STABLE ISOTOPE GEOCHEMISTRY AND ORIGIN OF WATERS IN SEDIMENTARY BASINS

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Formation waters with salinities ranging from about 5,000 mg/l to more than 350,000 mg/l dissolved solids play a fundamental role in the physical and chemical processes that occur in sedimentary basins. These waters are particularly important in: (a) the generation, transport, accumulation and production of petroleum, (b) the chemical aspects of mineral diagenesis, including dissolution, precipitation and mineral transformations leading to major increases and/or decreases in the porosity and permeability of reservoir rocks, (c) the transport and precipitation of Cu, U, and especially sediment-hosted Mississippi Valley-type Pb-Zn ore deposits, (d) tectonic deformations, (e) the transport of thermal energy for the geothermal and geopressured-geothermal systems, and (f) the interaction, movement and ultimate fate of large quantities of hazardous wastes injected into the subsurface. Despite clear economic and scientific importance, and about a century of investigations, there is still controversy regarding the origin and evolution of these saline waters (Hanor et al., 1988).

Our understanding of the origin of these waters and the

processes that modify their chemical and isotopic compositions, however, has increased considerably in the last 10 years as a result of: (a) improved analytical techniques, especially the use of inductively coupled plasma (ICP) alone or in combination with mass spectrometry (ICP/MS) for the determination of cations and metals, and the use of ion chromatography (IC), gas chromatography (GC) and GC/MS for the analysis of anions and organics (Hull et al., 1985; Hanor et al., 1988), (b) improved sampling methodologies, especially with the use of specially designed downhole samplers (Kharaka et al., 1988a), (c) increased availability and utilization of data on a variety of stable and radioactive isotopes (Fritz and Fontes, 1980, 1986; Faure, 1986; Valley et al., 1986; Hoefs, 1987; Kyser, 1987), (d) major improvements in the chemical thermodynamic data and procedures for applying them to brines and minerals, and (e) development and application of detailed geochemical, hydrological and solute transport codes (Cathles, 1981; Bethke, 1986; Hanor, 1987; Kharaka et al., 1988b; Melchior and Bassett, 1990). We now realize that these fluids are much more mobile and their interactions with rocks much more complex than previously realized. Also, the discovery of high concentrations (up to 10,000 mg/l) of reactive organic species in these waters has led to a new field of organic-inorganic interactions and developed bridges between geochemistries of aqueous fluids, organic matter and petroleum (Kharaka et al., 1985; Gautier, 1986; Surdam et al., 1989; Lundegard and Kharaka, 1990).

In this chapter we review the origin of water and the composition and sources of inorganic and organic solutes from several petroliferous sedimentary basins in North America. Variations in stable isotopes of oxygen and hydrogen in present-day and old meteoric waters are reviewed and used in conjunction with the isotopic and chemical compositions of deep basin waters to indicate their origin and chemical evolution. The isotopic composition of ocean water through geologic time is discussed in a separate contribution of this volume. The emphasis is on the main processes that are responsible for the modification of the chemical and isotopic compositions of these waters including: (a) mixing, (b) dissolution of evaporites, especially halite, (c) incorporation of bitterns, the residual water remaining after the precipitation of

evaporites, (d) dissolution and precipitation of minerals other than evaporites, (e) interaction with rocks, principally clays, siltstones and shales that behave as geological membranes, (f) activity of bacteria that can survive in sedimentary rocks to temperatures of up to about 80°C (Davis, 1967; Carothers and Kharaka, 1978), (g) interaction with organic matter, and (h) diffusion, especially in the presence of salt domes.

A number of excellent reviews on stable isotope and elemental geochemistry of waters in sedimentary basins have appeared in the last decade. Books written or edited by Fritz and Fontes (1980; 1986), Faure (1986), Hoefs (1987), Marshall (1987), and Chillingarian and Wolf (1988) contain several excellent chapters with information pertinent to this topic. Recent conference volumes with important contributions relevant to this chapter include Hitchon et al. (1986), Gautier (1986), Naeser and McCullough (1989), Miles (1989), and Melchior and Bassett (1990). Finally, several short-course volumes have recently appeared, including Gautier et al. (1985), Valley et al. (1986), Hanor (1987), Kyser (1987), and Hutcheon (1989). It is clear that water-rock interaction in sedimentary basins is receiving much attention from researchers in several fields of geology, hydrology and isotope geochemistry.

CHEMICAL COMPOSITION OF SUBSURFACE WATERS

Chemical composition of surface and shallow ground waters are highly variable. The waters are generally fresh (<1,000 mg/l dissolved solids) or brackish (1,000 to 10,000 mg/l dissolved solids), but the proportions of the major cations and anions are variable and dependent mainly on the mineral compositions of the rocks with which they come into contact (Freeze and Cherry, 1979; Hem, 1985). Many shallow ground waters are dominated by sulfate, which is replaced by carbonate in deeper ground waters. Dissolved sulfate in these waters is derived from dissolution of gypsum and anhydrite, or from oxidation of pyrite. Under reducing conditions prevalent in deeper waters, dissolved sulfate is reduced by bacte-

ria, and dissolved organic species are oxidized to bicarbonate. The net reaction may be represented by:

$$SO^{2-}_4 + CH_3COO^- \rightleftharpoons HS^- + 2HCO^-_3 \qquad (1)$$

The salinity of oil field waters from different sedimentary basins is highly variable (Table 1, Fig. 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 (Fig. 2). Water salinities in sedimentary basins range from about 5,000 to more than 350,000 mg/l dissolved solids. In any given basin, salinity generally increases with depth but the rate of increase is obviously variable (Fig. 1). For entire basins (e.g. Central Valley, California) or large areas within a basin (e.g. Corpus Christi area of Texas) that are devoid of evaporites and dominated by shales and siltstones, the salinities of formation waters show a general increase followed by a decrease with increasing depth of the reservoir rocks; salini-

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

Area	Sacramento			San Joaquin		North Slope		Central Mississippi	
Field	Grimes	Malton-Black Butte	San Emidio Nose	Wheeler Ridge	Kettleman North Dome	Barrow	Prudhoe Bay	Reedy Creek	West Nancy
Sample #	81-NSV-15	81-NSV-1	74-SEN-3	75-WR-5	912-1	78-AK-52	78-AK-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
Prod. Zone	Forbes	Forbes	Reef Ridge	Tejon	Lower McAdams	Barrow Sandstone	Sadlerochit Group	Rodessa	Smackover
Depth (m)	2,074	1,524	3,337	2,691	3,520	728	2,820	3,486	4,428
Temp. (°C)	65	58	148	117	141	16	94	102	118
TDS	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	980	8,500
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	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_2S	0.07	<0.1	0.02	0.11	3.02	<.1	<.1	<0.02	57.4
SiO_2	31	18	109	46	128	11	62	28	34
B	------	------	92	600	43	42	158	59	341
pH	7.6	7.6	7.7	6.9	7.4	7.2	6.5	5.08	5.48

Note: Depth is depth below ground level of mid-point of perforation. Production zone are those used by oil companies. TDS is calculated total dissolved solids. HCO_3 is field-titrated alkalinity and includes organic and inorganic species.

ties are relatively low reaching values of 5,000 mg/l in the deeper parts of the sections. Finally, a trend of constant water salinities is observed in the North Slope, Alaska, where the salinities are remarkably similar (19,000 to 24,000 mg/l dissolved solids, Table 1), considering the large areal extent of the sampled wells and the great variation in the depth (700 to 2,800 m) and lithologies of the reservoir rocks (Kharaka and Carothers, 1988).

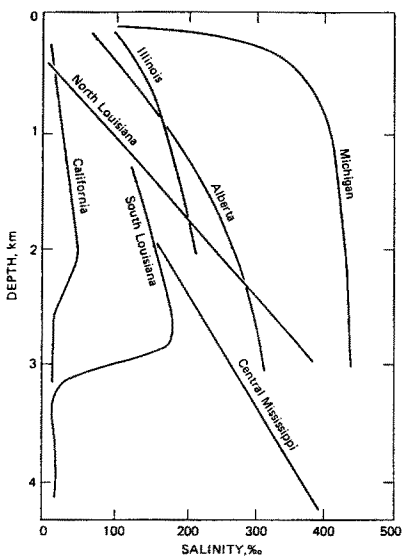


Figure 1: Salinity distribution with depth of reservoir rocks from some basins in North America. Note the different trends and the reversal of salinity in California and South Louisiana

Chloride is the dominant anion in nearly all formation waters associated with petroleum (Tables 1, 2, Fig. 3). The proportion of Cl to total anions (generally 70 to 90%) generally increases as the salinity of water increases reaching values of up to 99%. Acetate may comprise a high portion of total anions, especially in Na-Cl-CH_3COO type waters that are present mainly in Cenozoic reservoir rocks that are at temperatures of 80 to 100°C. In these waters, acetate and other organic acid anions can reach concentra-tions of up to 10,000 mg/l and contribute up to 99% of the measured alkalinities. The concentration of sulfate in oil field waters is low (generally <100 mg/l), even in connate waters of marine origin.

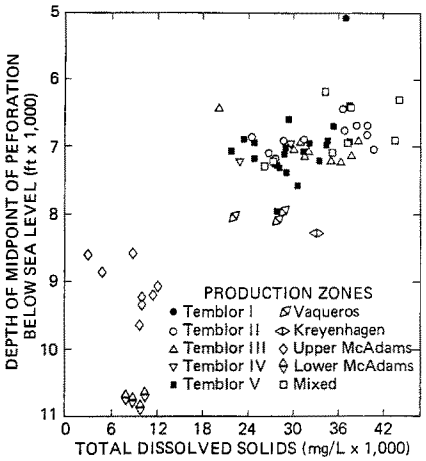


Figure 2: Distribution of salinity of formation waters from Kettleman North Dome oil field (California). Note the much lower salinity of water in the deeper McAdams Formation compared to Temblor Formation (Kharaka and Berry, 1974)

Table 2: Chemical composition (mg/l) and production data of formation waters in geopressured zones from coastal Texas and Louisiana

Area	Lafayette, LA		Houston-Galveston, TX		Corpus Christi, TX		McAllen-Pharr, TX	
Field	Weeks Island	Tigre Lagoon	Chocolate Bayou	Halls Bayou	Portland	East Midway	Pharr	La Blanca
Sample #	77-GG-19	77-GG-55	76-GG-7	76-GG-24	76-GG-63	77-GG-73	77-GG-73	77-GG117
Well Name	St.Un. A#9	Edna Delcambre #1	Angle #3	Houston "FF" #1	Portland A-3	Taylor E-2	Kelly A-1	La Blanca #12
Production Zone	S-Sand	Sand #3	Upper Weiting	Schenck	Morris	Lower Frio	Marks	7150 Sand
Depth (m)	4,275	3,928	3,444	4,161	3,514	3,662	3,018	2,903
Temp. (°C)	117	114	118	150	123	128	127	148
Pressure	43.1	75.8	52.4	80.0	58.0	62.2	52.4	56.6
Fluid Production								
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	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_2S	0.4	0.5	1.2	1.4	<0.1	0.04	<0.1	<0.1
HCO_3	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

Note: Depth is depth below ground level of mid-point of perforation. Temp. is measured subsurface temperature. Pressure is original bottom-hole pressure in MPa (1 psi = 6.9 kPa). Liquid production is in m^3/day. Production zones are names used by oil companies. TDS is calculated total dissolved solids. HCO_3 is the field titrated alkalinity and includes organic and inorganic species.

Sodium is the dominant cation in oil field waters, and it generally constitutes 70 to more than 90% of total cations (Tables 1, 2). Calcium generally is the second most abundant cation, and its proportions increase, especially in Na-Ca-Cl type waters in which it may reach concentrations of up to about 50,000 mg/l (Table 1). This increase with salinity, however, is variable in the same basin or in different basins. The concentrations and proportions of Mg are generally much lower than those in ocean water and generally decrease with increasing subsurface temperatures. The concentration and proportions of Sr, Ba, and Fe are generally higher than those in ocean water and generally increase with increasing Ca concentrations. The ratios of Li, K and Ce to Na generally increase with increasing subsurface temperatures, but again the proportions vary from basin to basin.

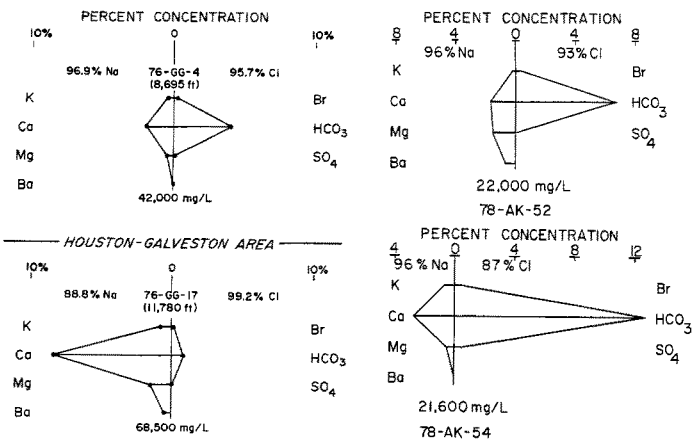


Figure 3: Modified Stiff diagrams showing the percent equivalent concentrations of the major cations and anions in formation waters from (a) normally pressured (upper) and geopressured (lower) zones of the Houston-Galveston area (Texas) and (b) North Slope (Alaska) (Kharaka et al., 1985)

It is clear from the discussion that the chemical composition of subsurface waters, including those of marine origin, is different from that of ocean water. Several investigators (Claypool and Kaplan, 1974; Gieskes, 1981) have noted major changes (with sulfate and Mg depletions and bicarbonate increases) in the chemical composition of sea water trapped in shallow sediments. These early changes become more pronounced with increasing depth of sediments and lead to chemical compositions found in oil field waters.

The chemical composition of formation waters from High Island field, offshore Texas, was investigated by Kharaka et al. (1985) to evaluate the early stages of diagenesis of marine waters (Table 3). The reservoir rocks in this field are present at depths that range from about 1,700 to 3,700 m and are marine sandstones of Pleistocene age. The chemical composition of the waters (Fig. 4), the δD and $\delta^{18}O$ values of the waters (to be discussed later), and the $^{87}Sr/^{86}Sr$ ratios of dissolved Sr show proportional mixing of two end members. The first is a Pleistocene marine connate water represented by samples 83-TX-6 and 83-TX-7 (Table 3); the second is a highly modified marine connate water (83-TX-5) that originated in Miocene sediments at a subsurface temperature of about 130°C (Kharaka et al., 1985).

Table 3: Chemical composition (mg/l) of formation waters from High Island Field (offshore Texas)

Sample #	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	B-12A	A-45-1
Depth (m)	2045	1876	2184	2140	1849	1838	1789	1741	2216	2052	3719
Temp. (°C)	70	55	66	67	53	52	50	49	77	64	98
TDS	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	15	----	----	----	<1	<1	3
H_2S-Titration	0.25	0.68	0.85	0.08	0.00	0.51	0.68	0.51	0.85	0.93	0.76
H_2S-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(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

Samples from High Island 573 field (Mobil Oil) except sample 83-TX-12, which is from High Island 571 field (Columbia Gas); Depth is that of mid-point of perforation below sea level (depth of water column is ~75m; Temp. is the measured subsurface temperature; TDS = mg/L total dissolved solids; field titrated alkalinity as HCO_3 comprises organic as well as inorganic species.

The concentrations of Na and Cl, total dissolved solids, and δD and $\delta^{18}O$ values of sample 83-TX-6 and 83-TX-7 are about equal to those of ocean water (Table 3). These parameters have behaved relatively conservatively since middle Pleistocene time. The present

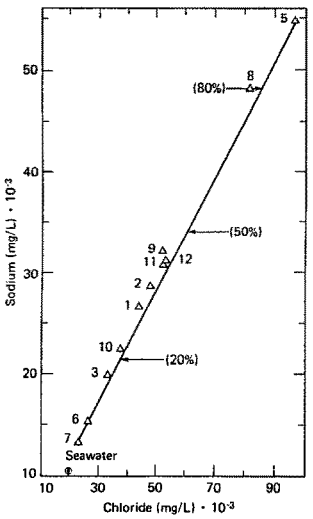


Figure 4: Concentrations of Na and Cl in formation waters from High Island field (offshore Texas) showing proportional mixing between a highly modified water (sample 83-TX-5) and an only slightly modified Pleistocene connate water (sample 83-TX-7). Sample numbers are from table 3 (Kharaka et al., 1985)

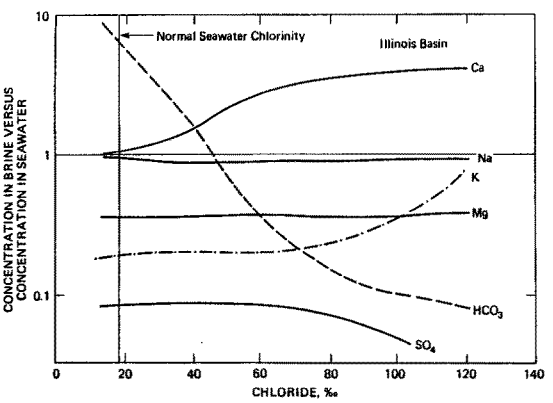


Figure 5: Generalized relative variations in the composition of major ions in formation waters from the Illinois basin. The normalized ratios indicate that the formation waters are depleted in SO_4, Mg and K relative to ocean water, and that they become progressively enriched in Ca and K and depleted in HCO_3 with increasing salinity (modified from Hanor, 1987)

subsurface temperature of these two samples is about 50°C. However, there are major differences between the chemical compositions of these two samples and that of ocean water. The concentrations of

sulfate in these waters is lower by about three orders of magnitude from that of ocean water, whereas those of Mg and K are about one third that of ocean water. The concentrations of iodide, organic species, B, Ba, Fe, Si, and Sr are many times higher that those of ocean water. The concentrations of Ca, bromide, and carbonate alkalinity are higher than those of ocean water (Table 3). These differences are even more pronounced when we compare the chemical composition of sample 83-TX-5 with that of ocean water. The concentrations of Cl (99,000 mg/l) and the Br/Cl ratios for this brine indicate dissolution of halite from the Louann Salt structures underlying the field (Kharaka et al., 1985). The variation of major ion concentrations with increasing Cl values (increasing depth) for samples from the Michigan basin continue the trends observed in data from High Island field (Fig. 5).

Metal-rich Brines

The concentrations of metals in oil-field waters, with the exceptions of Fe and Mn, are generally low. In the case of Pb and Zn, the concentrations are less than 100 mg/l, with the exception of fewer than half a dozen localities world-wide (Carpenter et al., 1974; Kharaka et al., 1987). The central Mississippi Salt Dome Basin is one of these metal-rich brine localities that is characterized by extremely high salinities that range to about 350,000 mg/l total dissolved solids (Tables 1, 4). The brines are Na-Ca-Cl type waters with very high concentrations of Ca (up to 50,000 mg/l) and other alkaline-earth metals, but with low concentrations of aliphatic acid anions. The metals are very concentrated in many water samples, reaching values greater than 100 mg/l for Pb, 250 mg/l for Zn, 500 mg/l for Fe and 200 mg/l for Mn. The samples with high metal contents have extremely low concentrations (less than 0.02 mg/l) of H sulfide. Samples obtained from the Smackover Formation (limestone) have low metal contents that are more typical of oil-field waters, but have very high concentrations (up to 85 mg/l) of hydrogen sulfide.

Table 4: Selected metal concentrations (mg/l; *μg/l) of formation waters from central Mississippi Salt Dome Basin (Kharaka et al., 1987)

Sample ID	Fe	Mn	Pb	Zn	Al*	Cd	Cu*
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-MS-8	194	69.3	22.8	107	132	0.67	34
84-MS-9	0.54	15.5*	<.5*	12.0*	---	<0.2*	<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*	<.5*	13*	---	0.08*	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*	10.6	1.05	1.04	12.6	---	0.08	<0.20

Organic Species in Subsurface Waters

In the last 15 years there has been considerable interest in the origin and interactions of dissolved organic acids in natural subsurface waters (Willey et al., 1975; Carothers and Kharaka, 1978; Kharaka et al., 1983, 1986; Crossey et al., 1986; Hanor and Workman, 1986; Lundegard and Land, 1986; Lundegard and Kharaka, 1990; MacGowan and Surdam, 1990). Geochemical interest in organic species stems from their important role in mineral diagenesis. In particular, they act as proton donors for a variety of pH-dependent reactions and as pH and Eh buffering agents. They also have the potential to form complexes with metals such as Al, Fe, Pb, and Zn. Finally, organic species have been studied for use as proximity indicators in petroleum exploration (Kartsev, 1974; Carothers and Kharaka, 1978) and as possible precursor for an important portion of natural gas (Kharaka et al., 1983). Kharaka et al. (1986), Lundegard and Kharaka (1990), and MacGowan and Surdam (1990) gave detailed recent reviews of the nature, origin, distribution and interaction of dissolved organics in subsurface waters.

The median concentration of dissolved organic species in shallow ground waters is about 1 mg C/l (Thurman, 1984). An important portion (20 to 40% and up to 90%) of this dissolved C consists

of high molecular weight fulvic and humic acids (Thurman, 1984). The proportion of these humic substances in organic species dissolved in the waters of the unsaturated zone is even higher, amounting to 50 to 60%. The median concentrations of dissolved organic C, however, are also higher, ranging from about 20 mg/l in the A soil horizon to 2 mg/l in the C soil horizon.

Concentrations of dissolved organic species in oil-field waters (40 to 200°C) are much higher than in ground waters and may reach values as high as 10,000 mg/l (as acetate) (Kharaka et al., 1986; Lundegard and Land, 1986; Crossey et al., 1986; Hanor and Workman, 1986; 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 lumped and recorded as bicarbonate alkalinity because they are titrated with H_2SO_4 used to measure field alkalinities. Willey et al. (1975) and Carothers and Kharaka (1978) showed that these organic acid anions can contribute up to 99% of the measured alkalinities (Fig. 6). Carothers and Kharaka (1978) and Kharaka et al. (1983) showed that the concentrations of these aliphatic acid anions were controlled mainly by the subsurface temperatures and the ages of the reservoir rocks. The distribution of aliphatic acid anions in oil field waters from several basins shows three distinct

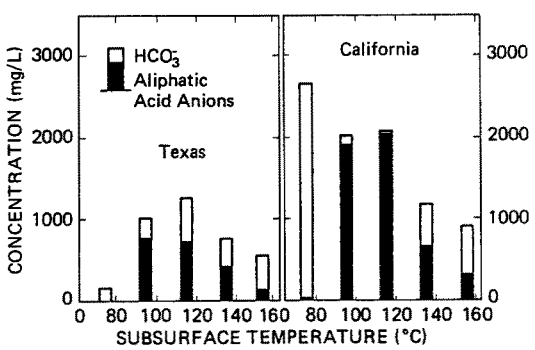


Figure 6: Average concentrations of aliphatic acid anions and bicarbonate alkalinity in oil-field waters from Texas and California (modified from Carothers and Kharaka, 1978). Note that organic acid anions contribute most of the total alkalinity at temperatures of 80 to 140°C

temperature zones (Fig. 7; Kharaka et al., 1988b). Zone 1 is characterized by concentrations of acid anions less than about 500 mg/l and temperatures less than about 800°C. The concentrations of acetate in this zone range from below detection limit to low values, whereas propionate generally predominates. Bacterial degradation is believed to be responsible for the absence of acetate and the low concentrations of organic species in Zone 1 (Carothers and Kharaka, 1978). The highest concentrations of aliphatic acid anions are present in the youngest and shallowest reservoir rocks of Zone 2 (temperature 80 to 100°C) and the concentrations generally decrease with increasing subsurface temperatures and ages of the reservoir rocks (Fig. 7). Acetate constitutes more than 90% of aliphatic acid anions with propionate comprising about 5% of anions (Carothers and Kharaka, 1978). The boundary of Zone 3, where no acid anions are present, is placed at about 220°C and is obtained by extrapolation of the least-squares line through the points of Zone 2 (Kharaka et al., 1986).

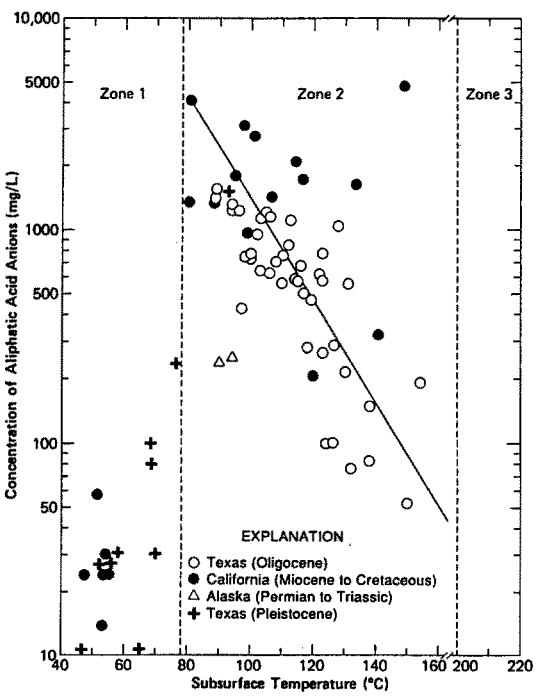


Figure 7: Concentrations of aliphatic acid anions (C125) in formation waters from three sedimentary basins. The highest concentrations are at about 80°C and decrease with increasing temperatures (Kharaka et al., 1988b)

The decrease in the concentrations of acid anions with increasing temperatures and ages of the reservoir rocks (Carothers and Kharaka, 1978) indicates thermal decarboxylation of acid anions to CO_2 and hydrocarbon gases (Fig. 7). Further evidence for thermal decarboxylation of acid anions is obtained from $\delta^{13}C$ values of dissolved bicarbonate, CO_2 and CH_4 in natural gas and diagenetic calcite and ankerite from Gulf Coast and California basins (Boles, 1978; Carothers and Kharaka, 1980; Lundegard and Land, 1986). These $\delta^{13}C$ values indicate that C in CO_2 gas, dissolved carbonate, and carbonate cements was derived largely from an organic source. Experimental studies of acetic acid show that decarboxylation rates are extremely sensitive to temperature and the types of catalytic surfaces available. Rate constants for acetic acid decarboxylation at 100°C differ by more than 14 orders of magnitude between experiments conducted in stainless steel and catalytically less active Ti (Kharaka et al., 1983; Drummond and Palmer, 1986). However, naturally occurring mineral surfaces provide rather weak catalysis effects. Decarboxylation rates calculated from field data provide more realistic half-life values of 10 to 60 million years at 100°C (Kharaka, 1986; Lundegard and Kharaka, 1990).

Table 5: Concentrations of dicarboxylic acids in formation waters from High Island Field, offshore Texas (Kharaka et al., 1985)

Dicarboxylic acid	Carbon No.	Sample number 83-TX-3 Concentration (mg/L)	83-TX-10	83-TX-12
Butanedioic acid	4	1.8	0.2	63
Pentanedioic acid	5	1.7	1.2	36
Hexanedioic acid	6	0.5	0.5	---
Heptanedioic acid	7	---	0.6	0.2
Octanedioic acid	8	---	0.7	5.0
Nonanedioic acid	9	---	1.4	6.0
Decanedioic acid	10	---	---	1.3

Dicarboxylic acid anions, which can be expected to form stronger complexes with metals, have also been identified in oil-field waters (Kharaka et al., 1985; Crossey et al., 1986; MacGowan and Surdam, 1990). The concentrations of dicarboxylic acid anions reported in formation waters of High Island Oil field, offshore Texas (Kharaka et al., 1986), are shown in table 5. Methybutanedioic and 2-methylpentanedioic acids were also identified but not

quantified in samples 83-TX-1 and 83-TX-12, the only samples tested. The highest concentrations and proportions of dicarboxylic acid anions are present in sample 83-TX-12 where they comprised about 6% by wt of total acid anions. In this sample, butanedioic (C_4) and pentanedioic (C_5) acids are dominant. MacGowan and Surdam (1990) reported values of up to 2,500 mg/l for propane-dioic (malonic) and up to 500 mg/l for ethanedioic (oxalic) acids.

A number of other reactive organic species were identified but not quantified by Kharaka et al. (1986). These include C_6 to C_9 monocarboxylic acid anions, phenol, 2-, 3-, and 4-methylphenol, 2-ethylphenol, 3, 4- and 3, 5-dimethylphenol, cyclohexanone, and 1, 2- and 1, 4-dimethylphenol, cyclohexanone, and 1, 2- and 1, 4-dimethylbenzene. Several amino acids including serine, glycine, alanine and aspartic acid have also been reported in low concentrations (up to 0.3 mg/l) in oil field waters (Rapp, 1976). Additional reactive organic species have been reported by Fisher and Boles (1990) and MacGowan and Surdam (1990).

ORIGIN AND CONTROLS ON SOLUTES IN SUBSURFACE WATERS

The chemical composition of subsurface water in a given basin is determined by the origin of the water and 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, however, generally is the solubility of the least soluble mineral of the solute. For example, the concentration of Ca in water from a given reservoir may increase because of membrane filtration, albitization of plagioclase feldspar and/or dolmitization of limestone. This water, however, will eventually attain saturation with calcite or another carbonate mineral that will be the ultimate control on the Ca (and carbonate) concentration.

The controls on the origins of sulfate and bicarbonate-type

waters, as already stated, are generally well understood. The origins of the great differences in the salinities and ion proportions of Na-Cl, Na-Cl-CH_3COO, or Na-Ca-Cl type waters, however, are not well understood. The main mechanisms proposed to account for their origins are a combination of the following: (a) dissolution of evaporites, especially halite, (b) diffusion, especially where halite and other evaporites are present, (c) incorporation of bitterns that were trapped in the sediments during the precipitation of evaporites, (d) dissolution and precipitation of minerals other than evaporites, (e) interaction of the waters with organic matter present in sedimentary rocks, and (f) interaction with rocks, principally clays, siltstones, and shales, that behave as geological membranes. Other mechanisms including density stratification, and mixing with brines from fluid inclusions were judged to be of minor importance (Mangelsdorf et al., 1970). A detailed discussion of these mechanisms, however, is beyond the scope of this chapter.

A detailed study of the basin that includes its geology, the mineral composition of the rocks, regional hydrology, as well as the chemical and isotopic compositions of the subsurface waters, is generally required to distinguish the different mechanisms responsible for the chemical and isotopic compositions of water. The chemical and other data should be carefully examined by: (a) using plots of various types, (b) subjecting the data to factor analyses (Hitchon et al., 1971), (c) computing the states of reactions of these waters at the subsurface conditions using geochemical models, such as SOLMINEQ.88 (Kharaka et al., 1988b), and (d) comparing the results from (c) with the mineral composition of the reservoir rocks. There have been recent attempts to quantify the results of water-rock interactions from the time of deposition to present, on field and basin-wide scales (Hanor et al., 1988).

ISOTOPIC COMPOSITION OF SURFACE WATERS

Application of stable isotopes has shown that subsurface

waters originate mainly from local meteoric water of different ages and marine connate water deposited with shales and siltstones. The isotopic compositions of present-day and old surface waters are discussed below because an understanding of these is needed in interpreting the origin of deep basin brines. A discussion of the isotopic composition of ocean water has been excluded from this part, but is covered in detail in a separate contribution.

Stable Isotope Compositions of Recent Meteoric Water

The relations governing the distribution of stable isotopes of O and H in present-day surface and shallow ground-waters are reasonably well known (Fig. 8). Craig (1961) showed that surface

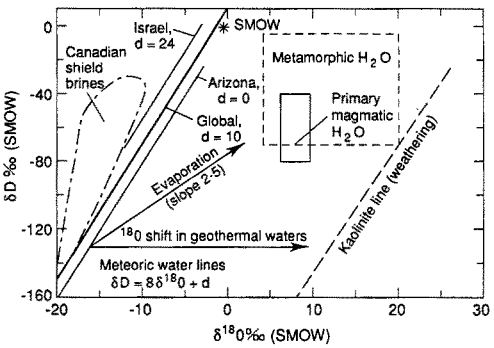


Figure 8: Isotopic compositions of ocean (SMOW), meteoric, metamorphic and primary magmatic waters. The field for the unusual Canadian Shield brines is shown. Also shown are the general trend for a meteoric water exchanging isotopes in a geothermal system and a trend for an evaporating meteoric water

water, other than that from closed basins undergoing extensive non-equilibrium evaporation and water from hot springs, have isotopic compositions that lie on the global meteoric water line (GMWL) that can be described by the equation:

$$\delta D = 8\ \delta^{18}O + 10 \qquad (1)$$

The δ values are given in the per mil (parts per thousand, o/oo) notation. Gat (1980) obtained essentially the same equation (slope

= 8.17, intercept = 10.6) from a plot of the mean δ D and $\delta^{18}O$ values of all precipitation samples from the Internatinal Atomic Energy Agency (IAEA) network.

A more general form of the equation describing the relationship between δD and $\delta^{18}O$ values of surface waters is:

$$\delta D = x\ \delta^{18}O + d \qquad (2)$$

where the value of x is generally equal to 8, but is about 6 for precipitation in tropical island stations (Yurtsever, 1975) and is 2-5 in closed basin-lakes undergoing non-equilibrium fractionation during evaporation. Dansgaard (1964) refers to the "d-parameter" in equation (2) as the "deuterium excess". The value of d is generally equal to 10, but may be less than 10 in many areas including wet coastal areas and tropical islands; its value is 22 in the dry eastern Mediterranean area (Gat and Carmi, 1970). The global meteoric water line, however, can be assumed to be applicable to surface and shallow ground waters in any area where no specific line has been established.

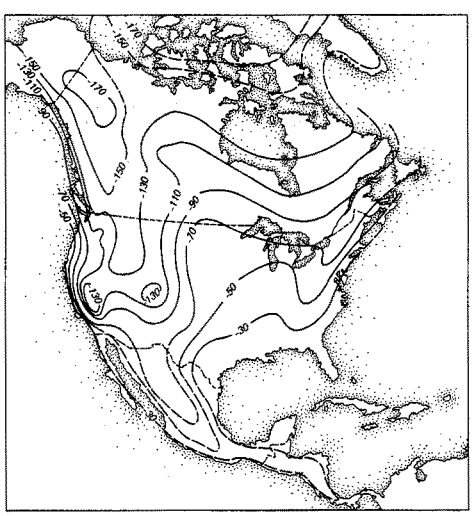


Figure 9: Map of North America showing the approximate distribution of mean annual δ D values of modern meteoric water (modified from Taylor and Margaritz, 1978). Data for Antarctic water from Yurtsever (1975) and Kharaka and Carothers (1988)

The distribution of the mean annual δD values of surface and shallow ground waters (the meteoric water) in North America (Taylor and Margaritz, 1978) is shown in figure 9. The distribution of the $\delta^{18}O$ values for these waters may be approximated, if not already available from equation (1) describing the GMWL. These values cannot be obtained by analyzing water samples from individual storms which, based on season, source of moisture and amount of precipitation, can have large isotopic variations (Fig. 10). Shallow ground waters and cold perennial springs are better representatives of local meteoric water as they give good time integrated samples of precipitation with relatively uniform isotope values (Fig. 10).

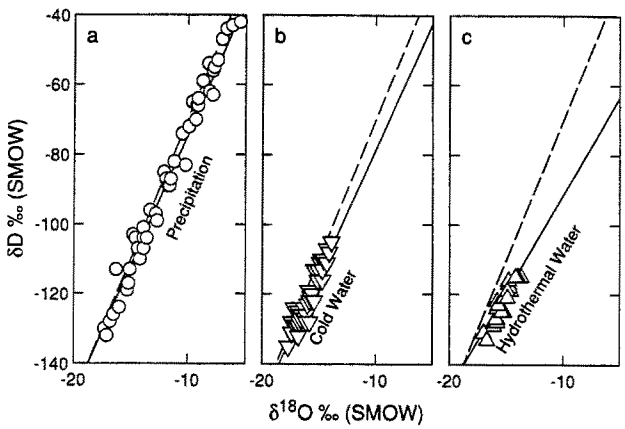


Figure 10: Isotopic composition of (a) precipitation, (b) cold surface and shallow ground waters, and (c) hydrothermal water. Dashed line is the Global Meteoric Water Line (Craig, 1961); solid lines are the least square lines. Note the wide range of isotope values for precipitation and some $\delta^{18}O$ shift for the hydrothermal water (modified from White et al., 1990)

The isotopic composition of mean annual precipitation is mainly controlled by geography (latitude, altitude, distance from the coast, and source of moisture). The most depleted precipitation occurs at high latitudes, high altitudes, and in the centers of large continents (Fig. 9). Yurtsever (1975) demonstrated a decrease in $\delta^{18}O$ of about 0.5 per mil per degree of latitude increase. The altitude effect is variable depending on local topography and climate, but depletions of 12-40 per mil in δD and 1.5-5 permil in $\delta^{18}O$ per km are typical (Gat, 1980). Where the altitude effect can be established, especially in coastal areas and on the windward

side of a mountain, it can be used to determine the recharge area for the deep subsurface water in the region (Kharaka et al., 1988a). Generally, the greater the distance from the source of moisture, the more depleted the precipitation. This depletion is caused by colder temperatures in the centers of large land masses during winter, by successive evaporation-condensation cycles as the moisture-laden air mass travels across the continent, and by the reevaporation of isotopically depleted water from continent.

The relationship between mean annual temperature and $\delta^{18}O$ values for northern Atlantic precipitation was given by Dansgaard (1964) as:

$$\delta^{18}O = 0.70t - 13.6 \qquad (3)$$

Combining equations (3) and (1) leads to:

$$\delta D = 5.6t - 98.8 \qquad (4)$$

As the temperature decreases, precipitation becomes more depleted in δD and $\delta^{18}O$ because the fractionation between liquid water and water vapor increases. Unfortunately, the above relationships are not universally applicable (Evans et al., 1978), but they may be used to estimate the mean annual temperatures of recharge during past time periods (Kharaka and Carothers, 1986).

Stable Isotope Compositions of Old Meteoric Water

Knowledge of the variations in the isotopic composition of surface waters through geologic time is necessary in order to study the origin of some deep basin brines which may have been recharged millions of years ago (Kharaka and Carothers, 1986; Knauth, 1988). These variations result from two main causes: changes in the isotopic composition of the oceans through geologic time (see next section), and changes in the climatic and topographic conditions at the area of recharge. These climatic changes in turn result from two factors: continental drift and the phenomena connected with it, including latitude changes, mountain building, and the ensuing changes in oceanic currents and wind circulation patterns, and as-

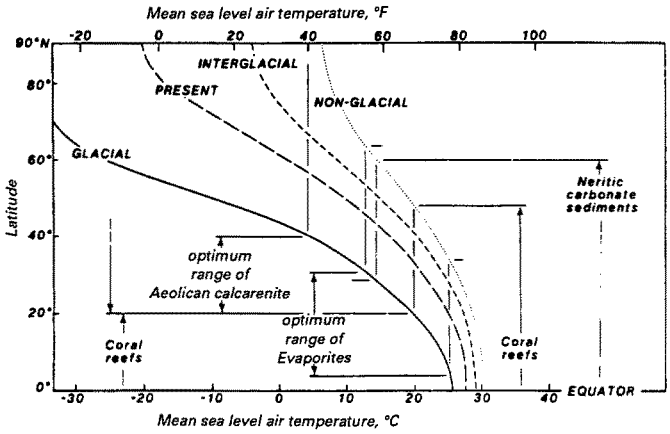


Figure 11: Surface mean temperatures for the present, glacial, non-glacial and interglacial periods at different latitudes (modified from Fairbridge, 1964)

tronomical factors and effects not related to continental drift that might include changes in the sun's radiation and changes in the composition of the earth's atmosphere.

It is generally recognized that "the present is not the key to the past" as far as climate is concerned (Lamb, 1977; Habicht, 1979; and others). This is illustrated by the general distribution of temperatures, as a function of latitude for the present, glacial, interglacial and nonglacial periods (Fig. 11). More detailed studies reported in Lamb (1977) and Gerasimov (1979) show temperature fluctuations of the order of $\pm$ 2°C in the middle latitudes within the Holocene Epoch alone. It should be noted that equations (3) and (4) indicate that present day precipitation changes in δD and $\delta^{18}O$ values by 5.6 and 0.7 per mil, respectively, for every 1°C change in mean annual temperature. This shows clearly that paleoclimatic and paleogeographic reconstructions (Habicht, 1979) should be attempted to aid in interpreting the isotopic data.

MODIFICATION OF STABLE ISOTOPES IN SUBSURFACE WATERS

Reactions between water and minerals, dissolved species,

associated gases, and liquids with which they come into contact, modify the isotopic composition of water and the other reactants. In addition to mixing between 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 membrane properties of rocks; (4) isotopic exchange between water and other fluids, especially petroleum.

Isotope Exchange between Water and Minerals

Authigenic minerals generally form in isotopic equilibrium with the associated pore waters at the temperature of their formation. Field data from many investigations show that carbonates, cherts and clay minerals undergo extensive isotopic alterations from reactions with pore waters at sedimentary temperatures (Clayton et al., 1968; Savin, 1980; Milliken et al., 1981; Kharaka and Carothers, 1986; Land and Fisher, 1987; Longstaffe, 1989; and many others). Because rates of diffusion in solid phases are extremely small at low temperatures, it is believed that these isotopic alterations result from chemical reactions involving water that include dissolution, precipitation, mineral transformations (e.g. smectite to illite, Mg-rich calcite to calcite) and recrystallization.

Field and experimental studies have demonstrated that isotopic exchange between water and quartz, feldspars and many other aluminosilicates are negligible at sedimentary temperatures in the absence of chemical reactions. For these minerals and others that have undergone no isotopic exchange with water, their isotope values can be used to calculate the temperature of their formation to study their diagenetic history (Milliken et al., 1981; Kharaka and Carothers, 1986; Longstaffe, 1989; and many others). It should be noted, however, that even in the case of quartz, the most stable and refractory mineral, extensive (generally up to 20% of detrital grains) intergranular pressure solution and reprecipitation is observed in some basins (Houseknecht and Hathon, 1987). The isoto-

pic composition of water and the newly formed quartz, of course, are different from the original values.

Table 6: Oxygen isotope fractionation factors between water and minerals as a function of temperature (T) in °K

Equation	Reference
$1000 ln\alpha(quartz\text{-}H_2O) = 3.38 \times 10^6 T^{-2} - 2.90$	Friedman and O'Neil (1977)
$1000 ln\alpha(amorph.\ silica\text{-}H_2O) = 3.52 \times 10^6 T^{-2} - 4.35$	Kita et al. (1985)
$1000 ln\alpha(albite\text{-}H_2O) = 2.39 \times 10^6 T^{-2} - 2.51$	Matsuhisa et al. (1979)
$1000 ln\alpha(K\ feldspar\text{-}H_2O) = 2.91 \times 10^6 T^{-2} - 3.41$	O'Neil and Taylor (1967)
$1000 ln\alpha(calcite\text{-}H_2O) = 2.78 \times 10^6 T^{-2} - 2.89$	Friedman and O'Neil (1977)
$1000 ln\alpha(dolomite\text{-}H_2O) = 3.34 \times 10^6 T^{-2} - 3.34$	Land (1983)
$1000 ln\alpha(protodolomite\text{-}H_2O) = 2.78 \times 10^6 T^{-2} + 0.11$	Land (1983)
$1000 ln\alpha(ankerite\text{-}H_2O) = 2.78 \times 10^6 T^{-2} + 0.32$	Dutton and Land (1985)
$1000 ln\alpha(siderite\text{-}H_2O) = 3.13 \times 10^6 T^{-2} - 3.50$	Carothers et al. (1988)
$1000 ln\alpha(anhydrite\text{-}H_2O) = 3.21 \times 10^6 T^{-2} - 4.72$	Chiba et al. (1981)
$1000 ln\alpha(kaolinite\text{-}H_2O) = 10.6 \times 10^3 T + 0.42 \times 10^6 T^{-2} - 15.34$	Savin and Lee (1988)
$1000 ln\alpha(smectite\text{-}H_2O) = 2.58 \times 10^6 T^{-2} - 4.19$	Savin and Lee (1988)
$1000 ln\alpha(illite\text{-}H_2O) = 2.39 \times 10^6 T^{-2} - 4.19$	Savin and Lee (1988)
$1000 ln\alpha(illite/smectite\text{-}H_2O) = (2.58 - 0.19 \times I) \times 10^6 T^{-2}$ -4.19; I = fraction of illite (0.0 - 1.0)	Savin and Lee (1988)
$1000 ln\alpha(chlorite\text{-}H_2O) = -8.38 \times 10^3 T^{-1} + 4.81 \times 10^6 T^{-2}$	Cole (1985)
$1000 ln\alpha(pyrophyllite\text{-}H_2O) = 1.08 \times 10^3 T^{-1} + 2.76 \times 10^6 T^{-2} - 5.37$	Savin and Lee (1988)

Formation of authigenic minerals and other mineral reactions discussed above are probably the most important processes that modify the original δD and $\delta^{18}O$ values of water in sedimentary basins. The extent of this modification depends on the following factors.

-The original isotopic compositions of the water and the various minerals with which the water reacts in the sedimentary section.

-The relative number of atoms of O and H in the water and the various minerals (the water/rock ratio) involved. In general, water is the main reservoir for H in sedimentary basins especially at shallow depths where the porosity and permeability of the rocks are high, whereas the minerals are normally the main reservoir for the O atoms. This is the reason why, in the case of water,

extensive "oxygen isotope shifts" are common and "hydrogen isotope shifts" are relatively rare.

-The subsurface temperatures at which chemical reactions and isotopic exchange between water and minerals occur. Temperatures are an important variable because the isotopic exchange rates between water and minerals increase with increasing temperature, and the magnitude of fractionation factors between water and minerals are strongly temperature dependent (Figs. 12 and 13, and Tables 6 and 7).

Table 7: Hydrogen isotope fractionation factors between water and minerals as a function of temperature (T) in °K

Equation	Temp. °C	Reference
$1000 ln\alpha(\text{kaolinite} - H_2O) = -4.53 \times 10^6 T^{-2} + 19.4$	<230	Lambert and Epstein (1980)
$1000 ln\alpha(\text{illite/smectite} - H_2O) = -19.6 \times 10^3 T^{-1} + 25$	29 - 120	Yeh (1980)
$1000 ln\alpha(\text{brucite} - H_2O) = 8.72 \times 10^6 T^{-2} - 3.86 \times 10^4 T^{-1} + 14.5$	144 - 510	Satake and Matsuo (1984)
$1000 ln\alpha(\text{brucite} - H_2O) = -33$	100	Satake and Matsuo (1984)
$1000 ln\alpha(\text{epidote} - H_2O) = 29.2 \times 10^6 T^{-2} - 139$	150 - 300	Graham et al. (1987)
$1000 ln\alpha(\text{epidote} - H_2O) = -36$	300 - 650	Graham et al. (1987)
$1000 ln\alpha(\text{zoisite} - H_2O) = -15.1 \times 10^6 T^{-2} - 28$	280 - 650	Graham et al. (1987)
$1000 ln\alpha(\text{glauconite} - H_2O) = -70$	6	Savin and Epstein (1970)
$1000 ln\alpha(\text{gibbsite} - H_2O) = -15 \text{ to } 0$	<25	Savin and Lee (1988)

The isotopic shifts resulting from reactions between water and minerals can be calculated using the law of conservation of mass. In a closed system, and for water reacting with a single mineral only, the equation is:

$$W\delta^{i}_{w} + M\delta^{i}_{m} = W\delta^{f}_{w} + M\delta^{f}_{m} \qquad (5)$$

where i and f are the initial and final δ values for water and minerals, respectively, and W and M are the mole fractions of atoms of O or H in water and minerals, respectively. Equation (5) may be rearranged to give:

$$\delta^{f}_{m} - \delta^{i}_{w} = M/W \quad (\delta^{i}_{m} - \delta^{f}_{m}) \qquad (6)$$

where M/W is the water/rock ratio and

$$M + W = 1 \qquad (7)$$

Assuming isotopic equilibrium between water and this mineral results in:

$$\alpha_{m\text{-}w} = \frac{1000 + \delta^{f}_{m}}{1000 + \delta^{f}_{w}} \qquad (8)$$

where $\alpha_{m\text{-}w}$ is the fractionation factor between water and this mineral at the temperature of reaction. Equation (7) can be approximated to:

$$\delta^{f}_{m} - \delta^{f}_{w} = 1000 \ln\alpha_{m\text{-}w} \qquad (9)$$

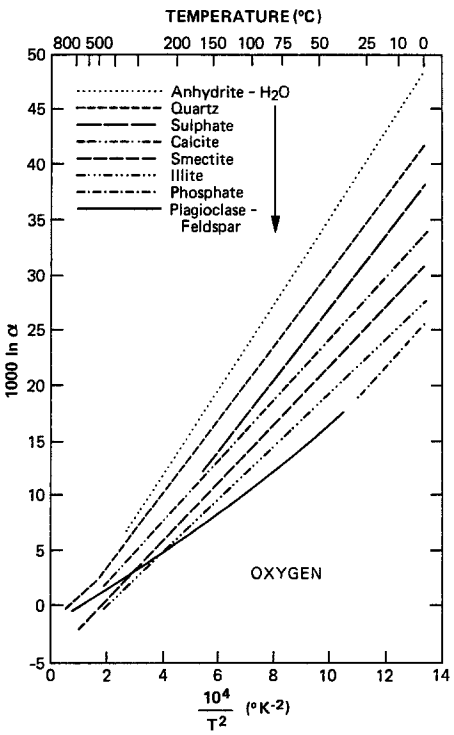


Figure 12: Oxygen isotope fractionations (α = fractionation factor between water and selected minerals plotted as a function of temperature (T in °K) showing the general decreases in the fractionation factors with increasing temperatures. Modified from Savin (1980) and Kharaka and Carothers (1986)

Equations (5) to (9) contain seven independent variables and three primary equations. Thus, all the unknowns can be calculated if values for four of the variables are known. In cases where several minerals are involved in isotopic exchange reactions, where only a portion of a given mineral has exchanged with water or where the section investigated must be treated as an open system, equations (5) to (9) can easily be modified for a more realistic treatment of field situations (Suchecki and Land, 1983; Criss et al., 1987; Dickson, 1987; Longstaffe, 1989).

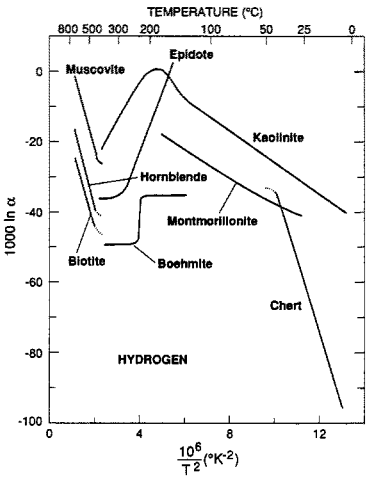


Figure 13: Hydrogen isotope fractionations (α = fractionation factor) between water and selected minerals plotted as a function of temperature (T in °K). Note the pronounced change in the slope of many curves around 200°C. Modified from Savin (1980), Kharaka and Carothers (1986) and Kyser (1987)

In sedimentary basins, reactions with carbonates and clay minerals are the main factors responsible for changes in the isotopic composition of formation waters because of mass balance considerations and the relative ease of isotope exchange. Formation of authigenic quartz, feldspars and other minerals, however, can be quantitatively important in the determination of the final isotopic composition of formation water. Material balance calculations that can be performed with equations (5) to (9) have only recently been attempted (Dickson, 1987; Longstaffe, 1989) because combined and detailed mineral and isotopic analyses simply have not been carried out on basin wide scales. Also, the permeabilities and thus the flow rates in the sedimentary section are often not available,

but these determine the effective water/rock ratios and thus the final isotopic composition of water and minerals. Qualitatively, however, the trends observed in the $\delta^{18}O$ values of formation waters in deep basins can be explained by isotopic exchange between water and minerals. Such exchange almost always results in an increase in the $\delta^{18}O$ value of the water and a decrease in the $\delta^{18}O$ values of the minerals involved (Fig. 14). The "oxygen isotope shift" in the case of water almost always increases as the subsurface temperature and depth of the reservoir rocks increase. This increased "oxygen isotope shift" with increasing temperatures result from an enhanced degree of exchange in the low water/rock ratio environment and the fact that the fractionation factors for O between water and all the important minerals with which the water may exchange in sedimentary basins decrease with increasing temperatures (Fig. 12).

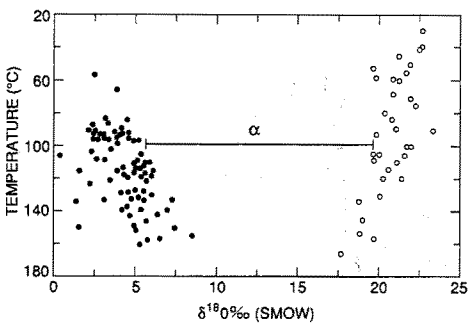


Figure 14: $\delta^{18}O$ values of formation water from Frio sandstones (dots), and the <1μm fraction (essentially smectite-illite) of Frio shale (circles). Line (a) gives the equilibrium fractionation between water and 50% smectite-illite at 100°C using the equation in Table 1. Modified from Land and Fisher (1987)

Hydrogen Isotope Exchange between Water and Clay Minerals

Clay minerals are the most important reservoirs of H in rocks. In many sedimentary basins (northern Gulf of Mexico, Central Valley, California, and others), shales comprise the bulk of the rocks in the basin, and the structural H in clay minerals comprises an important portion of the total H in these basins (Fig. 15). It should be noted that H isotope fractionation factors between clay minerals and water are less than 1.0, indicating that at equili-

brium the clay minerals will be depleted in D with respect to the water, and formation of clays from minerals with no structural H (e.g. feldspars) leads to enrichment of water in D (Fig. 13 and Table 6). Also the D values of detrital clay minerals in sedimentary basins generally vary between about -80 to -25 per mil and may be lower than that of the water with which they may exchange. Isotopic exchange between water and clays, thus, can result in increases or decreases in the δD of formation water (Kharaka and Carothers, 1986).

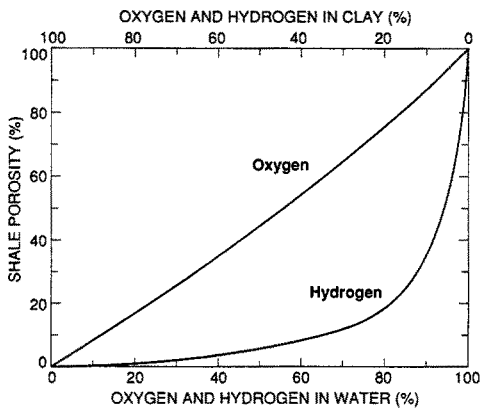


Figure 15: Relative abundance of O and H in pore water and structural illite (close to smectite) as a function of shale porosity. It is assumed that illite comprises 50% by weight of the shale. Note that there is more O and H in shale than pore water at porosities <40% and <6%, respectively

Experimental and field evidence indicate that significant H isotope exchange takes place between water and clay minerals with which they come into contact at all sedimentary temperatures, and that at temperatures higher than about 100°C equilibrium is generally reached in sedimentary basins. Bird and Chivas (1988) reported significant H isotope exchange for Permian kaolinite at temperatures of less than 100°C. Longstaffe and Ayalon (1990) reported H isotope reequilibration between formation water and kaolinite and illite at temperatures of less than 50°C. The clay minerals from three deep wells in the northern Gulf of Mexico basin reported by Yeh (1980) are in apparent isotopic equilibrium with the formation waters in the wells at temperatures higher than about 100°C. Isotopic equilibrium between water and clays in this basin, which

results from transformation of smectite to illite, is inferred from the decrease in the range of the δ D values of clays in the different size fractions from the same depth at temperatures higher than about 100°C and from the fact that the increase of δ D values of clays with increasing temperature are mirrored by, and can be related to the decrease in the δD value of formation waters (Fig. 16 and see Formation Waters of Connate Origin) from the same area (Kharaka et al., 1979; Kharaka and Carothers, 1986).

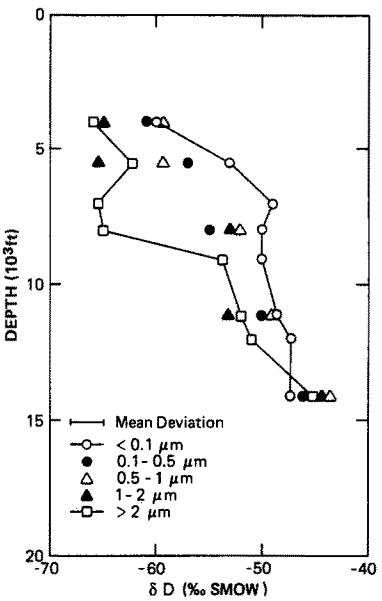


Figure 16: Variations in the δD values of shale with burial depth from CWRU Gulf Coast Well No. 10 (Yeh, 1980). Note the general increase in the δ D values of shale with increasing temperatures as a result of exchange with formation waters and that the smaller size particles (<0.1μm) are modified at shallower depths

Experiments on H and O isotopic exchange of illite, smectite, and kaolinite with water conducted by O'Neil and Kharaka (1976) in the temperature range 100-350°C showed significant (up to 28% for smectite) H isotope exchange even at 100°C. The exchange increased with increased temperatures and duration of runs (up to about 2 years) and were much higher for smectite than for the other minerals at all temperatures. At 200°C the maximum H isotope exchange for kaolinite, illite and smectite were 29, 28, and 82%, respectively. These extensive isotope exchanges took place with no

detectable changes in the minerals. Oxygen isotope exchange in the same systems was minor to negligible at all temperatures, indicating that H isotope exchange occurred by a mechanism of proton exchange. These experiments showed near complete O isotope exchange at 350°C between kaolinite and water, however, this resulted from the complete transformation of kaolinite to pyrophyllite and diaspore.

Evaporation and Condensation

Evaporation and boiling concentrate the light isotopes of O (at all temperatures) and H (at temperatures less than about 240°C) in the vapor phase, and result in higher δD and $\delta^{18}O$ values of the remaining water with increasing evaporation and boiling. Evaporation from surface waters, especially from lakes in closed basins and in the unsaturated zone, is very important in determining the isotopic composition of these waters. The δD and $\delta^{18}O$ values from these evaporating waters generally plot on straight lines with slopes that vary (depending on humidity and local conditions of evaporation) from 2 to 5, and that intersect the "meteoric water line" at the initial (unevaporated) values characteristic of the area. Boiling and evaporation modify the isotopic composition of water in many geothermal systems (Truesdell and Hulston, 1980), however, these processes probably are not important in sedimentary basins except in the case of gas wells. The isotopic and chemical composition of formation waters produced from many gas fields can be modified significantly by mixing with variable amounts of condensed water which is present as water vapor in the gas phase at subsurface conditions but condenses to liquid water as the gas cools on entering the well. The amount of this condensed water, which can be calculated, increases as the subsurface temperatures increase and pressures and salinities decrease (Kharaka and Carothers, 1986).

Membrane Properties of Rocks

There is field, laboratory, and theoretical evidence sugges-

ting that shales and clays act as membranes fractionating the stable isotopes of water (Graf et al., 1965; Kharaka et al., 1973; Coplen and Hanshaw, 1973; Phillips and Bentley, 1987; Demir, 1988). The concentrations of δD and $\delta^{18}O$ are lower in the effluent water compared to their concentrations in the hyperfiltrated water. Graf et al. (1965) showed isotopic fractionations resulting from the passage of water through shales in the Illinois, Michigan, Gulf Coast and Alberta basins (Fig. 17). The δD and $\delta^{18}O$ values shown in figure 17 are residual values as the data from different basins were normalized to the value for meteoric precipitation at Chicago and to the value at 25°C for equilibrium with pre-Tertiary marine limestone. This normalization was carried out in order to separate the membrane fractionation from other effects. Hitchon et al. (1971) and Kharaka et al. (1973) reported isotopic compositions of waters from the western Canada and California basins, respectively, that indicated isotopic fractionations resulting from the passage of water through shale membranes.

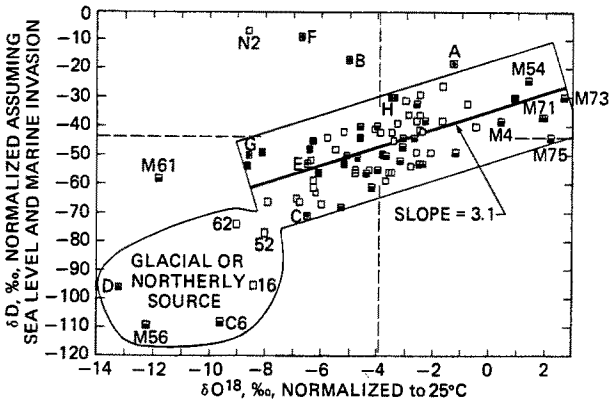


Figure 17: The residual regularity between normalized (see text) δD and $\delta^{18}O$ values of formation waters from Illinois (open squares), Michigan (half full squares), Gulf Coast (full squares) and Alberta (squares with dots) basins showing the membrane effects of shales (Graf et al., 1965)

Results of laboratory experiments (Coplen and Hanshaw, 1973) show that the effluent waters were depleted by 2.5 per mil and 0.8 per mil in δD and $\delta^{18}O$, respectively, relative to the hyperfiltrated (residual) solutions when distilled water and dilute NaCl solution were forced through compacted montmorillonite at ambient temperatu-res. A plot of δD versus $\delta^{18}O$ values from these

experiments fall on a line with a slope of 3.1 (Fig. 18). The slope of this line, it should be noted, is exactly the same as that given by Graf et al. (1965) for the residual δD and $\delta^{18}O$ values of formation water that they attributed to membrane effects (Fig. 17). Benzel and Graf (1984) and Demir (1988), however, obtained somewhat different isotopic fractionation factors as functions of temperature, compac-tion and hydraulic pressures and water compositions.

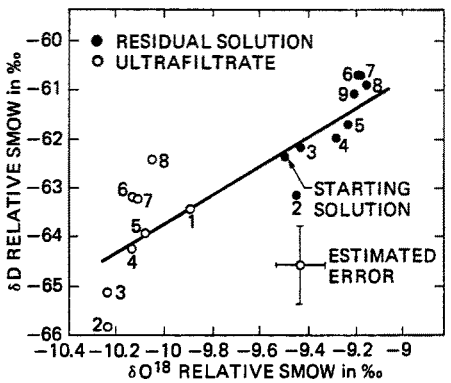


Figure 18: Isotopic compositions of residual (hyperfiltrated) and ultra-filtrate (effluent) solutions of 0.01N NaCl forced through compacted clay (Coplen and Hanshaw, 1973). The slope of the line (3.1) in this figure is equal to that obtained from natural systems (Fig. 17)

Isotope Exchange between Formation Water and other Fluids

Hydrogen isotope exchange between H_2S and water and O isotope exchange between CO_2 and water will occur in nature where water comes in contact with H_2S or CO_2 rich gases. In general, however, isotopic exchange with these gases will not be quantitatively important in significantly modifying the isotopic composition of formation waters from deep sedimentary basins. On a local scale, isotopic exchange between water and these gases may be significant, especially in the case of H_2S in sour gas fields (Hitchon and Friedman, 1969) because of the large fractionation factor between H_2S and water. Isotopic exchange between water and gaseous or liquid hydrocarbons is probably not quantitatively important because exchange rates are extremely low at sedimentary temperatures, but additional investigations are needed to properly

evaluate these effects (Kharaka and Carothers, 1986). Finally, isotopic exchange between water and H gas may be very important in sedimentary basins because the fractionation factors are large ($\alpha_{H2O(v)} - H_{2(g)}$ = 1,400-640 at 0 to 200°C; Bottinga, 1969) and H gas may be an important component in basins with their rich organic matter, but the importance of this reaction needs investigation (Sheppard, 1986).

ORIGIN OF WATER IN SEDIMENTARY BASINS

Oxygen and H isotopes of water are the most useful tool in the study of the origin of subsurface waters. Prior to the use of isotopes, it was generally assumed that most of the formation waters in marine sedimentary rocks were connate marine (White, 1965). Clayton et al. (1966) were the first to use stable isotopes to show that waters from several sedimentary basins were predominantly of local meteoric origin, the original connate water being lost by compaction and flushing. The extensive use of water isotopes, solutes and associated minerals coupled with studies of regional geology and paleohydrology have led to the realization that subsurface waters generally have complicated histories and frequently are mixtures of waters with different origins (Kharaka and Carothers, 1986; Knauth and Beeunas, 1986; Sheppard, 1986; Hanor, 1987; Longstaffe, 1989; and many others.)

Formation Waters from Holocene Meteoric Waters

The isotopic compositions of formation waters associated with petroleum were shown to be related principally to recent local meteoric water (Clayton et al. 1966; Hitchon and Friedman 1969; Kharaka et al. 1973). Their δD values show a "hydrogen isotope shift" in addition to the generally observed "oxygen isotope shift" (Fig. 19). The origins of the shifts vary from basin to basin, but the lines fitted to the δD and $\delta^{18}O$ plots always intersect the meteoric water line (Craig, 1961) at values that approximate those

of present-day meteoric water in the area of recharge (Fig. 19).

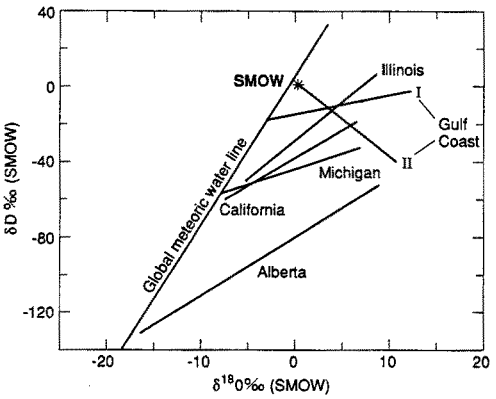


Figure 19: Isotopic compositions of oil-field waters from several basins in North America. Original lines from Clayton et al. (1966), Hitchon and Friedman (1969), Kharaka et al. (1973) and Kharaka et al. (1979). The isotope lines intersect the GML at points with isotope values of present-day meteoric water, except for Gulf Coast II

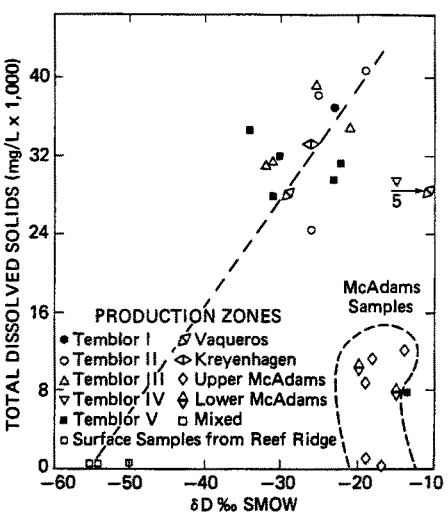


Figure 20: Relationship between δD and salinity of formation and ground waters from the Kettleman North Dome (California). The data from the McAdams samples fall on a separate grouping from the remainder of the samples (Kharaka et al., 1973)

Oxygen and H isotopes of water are not sufficient by themselves to indicate the origin of water. Kharaka et al. (1973) showed that plots of δD values and total dissolved solids indicated a

connate marine origin for the waters from McAdams Formation (Eocene) and a meteoric origin for those from overlying formations (Fig. 20); the isotope data alone could indicate a meteoric origin for all the waters as they plot on the same trend (Fig. 21). Also, a recent detailed study (Connolly et al., 1990) of δD and $\delta^{18}O$ values of water and minerals, combined with Cl and Sr concentrations and $^{87}Sr/^{86}Sr$ ratios, suggests that the formation waters in the Alberta basin, Canada, are not all meteoric as may be indicated by figure 19, but that they form 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.

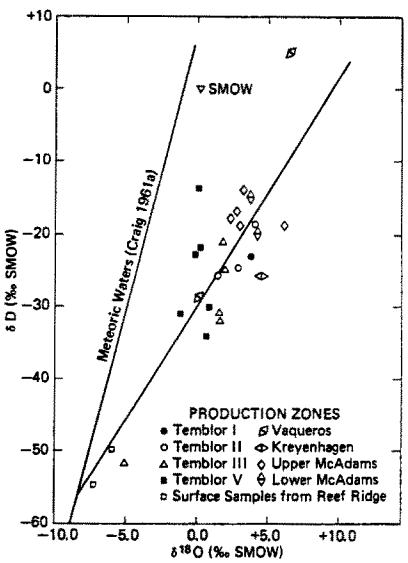


Figure 21: Isotopic composition of formation and ground waters from Kettleman North Dome oil field, California. The solid line is the least-squares line drawn through the data for the formation waters (Kharaka et al., 1973)

Formation Waters from "Old" Meteoric Water

Stable isotopes of water in addition to age determinations using ^{14}C, ^{36}Cl and other isotopes and flow rates, have shown that the waters in many aquifers are "old" meteoric water, i.e., older than Holocene and probably recharged during the Pleistocene Epoch

(Pearson and White, 1967; Bath et al., 1978; Fontes, 1980; Coplen, 1989). Clayton et al. (1966) showed that a number of formation waters from the Michigan and Illinois basins were probably recharged during the Pleistocene Epoch because they had $\delta^{18}O$ values that were much lower than those for present-day meteoric water in the respective areas.

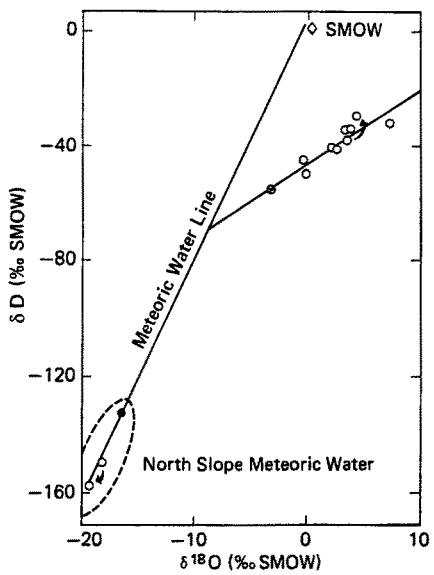


Figure 22: Isotopic composition of formation waters from the North Slope, Alaska. The solid line is the least-squares line drawn through the data. Also shown are values for SMOW, meteoric water in the area and the GMWL. The line through the data does not pass through SMOW or the local meteoric water

Kharaka and his colleagues, (Kharaka et al., 1979; Kharaka and Carothers, 1988) were probably the first to give evidence of meteoric water older than the Pleistocene Epoch in sedimentary basins. These authors presented isotopic and chemical data of formation waters from exploration and producing oil and gas wells from the North Slope of Alaska. The water samples were obtained from reservoir rocks varying in depth from 700 to 2,800 m and in age from Triassic to Mississippian. The chemical data show that the formation waters, regardless of the wells sampled and the age, depth, or lithology of the reservoir rocks, are remarkably similar in total dissolved solids (19,000-24,000 mg/l) and distribution of major cations and anions. The δD and $\delta^{18}O$ values for these waters with the least-squares line drawn through them are shown in figure

22. The least-squares line intersects the meteoric water line at δD and $\delta^{18}O$ values of -65 and -7 per mil, respectively. This line for formation waters, it should be noted, does not pass through the values for standard mean ocean water (SMOW) or 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 the recharge occurred when North Slope had an entirely different climate. This climate may be inferred from the data of Dansgaard (1964), who showed that present day meteoric waters change in δD and $\delta^{18}O$ by 5.6 and 0.7 per mil, respectively, for every 1°C change in mean annual temperature. This relationship, which is rather approximate, suggests that the mean annual temperature at the Brooks Range (the most likely recharge area) was 15° to 20°C higher at the time of recharge than today.

Two possibilities were considered by Kharaka and his colleagues: the first assumes topographic conditions at the time of recharge were similar to present, but that the North Slope was at a latitude of 48°N or further south. A more plausible explanation, however, would keep northern Alaska in its present location, but requires changing the climatic conditions so that the mean annual temperatures were significantly higher, perhaps 15 to 20°C higher than their present values. Mean annual temperatures during parts of interglacial periods may have been higher in northern Alaska than their present values, but the increases were far less than those required by waters of this study (Fig. 11; Habicht, 1979). However, paleoclimatic indicators show that North America (including northern Alaska) had warmer climates than that of the present through most of the Mesozoic and Tertiary (Habicht, 1979; Wolfe, 1980). These studies show that the mean annual temperatures in northern Alaska required by the recharge waters of this study (15 to 20°C higher than at present) were reached as recently as the Miocene, but were also present throughout most of early Cenozoic and Mesozoic. The actual time of recharge cannot be determined for formation waters in northern Alaska, but it is clear that extremely old meteoric waters are present in this and other basins (Knauth, 1988; Connolly et al., 1990).

Formation Waters of Connate Origin

There are several sedimentary basins in the world where geological and hydrodynamic considerations indicate that formation waters are connate in origin. The Gulf of Mexico is a prime example of such basins. The extensive drilling for petroleum, especially in the northern half of this basin, has shown a very thick sequence (up to 15,000 m) of terrigenous shales, siltstones and sandstones of Cenozoic age that lack major unconformities. A thick sequence of fine-grained sediments in the basin is important because these sediments contain the largest portion of connate water at the time of deposition (initial porosity up to 80% for clays), and most of this water is squeezed out into the interbedded sandstones by subsequent compaction.

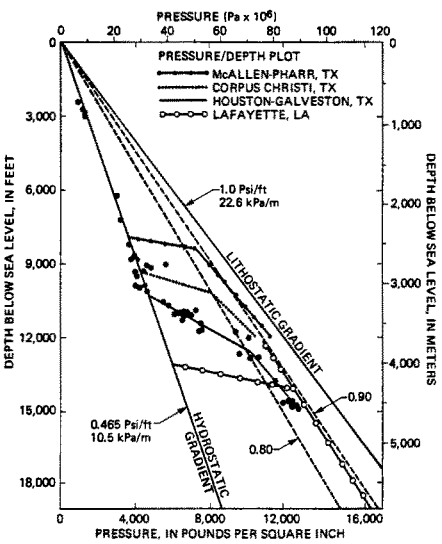


Figure 23: Original bottom-hole pressure from oil and gas wells in coastal Texas and Louisiana plotted against depth below sea level. Note the different depths at which the geopressured zone is encountered in different areas of the Gulf Coast, USA (Kharaka et al., 1978)

Abnormally high fluid pressures (geopressured zones) are another important characteristic of these basins. In the northern Gulf of Mexico basin (Fig. 23), geopressured zones with hydraulic pressure gradients higher than hydrostatic [10.5kPa m 1 (0.465psi

ft 1)] are encountered at depths that range from about 2,000m in south Texas to more than 4,000m in parts of coastal Louisiana (Kharaka et al., 1985). Fluid potentials calculated from the pressures give hydraulic heads that are higher than any recharge areas in the basin, indicating water flow upward and updip in this section. 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 northwest, indicating that the water, at least in the geopressured zones, is connate water squeezed from the marine shales and siltstones in the basin (Kharaka and Carothers, 1986; Land and Fisher, 1987).

The isotopic compositions of formation waters from the geopressured and normally pressured zones and local ground waters from the northern Gulf of Mexico basin are shown in figure 24. The data for formation waters 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 geopressured and normally pressured zones are not meteoric in origin nor are they the result of mixing of meteoric and ocean waters. These data indicate that the formation waters are connate and represent the original marine water of deposition.

The trend observed in figure 24 is unusual in that the δ D values decrease (are lighter) instead of increase with increasing $\delta^{18}O$ values, which in turn increase with increasing subsurface temperatures. Kharaka and Carothers (1986) use equations based on conservation of mass (equ. 5 to 9) to show that isotopic interaction between connate marine water and clay minerals having very light original δ D value of -70 per mil (Yeh, 1980) is responsible for this unusual shift. Isotopic exchange with clays appear also to control the $\delta^{18}O$ values of water (Fig. 14) in this basin (Yeh, 1980; Kharaka and Carothers, 1986; Land and Fisher, 1987).

The concentrations and isotopic compositions of noble gases in natural gas produced from geopressured geothermal and natural gas wells in the northern Gulf of Mexico basin also support the conclusion that the formation waters from this basin are marine connate in origin (Mazor and Kharaka, 1981). These authors show

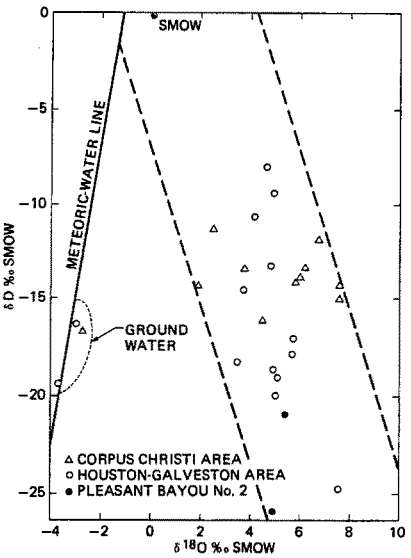


Figure 24: Isotopic composition of formation waters from northern Gulf of Mexico basin. The trend shows decreased δ D values with increasing $\delta^{18}O$ values and it goes through SMOW and away from the local meteoric water (Kharaka et al., 1979)

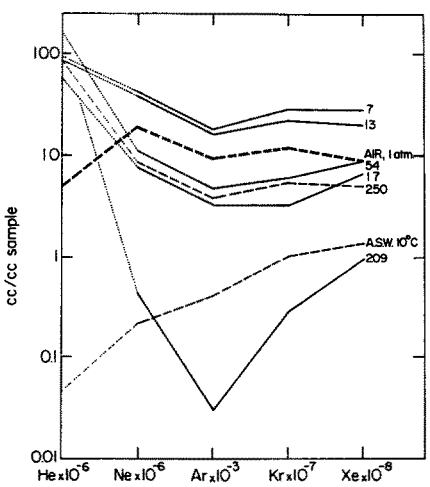


Figure 25: Abundance patterns for noble gases from geo-pressured-geothermal and natural gas wells from coastal Texas and Louisiana, and for air and sea water saturated at 10°C. For Ar, only the atmospheric component is plotted and that the concentration units (cc of gas per cc of water) are at standard conditions (Mazor and Kharaka, 1981)

that the abundance pattern from sample No. 209 (where all the gas produced is solution gas because no separate gas phase is present at depth) is essentially identical to that of air saturated sea water (Fig. 25). The abundance patterns for the other samples where separate gas phases are present, are similar to that of air, indicating degassing of a small fraction (up to about 1%) of dissolved noble gasses from a large volume of connate water of marine origin.

Bittern Connate Water in Evaporites

Evaporated ocean water trapped in salt and associated sediments and adjacent rocks at the time of evaporite precipitation (bittern water) is probably an important component of water in several sedimentary basins that contain thick evaporite sequences (Carpenter et al., 1974; Knauth and Beeunas, 1986; Kharaka et al., 1987; Connolly et al., 1990). The central Mississippi Salt Dome basin represents such a basin and the isotopic composition of its formation water is plotted in figure 26. The isotope values fall into three main groups. Samples from rocks of Jurassic age (Smackover and Norphlet Formations) have δD values (-1 to -3 per mil) that are approximately equal to that of SMOW; they have $\delta^{18}O$ values (5.1 to 7.3 per mil) that are highly enriched in ^{18}O. Samples obtained from rocks of Cretaceous age have δD values (-9 to -13 per mil) that are depleted in D relative to both SMOW and the samples from rocks of Jurassic age. Finally, samples obtained from shallow ground waters in the area have δD and $\delta^{18}O$ values that plot close to the Global Meteoric Water Line (GMWL). The $\delta^{a}D$ values give the D/H measurements in terms of the activities of D in solutions (Fig. 26). These were calculated from the δD values using a correction factor $\Delta\delta$ (Sofer and Gat, 1972) given by:

$$\Delta\delta = 6.1\ m_{Ca} + 5.1\ m_{Mg} + 2.4\ m_{K} + 0.4\ m_{Na} \qquad (10)$$

where m is the molality of the subscripted cation. The correction factors for the formation waters are high, ranging from 2.3 per mil to 10.1 per mil. The $\delta^{a}D$ versus $\delta^{18}O$ (^{18}O values are always reported in terms of activities) plot shows a more linear trend than that obtained using δD values (Fig. 26).

The isotopic compositions of the waters support the conclusion, based on plots of Br versus Cl and combinations of other chemical constituents (Carpenter et al., 1974; Stoessell and

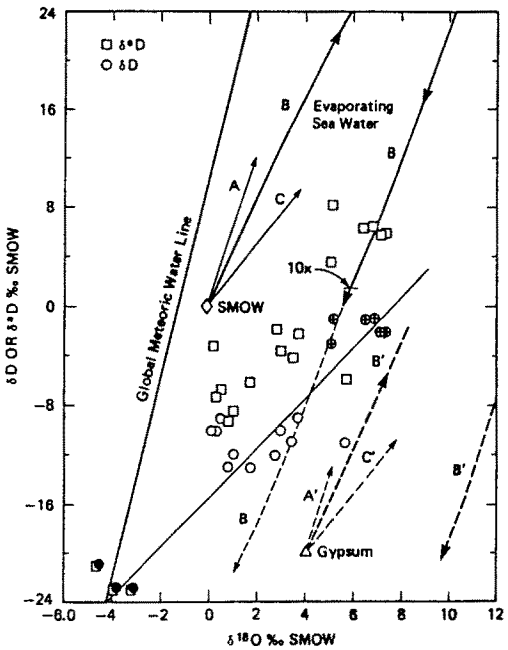


Figure 26: Isotopic composition of ground (solid circles) and formation waters from Jurassic (open circles with +) and Cretaceous (open circles) rocks from central Mississippi Salt Dome basin. $\delta\ ^{a}D$ values were computed from δD values and a correction factor obtained using equation (10) in the text. Lines originating from SMOW and gypsum are the range of trajectories for sea water undergoing evaporation and for hydration water in gypsum precipitated at corresponding points on the evaporation trajectories, respectively. Line B is Holser's (1979) estimate of evaporating sea water in the Gulf Coast. The least-squares line for the δD and $\delta^{18}O$ values is also indicated (from Kharaka et al., 1987)

Carpenter, 1986; Kharaka et al., 1987) that 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 then the trend reverses describing a loop on the δ-diagram (Fig. 26; Lloyd, 1966; Holser, 1979). The actual trajectory formed on the -diagram is variable depending on the local conditions of temperature, humidity and wind velocity at the evaporation site. Holser (1979) and Knauth and Beeunas (1986) have shown that line (B) is probably the most likely trajectory for evaporating seawater at the Gulf Coast (Fig. 26). Line (B) passes

very close to the point giving the δ-values for the water in the Norphlet Formation. The δ-values for the bittern water at that point are those expected from evaporating seawater at the point of halite precipitation (ratio of remaining water to the original water, R, equal to 11x). The δ-values of the samples from the Smackover Formation were initially approximately equal to those from the Norphlet Formation; the 1 to 2 per mil shifts in $\delta^{18}O$ values are likely related to isotopic interactions with the enclosing carbonate minerals (Heydari and Moore, 1989).

The lower δD and $\delta^{18}O$ values of water from rocks of Cretaceous age can be explained as bittern seawater taken past the point of evaporation for water from rocks of Jurassic age or as a mixture between meteoric water and bittern seawater (Fig. 26). The origin of these waters cannot be explained by mixing between bittern and unevaporated seawater (SMOW), or by water released from the dehydration of gypsum (Fig. 26). The chemical composition of water can be used to show that increased evaporation leading to higher salinities is not a plausible explanation for the origin of waters in rocks of Cretaceous age. The salinities of these waters are considerably lower than those of waters from Jurassic rocks and are likely the result of mixing with meteoric water. A more detailed treatment of the geochemistry of water in this basin (Kharaka et al., 1987) shows that 20 to 80% of the water in Cretaceous rocks is of meteoric origin.

Deep Basin Brines from Mixing of Different Waters

Formation waters in sedimentary basins are highly mobile, resulting in the mixing of waters of the same origin but different age or different origin and age (Kharaka and Carothers, 1986). 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 of D and total dissolved solids, they concluded that the observed distribution of D in the formation waters could best be derived through mixing of diagenetically modified seawater with not more than 2.9 times as much fresh meteoric water. They attributed the ^{18}O enrich-

ment of formation waters to extensive exchange with the carbonate rocks (see also the recent study by Connolly et al., 1990).

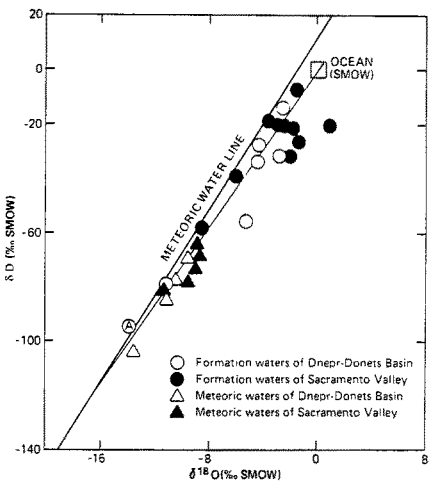


Figure 27: Isotopic composition of meteoric (triangles) and formation waters (circles) from Dnepr-Donets basins, USSR (Vetshteyn et al., 1981), and Sacramento Valley, California, USA. In both basins the formation waters are probably mixtures of meteoric and connate (marine) waters (Kharaka and Carothers, 1986)

Examples of deep-basin waters that can be related to simple proportional mixing between meteoric water and marine connate waters are shown in figure 27. Vetshteyn et al. (1981) showed that the waters from the Dnepr-Donets basin and the Ukrainian Shield are essentially a mixture of meteoric and connate waters (line A-SMOW, Fig. 27). Rozkowski and Przewlocki (1974) reported the isotopic composition of brines from the Upper Silesian Coal basin, Poland, which lie on a simple mixing line between local meteoric water and SMOW. The isotopic data for the Sacramento Valley, California, also shown in figure 27, again indicate mixing of meteoric and marine connate waters, accompanied by some ^{18}O enrichment. Mixing of meteoric and ocean water in the Sacramento Valley basin is supported by geological, hydrologic and isotope evidences. Berry (1973) and Kharaka et al. (1985) used evidence from the chemical composition of formation waters, fluid hydrodynamics, and regional geology to show that connate water was being squeezed from shales in this basin. This water moved upward in the section and mixed with

meteoric water that was present in the sandstones from which the samples were obtained.

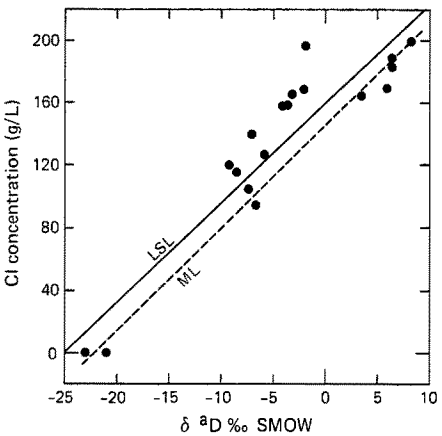


Figure 28: The mixing (ML) and least-squares (LSL) lines based on the concentrations of Cl and $\delta^{2}D$ values for formation waters from central Mississippi Salt Dome basin. Samples from Cretaceous rocks plot above the mixing line, indicating halite dissolution (Kharaka et al., 1987)

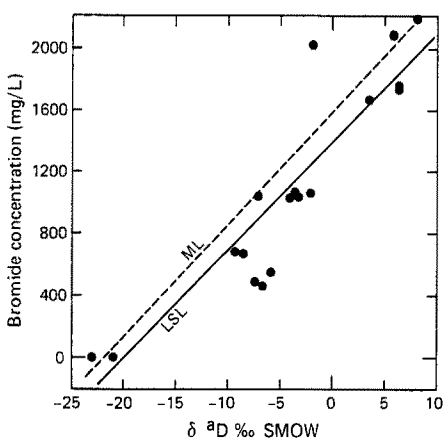


Figure 29: The mixing (ML) and least-squares (LSL) lines based on the concentrations of Br and $\delta^{2}D$ values for formation waters from central Mississippi Salt Dome basin. Samples from Cretaceous rocks plot below the mixing line, indicating halite dissolution (Kharaka et al., 1987)

Mixing between meteoric water and bittern connate water was

demonstrated by Kharaka et al. (1987) for formation waters from central Mississippi Salt Dome basin. They used plots of Cl and Br concentrations and $\delta^{a}D$ values to show that meteoric water comprised up to 20% of pore water in Jurassic rocks (Fig. 28, 29); meteoric water comprised 20 to 80% of water in Cretaceous rocks. Knauth (1988) also 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 having 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 that the formation waters in Pleistocene reservoir rocks originated by mixing of two marine connate waters (Fig. 30). One end member is an essentially unmodified marine connate water of Pleistocene age (samples 6 and 7 in Fig. 30) where as the other (sample 5) being highly modified marine connate water possibly of Miocene age. Approximately the same mixing proportions were obtained using stable isotope values (Fig. 30) and concentrations of Na, Cl, Ca, and Li (Fig. 4).

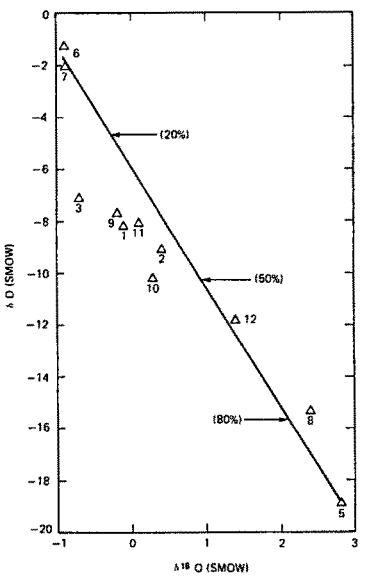


Figure 30: Isotopic composition of formation waters from High Island field, offshore Texas. Percentages representing mixing proportions of the deep brine with Pleistocene connate water (Kharaka et al., 1985). Sample numbers are from Table 3

SUMMARY AND CONCLUSIONS

Formation waters with salinities ranging from about 5,000 mg/l to more than 350,000 mg/l 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 O and H isotope geochemistry of water and a diverse suite of other stable and radioactive isotope compositions have been reported for formation waters from many sedimentary basins worldwide. Application of these determinations together with local and regional geology and 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 previously realized.

The formation waters in the majority of 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-CH_3COOO, or Na-Ca-Cl type waters by a combination of the following main processes: (a) dissolution of halite, (b) incorporation of bitterns, (c) dissolution and precipitation of minerals other than halite, (d) interaction of the waters with organic matter present in sedimentary rocks, (e) interaction with rocks, principally clays, siltstones, and shales, that behave as geological membranes, and (f) diffusion, which appears more important than previously realized. The important processes responsible for the chemical evolution of water and mineral diagenesis in each basin, however, can be identified using "chemical markers" and isotopes.

The discovery in these waters of high concentrations (up to 10,000 mg/l 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 these organics are degraded by bacteria and by thermal decarboxylation. Decarboxylation rates estimated from field data for acetate, the dominant species, give half-life values of 20 to 60 million years at 100°C.

The concentrations of Pb, Zn, Cu, Hg, and several other metals (excluding Fe and Mn) are almost always very low (<1 mg/l) in oil field waters because they are controlled by the very low solubilities of their respective sulfide minerals. Exceptionally rich sources of metals such as redbeds are probably present in the few localities worldwide where metal concentrations are high. Metals leached from these beds first precipitate along with available reduced sulfur; dissolved metal concentrations increase to high values only when the concentrations of H_2S decrease to extremely low values (<0.01 mg/l).

Water-rock interaction in sedimentary basins is and will continue to be the subject of intensive research. The following are several areas that are receiving more attention because of their scientific or economic importance, or the availability of new and applicable equipment.

(1) A plethora of stable and radioactive isotope data are 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 at sedimentary conditions are needed for a better interpretation of the isotope data.

(2) Major advances have been made during the last decade documenting the nature, distribution, and interactions of reactive organic species. Additional investigation is needed, especially in determining the stability of organic-inorganic complexes, the rates of decarboxylation in 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, solid-solution minerals, and brines. Also needed are dissolution-precipitation kinetic data that are applica-

ble to field situations.

(4) Geochemistry of Al is poorly understood, especially the transport of Al in formation water.

(5) Membrane behavior of shales in sedimentary basins is also poorly understood and requires additional study.

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