Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin.
I. Chemistry

CATHY A. CONNOLLY

Department of Geology, The University of Alberta, Edmonton, Alberta T6G 2E3, Canada

LYNN M. WALTER

Department of Geological Sciences, The University of Michigan, Ann Arbor, MI 48109, U.S.A.

H. BAADSGAARD

Department of Geology, The University of Alberta, Edmonton, Alberta T6G 2E3, Canada

and

FRED J. LONGSTAFFE

Department of Geology, The University of Western Ontario, Biological and Geological Sciences
Building, London, Ontario N6A 5B7, Canada

Abstract—Inorganic chemical analyses and short-chain aliphatic acid content are used to interpret the origin and compositional evolution of formation waters in the Alberta portion of the Western Canada Sedimentary Basin. Forty-three formation water samples were obtained covering a stratigraphic interval from Devonian to Cretaceous. The data show that: (1) there is a subaerially evaporated brine component that shows no apparent contribution of waters derived from evaporite dissolution; and (2) formation waters have maintained characteristics indicative of subaerially evaporated waters, despite subsequent flushing by gravity-driven meteoric waters in the basin.

Formation waters are predominantly Na–Cl brines that contain 4–235 g/l total dissolved solids (TDS). Short-chain aliphatic acids (SCA) range up to 932 mg/l, with the following abundance: acetate ≫ propionate > butyrate. Their number varies randomly with subsurface temperature, depth, geological age and salinity. Instead, SCA distributions appear related to proximity to Jurassic and Mississippian source rocks and to zones of active bacterial SO_4 reduction.

Based on chemical composition, the formation waters can be divided into three groups. Group I waters are from dominantly carbonate reservoirs and Group II from clastics. Groups I and II are differentiated from Group III in that they are composed of a brine end member, formed by evaporation of sea water beyond the point of halite saturation, that has been subsequently diluted 50–80% by a meteoric water end member. Group III waters are from clastic reservoirs and are dilute, meteoric waters that are decoupled from the more saline, stratigraphically lower, waters of Groups I and II.

Group I waters have been influenced by clay mineral transformations in shales surrounding the carbonate reservoirs, ankeritization reactions of reservoir dolomites and calcites, and possible decarboxylation reactions. Group II waters indicate significant leaching reactions, particularly of feldspar and clay minerals. Group I and Group II waters both indicate ion exchange reactions were also possible. The waters are near equilibrium with respect to quartz, calcite, dolomite and barite, but are undersaturated with respect to evaporite minerals (halite, anhydrite). Occurrence of feldspar (predominantly albite) and kaolinite seems to control the population of the water cations. Post-Laramide invasion of meteoric waters provided an impetus for many of the diagenetic reactions in both carbonate, but especially in clastic reservoirs. Subsequent hydrochemical isolation of Group I and II waters from further meteoric influences occurred, resulting in pronounced mixing relations and cross-formational fluid flow replacing the once dominant lateral flow.

INTRODUCTION

THE ORIGIN of saline brines in sedimentary basins is a controversial topic. Early investigators advocated a simple connate origin (WHITE, 1965). More recently, the concept of complete flushing of sedimentary basins by meteoric waters was introduced in an attempt to explain isotopic data (CLAYTON et al., 1966) and later, the importance of flushing of sedi-

mentary basins by gravity driven flow was stressed by hydrodynamic flow models (TOTH, 1980; GARVEN, 1985; BETHKE, 1986). However, there is now growing chemical and isotopic evidence that in some settings, waters may still be present that have been hydrologically isolated since entrapment during sedimentation (KNAUTH and BEEUNAS, 1986; KHARAKA et al., 1987; KNAUTH, 1988). Amalgamation of these two ideas has resulted in hypotheses that call

for mixing of meteoric and modified connate waters (HITCHON and FRIEDMAN, 1969) and suggestions that a component of dense connate water may not be completely removed from an aquifer (DOMENICO and ROBBINS, 1985). As a result, a wide variety of interpretations for the provenance of basinal waters has been offered, with most discussions focusing on three mechanisms for the production of the basinal brines: shale membrane filtration, infiltration of subaerially evaporated sea water, and dissolution of evaporite deposits (GRAF *et al.*, 1966; CARPENTER, 1978; HANOR, 1979). Regardless of which model is favored, it is known that water undergoes chemical and isotopic changes through movement and mixing, mineral dissolution and precipitation, diffusion from adjacent shales, and organic maturation reactions, all of which are reflected in the present chemical compositions of the formation waters.

The Western Canada Sedimentary Basin is considered to be a classic example of a gravity driven flow basin and many studies have been made on the basinal fluids. BILLINGS *et al.* (1969) examined the water chemistry and concluded that membrane filtration was the dominant control on salinity. In a more detailed investigation, HITCHON *et al.* (1971) used statistical analyses to arrive at a chemical model whereby original sea water evolved in composition and was influenced by recharged meteoric water, exchange with carbonates, membrane filtration, solution of evaporites, formation of new minerals and exchange with clays and organic matter. Recently, SPENCER (1987) speculated that residual evaporite brines played a major role in the evolution of Devonian brines in the basin and were modified by reaction with the Precambrian basement and subsequently diluted by meteoric waters. The study presented here examines formation waters from reservoirs comprising the whole stratigraphic column in the Alberta Basin and focuses on interdependence and water–rock interactions in the Devonian–Cretaceous section. The study is spatially restricted

to the central region of the Alberta Basin so lateral variations inherent in some basin-wide studies are avoided.

This paper is the first of two (CONNOLLY *et al.*, 1990) and concentrates on the chemistry, origin and evolution of Alberta formation waters. Forty-three water samples from Devonian through Cretaceous strata, were analyzed for alkalinity, major, minor and trace cation compositions, anion compositions, H_2S content and S isotopes, and short-chain aliphatic acids (SCA). Other than the studies of KHARAKA *et al.* (1985) and KHARAKA and CAROTHERS (1986) no information has been hitherto reported on the distribution of SCAs in oil field waters from reservoirs older than Mesozoic. Furthermore, no SCA data exist for the Alberta Basin formation waters. Present water chemistries and late diagenetic events are discussed in terms of water mixing and water–rock interactions. Radiogenic and stable isotope data are discussed in the second paper (CONNOLLY *et al.*, 1990). Both papers exhibit three distinct water groups in the basin and discuss the degree of inter-relationship among them.

GEOLOGICAL SETTING OF THE ALBERTA BASIN

The Alberta Basin is part of the Western Canada Sedimentary Basin, bordered to the west by the Rocky Mountain Thrust Belt, to the northeast by the Precambrian Shield, and to the southwest by the Sweetgrass Arch (Fig. 1). The Alberta Basin is a simple monocline comprised of essentially undeformed, northwesterly trending Mesozoic and Paleozoic sedimentary rocks which rest unconformably on Precambrian rocks of the Canadian Shield (Fig. 2). Adjacent to the Rocky Mountain Foothills, the sedimentary package exceeds 5700 m, but thins to the east owing both to depositional thinning and erosion. Mesozoic strata include Cretaceous sedimentary rocks composed of thick shale and silt units interbed-
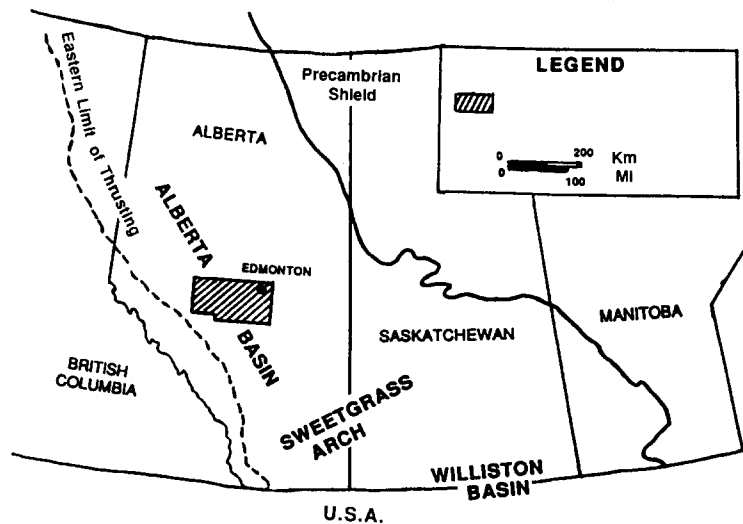

FIG. 1. Map of the Western Canada Sedimentary Basin, showing location of the study area.
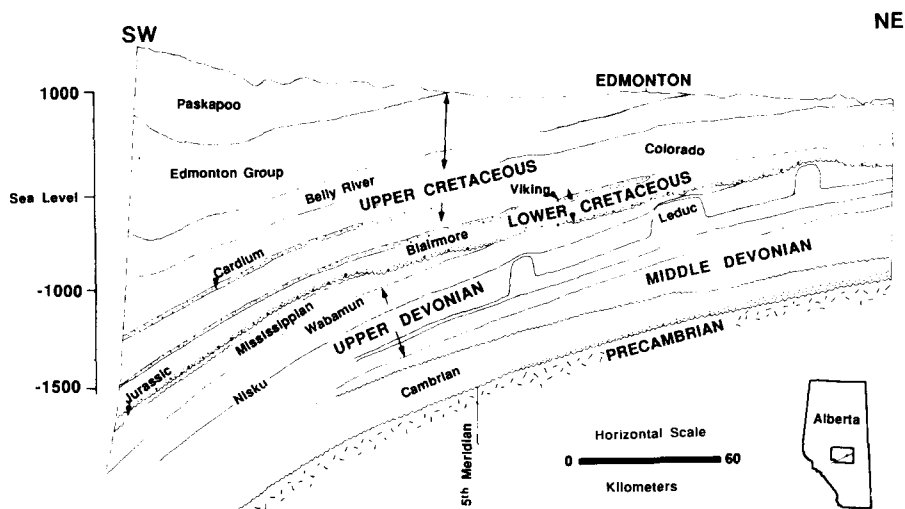
FIG. 2. Geological cross section from SW to NE through the Alberta Basin showing the major stratigraphic units and unconformities.

ded with thin sandstones (Table 1). A major regional unconformity separates these rocks from eroded Jurassic and Paleozoic carbonates, shales and evaporites. A more subtle unconformity separates Mississippian from Jurassic rocks. Upper Mississippian, Pennsylvanian, Permian, Triassic and most of the Jurassic have been eroded from the central plains of Alberta.

The tectonic history of the Western Canada Sedimentary Basin has been strongly influenced by the Canadian Cordillera, with the present day morphology originating via orogenic forces in the Jurassic–Cretaceous period (NELSON, 1970). The Columbian Orogeny occurred near the end of the Jurassic as a result of subduction of the Pacific Plate beneath the edge of the North American Plate and shortening across the orogen initiated formation of the Rocky Mountains (PRICE, 1973; DICKINSON and SNYDER, 1978; BEAUMONT, 1981; JORDON, 1981). The Late Cretaceous was marked by the first pulse of Laramide tectonism with thrusting and uplift occurring along the eastern Cordillera (TAYLOR et al., 1964). The major pulse of the Laramide Orogeny occurred in Late Paleocene or Early Eocene, resulting in maximum burial of the foreland basin (TAYLOR et al., 1964; PORTER et al., 1982; HITCHON, 1984). Subsequent erosion of accumulated Tertiary and Upper Cretaceous rocks has occurred.

The current hydrodynamic regime in the Alberta Basin was initiated by the second orogenic pulse of the Laramide Orogeny. Associated overthrusting effected a large hydraulic head in the eastern Foothills, creating a mechanism for deep penetration of meteoric waters which discharged eastward (HITCHON, 1969a, 1984). Prior to the Laramide Orogeny, it is doubtful that a hydraulic head greater than that generated by the present Canadian Cordillera ever existed (HITCHON and FRIEDMAN, 1969). It has been suggested that the Upper Devonian–Carboniferous

carbonate rocks channel flow from most of the Alberta Basin toward the northeast in the role of low fluid potential drain for the basin (HITCHON, 1969b, 1984). However, GARVEN (1989) suggests that the regional flow system has undergone dissipation and partitioning, at least since the Pliocene, with younger, shallower formations developing smaller flow sub-systems.

SAMPLE COLLECTION AND ANALYSIS

Prior to sampling, care was taken to ensure that the oilfield waters collected were not exposed to water flood or potential sources of anthropogenic contamination, such as swabbing or acidizing. All water samples were collected exclusively from oil fields to avoid dilution problems associated with gas wells. Oil–water emulsions were collected in large acid-cleaned bottles from the well-head of producing oil-wells and the two phases were allowed to separate. The waters were filtered through glass wool to remove any solids and oil droplets. If H_2S gas was present, two filtered aliquots were immediately collected in 500 ml glass jars containing excess cadmium acetate (1.5 g) to precipitate dissolved sulfide as CdS.

Water from the macroporous filter was subsequently passed through a 0.22-μm filter using a pressure-driven automated filtration device. A 125 ml aliquot was collected for pH, density, total alkalinity and Cl measurements, with the former three determinations being performed immediately in the field. The pH was measured using a combination electrode and portable pH meter, density with a portable densitometer, and total alkalinity potentiometrically by Gran titration (GIESKES and ROGERS, 1973). The Cl measurement was done by $AgNO_3$ potentiometric titration in the laboratory. A reverse alkalinity measurement was made by back-titrating the forward total alkalinity sample solution with a weak base (0.05 N NaOH), using a potentiometric technique to select the endpoint. Reverse alkalinity is primarily contributed by short-chain aliphatic acids (SCA) (WILLEY et al., 1975). Subtracting the reverse alkalinity from the total alkalinity provides a good estimate of the carbonate alkalinity because of the low concentration of other protolytic species at low pH values of these brines.

Samples for SCAs were collected in 125 ml glass amber

Table 1. Stratigraphic column for the study area in the Alberta Basin. Waters were collected from Upper Devonian–Upper Cretaceous units

System	Stratigraphic unit	General lithology and depositional setting
Upper Cretaceous	Basal Belly River	Carbonaceous sandstone interbedded with shale and sandstone.
	Lea Park	Shales becoming more marine toward base.
	Cardium	Three sandstone members separated by dark shales. Sandstone members may have conglomerate at the top and be interspersed with shale lenses.
Lower Cretaceous	Viking	Varies from fine salt and pepper sandstone to siltstone to silty shale; sandstone generally interspersed with shale.
	Glauconitic	Very fine to medium quartz sandstone mixed with coarser salt and pepper sandstone. Clay and calcareous cement vary.
	Ostracod	Predominantly shale that is partly calcareous, containing bands of argillaceous limestone.
	Basal Quartz	Essentially sandstone varying greatly in colour and texture. Upper beds are more calcareous. Contains lenses of shale.
Middle Jurassic	Rock Creek	Calcareous sandstone and rusty weathering shale; argillaceous limestone lenses.
	Poker Chip Shale	Black calcareous shales with thin limestone beds.
Lower Jurassic	Nordegg	Black limestone and black calcareous shales with abundant chert fragments; top highly fossiliferous.
	Fernie	Shale; commonly sandy, in places calcareous, and occasionally bituminous.
Mississippian	—	Massive coarse-grained limestone, alternating with beds of black fine-grained limestone; may contain chert nodules.
Upper Devonian	Wabamun	Limestone dominant in the upper part of the group and dolomite in the middle and lower parts; however, may consist of all one lithology or the other.
	Nisku	Dolomite, variably silty and anhydritic.
	Leduc	Semi-fragmental and reef-like; crystalline dolomite with scattered vugs.
Middle/Lower Devonian	Elk Point	Anhydritic dolomite, fossiliferous.
Cambrian	—	Calcareous grey to black shale. Buff to glauconitic sandstone; shale partings.
Precambrian	—	Crystalline basement.

bottles containing a bactericide (cupric chloride; 0.5 g). These samples were immediately refrigerated until analysis. Concentration and identification of SCAs were conducted by ion exclusion chromatography (ICE) on a Dionex 4000i series ion chromatograph, using an ICE-AS1 column. Conditions selected do not differentiate between isomers of butyrate or valerate. Each water solution was diluted and pretreated with an On Guard-Ag cartridge containing a high capacity, strong acid cation exchange resin in Ag form, which removed Cl, Br and I (and other Ag insoluble species) from sample matrices. The sample was injected into the AS1 exchange column and eluted at 0.8 ml/min flow with 0.2 mN HCl eluant (2% 2-propanol). Suppressed background conductivity detection (anion micro-membrane suppressor; 6 mM tetrabutylammonium hydroxide, approximately 2 ml/min) was used. Retention times were approximately: acetate 13 min; propionate 15 min; butyrate 18 min; valerate 27 min. Recovery was >98%, so no correction has been made to the data. Precision is ±5% for acetate and ±20% for propionate and butyrate.

A 250 ml aliquot was acidified to pH <2 using HNO_3 for analysis of cations by a Leeman Labs Plasma-Spec III inductively coupled plasma–atomic emission spectrometer (ICP–AES). The samples were analyzed in simultaneous mode and in two separate groups; (1) major elements (Ca, B, Ba, Mg, Na, Sr) at 1:100 and 1:50 dilution and (2) minor and trace elements (Fe, K, Li, Mn, Pb, Si, Zn) at 1:10 or undiluted. Replicate analyses of gravimetric standard solutions indicate a precision better than ±2%.

A 125 ml aliquot containing 0.5 g cadmium chloride was used for Br and SO_4 analysis by ion chromatography. Bromide was measured on an AS2 column at an eluant flow rate of 2.5 ml/min and SO_4 was measured on an AS5 column at an eluant flow rate of 1.5 ml/min. Suppressed background conductivity detection (anion micro-membrane suppressor; 25 mN H_2SO_4, ~4 ml/min) was used. The eluant was 2 mM NaOH; 4.5 mM Na_2CO_3; 2% CH_3CN; and 0.8 mM 4-cyannophenol. Precision of anion analyses is better than ±2%.

Samples for S isotopic analyses of dissolved SO_4 and S^- were collected in a 250 ml bottle containing 1.5 g of cadmium acetate. The Cd-acetate present exceeded the molality of dissolved H_2S, thus all H_2S was trapped as CdS. The CdS was filtered and barium chloride added to the filtrate to precipitate sulfate as $BaSO_4$ (LONGINELLI and CRAIG, 1967).

The H_2S collected and precipitated with cadmium acetate at the wellhead was quantitatively converted in the labora-

tory to Ag_2S by acidification and sparging into a 1 M $AgNO_3$ solution. The SO_2 gas for S isotope analyses was produced by combustion of Ag_2S with Cu_2O at 950°C under vacuum, and $BaSO_4$ was reacted with sodium metaphosphate at 950°C under vacuum. Sulfur isotope ratios were measured on a VG mass spectrometer and results are reported in the standard δ notation relative to Canyon Diablo troilite (CDT).

Depths and temperatures were determined from logs. Depths were set as the mid-point between perforations. Maximum bottomhole temperatures recorded from the logs were corrected for cooling by drilling processes (KEHLE, 1971) and extrapolated back to the depth of the formation of interest assuming a geothermal gradient of 30°C/km (HITCHON, 1984).

RESULTS AND DISCUSSION

General

Chemical compositions, densities, temperatures and depths of Alberta Basin formation waters are summarized in Table 2. Most samples have charge balance errors <±2%, as determined by direct analysis. Total dissolved solids (TDS) were calculated by summing the concentrations of all the major and minor ions, and are in the range 4–235 g/l. The average TDS is 80 ± 47 g/l, making the waters relatively dilute and variable in salinity compared to waters in some other basins which have been extensively studied, such as in the Palo Duro Basin (FISHER and KREITLER, 1987), the Appalacian and Michigan Basins (McNUTT et al., 1987) and the Mississippi Interior Salt Basin (KHARAKA et al., 1987). Formation water temperatures in the study area range from 35 to 75°C; the average temperature being 53 ± 10°C. Samples were obtained from depths of 680–1970 m; the average depth is 1333 ± 312 m.

According to the water classification of HEM (1970), all of the waters are brines (TDS > 35 g/l), except those from the Rock Creek, Belly River and Cardium stratigraphic units. The former two formation waters are classified as saline (TDS = 10–35 g/l) and the latter as brackish (TDS = 1–10 g/l). Location in the basin, stratigraphic position and lithological composition of the reservoir rocks appear to be more important than depth in controlling the TDS. Most of the waters are Na–Cl brines, with Na comprising >90% of the total cations and Cl comprising >98% of the total anions. Exceptions to this are: (i) several Devonian samples, which are actually Na–Ca–Cl brines (CARPENTER, 1978) and are the most concentrated of all the samples; and (ii) all of the Cardium waters which are HCO_3^-–Na waters and are the most dilute. Sodium and Cl are extremely well correlated in all the formation waters ($r = 0.98$). Figure 3 shows a cross section through the study area illustrating the formation water concentration distribution within the basin, with contours showing equal values of Cl concentration. The contour lines dip in accordance with the rocks, with more dilute waters extending to

greater depths towards the southwest, closer to the potentiometric high for the basin. A <5 g/l concentration contour is shown toward the SW, which approximates the distribution of the Cardium Formation (Fig. 2). This formation is more permeable than surrounding shale units and meteoric fluids are likely directed toward the Cardium in the direction of decreasing free energy.

Alkalinity and short-chain aliphatic acids

Short-chain aliphatic acid anions (SCA) are water-soluble volatile fatty acids with six or fewer C atoms (C_2–C_5) per molecule. The observed order of aliphatic acid anion abundance for most basin brines is acetate >> propionate > butyrate > valerate. Total SCA concentrations for Alberta Basin waters vary from 0 to 932 mg/l over a temperature range of 40–75°C (Table 2). As in other sedimentary basins, acetate is by far the most abundant SCA ranging from 0 to 844 mg/l. However, at low total SCA concentrations, the weight per cent of acetate is more variable, with other SCA species commonly becoming more significant (Fig. 4). Propionate concentrations range from 0 to 74 mg/l, becoming more abundant in stratigraphically younger, though not necessarily lower temperature, units. Values up to 17.1 mg/l were obtained for butyrate. Valerate and dicarboxylic acid anion concentrations were below detection limits.

Influence of SCAs on alkalinity. Alkalinity is a key parameter in controlling carbonate mineral saturation states and the pH buffer capacity of subsurface waters. Short-chain aliphatic acids may contribute significantly to the total titration alkalinity, as evidenced in many other sedimentary basin brines, including those from the San Joaquin Valley, Houston and Corpus Christi (WILLEY et al., 1975; CAROTHERS and KHARAKA, 1978; SURDAM and CROSSEY, 1985); south Louisiana (WORKMAN and HANOR, 1985; HANOR and WORKMAN, 1986); and offshore Texas (KHARAKA et al., 1985).

The reverse alkalinity measurement was used as a reasonable approximation of the total SCA content in the waters. This value made it possible to compensate for SCA effects to the titration alkalinity measurement, thereby omitting pre-analytical sample treatment usually required to isolate organic from alkaline species. This is advantageous because SCAs are easily volatilized during the isolation procedure. The reverse alkalinity value agrees reasonably well with the summation of individual SCA species as determined by ion chromatography (Table 2). Figure 5 illustrates the variable influence of SCA concentration on total titration alkalinity measurements in the Alberta Basin. Short-chain aliphatic acid anions can constitute up to 91% of the total titration alkalinity.

Table 2. Sample locations, depths, temperatures, chemical compositions, alkalinities and organic acid content of Alberta Basin waters. All ionic concentrations are in mg/l. Lead analyses were conducted, but levels were below detection in all the formation water samples. nd = Below detection limit; (—) = not analyzed; A_T = titrated alkalinity; A_R = reverse alkalinity; A_C = carbonate alkalinity; Org acids = total short chain aliphatic acids; Form = formate; Ace = acetate; Prop = propionate; But = butyrate. The alkalinities are presented in meq/l and the organic acids in mg/l and meq/l

System	Stratigraphic unit	Location	Depth (m)	Temp (°C)	TDS (g/l)	pH	Density (g/l)	Na	Ca	Mg	K	Sr	Ba	Li	B
Upper Cretaceous	Belly River	6-5-49-6W5	1078	35	15	7.9	1.008	5690	163	47	72	17	43	1	5
	Belly River	8-29-48-6W5	1090	49	16	7.5	1.009	6050	179	50	33	21	47	1	21
	Belly River	2-28-48-6W5	1076	45	16	8.4	1.008	5990	186	52	47	21	41	1	5
	Belly River	16-22-47-4W5	984	48	11	8.0	1.005	4210	125	30	34	15	27	1	3
	Cardium	3-24-49-5W5	1245	43	5	8.8	1.002	2450	32	11	28	7	5	1	6
	Cardium	14-20-48-6W5	1426	54	4	8.3	1.002	2040	8	3	9	1	4	1	5
	Cardium	16-30-49-6W5	1304	47	4	8.5	1.002	2150	9	3	22	1	4	1	5
Lower Cretaceous	Viking	12-20-49-21W4	999	41	55	7.4	1.036	20800	431	233	107	104	175	5	8
	Viking	15-21-56-24W4	1050	47	60	7.3	1.040	22000	1070	416	102	182	365	5	7
	Viking	8-32-55-20W4	703	40	74	7.1	1.050	25100	2020	884	209	230	203	8	8
	Viking	6-7-56-20W4	676	44	74	7.9	1.049	25200	2040	942	275	217	189	9	8
	Glauconitic	4-36-49-4W5	1630	59	67	7.1	1.044	24700	1030	280	348	234	350	11	5
	Glauconitic	12-16-51-4W5	1574	65	65	6.9	1.043	24800	510	207	489	88	7	12	7
	Glauconitic	14-4-51-25W4	1293	—	96	—	1.063	31900	4040	867	576	360	176	19	8
	Ostracod	16-20-49-3W5	1609	65	72	7.1	1.048	25900	1350	390	330	264	395	12	5
	Ostracod	5-30-49-3W5	1640	67	62	7.7	1.041	22600	888	236	354	151	72	11	7
	Basal Quartz	10-29-56-24W4	1067	46	73	6.2	1.048	25100	2100	795	478	180	83	—	17
	Basal Quartz	13-21-56-24W4	1060	—	91	6.8	1.061	30600	2870	1178	740	199	14	19	27
	Basal Quartz	14-23-52-26W4	1253	—	111	7.2	1.075	35000	5780	1307	944	375	3	27	37
	Basal Quartz	15-33-51-25W4	1359	56	113	6.9	1.078	35900	4030	1344	1050	376	2	30	39
	Basal Quartz	2-25-52-26W4	1237	52	94	7.6	1.069	24900	4570	1154	818	289	2	24	32
	Basal Quartz	16-34-49-5W5	1700	63	60	7.1	1.040	22900	626	150	390	64	27	11	7
Middle Jurassic	Rock Creek	10-25-54-13W5	1969	75	22	7.5	1.014	8470	123	46	119	26	14	4	15
	Rock Creek	16-24-54-13W5	1964	64	21	7.1	1.014	8440	240	49	134	38	36	4	11
	Middle Jurassic	8-34-49-5W5	1699	57	59	7.0	1.040	22300	698	155	395	60	2	11	8
	Middle Jurassic	6-34-49-5W5	1706	61	62	7.9	1.042	23600	793	179	555	54	2	16	8
Lower Jurassic	Nordeg	14-13-49-5W5	1703	—	107	6.9	1.072	35300	4240	1039	1050	239	2	33	37
	Nordeg	1-18-52-5W5	1647	67	100	6.8	1.066	33800	3180	1038	573	463	105	17	13
Mississippian	Banff	6-31-50-4W5	1621	58	103	8.5	1.068	36900	2180	800	924	323	2	25	14
	Banff	14-30-50-4W5	1640	62	87	8.1	1.057	31100	1250	568	659	208	2	19	10
Upper Devonian	Wabamun	9-16-57-3W5	1340	50	93	7.0	1.063	30700	3550	1051	714	325	4	18	17
	Wabamun	2-4-57-3W5	1334	50	102	7.1	1.070	33200	3890	1292	714	359	5	22	15
	Wabamun	13-20-56-3W5	1399	52	137	6.8	1.093	41200	7380	2071	1480	446	4	36	53
	Wabamun	3-7-57-1W5	1247	44	108	6.9	1.074	33600	4810	1498	992	393	2	26	43
	Nisku	15-29-49-26W4	1596	69	178	6.9	1.119	50600	12200	2545	3200	365	2	55	103
	Nisku	14-3-56-24W4	1179	45	113	6.4	1.076	33300	6720	1841	1930	187	1	37	68
	Nisku	16-10-56-24W4	1170	45	111	6.0	1.075	32700	6400	1768	1840	184	1	36	62
	Leduc	11-14-57-21W4	972	41	106	6.2	1.070	34200	4380	1870	896	219	1	20	43
	Leduc	6-20-57-21W4	978	39	99	6.5	1.067	31100	4260	1582	842	168	1	19	35
	Leduc	7-6-58-21W4	979	42	108	6.1	1.073	33000	4850	1862	1000	187	1	22	42
	Leduc	11-12-58-22W4	985	42	111	6.0	1.074	34900	5220	1987	1080	198	1	23	48
	Leduc	11-15-50-26W4	1623	63	235	6.2	1.161	50000	30000	5035	3640	1190	7	50	142
	Leduc	6-23-52-26W4	1536	65	129	6.7	1.088	34500	11100	2109	1560	397	3	28	56

(continued).

Occurrence and distribution of SCAs. In sedimentary basins, SCAs may be produced by bacterial SO_4-reduction and methanogenesis (HATTON and HANOR, 1984) or they may be formed abiotically during thermal maturation of organic matter (SURDAM *et al.*, 1984). Conversely, SCAs can also be consumed by bacteria or, if temperatures are >85°C, degraded by thermal decarboxylation into methane, ethane, propane or butane. CAROTHERS and KHARAKA (1978) suggested that concentrations of SCAs define three temperature zones. Zone 1 is characterized by temperatures <80°C and SCA concentrations of <60 mg/l, consisting principally of propionate.

Zone 2 corresponds to temperatures of 80–200°C and much higher concentrations of SCAs (up to 4900 mg/l). Acetate forms 90% or more of the total SCAs and the concentration of all SCAs decrease with increasing temperature. Zone 3 has temperatures >200°C and is inferred to have no aliphatic acid anions present. Microbiological degradation of acetate by methanogenic bacteria and dilution by mixing with meteoric waters were postulated to explain the composition and concentration of SCAs in zone 1; thermal decarboxylation of SCAs was thought to decrease the concentration of SCAs in zone 2.

Although the temperatures of the formation

Table 2. *Continued*

Cl	SO_4	Br	Fe	Mn	Zn	H_2S	A_T	A_R	%A_T	A_C	Org acids (mg/l)	Form (mg/l)	Ace (mg/l)	Prop (mg/l)	But (mg/l)	Org acids (meq/l)	SO_4^{-2} $\delta^{34}S$	H_2S $\delta^{34}S$
8890	nd	118	0.01	0.34	nd		10.42	0.23	2.21	10.19	—	—	—	—	—	—		
9590	nd	126	0.02	0.42	0.69		6.11	0.10	1.64	6.01	0.5	0.5	nd	nd	nd	0.01		
9500	nd	—	0.21	0.34	nd		5.17	0.02	0.39	5.14	—	—	—	—	—	—		
6250	nd	72	2.46	0.17	0.01		13.98	0.76	5.44	13.22	18.2	nd	17.9	0.3	nd	0.31		
2140	nd	31	0.03	nd	nd		41.44	0.06	0.14	41.38	44.2	2.6	41.1	0.5	nd	0.76		
1860	nd	26	0.11	0.01	nd		32.43	0.06	0.19	32.37	—	—	—	—	—	—		
1930	nd	26	0.02	0.03	nd		43.24	0.30	0.69	42.95	16.8	0.9	13.6	2.3	nd	0.29		
33300	nd	181	30.11	0.50	nd		9.91	0.45	4.54	9.46	60	nd	18.6	41.4	nd	0.88		
36100	nd	172	7.13	0.62	0.04		18.29	16.73	91.47	1.57	931.8	1.4	843.5	71.2	17.1	15.49		
44700	nd	191	8.20	1.19	0.93		5.41	3.63	67.1	1.78	151.4	nd	77.4	74	nd	2.32		
44500	nd	184	0.21	0.41	0.18		3.18	1.48	46.54	1.71	97.4	2.5	27.9	67	nd	1.45		
39700	nd	123	59.94	2.64	0.02		13.86	6.68	35.42	7.18	296.1	nd	245.2	46.4	4.5	4.84		
38900	36	153	20.19	0.21	0.05		26.70	0.97	3.63	25.73	—	—	—	—	—	—		
58300	—	—	0.50	1.55	0.18		7.54	4.87	64.59	2.67	284.2	6.3	238.8	30.4	8.7	4.7		
42700	10	137	36.74	0.99	0.07		11.90	5.16	43.36	6.74	377.8	9.1	336.3	26.9	5.5	6.33		
37200	17	129	0.21	1.03	0.06		12.91	8.52	66	4.39	496.1	7.1	452.1	28.6	8.3	8.31		
44100	102	174	85.94	2.35	0.06		8.17	5.69	69.65	2.48	—	—	—	—	—	—		
54400	269	211	18.39	0.60	0.02		15.10	0.01	0.07	15.09	—	—	—	—	—	—		
67400	215	280	0.26	5.11	nd	122	6.82	0.25	3.67	6.58	15.7	0.8	9.7	5.2	nd	0.25	37.2	17.8
69500	281	267	0.18	6.59	nd	54	7.59	0.44	5.80	7.16	11	0.2	5.7	5.1	nd	0.27		
61700	339	242	0.20	4.01	nd	38	6.11	1.10	18.00	5.01	—	—	—	—	—	—		
35900	—	—	93.05	1.69	0.44		23.60	10.03	42.5	13.57	542.2	1.5	535	5.7	nd	9.18		
12700	11	28	0.15	0.09	0.06		34.67	5.14	14.83	29.54	327.6	4.3	278.9	37.5	6.9	5.42		
12300	20	30	52.20	0.70	0.02		26.55	8.07	30.4	18.48	433.6	0.9	391.3	30.1	11.3	7.06		
34800	170	100	129.17	1.42	0.01		27.02	12.91	47.78	14.11	708.1	2.2	627.6	62	16.4	11.72		
36800	295	113	0.25	1.02	0.03		29.49	13.76	46.66	15.73	—	—	—	—	—	—		
64100	520	225	0.24	1.87	nd		11.80	4.91	41.61	6.9	296.9	1.6	259.1	30.9	5.3	4.91		
60700	—	237	63.59	1.25	2.88		29.03	7.43	25.59	21.6	425.6	1.2	389	32.1	3.3	7.09		
61700	273	224	0.16	0.15	nd		9.98	8.11	81.26	1.87	446.4	1.1	394.7	45.6	5	7.39		
52500	222	181	1.76	0.19	nd		10.29	8.91	86.59	1.39	511.2	1.3	461.2	43.8	4.9	8.5		
55900	87	467	2.18	2.46	0.03		9.52	0.66	6.93	8.86	36.3	1	33	2.3	nd	0.31		
62600	56	244	11.87	1.30	0.02		8.35	2.65	31.74	5.7	—	—	—	—	—	—		
84100	140	335	9.34	0.66	nd	5	3.55	0.66	18.59	2.89	30.1	1.2	23.3	5.6	nd	0.5		
66100	151	269	0.27	0.26	nd	20	8.71	0.97	11.14	7.74	—	—	—	—	—	—		
108000	624	514	0.26	0.15	nd	136	5.81	—	—	—	29.9	1.7	20	8.2	nd	0.49		
67600	1080	354	0.27	0.19	nd	199	12.79	0.21	1.64	12.58	7.5	nd	nd	7.5	nd	0.1	42.2	14.3
67000	1000	335	0.34	0.27	nd	252	10.32	1.07	10.37	9.25	—	—	—	—	—	—		
63100	880	241	0.31	0.07	nd	367	9.61	0.10	1.04	9.51	—	—	—	—	—	—		
60000	1280	227	0.28	0.07	nd	415	9.02	0.03	0.33	8.99	—	—	—	—	—	—	37.7	20.8
65100	1170	258	0.28	0.08	nd	367	9.59	0.06	0.63	9.53	—	—	—	—	—	—		
66100	1240	274	0.27	0.08	nd	347	8.45	0.55	6.51	7.9	—	—	—	—	—	—		
144000	294	1260	17.48	0.49	0.83		4.76	3.20	67.23	1.56	—	—	—	—	—	—		
78300	837	485	0.62	1.42	nd	4	4.29	2.23	51.98	2.07	120.6	0.3	116.3	4	nd	2.03		

waters in the Alberta Basin (35–75°C) correspond to zone 1 of the classification of CAROTHERS and KHARAKA (1978), the predominant SCA is acetate, with concentrations often >60 mg/l. Bacterial action can alter the order of aliphatic acid anion dominance, with acetate preferentially degraded relative to propionate, and propionate preferentially degraded relative to butyrate and valerate. However, the general observation that longer chain aliphatic acid anions dominate in low temperature reservoirs (CAROTHERS and KHARAKA, 1978; WORKMAN and HANOR, 1985) is not substantiated by data for the Alberta Basin, or in some other basins (KHARAKA *et al.*, 1985;

MEANS and HUBBARD, 1987; FISHER, 1987). High acetate concentrations can result from a lack of methanogenic bacteria (KASPER and WUHRMANN, 1978). Thus acetate dominance, rather than suggesting a lack of bacterial activity, may indicate the type of bacteria that is or is not present. Propionate and butyrate appear to become more significant in Alberta Basin waters in stratigraphically younger units that have relatively lower total organic acid contents (Fig. 4b), but there is insufficient data to define distinct relations.

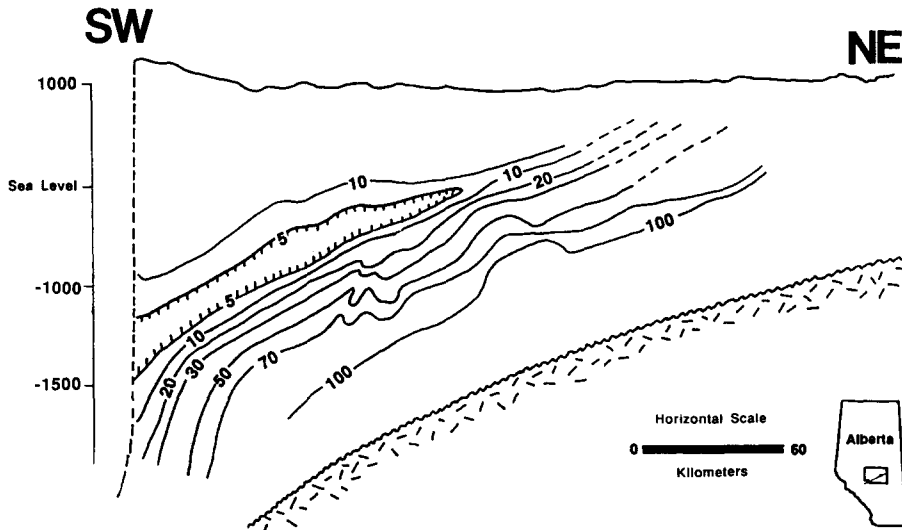Short-chain aliphatic acid concentrations, within a given formation, are significantly lower in waters

FIG. 3. Cross section from SW to NE through the Alberta Basin with contours showing equal values of Cl concentration (g/l).
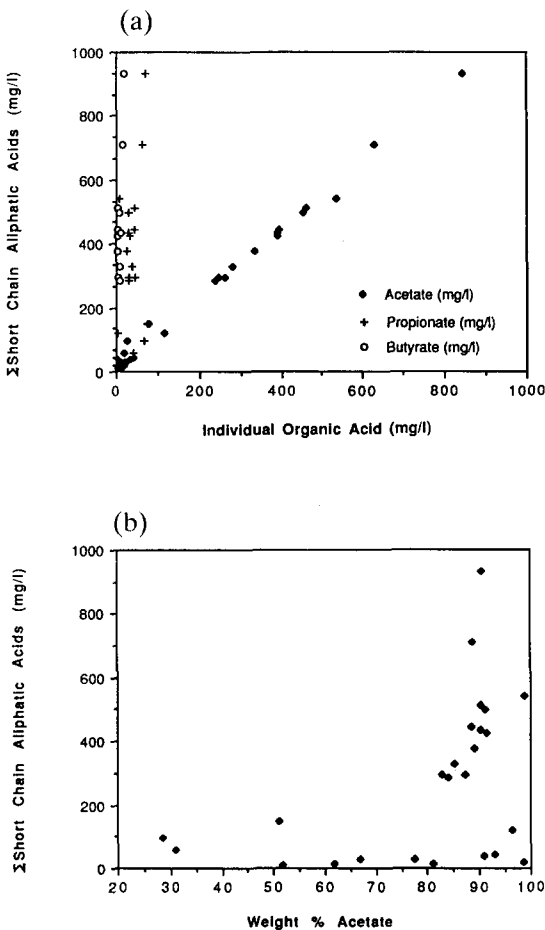

FIG. 4. (a) Distribution of total SCA vs the individual species. The correlation coefficient of total SCAs vs acetate is 0.996, illustrating the dominance of acetate concentration. (b) Total SCA vs wt% acetate. Acetate is generally the dominant anion as shown in Fig. 4a, but at lower total SCA concentrations, acetate comprises less of the total wt % of the SCAs.

containing H_2S (see Table 2). Sulfate-reducing bacteria are likely depleting the SCA concentration (MEANS and HUBBARD, 1987) by reaction (1):

$$CH_3COO^- + SO_4^{-2} \leftrightarrow 2HCO_3^- + HS^-. \quad (1)$$
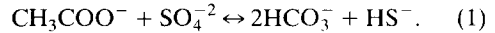
In support of this mechanism, those waters containing H_2S and lower SCA concentrations also have higher carbonate alkalinities (Table 2).

Both bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR) have been cited as mechanisms responsible for H_2S generation in Devonian reservoirs of the Alberta Basin (KROUSE, 1980; MACHEL, 1987; KROUSE *et al.*, 1988). Sulfur isotopic data obtained in this study (Table 3) can be used in concert with data from KROUSE (1980) for waters in the study area, to evaluate the relative importance of these mechanisms. KROUSE (1980) noted in a survey of $\delta^{34}S$ values for SO_4, that there was a marked transition from BSR to TSR at present reservoir temperatures near 80°C. This is reflected in the $\delta^{34}S$ values for SO_4 in formation waters, which
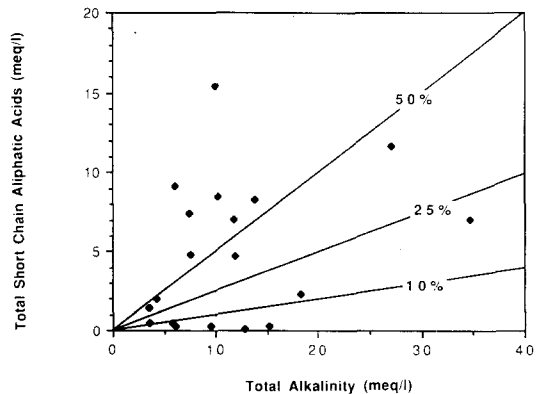
FIG. 5. Plot of SCA alkalinity vs total titration alkalinity for Alberta Basin brines. The SCAs comprise a widely varying percentage of the total alkalinity.
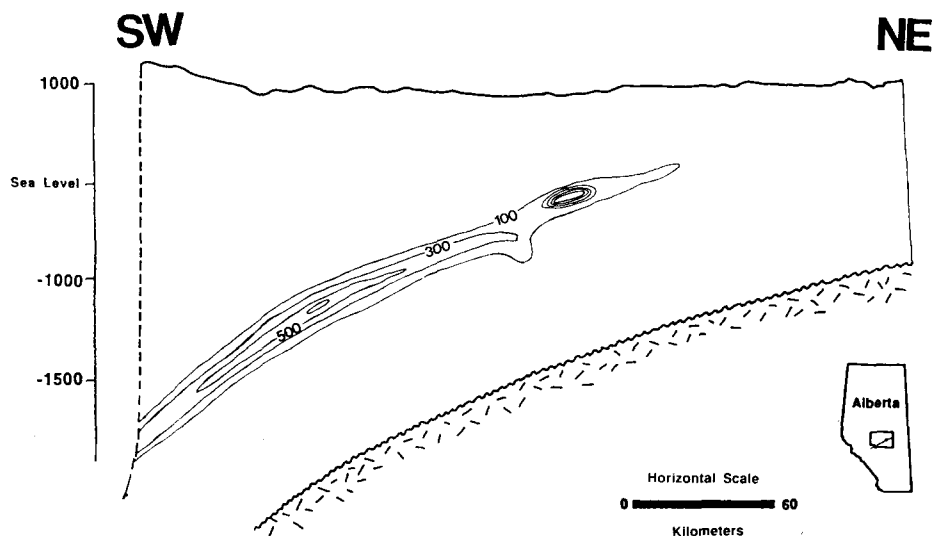
FIG. 6. Cross section from SW to NE through the Alberta Basin with contours showing equal values of total SCA concentration. Contour interval is 200 mg/l.

are approximately $+40\%o_{CDT}$ at lower temperatures and $+20\%o_{CDT}$ at higher temperatures. All of the waters sampled in this study resided in low temperature reservoirs ($<75°C$). The few samples analyzed here are similar to those of KROUSE (1980) and corroborate the hypothesis that these waters are undergoing BSR as shown by Eqn (1). Furthermore, the $\Delta\delta^{34}S$ for SO_4^{-2}–H_2S are relatively high in the waters examined in this study, which is characteristic of the lower temperature, BSR zone.

The concentration of SCAs in Alberta Basin formation waters are not directly interpretable in terms of temperature, depth, salinity, or geological age, but they do exhibit a strong relation with proximity to source rock, primarily the Jurassic, but also the Mississippian shales (Fig. 6). These are the most organic-rich shales in the Alberta Basin (DEROO et al., 1977; MOSHIER and WAPLES, 1985). Devonian shales are also important source rocks in the basin but many Devonian waters contain H_2S, likely of bacterial origin. Thus, it is likely that even if SCA generation had been important in Devonian source rocks, SO_4 reducing bacteria would have utilized them. Reverse alkalinity measurements suggest that most of the Devonian waters, other than one sample with a low H_2S content, had extremely low SCA abundances (Table 2).

In other studies of oil field brines, $\delta^{18}O$ values and Br concentrations have been related to SCA concentrations (MEANS and HUBBARD, 1987). Little correlation between SCAs and these chemical parameters is observed for Alberta Basin formation waters. Anomalously high values of Br are observed in some of the high SCA waters, particularly those in the Jurassic and Mississippian. However, there is no consistent trend established, possibly because of variable amounts of bacterial degradation affecting the SCA concentration in a non-linear fashion. Values of $\delta^{18}O$ become slightly more positive with increasing

total SCA content, suggesting that water-washing and dilution decrease the total SCA concentrations.

Anomalous alkalinity in the Cardium Formation. Anomalously high alkalinity values exist in the formation waters sampled from the Cardium Formation. These waters are dilute and are derived from fluid movement upward into the formation through a shale membrane (Fig. 7), the Second White Speckled Shale. GRAF et al. (1966) and GRAF (1982) have proposed a model for shale membrane filtration that may be considered as a cause of the Cardium Formation water chemistry; however, this model necessitates $NaHCO_3^0$ passing through shale membranes to remove excess Na and aqueous carbonate from the input to effluent solutions and this complex is very weak and likely ineffective.

DEMIR (1988) has shown that the concentration drop of Na molality across a compacted smectite membrane is only 0.8 for a transient period and 0.3 molality units at steady state. A number of smectite-enriched bentonite beds in the Lower Cretaceous units of Alberta have been documented (AMAJOR, 1978, 1980; TIZZARD and LERBEKMO, 1975); however, these units are rare in the study area, with smectite being found in only one Blairmore and one Viking sample. Thus, shales in the study area would be much less efficient than those in the study of DEMIR (1988). The difference in molality on the immediate influent and effluent sides of the Cardium Formation is a little more than 0.8 molality, which is too large a variation considering the shale mineralogy does not provide the most efficient filtration. Furthermore, the shale zone containing the most smectite in the Lower Cretaceous (the Joli Fou Formation) is stratigraphically lower than the Viking Formation. This shale unit would provide the most efficient membrane in the study area and if membrane filtration is the significant cause of the Cardium Formation water

chemistry, similar concentrations and alkalinities should then be observed in the waters of the Viking Formation. Therefore, although membrane filtration may affect Cardium waters to a minor degree, the process does not completely explain the chemistry observed, so other processes must be considered.

The Cardium alkalinity values are better understood when examined in conjunction with data on the existing flow regime and the geometry and distribution of lithologies (Fig. 7). The Cardium Formation is a marine sandstone bounded by low permeability shales. Meteoric waters flushing through the Cardium Formation, as indicated by hydrologic, chemical and isotopic data, would cause oxidation of organic matter in surrounding shales to CO_2 (MACHEMER and HUTCHEON, 1988). Solution of this CO_2 would increase fluid buoyancy and CO_2-charged waters would migrate through the Cardium Formation and be trapped by overlying shales. The pH of the water would remain relatively constant, buffered by organic debris or mineral assemblages (BERNER, 1981) and high alkalinity values would result. Furthermore, it has been demonstrated that dilute meteoric waters are dominated by Na, Ca and HCO_3^- and contain little Cl (GARRELS, 1967; GARRELS and MACKENZIE, 1967; NESBITT, 1985). Cardium Formation waters have compositions similar to meteoric waters, except for the Ca concentration. The lack of Ca is likely a result of calcite cementation and clay mineral cation exchange reactions. Dilute meteoric waters invoke cation exchange reactions on clay minerals causing increased concentration of Na in the fluid phase and Ca on the clays (CERLING *et al.*, 1989).

Solution—mineral equilibria

Thermodynamic controls on formation water composition must be investigated before evaluating potential sources of water molecules and solutes. Stability relations between subsurface waters and various

mineral phases can be evaluated by calculating the ion activity product (IAP) of the minerals in each analyzed water and comparing this value to the equilibrium constants of the mineral (K_T) at a specific temperature. This is referred to as the saturation index (S.I.) and is technically defined as S.I. = log (IAP/K_T). A positive S.I. value indicates supersaturation of the solution with respect to the mineral, a negative S.I. value undersaturation, and zero indicates equilibrium.

Aqueous species distribution and mineral saturation states were computed using the computer code EQ3NR (WOLERY, 1983). In this program, the $\dot{B}$ equation (HELGESON, 1969) is used to approximate activity coefficients of aqueous species. These approximations should be limited to applications in which the true ionic strength is <1 molal. Due to complexing, the true ionic strength is much less than the stoichiometric ionic strength and solutions having stoichiometric ionic strengths up to ~3 can be evaluated with confidence. Except for one Leduc (11-15-50-26W4) and one Nisku (15-29-49-26W4) sample, this stipulation is met by all the samples discussed here.

All Alberta Basin formation waters are saturated with respect to quartz (Fig. 8), regardless of the TDS value or whether they are from carbonate or clastic rocks. This confirms that the salinities represent *in-situ* conditions and have not been diluted by condensed water vapor during sample collection.

Although the formation waters are predominantly of the Na–Cl type, they are several orders of magnitude undersaturated with respect to halite. Saturation indices range from −1.45 to −4.19 (mean value = −1.89), with values approaching saturation with increasing ionic strengths.

Saturation with respect to carbonate minerals cannot be calculated directly because measured pH values are affected both by degassing due to pressure release during sampling and by oxidation of Fe. The former effect results in an increase in pH and S.I. in
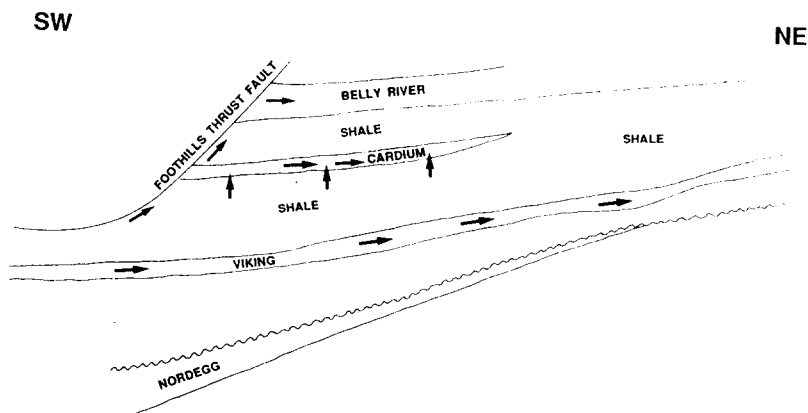

FIG. 7. Schematic cross section from SW to NE in the Alberta Basin illustrating proposed migration pathways for oil and gas derived from source rocks for the Cretaceous–Jurassic section (modified from CREANEY and ALLAN, in press).
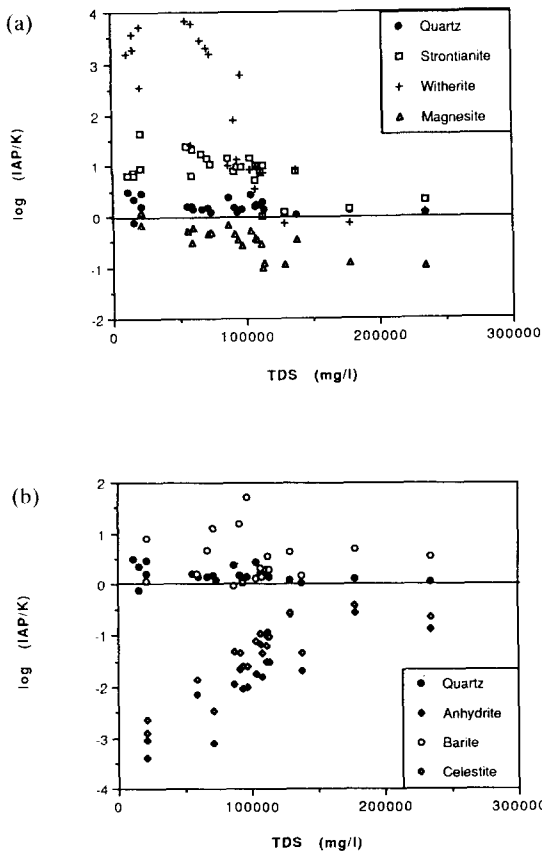
(a)

(b)

FIG. 8. Saturation index (S.I. = log (IAP/K)) vs total dissolved solids. Quartz is on plots (a) and (b) for reference. (a) Depicts saturation states of the carbonate minerals for Alberta Basin waters assuming pH is set by calcite phases in the host lithology. (b) Depicts saturation states of sulfate minerals in Alberta Basin waters.

the waters; the latter causes a decrease in these values (FISHER and KREITLER, 1987). Regardless of these uncertainties, equilibration of the formation waters with respect to calcite and some with respect to dolomite, is probably a reasonable assumption considering the following arguments.

First, carbonate minerals and groundwater exhibit rapid equilibration relative to the residence time of deep basin brines (PALCIAUSKAS and DOMENICO, 1976; PLUMMER et al., 1978, 1979; BUSENBERG and PLUMMER, 1982). Correspondingly, the kinetics of calcite and dolomite dissolution suggest that if the brines have been in residence since the Pliocene, it is likely that saturation by dissolution has been attained, although water–carbonate oxygen isotopic equilibrium has not been reached (CONNOLLY et al., 1990).

Second, the Paleozoic section of the Alberta Basin is dominated by carbonates and all of the Mesozoic clastic units contain calcite cements throughout the paragenetic sequence of their assemblage. The latest diagenetic phases in many of the clastic units are carbonate cements, implying carbonate saturation. The oxygen isotopic compositions of these cements

(LONGSTAFFE, 1986; AYALON and LONGSTAFFE, 1988) indicates that they were formed during and subsequent to the Laramide orogeny and concomitant flushing of meteoric waters. At this time the waters were at their most dilute in many parts of the basin, yet carbonate precipitation still occurred.

Finally, saturation indices estimated from measured parameters (Alk_C and Ca) and activities determined using EQ3NR, show the brines to be generally saturated or oversaturated with respect to both calcite and dolomite even when the pH values are manipulated to very low values. When the pH was set assuming calcite or dolomite equilibrium at the measured carbonate alkalinity, Ca concentration and temperature, the equilibrium pH value decreased from the field measured value by between 0.58 and 1.57 pH units (average = 1.04 ± 0.2). Hence, the assumption of saturation is supported, as it is unlikely that measured pH values are much more than a log unit higher than the true subsurface values.
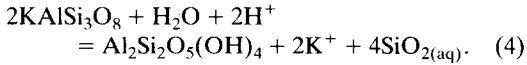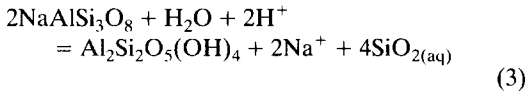
Figure 8a shows the S.I. for some of the carbonate phases in the waters, with quartz plotted for reference. Equilibration of the waters with subsurface calcite was used to calculate pH, using the following equation:

$$CaCO_3 + H^+ \leftrightarrow Ca^{+2} + HCO_3^-. \quad (2)$$
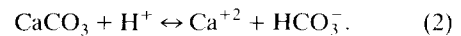
Considering the uncertainty on the measured pH values, this appears the best way to represent *in situ* pH values. Examining the carbonate phases, magnesite is undersaturated in all the waters, whereas strontianite and particularly witherite are oversaturated.

Low levels of SO_4 (below the detection limit) characterize the stratigraphically highest, most dilute waters in the Alberta Basin (from Belly River, Cardium, and Viking units). When SO_4 is present in waters, they are saturated with respect to barite, but undersaturated with respect to celestite and anhydrite, with the degree of undersaturation becoming more significant in stratigraphically higher, more dilute, clastic-hosted waters (Fig. 8b). Barite is extremely insoluble and only a low Ba concentration (0.2 mg/l) is required to saturate and precipitate this phase. As a result, barite controls the S.I. of witherite to some extent. Witherite has very high S.I. in the dilute formation waters that lack SO_4. However, when SO_4 become significant, Ba is precipitated with SO_4 and witherite shows a corresponding decrease in S.I. Celestite is also a very insoluble mineral phase, but strontianite precipitates most of the Sr from solution and barite most of the SO_4, so celestite does not come close to saturation.

Feldspars and clay minerals are the most likely buffers of Na and K, but silicate mineral equilibria in saline brines at slightly elevated temperatures cannot be quantitatively evaluated at present (FISHER and KREITLER, 1987). Furthermore, Al is difficult to measure accurately in these waters. However, Al may be conserved in the reactions, as shown below:

$$2NaAlSi_3O_8 + H_2O + 2H^+$$
$$= Al_2Si_2O_5(OH)_4 + 2Na^+ + 4SiO_{2(aq)}$$
$$(3)$$

$$2KAlSi_3O_8 + H_2O + 2H^+$$
$$= Al_2Si_2O_5(OH)_4 + 2K^+ + 4SiO_{2(aq)}. \quad (4)$$

By comparing brine ion activity ratios with those predicted by equilibria phase relations at *in-situ* temperatures (SUPCRT data base; HELGESON *et al.*, 1978; SHOCK and HELGESON, 1988) the directions of reactions (3) and (4) can be evaluated. The IAP/K values derived for Eqn (3) suggest kaolinization of albite is occurring which is corroborated by thin section petrography. Kaolinization of K-feldspar (4) is not occurring significantly but its values approach initiation of the reaction (IAP/K = 0.2). The albitization of plagioclase feldspar is indicated for all of the formation waters; however, albitization of K-feldspar is not suggested. The above reactions give only the direction of the reaction. Such representation is one dimensional and does not consider other reactions which are occurring concurrently. Thus, it is recognized that stability relations are more accurately portrayed on activity–activity diagrams (CONNOLLY, in prep.).

Trace and major element constraints on water origins

The formation water samples from the Alberta Basin can be divided into three groups based on isotopic (CONNOLLY *et al.*, 1990) and water chemistry (Fig. 9). Group I waters are dominantly carbonate-hosted (Devonian, Mississippian and lowermost Jurassic (Nordegg Formation) carbonates) but also include waters from the lowermost Cretaceous (Basal Quartz Formation) clastic assemblage. Group II waters are from dominantly clastic, partially carbonate reservoirs, comprised of the Middle Jurassic

Fernie Group, and Lower Cretaceous Ostracod, Glauconitic and Viking Formations. Group III waters are from clastic rocks of the Rock Creek (Jurassic) and Upper Cretaceous Cardium Formation, and Belly River Group.

The above groups do not necessarily follow the order of the stratigraphic units in the subsurface, with the Middle Jurassic being placed in Group II and the Rock Creek Formation in Group III, although they are stratigraphically lower than the Basal Quartz Formation of Group I. The Jurassic is represented by a small lens of sedimentary rocks in the western part of the basin that are not found at most of the sampling locations. The dip of Cl concentration contours (Fig. 3) and of the hydrologic groups toward the southwest (Fig. 9) indicate that dilute waters extend to greater depths in this direction. Thus, when water chemistry is considered, Jurassic waters, because of their more westerly sampling locations, are more akin to shallower, less saline waters to the east.

Because the sedimentary rocks in the Alberta Basin are predominantly marine, sea water is an appropriate reference solution with which to compare the formation waters. Such a comparison is justified because sea water is considered to have been constant since the Cambrian (HOLLAND, 1984). To test the origin and modification of basinal waters, compositional relations were examined to help determine whether waters originated by one or more of the following: (1) subaerially evaporating sea water; (2) dissolution of evaporite deposits; (3) complete or partial flushing of meteoric waters by gravity driven flow; or (4) interaction of formation waters with enclosing sedimentary rocks. These graphs are also useful to distinguish the degree of diagenetic reactions and subsequent water equilibration with host rocks. Osmotic and reverse osmotic processes (GRAF, 1982) are relatively ineffective in the Alberta Basin, for reasons that were addressed earlier in the paper.
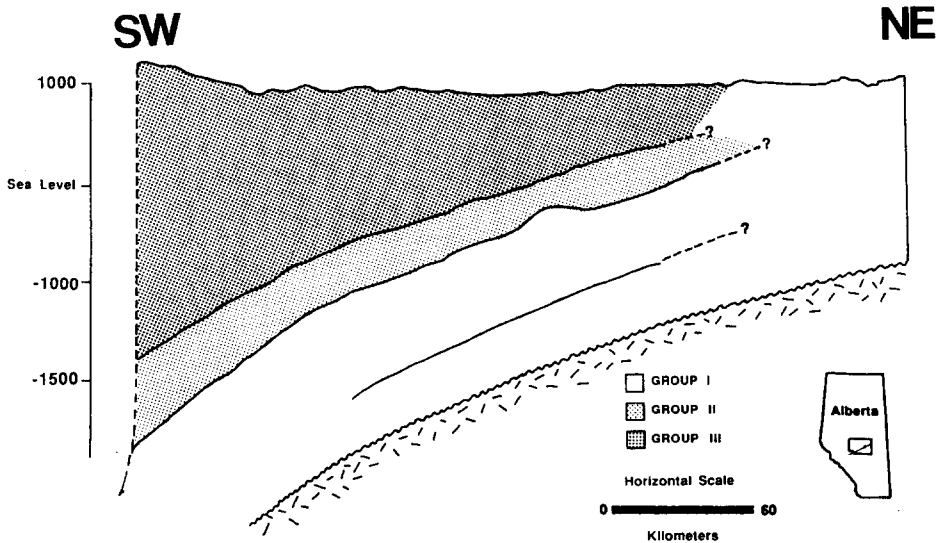

FIG. 9. Geological cross section from SW to NE through the Alberta Basin illustrating the division of formation waters into Groups I, II and III.

Thus, mixtures of water molecules and solutes and their sources are evaluated.

Components of subaerially evaporated sea water or dissolution of evaporites. During evaporation of sea water, the ratio Cl:Br is constant until halite saturation is reached, at which point Cl is preferentially removed from the fluid and Br is concentrated in the residual solution. The sea water evaporation trajectory (S-E-T) (CARPENTER, 1978) in Fig. 10 depicts this relation. The distribution of formation waters on this graph, relative to the S-E-T, can indicate the different origins and processes which have affected water chemistry. Waters which plot directly on the log Cl versus log Br S-E-T, at concentrations greater than sea water, can be tentatively interpreted as subaerially evaporated brines. Waters affected by halite dissolution have an excess of Cl relative to Br and plot above the S-E-T. If waters plot below the S-E-T, they may have evaporated past the onset of halite precipitation and been subsequently diluted by meteoric water or sea water.

Meteoric water is the most likely diluting solution in the Alberta Basin (CONNOLLY *et al.*, 1990). Addition of meteoric water to sea water evaporated past the point of halite precipitation causes the mixture to move off the evaporation trajectory along a straight line parallel to the sloping portion of the S-E-T
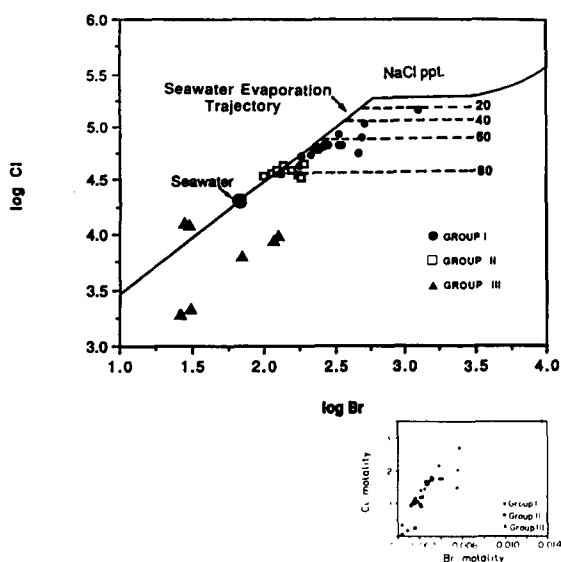

FIG. 10. Log Cl vs log Br for Alberta Basin formation waters with the sea water evaporation trajectory for reference (CARPENTER, 1978). None of the samples plot above the S-E-T indicating salinity was not achieved by dissolution of halite. Group I brines plot to the right of the S-E-T indicating they have a sea water component that reached halite precipitation and was subsequently diluted with meteoric water. Isopleths showing remixing proportions of 20, 40, 60, and 80% are given for reference. Most of the brines for Groups I and II plot between 50 and 80% dilution. Group III waters are all more dilute than sea water. Inset provides a graph of the molality of Cl versus the molality of Br.

(CARPENTER, 1978). Such dilution reduces Br and Cl concentrations in percentages shown by the isopleths in Fig. 10. Therefore, formation waters which plot to the right and below the S-E-T may be interpreted as having an evaporite brine component. Recently, the conservative nature of Br in sedimentary basins and its utility in determining the origin of formation water has been questioned. Reverse partitioning of Br can cause an enrichment of Br relative to Cl during halite recrystallization (LAND and PREZBINDOWSKI, 1981; STOESSELL and CARPENTER, 1986). Hence, it is possible that waters derived from halite recrystallization can plot to the right and below the S-E-T.

KHARAKA *et al.* (1987) have also suggested that waters derived from the dissolution of halite and mixed with meteoric or marine waters could result in a water plotting beneath the S-E-T. This possibility was considered by examining the chemistry of some shallow waters in the Alberta Basin (HOLYSH, 1989) and some Belly River formation waters (HITCHON *et al.*, 1971), both of which are dominated by meteoric fluids. Hypothetical mixing lines joining these waters with those derived from salt dissolution indicate that the hypothesis of KHARAKA *et al.* (1987) is a highly unlikely explanation for Alberta Basin waters. Greater than 85% meteoric water is required just to have the dissolution of halite–meteoric-water mixture reach the S-E-T, let alone have it plot to the right of it. Furthermore, if the mixture did plot beneath the S-E-T, it would be extremely dilute and require additional mixing with unreasonably large volumes of sea water, which had passed the onset of halite precipitation, in order to explain the present position of the waters (Fig. 10).

Formation waters from the Alberta Basin cluster in several distinct groups in Fig. 10. None of the water samples plot above the S-E-T, suggesting that none of them are derived from congruent halite dissolution despite abundant salt deposits found in the Middle Devonian within and to the east of the study area. HITCHON *et al.* (1971) suggest that halite dissolution in the subsurface accounts for the high salinity of some formation waters, but that this affect is minimized by the development of channel flow in the low fluid potential drain lying above Middle Devonian strata. Whether this channel flow is presently active or not remains controversial (HITCHON *et al.*, 1971; DEROO *et al.*, 1977; HITCHON, 1984; GARVEN, 1985, 1989). Nevertheless, dissolution of underlying salt does not appear to be affecting the chemistry of the overlying formation waters, regardless of the fact that the salt edge in many of the underlying evaporite units is in the study area.

Most of the waters from the dominantly carbonate rocks of Group I plot to the right of the S-E-T, with some plotting directly on it. Although congruent dissolution of halite cannot explain these trends, it is important to consider whether these waters have resulted from reverse partitioning of Br during recrystallization of halite. In addition to the unreasona-

bly large water–rock ratio required (>5; see STOES-SELL and CARPENTER, 1986, Table 2) to generate the existing Br concentrations (STOESSELL and CARPENTER, 1986; SPENCER, 1987) additional chemical evidence argues against halite recrystallization.

First, increasing Br concentrations via halite recrystallization can be recognized by decreasing K/Br ratios (STOESSEL and CARPENTER, 1986) and increasing Na/Br ratios (FISHER and KREITLER, 1987) because of the variable distribution coefficients of these elements in this scenario. A plot of log K versus log Br (Fig. 11a) illustrates that Group I waters, which demonstrate the largest degree of evaporation, have the highest K/Br ratio of the groups. Thus, waters with largest Br enrichments are similarly enriched in K, contrary to what would result from halite recrystallization. Similarly, on a log Na versus log Br plot (Fig. 11b), all the water groups plot under the S-E-T. Sodium depletion is unlikely if the waters were derived from the recrystallization of halite.

Second, the summation of divalent cations charge-
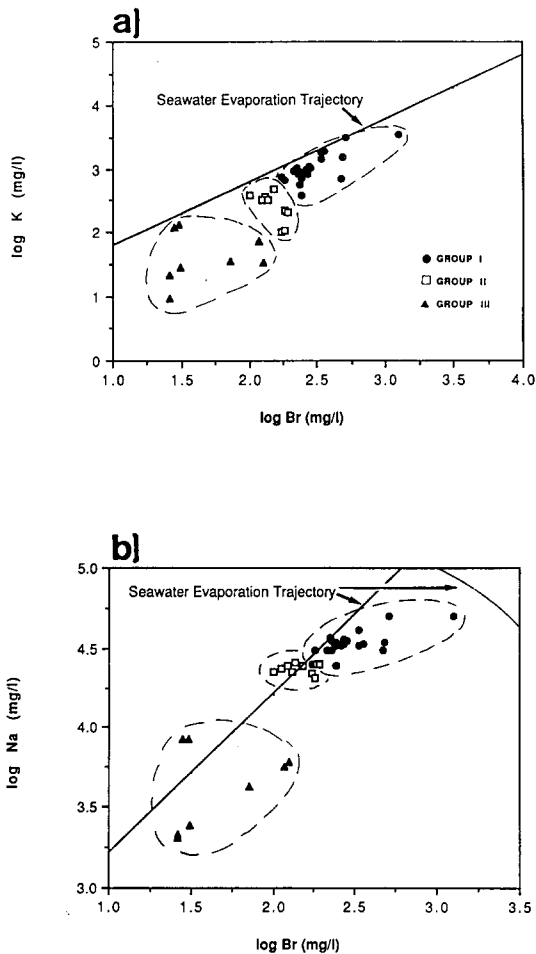
FIG. 11. (a) Log K vs log Br for Alberta Basin brines. Fluids which show the greatest enrichment in NaCl from sea water evaporation plot closest to the S-E-T in this figure. Note that Group I waters plot closest to the S-E-T. (b) Log Na vs log Br for Alberta Basin brines.
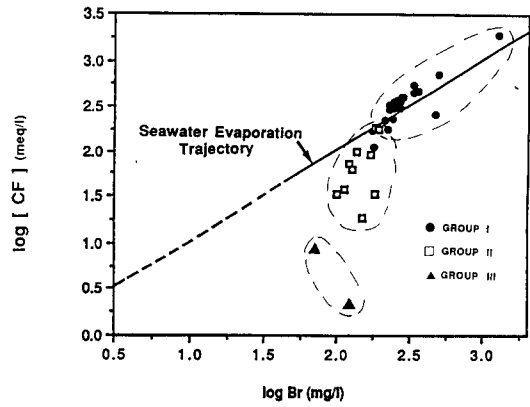
FIG. 12. Log CF vs log Br for Alberta Basin formation waters.

balanced with respect to Cl (denoted CF on the graph) versus log Br (CARPENTER, 1978), plotted in Fig. 12, shows waters from Group I plot above, not below, the S-E-T. Bromide enrichment from halite recrystallization would force waters below the S-E-T, exhibiting an enrichment in Br and a corresponding depletion in divalent cations (STOESSELL and CARPENTER, 1986).

Finally, the oxygen isotopic composition of the waters (CONNOLLY *et al.*, 1990) exhibit a positive relation with Br. Values of $\delta^{18}O$ enriched in ^{18}O cannot be achieved by simple salt dissolution at low temperatures but require initial evaporative processes to enrich the water in the heavy isotope. Waters in the Alberta Basin which exhibit the highest degrees of evaporation on Fig. 10 are the most enriched in ^{18}O.

From the above discussion, it appears reasonable to suggest that Group I waters originated by varying degrees of sea water evaporation to beyond halite saturation, and subsequent mixing with meteoric waters introduced to the Alberta Basin in response to gravity-driven flow during the Laramide Orogeny. Although Group II waters were sampled from stratigraphically higher units than Group I, some of these waters plot to the right of the S-E-T in Fig. 10. This is likely the result of desorption of Br from organics (MEANS and HUBBARD, 1987), because these waters are closest to the dominant source rocks in the basin, the Jurassic shales, and show the highest SCA concentrations. It is unlikely that these waters were evaporated past the onset of halite saturation and were subsequently diluted, when stratigraphically lower waters from Group I, directly beneath and closer to halite deposits, plot on the S-E-T. Other Group II waters plot directly on the S-E-T, suggesting they migrated up the S-E-T, never reaching halite precipitation and were subsequently diluted back down the trajectory. The proximity of the Group II waters to those from Group I on the graph, suggests that the former waters were close to halite saturation, prior to dilution. Based on the approximate maximum degrees of evaporation of Group I

and II waters, the majority of these brines have experienced about 50 to 80% dilution by meteoric water.

Together, Groups I and II exhibit a strong correlation in Fig. 10 at a slight angle to the S-E-T, which seems to define the waters as two component mixtures between a Br-enriched brine and a more dilute water. Conservative mixing phenomena yield straight line relations on linear scales that can develop curvature on log–log plots (HANOR, 1987). However, over the concentration range in these plots, a linear relation would be maintained regardless of scale (Fig. 10, inset). Log scales are used here to be consistent with the original work on compositional trends of sea water (CARPENTER, 1978).

Cretaceous formation waters (five samples) from Group III form a linear relation beneath the S-E-T and are more dilute than sea water. Group III Rock Creek water samples (two samples) plot slightly above the S-E-T and are also more dilute than sea water. All of the waters from Group III appear chemically unrelated to Group I or II, and the Cl/Br ratio cannot be used to establish the identity of dilute end members, because meteoric waters are known to be compositionally distinct from dilute formation waters (GARRELS, 1967; GARRELS and MACKENZIE, 1967; NESBITT, 1985).

Diagenetic modifications of waters. The chemistry of divalent cations in waters can be monitored by considering the amount of divalent cations charge balanced by Cl. This relation is also referred to as the Carpenter Function (CF) (CARPENTER, 1978), and is defined below as:

$$CF = Ca + Mg + Sr - SO_4 - HCO_3 \text{ (in meq/l)}.$$

Dolomitization of calcite, reduction of SO_4 and precipitation of gypsum or halite are common reactions in evaporite settings. Despite the affect these processes have on individual ionic concentrations, the CF relative to Br remains unchanged during the specified reactions as sea water is evaporated (Fig. 12). Furthermore, dilution by meteoric water or sea water does not displace a brine from the S-E-T. Hence, the relation of CF to Br can be used, in conjunction with log Cl versus log Br relations, as a basis for determining whether a brine originated from evaporation of sea water and subsequently underwent (i) water–rock interaction or (ii) mixing with waters of different origins. The relation of CF versus log Cl (Fig. 13) is also useful because Cl is a conservative element in sedimentary basins.

Elemental plots also maintain standard compositional trends during evaporation (Figs 11 and 14). If a solution containing several different ions is concentrated by evaporation, the ratios of the various ions, with respect to each other, remain constant except in cases where ions are precipitating or reacting with the substrate in which the brine is contained. Thus, various diagenetic reactions may be inferred by exa-
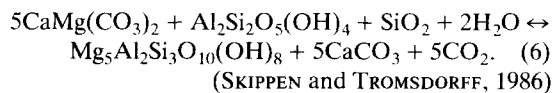
mining ion ratios relative to sea water evaporation trajectories in conjuction with Figs 10, 12 and 13.

Some of the formation waters in Group III are characterized by negative CF values and are not represented in Figs 12 and 13. These include all of the waters from Cardium and Rock Creek reservoirs, and one from the Belly River (16-22-47-4W5). These waters are in the $Na-HCO_3$ class, and are of meteoric origin. The extremely high alkalinity and high proportions of Na relative to divalent cations (i.e. Na/Ca > 34) particular to these formation waters results in negative CF values; therefore, these waters are not represented in the graphs on Figs 12 and 13.

Most of the Alberta Basin formation waters from Group I plot slightly above the S-E-T on the log CF versus log Br plot (Fig. 12). This suggests that these waters are slightly enriched in divalent cations because they are not depleted in Br (see Fig. 10). Divalent cations must be a result of other reactions occurring in Devonian and Cambrian shales, adjacent to and underlying Devonian carbonate reservoirs. For example, silicate hydrolysis reactions (HUTCHEON, 1989), in which a clay mineral, such as kaolinite, reacts to form illite, obtaining K from coexisting pore water and releasing protons, provide a potential source of acid (reaction 5):

$$3Al_2Si_2O_5(OH)_4 + 2K^+ \leftrightarrow$$
$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O. \quad (5)$$
$$\text{(BJORLYKKE, 1984)}$$
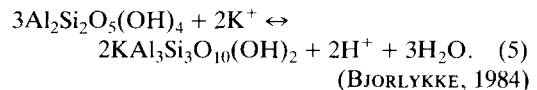
Clay–carbonate reactions provide another potential source of acid, via CO_2, in sedimentary systems (HUTCHEON, 1989; HUTCHEON *et al.*, 1980). Reactions such as the conversion of kaolinite and dolomite to chlorite and calcite (reaction 6) are likely occurring in Devonian and Cambrian shales:

$$5CaMg(CO_3)_2 + Al_2Si_2O_5(OH)_4 + SiO_2 + 2H_2O \leftrightarrow$$
$$Mg_5Al_2Si_3O_{10}(OH)_8 + 5CaCO_3 + 5CO_2. \quad (6)$$
$$\text{(SKIPPEN and TROMSDORFF, 1986)}$$

Numerous reactions of this kind, including those that involve smectite or illite may also occur. Similarly,
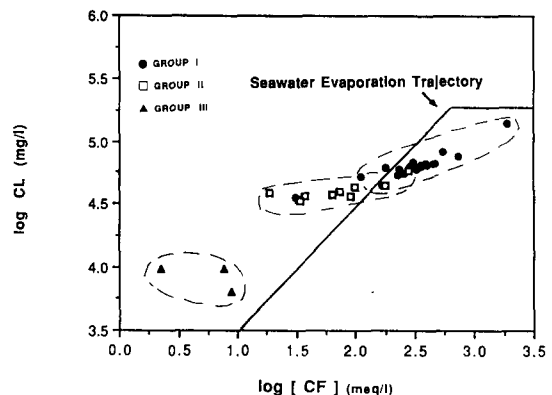

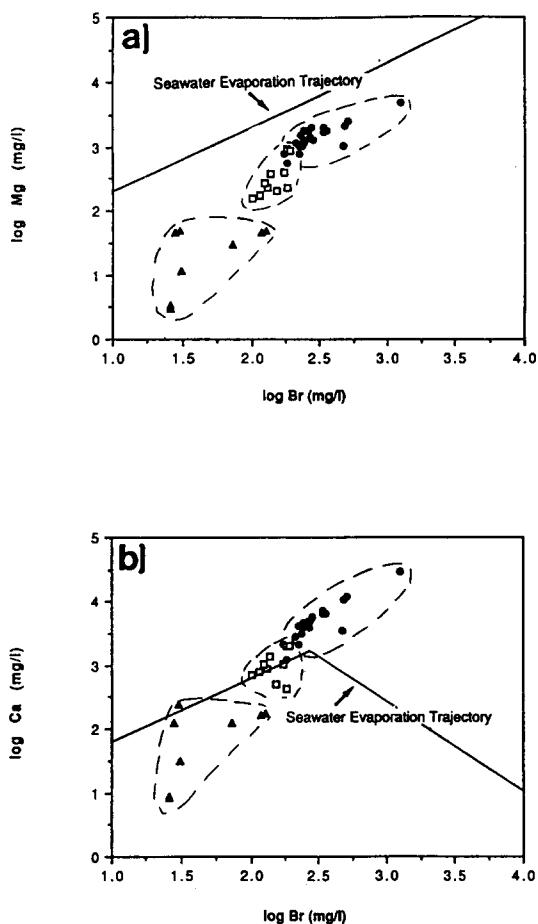FIG. 13. Log Cl vs log CF for Alberta Basin formation waters.

FIG. 14. (a) Plot of log Mg vs log Br for Alberta Basin waters. Note a depletion of Mg relative to the S-E-T for all formation water groups. (b) Plot of log Ca vs log Br for Alberta Basin waters. There is a significant increase in Ca relative to S-E-T, for Group I waters.

chlorite, ankerite and calcite may contain Fe and Mg, and a parallel reaction to (6) can be written for the Fe end member:

$$5FeCO_3 \cdot Al_2Si_2O_5(OH)_4 + SiO_2 + 2H_2O \leftrightarrow Fe_5Al_2Si_3O_{10}(OH)_8 + 5CO_2. \quad (7)$$
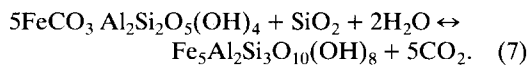
Other reactions providing a source of CO_2 to formation fluids would be decarboxylation reactions in Devonian hydrocarbons.

Although temperatures greater than present day reservoir conditions are required to initiate these reactions, it is possible that temperatures in the Cambrian and Devonian shales were sufficiently high at one time, prior to the maximum burial of the basin, when the topographically controlled hydrodynamic regime, induced by the second pulse of the Laramide Orogeny, cooled down the basin. Reactions 6 and 7, and similar ones generate CO_2 in solution, a source of acid for the dissolution of carbonate in Group I reservoirs, which would cause a corresponding increase in divalent cations not compensated for by the CF. These reactions are indicated on elemental plots

(Figs 11 and 14) used in conjunction with Fig. 12. Potassium and Mg are depleted relative to the S-E-T, whereas Ca is enriched in most of the waters with the exception of Group III. Thus, rather than attributing Group I water chemistry solely to dolomitization reactions (SPENCER, 1987), Fig. 12 indicates other processes are influencing the water composition. Ion exchange reactions in shales surrounding carbonate reservoirs may also explain an excess of divalent cations as is shown below.

Ankeritization of the dolomite and calcite in the Devonian carbonate assemblages may provide a further explanation for the excess of divalent cations. BOLES (1978) and BOLES and FRANKS (1979) suggested the following reaction

$$4CaCO_3 + Fe^{+2} + Mg^{+2} \leftrightarrow 2CaFe_{0.5}Mg_{0.5}(CO_3)_2 + 2Ca^{+2} \quad (8)$$
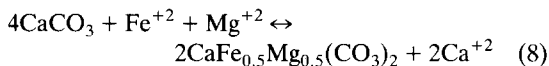
and noted that adjacent shales could provide the Fe and Mg necessary for the reaction. Most of the dolomite in the study area has been identified to be Fe-rich (ankerite) (CONNOLLY, in prep.) and reaction (8) would cause an increase in the CF value relative to S-E-T as Fe is not compensated for in the function.

Samples from Group II fall below the S-E-T suggesting that along with minimal enrichment in Br (Fig. 10), these waters also have a marked depletion in divalent cations. This depletion is further indicated by the high Na/Ca ratios for all of these brines. Albitization or the formation of K-feldspar removes monovalent cations from solution and replaces them with divalent cations, causing an increase in the CF. However, processes such as kaolinization of feldspar and clay mineral stabilization reactions are indicated by a depletion of divalent cations in Group II waters. These processes are typical in sedimentary zones penetrated by meteoric water (HURST and IRWIN, 1982). Meteoric waters are dilute and acidic, and kaolinization reactions (e.g. of albite) would generate high Na contents, particularly because a higher fraction of volcanic fragments and Na-plagioclase are present in these reservoirs (CONNOLLY *et al.*, 1990).

Cation exchange processes may also explain the water chemistry. CERLING *et al.* (1989) noted that when clay minerals in shales and sandstones are weathered by meteoric waters, a release of Na ions, previously held as exchangeable ions, occurs. To examine the potential for cation exchange processes, the parameter $mCl - mNa$ (molality of Cl minus molality of Na), defined as the Na deficiency (FISHER and KREITLER, 1987), is used (Figs 15a and 15b). High Na concentrations in basin brines, such as those of the Alberta Basin, would promote ion-exchange reactions such as simple exchange on clays, conversion of calcic plagioclase to albite, and alteration of detrital clays to Na-clays. Clays equilibrated with waters of high ionic strength have higher Na/Ca ratios than do those equilibrated with waters of low ionic strength (CERLING *et al.*, 1989). Charge balance requires that for each divalent cation released to sol-

ution, two monovalent ions are removed from solution. Sodium exchange is indicated by the relation between Na deficiency and the sum of major divalent cations (Fig. 15). All samples shown in Fig. 15a fall on or above the S-E-T, with the most saline waters from Group I exhibiting the greatest degree of Na removal. This suggests that in addition to the processes described earlier, ion-exchange may account for high concentrations of divalent cations in Group I.

If Na and Cl behave relatively conservatively during evaporation, waters having high Cl contents probably had high initial Na contents. However, high Na concentrations would more effectively drive exchange reactions and cause Na loss. Figure 15b shows that many of the Group I waters have lost Na, indicating exchange processes may have been active. Both Group II and III waters show enrichment rather than removal of Na. This is likely because these waters are dilute, resulting in Ca being removed from solution (Fig. 14b) and replaced by Na. Figure 10 clearly illustrates that Group II waters are all ~80% diluted, with Group I being much more concentrated. This difference in ionic strength may be sufficient to divide the ion-exchange processes.

A strong linear relation between Group I and Group II is observed in Figs 10, 11, and 12 which is maintained on linear molar scales. Plotting log Cl versus CF (Fig. 13) more clearly demonstrates a distinct break between Group I and Group II. Group I waters plot predominantly under the S-E-T providing additional evidence that these waters are concentrated sea water that has been diluted by meteoric water. Group II plot above the S-E-T confirming a depletion in divalent cations and exhibiting a strong diagenetic component responsible for altering the original sea water composition of the deposited sediments. Samples of Group III plot separately from the other two groups.

closed system behavior and do not consider diagenetic disturbance of any kind.

Cation cross-plots were constructed to determine whether mixing relations could be distinguished among Alberta Basin waters. Figure 16a is such a plot of Ca versus K and exhibits a linear array directed toward the origin. Waters of Group II plot closer to the origin than Group I, and Group III waters are so dilute relative to the other two groups that they can barely be observed at the scale of the graph. This behavior suggests that Alberta Basin formation waters are composed of a single brine of constant composition diluted by meteoric water. Most elemental plots are similar to Fig. 16a, with correlation coefficients >0.93, both with and without plotting the two most concentrated waters. However, if Na is plotted versus other elements (e.g. K, Mg, Ca, Sr), a relation such as exhibited in Fig. 16b is observed. A linear relation between Group I and Group II is apparent with a non-zero intercept; Group III is completely removed from the trend. A mixing triangle is not indicated, but rather mixing between two brines, Group I and Group II, with Group III waters
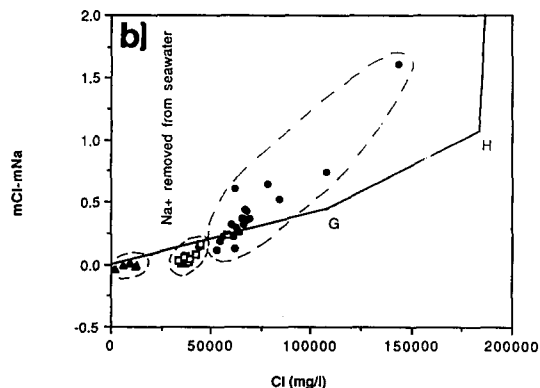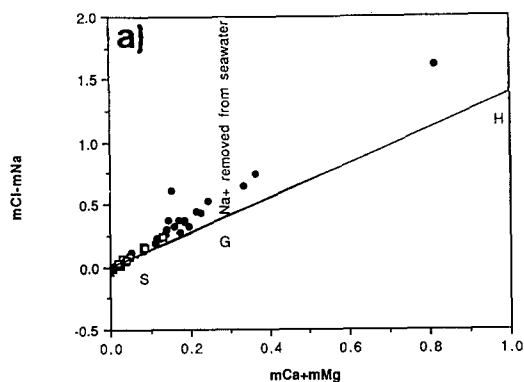

Mixing relations–elemental relations

Figures 10 through 15 strongly suggest a mixing relation between Group I and Group II waters, while Group III waters appear unrelated to them. The principles governing mixing systematics are reviewed by FAURE (1986). Briefly, when a brine of constant composition is mixed with dilute meteoric water, concentrations of elements (Na, Ca, K, Mg, Sr) on an x–y plot form a linear array directed toward the origin. When two brines of differing composition mix, a similar relation is observed on an x–y plot, but with a non-zero intercept. When the two-brine mixture is diluted with meteoric water, a triangle of mixing is introduced encompassing a scatter of points, with the three end-member components forming the apices of a triangle (LOWRY et al., 1988). These relations are only formed, however, during

FIG. 15. (a) Plot of (mCl–mNa) vs (mCa + mMg) for Alberta Basin brines. (b) Plot of (mCl–mNa) vs Cl. Line SGH shows the evaporating sea water trajectory: S = sea water, G = start of gypsum precipitation, H = start of halite precipitation.
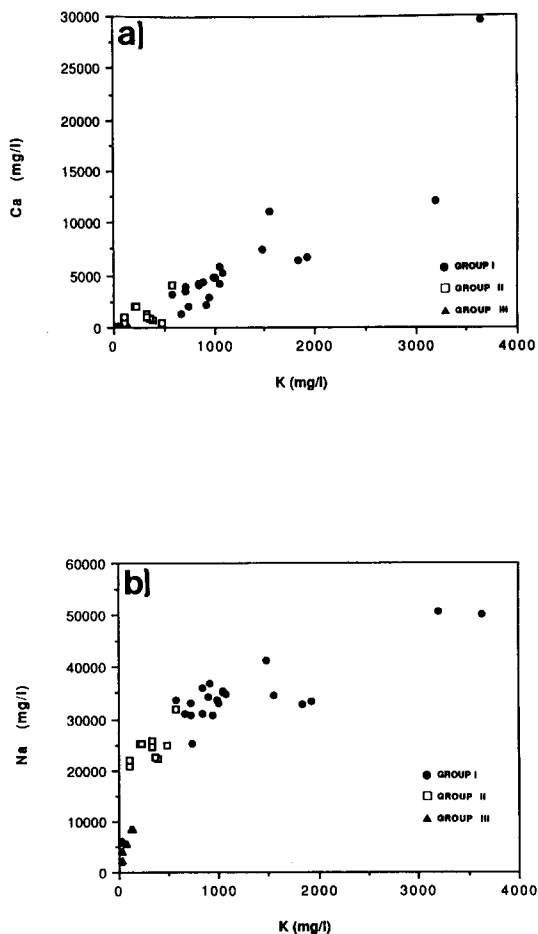
FIG. 16. (a) Plot of Ca vs K which form a linear array intersecting close to the origin. A least squares fit to the data yields $r = 0.91$. (b) Na vs K in Aberta Basin brines. A linear array is observed between Group I and Group II; however, Group III belongs to a separate system.

apparently acting as an independent, much more dilute system. Plots of Na versus other elemental concentrations provide a more accurate indication of the mixing relations because Na is the most abundant cation in the waters, and therefore the least likely to be masked by diagenetic reactions, and it is a very conservative element in sedimentary systems.

Diagenetic reactions affect water chemistry in the Alberta Basin (Figs 12 and 13), but linearity of all $x-y$ plots for major elements of the waters (Na, Ca, K, Mg, Sr) suggests that mixing occurred subsequent to these reactions. Many of the diagenetic reactions, particularly in the clastics, were driven by meteoric recharge in response to Laramide tectonism. Because Group I and II waters appear to have mixing relations, this suggests that mixing occurred after this major flushing event. The regional flow system underwent dissipation and partitioning in the Pliocene (GARVEN, 1989) and this is probably when the Group I and Group II waters became isolated from Group III (CONNOLLY et al., 1990). If meteoric waters were still influential today in the stratigraphically

lower fluid system, all of the major element $x-y$ plots would have intersections at the origin.

CONCLUSIONS

Formation waters from Devonian through Cretaceous carbonate and clastic reservoirs in the Alberta Basin were examined for SCAs and major and minor elements. The abundance and distribution of SCAs in Alberta Basin formation waters do not appear influenced or related to reservoir temperature, sampling depth or geological age. However, a strong association between SCA concentration and proximity to the Jurassic shales is evident, with water-washing and meteoric flushing providing a contributing influence.

Three distinct water groups are evident in the Alberta Basin: Group I waters are dominantly carbonate-hosted and are stratigraphically the lowest; Group II waters are primarily from clastic reservoirs; and Group III waters are completely clastic-hosted and comprise the stratigraphically highest zone. Group I and II form a distinct hydrochemical regime, which is decoupled from the dilute waters of Group III.

Group III water chemistry is dominated by Na and HCO_3^- (alkalinity) and there is no evidence of a sea water or an evaporated brine end-member. Reservoirs containing these waters were deposited in sea water; however, the dilute nature of these $Na-HCO_3^-$ waters argue for complete flushing of any residual marine waters in these reservoirs by meteoric waters.

Formation waters from Group I and Group II form two component mixtures of (i) a residual evaporite brine and (ii) post-Laramide but pre-present day meteoric water. The brine end-member was formed by evaporation of sea water beyond the point of halite saturation and was not influenced by congruent dissolution of evaporite deposits. These carbonate-hosted waters were subsequently influenced by silicate hydrolysis and clay–carbonate reactions in surrounding shales and ankeritization reactions of reservoir carbonates. The clastic-hosted waters of Group II were affected by feldspar–clay mineral leaching reactions initiated by gravity driven flow of meteoric waters, resulting from Laramide orogenesis. Both Group I and Group II waters may also have been altered by ion exchange processes. Group I and Group II waters define a two component mixture, which was established subsequent to hydrochemical isolation in the Pliocene. At this point cross-formational flow began to become significant relative to lateral flow.

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