measurements of the oxygen and hydrogen isotopes in water and of a diverse suite of other stable and radioactive isotopes, have been reported for formation waters from many sedimentary basins worldwide. Application of these data, together with information on data for the local and regional geology and on the recent and paleohydrology, have shown that these fluids are much more mobile, and their origins and interactions with rocks and sediments much more complex than realized previously.

The formation waters in sedimentary basins are dominantly of local meteoric or marine connate origin. However, bittern (residual) water, geologically old meteoric water, and especially waters of mixed origin are important components in many sedimentary basins. The original waters have evolved to Na-Cl, Na-Cl-CH₃COO, or Na-Ca-Cl-type waters by a combination of several major processes: (1) dissolution of halite; (2) incorporation of bitterns; (3) dissolution and precipitation of minerals other than halite; (4) interaction of the waters with organic matter present in sedimentary rocks; (5) interaction with rocks, principally clays, siltstones, and shale, that behave as geological membranes; and (6) diffusion, which appears to be more important than previously thought. The important processes responsible for the chemical evolution of water and mineral diagenesis in each basin can be identified using "chemical markers" and isotopes.

The discovery, in these waters, of high concentrations (up to $1 \times 10^4 \text{ mg l}^{-1}$) of mono- and dicarboxylic acid anions, phenols, and other reactive organic species has led to numerous field and laboratory studies to determine their distribution and importance in inorganic and organic interactions. The observed concentrations are minimum values, because the organics are degraded by bacteria and by thermal decarboxylation reactions. Decarboxylation rates estimated from field data for acetate, the dominant species, give half-life values of 20–60 Myr at 100 °C.

The concentrations of lead, zinc, copper, mercury, and several other metals (excluding iron and manganese) are almost always very low ($<1 \text{ mg l}^{-1}$) in oil-field waters, because they are limited by the very low solubility of their respective sulfide minerals. Exceptionally rich sources of metals such as redbeds are probably present in the few localities worldwide, where dissolved metal concentrations are high. Metals leached from these beds precipitate along with available reduced sulfur; dissolved metal concentrations increase to high values only when the concentration of H₂S is extremely low ($<0.01 \text{ mg l}^{-1}$).

Water-rock interaction in sedimentary basins is and will continue to be a subject of intensive research. The following are areas that are receiving particular attention because of their scientific or economic importance, and/or the arrival of new equipment and techniques:

1. A plethora of stable and radioactive isotope data is being used to study mineral diagenesis and the origin and age of water and the sources and sinks of solutes in these basins.

Determination of accurate fractionation factors and rates of isotopic exchange between waters and minerals under sedimentary conditions are needed for a better interpretation of the isotope data.

2. Major advances have been made since the early 1990s documenting the nature, distribution, and organic and inorganic interactions of reactive organic species. Additional investigation is needed, especially in determining the stability of organic-inorganic complexes, rates of decarboxylation under field conditions, and the importance of dissolved organic sulfur and nitrogen compounds.
3. Geochemical, hydrologic, and solute transport codes are being applied to sedimentary basins. To obtain reliable information from this endeavor, accurate, detailed data on aqueous and solid phases must be available and more accurate thermodynamic data are needed for clay minerals, minerals of highly variable composition, and brines. Data are also needed for the kinetics of dissolution/precipitation in the field.
4. Chemical and physical processes that control the geochemistry of aluminum, especially its transport in formation water.
5. Evaluation of reaction kinetics by integrating field and reservoir-scale spatial variations in fluid compositions with quantitative fluid flow models and sediment mineralogy.
6. Chemical and isotopic evolution of aqueous wastes, including produced water injected into the subsurface. What can be deduced about the fate of these wastes from what is known about the composition and interactions of formation water?
7. Chemical and physical processes that decrease formation water salinity.
8. Mechanisms by which basinal brines are expelled back up into near-surface environments. Can it be done without tectonics? What impact do major brine-expulsion events have on the exogenic geochemical cycle?

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