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Fluorine in formation waters, Alberta Basin, Canada

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Abstract—Fluorine is a common minor constituent of formation waters throughout the Alberta Basin, and it was detected in each of the 469 samples analyzed for it. Contents range up to 22 mg/l, with an arithmetic mean of 1.83 mg/l and a median value of 1.20 mg/l. There is a trend toward increased mean and median contents of F from the shallower, cooler, less saline formation waters to the deeper, hotter, more saline formation waters. This trend parallels a trend of increasing saturation with respect to fluorite, with most of the less saline formation waters being undersaturated with respect to fluorite. At the same time, the major portion of F occurs as F^- in the less saline formation waters, with increasing amounts held as MgF^+ as the Ca content, ionic strength and temperature increase. Complexes between Al and F, and VO and F account for only a relatively minor portion of the complexed F. A significant portion of the F in high-salinity formation waters from marine strata could well have originated from the initial seawater. However, it is speculated that water–rock reactions with bentonite or bentonitic shales may have to be invoked to account for the very high contents of F in the less saline formation waters from some of the shallow, cooler, non-marine aquifers of the Upper Cretaceous post-Colorado aquifer-aquitard system. Finally, it is possible to use knowledge of the distribution of F in formation waters from individual aquifers to check on the “correctness” of F determinations (primarily when formation waters of similar composition show saturation with respect to fluorite), and in the same case to predict the F content of formation waters in the Alberta Basin for which only the appropriate major ions have been determined.

INTRODUCTION

Fluoride is commonly determined in shallow, potentially potable groundwater because contents >1.5 mg/l are generally considered to be deleterious to human health. Deeper formation waters are seldom analyzed for F, as observed by Collins (1975) who reported that “a few are known to contain up to 5 mg/l”. He did not discuss further the geochemistry of F in formation waters. Determination of F in aqueous solutions was rendered much easier with the development of the fluoride ion-sensitive electrode in 1968. More recently, ion chromatographic techniques allow simultaneous multi-anion determinations in aqueous solutions. Campbell (1987) provided a short overview of the determination of fluoride in various matrices. As part of a continuing study of formation waters in the Alberta Basin, F was determined in 469 samples using the fluoride ion-sensitive electrode technique, together with analysis for all major and many minor components. When using a fluoride ion-sensitive electrode it is normal to add a Total Ionic Strength Adjustment Buffer to provide a constant ionic strength background, thus minimizing variations between samples and standards. In the case of most saline formation waters this can be accomplished by dilution to about seawater salinity; this has the dual effect of ensuring adequate buffering at

constant ionic strength and of breaking down any fluorine complexes to F^- . Thus the F reported here is total F.

The objectives of this paper are: (1) to summarize information on the content and distribution of F in formation waters from the Alberta Basin in terms of basin-scale hydrostratigraphic units; (2) to determine the controls on the content of F in terms of saturation with respect to fluorite and the presence of F complexes; (3) to provide a geochemical background to any future study of F in shallow potable groundwaters of Alberta.

ALBERTA BASIN

The Western Canada Sedimentary Basin (see inset map in Fig. 1) comprises the Alberta Basin and the Canadian portion of the Williston Basin. The Alberta Basin (Fig. 1) is bounded on the northeast by the exposed Canadian Shield and on the west by the Foreland Fold and Thrust Belt. It is separated from adjacent sedimentary basins by the Bow Island Arch in the southeast and the Tathlina Arch in the north. It covers most of Alberta, northeast British Columbia, and the western edge of Saskatchewan. Phanerozoic strata form a wedge with a zero edge at the exposed Canadian Shield and range up to about 5.5 km thickness near the edge of the disturbed belt (Fig. 1). There is a similarity and correlation between the basin fill isopach and the temperature at the Precam-

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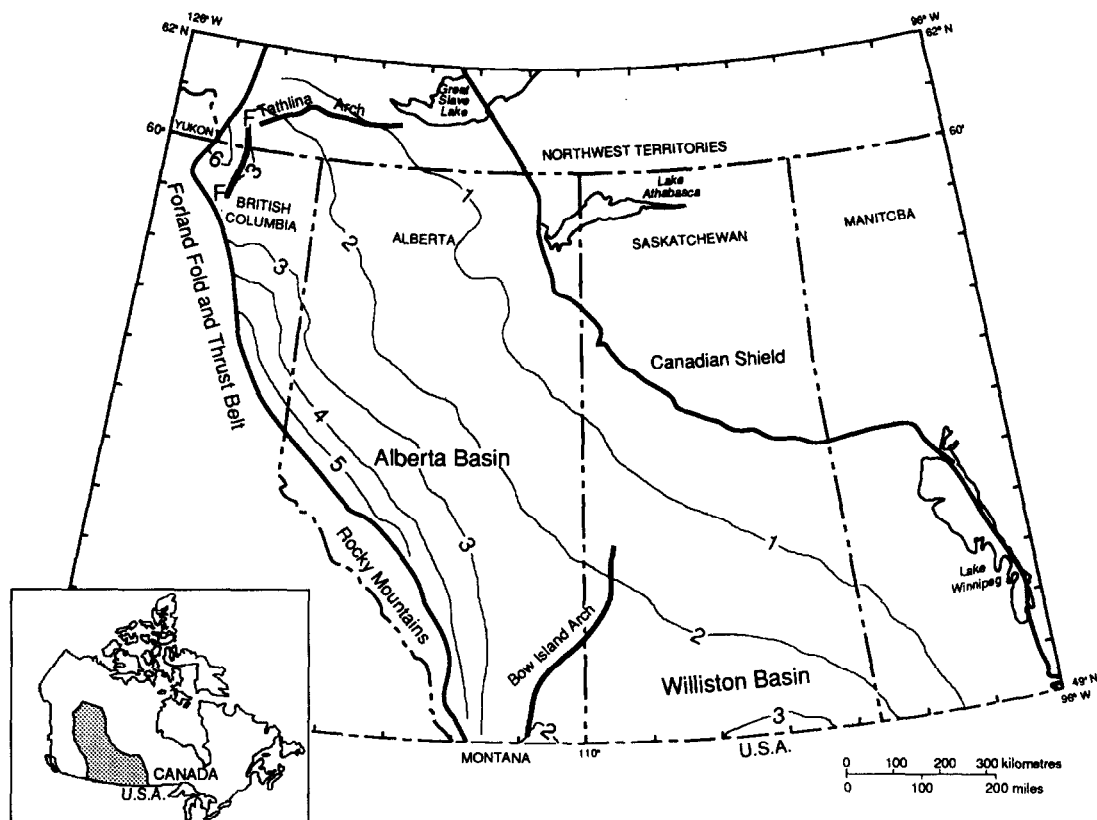


Fig. 1. Alberta Basin: showing location, bounding structural elements, and Phanerozoic isopach (km) from Wright *et al.* (1994, Fig. 3.2).

brian basement, which is up to 160°C in the deepest strata near the Foreland Fold and Thrust Belt, <60°C over the Bow Island Arch and generally <30°C in the shallow basement. Formation temperature is thus depth controlled.

DATA BASE AND DATA PROCESSING

Effectively all of the >141,000 formation water analyses in the files of the Alberta Energy Resources Conservation Board are "standard" analyses in which Na is calculated as the difference between the analyzed anions and cations, therefore including accumulated analytical and other errors; rarely are trace elements reported. As such, these analyses are of limited utility and certainly not generally suitable for studies of trace elements in formation waters or water-rock interaction.

Ideally, two things are required if a formation water analysis is to be of value to petroleum or mineral exploration, or to studies of water-rock interaction. First, the sample should be partially analyzed in the field for "time-sensitive" components and aliquots preserved for subsequent laboratory analysis. Second, appropriate minor and trace elements should be determined, and a complete analysis made of major elements so that a proper ionic (charge) balance can be determined. Few analyses from the Alberta Basin meet both requirements, and of those that do it is clear that at least some are not even representative of the *in situ* formation water because of a variety of effects such as contamination with water floods.

The data base used in this study comprised unpublished analyses in the so-called RCAH-series (Research Council of

Alberta Hitchon-series). These samples were collected in 1975–1977 through a cooperative project with the Alberta Energy Resources Conservation Board; all were from drill-stem tests. The produced formation water was sampled by the operating company for the Alberta Energy Resources Conservation Board and the Alberta Research Council, though it was clear from the descriptions on the provided plastic containers that the samples taken for the Alberta Energy Resources Conservation Board were not always from the same drillstems as those taken by the companies for their own "standard" analyses. Often this made effectively little difference when the analyses were subsequently compared but it did allow a check to be made against samples for which a significant loss of CO₂ had resulted in possible precipitation of calcium carbonate prior to trace element determination. Major components were determined by the Alberta Energy Resources Conservation Board, and selected minor and trace elements by the Alberta Research Council. The majority of the trace elements were determined by Chemical and Geological Laboratories Ltd. of Edmonton using ICP methods.

The RCAH-series samples were collected under a wide variety of conditions, they were untreated in the field, and often several weeks elapsed before they could be treated for preservation of trace elements. As a result, CO₂ loss was sometimes significant, even to the extent of causing precipitation of calcium carbonate. Normally, the presence of CO₃²⁻ in formation water indicates contamination with drilling mud or, less commonly, they have been subject to extensive CO₂ loss due to delay in analysis (see discussion in Hitchon *et al.*, 1990, Appendix 1). Because the "standard" analysis reported by the operating company was made within a day or two of sampling, it acted as a check with respect to possible extensive CO₂ loss, and consequent calcium carbonate precipitation, in the RCAH-series

samples. Thus only analyses without evidence of excessive CO_2 loss were included in the data base, even though they may report some CO_2 . Where the RCAH-series samples fell in the areas studied by Hitchon (1990, 1991) they were also checked against the regional trend maps and if anomalous were rejected. They were then run through the computer program SOLMINEQ.88 (Kharaka *et al.*, 1988), and those with a charge imbalance $>15\%$ were rejected. Of the analyses retained, $\sim 66\%$ had a charge imbalance $<5\%$, and $\sim 23\%$ had a charge imbalance in the range 5–10%.

In order to compensate for the loss of CO_2 and to determine the mineral solubility characteristics at formation temperatures, two procedures were carried out. First, the formation temperature was calculated from the depth of the drillstem test, and the integral regional geothermal gradient and annual ground temperature from Bachu and Burwash (1994). Second, the CO_2 option in SOLMINEQ.88 was used to add back CO_2 until the solution was saturated with respect to calcite. Thus the information reported here reflects that of formation waters saturated with calcite at formation temperature.

SOLMINEQ.88 reports the saturation of the water sample with respect to a large suite of minerals in terms of the Gibbs free energy difference ($\Delta G_{\text{diff}} = RT \ln (Q/K)$) between the actual and equilibrium states of the mineral. A positive value of ΔG_{diff} indicates that the mineral should precipitate from the water; a negative value of ΔG_{diff} indicates that the mineral should dissolve in the water; $\Delta G_{\text{diff}} = 0.0$ indicates that the mineral is in equilibrium with the water. The calculation is strictly an equilibrium calculation. If the water is supersaturated with respect to the mineral, the mineral may not precipitate because of kinetic considerations. However, the greater the supersaturation, the more likely it is to precipitate. In order to provide an indication of the degree to which any specific mineral is saturated in the formation waters under consideration, the classification of ΔG_{diff} shown in Fig. 2 will be used throughout this paper, rather than reporting the actual ΔG_{diff} values. This is purely a convenience for the purposes of this paper.

FLUORINE GEOCHEMISTRY

Content and distribution

The 469 analyses in the data base were assigned to their respective basin-scale hydrostratigraphic unit, as defined by Bachu (1995) and shown in Fig. 3. Table 1 shows the minimum, mean, median and maximum content of F in formation water in each of these hydrostratigraphic units, as well as comparable information for the Alberta Basin. Although the number of samples in any of the basin-scale hydrostratigraphic units varies widely, and therefore may not be entirely representative of that unit, at the scale of the mega-stratigraphic successions recognized by Bachu (1995) the distribution is fairly uniform across the Alberta Basin (Fig. 4). Therefore, at least at the scale of the major flow units, the data in Table 1 can be considered representative.

Fluorine was detected in all the samples analyzed for it. Contents range from the detection limit (0.01 mg/l) to 22 mg/l. Although the minimum contents in the basin-scale hydrostratigraphic units vary widely, maximum contents are generally >5 mg/l. As a general observation, there is a trend toward

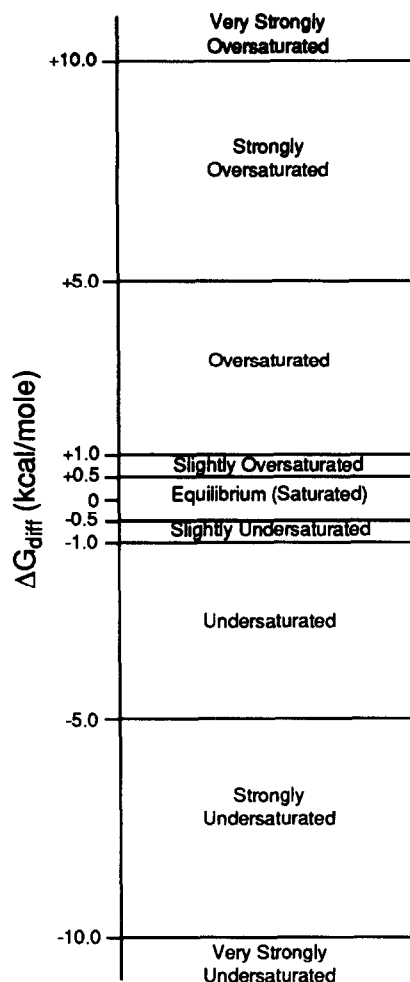


Fig. 2. Scheme for classification of ΔG_{diff} values determined by SOLMINEQ.88 in terms of mineral saturations.

increased mean and median contents with depth (age of the unit) and hence formation temperature. The mean content of F in formation waters in the Alberta Basin is 1.83 mg/l.

Saturation with respect to fluorite

The saturation with respect to fluorite was calculated for each of the analyses based on solutions saturated with respect to calcite at formation temperature. Within each basin-scale hydrostratigraphic unit the ΔG_{diff} values were classified using the scheme shown in Fig. 2, and the percentage of values falling within each class is reported in Table 1. The most important observation is the gradual trend from mainly undersaturation with respect to fluorite in the shallower, cooler, less saline formation waters with lower contents of Ca, to saturation and oversaturation in the deeper, hotter, more saline, Ca-rich formation waters. This is well illustrated by a scatter plot of Ca content against ΔG_{diff} for fluorite (Fig. 5). The greatest undersaturation (maximum negative

Stratigraphic nomenclature						Hydrostratigraphy	
Period		Group		Formation			
Tertiary				Paskapoo		Scollard - Paskapoo aquifer	
Cretaceous		Upper		Edmonton	Scollard		Battle aquitard
					Battle		
					Whitemud		
					Horseshoe Canyon		
					Bearpaw		Bearpaw aquitard
					Belly River		Belly River aquifer system
					Lea Park		Lea Park aquitard
				Milk River	Milk River aquifer		
		Lower		Colorado	Cardium		Colorado aquitard system
					Second White Speckled Sandstone		
					Viking		
				Mannville		Clearwater	Upper Mannville aquifer
					Clearwater aquitard		
				Lower Mannville aquifer			
				Jurassic aquitard			
Jurassic		U			Mississippian - Jurassic aquifer system		
		M					
		L					
Triassic							
Permian							
Pennsylvanian							
Mississippian				Stoddart		Exshaw - Banff aquitard	
				Rundle			
				Banff			
				Exshaw			
Devonian		Upper		Wabamun		Upper Devonian aquifer system	
				Winterburn			
				Woodbend	Ireton		
		Middle		Leduc	Cooking Lake	Middle - Upper Devonian aquifer system	
				Beaverhill Lake		Prairie aquiclude - aquitard system	
				Elk Point	Upper	Prairie	
	Winnipegosis						
Lower		Elk Point	Lower			Elk Point aquiclude system	
				Not deposited			
Silurian						Cambrian aquitard system	
Ordovician							
Cambrian		U			Basal aquifer		
		M	Basal Sandstone				
		L	Not deposited				
Pre - cambrian						aquiclude	

Fig. 3. Basin-scale stratigraphic and hydrostratigraphic nomenclature, Alberta Basin (modified from Bachu, 1995).

ΔG_{diff} value) is -3.6 , though the majority of formation waters that are undersaturated with respect to fluorite have ΔG_{diff} values in the range -1.0 to -2.5 (although two ΔG_{diff} values in fact exceed -3.6 , there is the possibility that the F values are in error). The ΔG_{diff} is never $>+2.0$, even for samples with $F > 10 \text{ mg/l}$.

Fluorine complexes

It is quite clear from the information just presented on saturation with respect to fluorite that factors in addition to fluorite saturation control the content of F in formation waters. The degree to which F complexes are important is illustrated by the data in Table

Table 1. Summary of F (mg/l) and ΔG_{diff} values for fluorite in formation waters, Alberta Basin, Canada, by basin-scale hydrostratigraphic units; see Fig. 3 for stratigraphic nomenclature

Hydrostratigraphic unit	No.	F (mg/l)				ΔG_{diff} Fluorite* (% by class)				
		Min.	Mean	Median	Max.	USat	SIUSat	Sat	SIOSat	OSat
post-Colorado aquifer-aquitard system	26	0.42	2.16	1.21	19.1	79	8	13	—	—
Colorado aquitard system	124	0.01	1.22	0.80	12.6	75	15	8	—	2
U. Mannville aquifer	55	0.13	1.29	0.80	8.0	42	23	31	4	—
Clearwater aquitard	—	—	—	—	—	—	—	—	—	—
L. Mannville aquifer	81	0.30	1.39	1.15	16.5	53	29	16	1	1
Jurassic aquitard	—	—	—	—	—	—	—	—	—	—
Mississippian-Jurassic aquifer system	86	0.13	2.14	1.80	11.7	21	21	51	4	3
Exshaw-Banff aquitard	—	—	—	—	—	—	—	—	—	—
U. Devonian aquifer system	47	0.58	2.07	1.30	7.0	10	37	47	3	3
Ireton aquitard	—	—	—	—	—	—	—	—	—	—
Middle-upper Devonian aquifer system	26	0.32	3.94	3.90	8.8	11	—	50	17	22
Prairie aquiclude-aquitard system	7	1.19	2.21	2.30	3.6	—	20	80	—	—
Winnipegosis aquifer	11	0.46	2.90	3.00	5.5	—	—	14	57	29
Elk Point aquiclude system	—	—	—	—	—	—	—	—	—	—
Cambrian aquitard system	1	—	2.80	—	—	—	—	—	100	—
Basal aquifer	5	1.70	6.80	3.30	22.0	—	—	—	25	75
ALBERTA BASIN	469	0.01	1.83	1.20	22.0	47	19	26	4	4

*USat = undersaturated (ΔG_{diff} -1.0 to -5.0); SIUSat = slightly undersaturated (ΔG_{diff} -0.5 to -1.0); Sat = saturated (ΔG_{diff} +0.5 to -0.5); SIOSat = slightly oversaturated (ΔG_{diff} +0.5 to +1.0); OSat = oversaturated (ΔG_{diff} +1.0 to +5.0).

2. The samples were classified by Ca content, and the percentage of F present as F^- calculated for each sample using output from SOLMINEQ.88. The columns in Table 2 sum to 100; thus, for example, 95% of formation waters with <100 mg/l Ca have >90% of the F present as F^- . The bold numbers outline the trend of decreasing percentage of F present as F^- with increasing content of Ca; or in other words, increased Ca (and salinity) result in the presence of a higher percentage of F complexes.

The computer code SOLMINEQ.88 calculates the amount present as F^- , six Al-F complexes, HF^0 , MgF^+ , NaF^0 , ten complexes which include U and F, VO_2F^0 , VO_2F_2^- , VOF^+ , VOF_2^- , FeF_2^{2+} and SiF_6^{2-} , depending, of course, on the presence of pertinent input data. Kharaka *et al.* (1988, Table 1A, pp. 122–124) provide molecular weights for these complexes, from which the amount of F held by each complex can be calculated. It should be pointed out that calculations by SOLMINEQ.88, and by many geochemical computer codes, assume equilibrium, which is not necessarily the case. Organic solutes were not determined in any of the samples studied and their effect, if any, on the complexing of F is not taken into account. Nevertheless, the information provided by the SOLMINEQ.88 calculations is the best available at this time.

Salinity, Ca content, formation temperature, and possibly other factors, all affect the way in which F occurs in formation waters. The five detailed analyses in Table 3 illustrate the decrease in the amount of F present as F^- , concomitant with the increase in the

importance of the MgF^+ complex, as salinity, Ca content, and to some extent formation temperature increase. Note that V was below detection in all but the first sample (RCAH25-874A), so V-F complexes are only reported for this sample. The Appendix provides information on the content of V in formation waters in the Alberta Basin, organized by the same basin-scale hydrostratigraphic units as Table 1. The generally low content of V (below detection in 59% of the samples) means that V-F complexes will seldom be important hosts for F in formation waters.

The determination of Al in formation water is notoriously difficult and the results subject to uncertainty as to their reliability. This difficulty can be overcome by correcting the analysis, using a computer code such as SOLMINEQ.88, based on the assumption of equilibrium of the formation water at formation temperature with the minerals present in the rock. Some of the limitations of this approach are outlined by Bachu *et al.* (1989, pp. 11–12). The information in Table 4 illustrates the effect of such an adjustment on F complexes. Full details of the analysis appear in Hitchon (1993, Table 19), but pertinent information for the purposes of this study are as follows: salinity, 196,208 mg/l; Na, 60,400 mg/l; Ca, 14,800 mg/l; Mg, 960 mg/l; F, 5.5 mg/l; Fe, 1.1 mg/l; V, 1.3 mg/l; SiO_2 (anal.), 12 mg/l; SiO_2 (calc.), 10.8 mg/l; Al (anal.), <2 mg/l; Al (calc.), 0.027 mg/l. First, data on the unadjusted analysis at room temperature are clearly spurious. Second, the distribution of the major F complexes is not significantly different between the analysis adjusted only for cal-

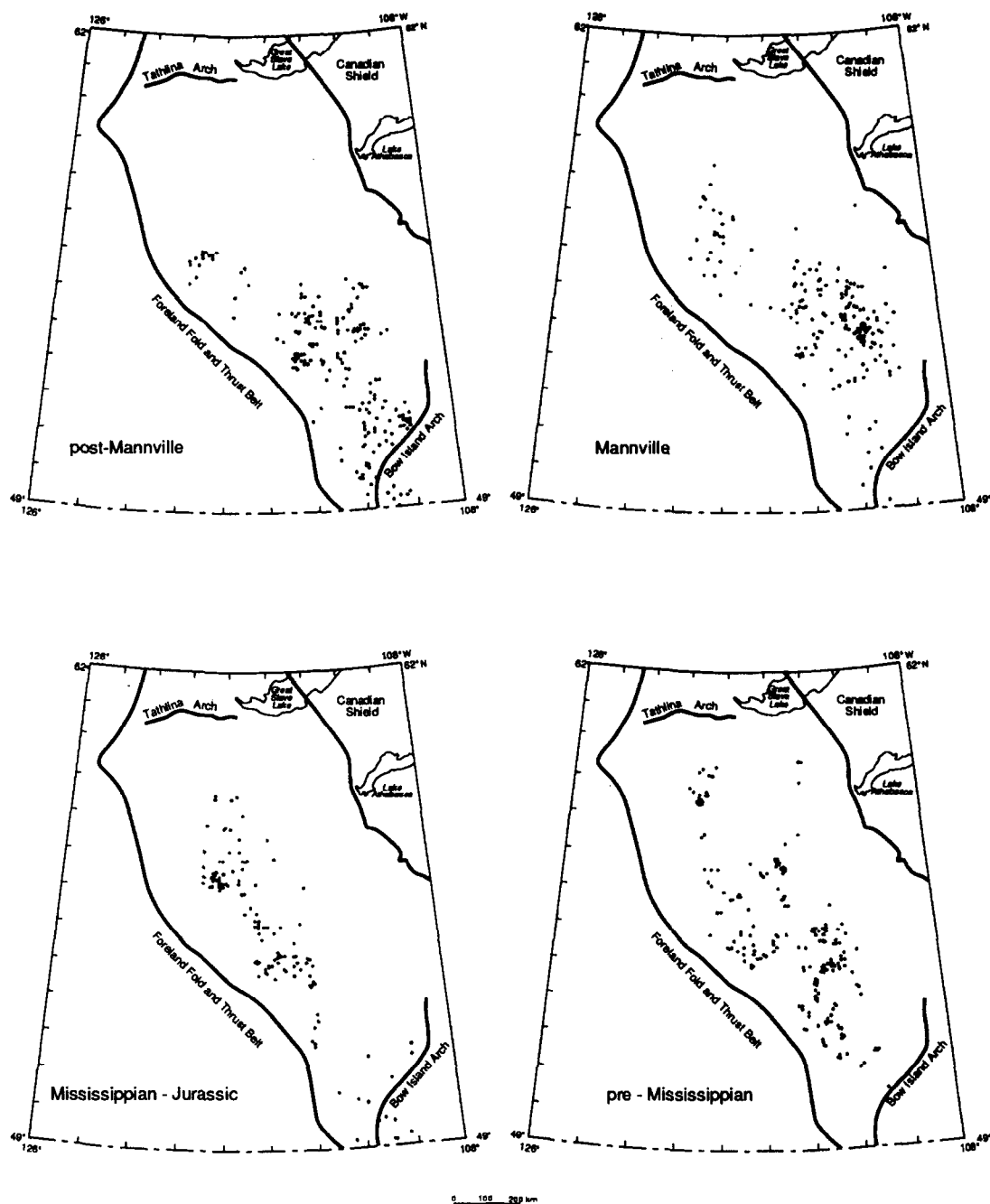


Fig. 4. Distribution of formation waters in the data base classified by the major hydrostratigraphic successions identified by Bachu (1995).

cite saturation at formation temperature (similar to all analyses used in this study) and that adjusted for calcite, quartz and illite saturation at formation temperature. Interestingly, the only significant V-F complex is VO_2F , which accommodates 7.59% of the total F in both the unadjusted and adjusted cases. Complexes of Al and F accommodate 0.59% of the total F, with AlF_2^+ being the dominant complex. As the adjusted pH decreases with the addition of CO_2 to achieve equilibrium with calcite (0.3219×10^{-2}

mol/kg water added in the case of the data reported in Table 4), small amounts of F occur as HF^0 .

DISCUSSION

The 469 unpublished analyses used in this study were each examined using SOLMINEQ.88. Such detailed evaluation is not practical for the >141,000 formation water analyses from the entire Western

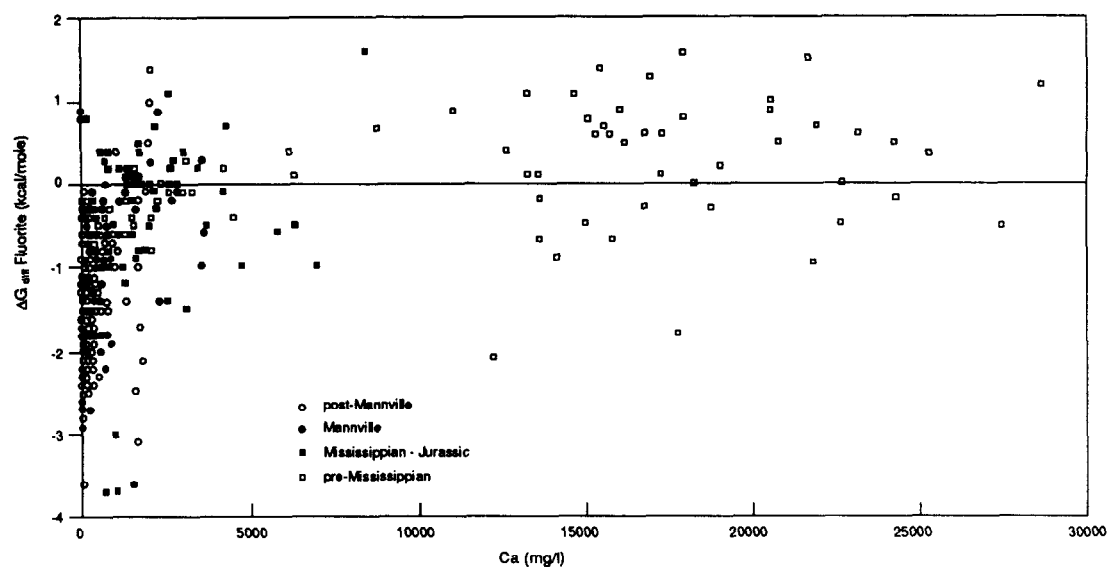


Fig. 5. Scatterplot of Ca (mg/l) against ΔG_{diff} fluorite, with the formation waters classified by major hydrogeological units. Many data points with Ca < 1000 mg/l represent several individual analyses which could not be plotted separately.

Table 2. Summary of percent F^- to total F in formation waters, Alberta Basin, Canada, in relation to Ca content (see text for details)

Percent F^- of total F	Ca (mg/l)							
	<100	100–199	200–299	300–399	400–499	500–999	1000–4999	>5000
>90	95	80	39	25		3	3	
80–89	5	20	48	50	75	26	1	
70–79			10	25	25	60	26	
60–69			3			11	23	
50–59							33	3
40–49							8	3
30–39							5	8
20–29							1	30
10–19								40
<10								16

Canada Sedimentary Basin presently held in the Alberta Geological Survey Well Data Base; apart from this only relatively few report F. Using the culling criteria of Hitchon and Brulotte (1994), the culled data were searched for analyses reporting F. The frequency percent histogram for the Western Canada Sedimentary Basin (not shown) is similar to that for the Alberta Basin (Fig. 6). Because F was found as a minor constituent in all formation waters analyzed in this study, it is likely ubiquitous at these levels in all formation waters in the Western Canada Sedimentary Basin.

Based on the information presented in this paper it is clear that the content of F in formation waters is controlled by a complex relation among saturation with respect to fluorite and the content of other components which can combine with F to form complexes—and both formation temperature and ionic strength are part of this control scenario. For analyses which are undersaturated with respect to

fluorite, the dissolution/precipitation option in SOLMINEQ.88 can be used to calculate the amount of F to be added to reach saturation. For the two samples (RCAH25-874A and RCAH20-974) from the Milk River aquifer in Table 3, the amounts to be added are 3.3 and 3.57 mg/l F, respectively. In the former example the amount of F present as F^- increases by 0.2%, with a corresponding decrease in the amount held as VO_2F^0 . The distribution of F was unchanged in sample RCAH20-974. For the formation water from the Basal aquifer with 22 mg/l F (see Table 1) and $\Delta G_{\text{diff}} = 3.21$, saturation with respect to fluorite occurs at a F content of only 2.16 mg/l. The distribution of F is generally similar, i.e. the majority (~66%) occurs as MgF^+ . One cannot help but wonder if the reporting analyst missed a decimal place, i.e. 2.2 reported as 22; unfortunately the analysis cannot be repeated; this sample is not shown in Fig. 5. These observations lead to the suggestion that if F is reported in a few analyses in an aquifer and

Table 3. Chemical composition (mg/l), physical properties and production data for selected formation waters, Alberta Basin, Canada

Sample number	RCAH25-874A	RCAH20-974	RCAH33-576	RCAH37-1075B	RCAH103-475A
Stratigraphic unit	U. Cretaceous Milk River Fm.	U. Cretaceous Milk River Fm.	Triassic Halfway Fm.	Triassic Charlie Lake Fm.	M. Devonian Slave Point Fm.
Location	6-27-5-3-W4	10-7-13-15-W4	C-100-1-94-H-3	7-2-80-5-W6	10-33-86-15-W5
Depth (m)	586.7–606.6	240.8–259.1	1239.0–1266.7	1121.1–1128.7	1623.1–1642.9
Formation temp. (°C)	19	11	51	40	46
Source	DST 1 320 m mc fw GTS 240 m ³ /d	DST 1 109.7 m mc fw GTS 240 m ³ /d	DST 2 132.6 m sw	DST 1 990.6 m sw 54.9 m gc wc mud	DST 1 514.2 m sw 171.6 m wcush
Li	0.3	0.5	46	43	26
Na	1090	2500	31600	51200	47000
K	9	14	665	1040	545
Mg	3	8	225	779	2490
Ca	12	19	859	2900	13380
Sr	0.25	1.1	205	100	300
Ba	0.09	1.2	0.8	0.56	1.2
Cu	0.03	0.01	*	*	*
Zn	*	*	*	3.1	*
Pb	0.05	0.03	0.9	4.1	15
Fe	0.03	*	*	*	*
Mn	0.005	*	*	0.63	3.4
As	0.2	0.3	*	11	*
B	3.1	2.5	20	24	24
PO ₄	8.5	*	*	*	43
NH ₃	—	—	151	211	51.7
SiO ₂	12	8.8	4.7	5.4	16
F ₂	3.02	1.46	3.56	1.8	2.15
Cl	1050	3000	53000	90000	100900
Br	11	37	105	165	334
I	11	26	19	16	12
SO ₄	301	48	457	1750	1264
HCO ₃	395	436	1171	229	89
CO ₃	250	232	*	*	*
Total solids (calc.)	3152.40	6284.90	88503.35	148423.22	166263.73
Imbalance (%)	−2.6	+4.8	−2.0	−2.1	+1.1
pH (laboratory)	8.80	8.60	7.60	7.05	6.82
pH (calc., formation temp.)	7.79	7.76	5.91	6.28	6.13
Density (15.56°C)	1.0066	1.0067	1.0631	1.1075	1.1223
Refractive index (25°C)	1.3337	1.3341	1.3480	1.3578	1.3626
F distribution (% total F)					
F [−]	99.0	98.8	72.3	51.7	23.0
HF ⁰	<0.1	<0.1	0.1	<0.1	<0.1
MgF ⁺	0.3	0.6	21.9	43.4	74.8
NaF ⁰	0.4	0.6	5.7	4.9	2.2
VO ₂ F ⁰	0.3	—	—	—	—
ΔG _{diff} fluorite	−0.9	−1.4	0.3	0.0	0.1

fw = fresh water; gc = gas-cut; mc = mud-cut; sw = salt water; wc = water-cut; wcush = water cushion.

Additional determinations: RCAH 25-874A (Co 0.01, Cr 0.02, Mo 0.13, Ti 0.007, V 0.03); RCAH 20-974 (Mo 0.08); RCAH 103-475A (Co 2.2, Cr 3.0).

— = not determined.

* = below detection.

the formation water is generally close to saturation with respect to fluorite, then a reliable estimate can be made of the F content of formation waters without F determined simply by calculating the F needed to achieve fluorite saturation at formation temperature. Only major ions (Na, K, Ca, Mg, Cl, SO₄, HCO₃) would be needed to give a fairly reliable estimate. And using the example above from the Basal aquifer, calculation of saturation with respect to fluorite can be used to check on the general "correctness" of a F determination when it is known that formation

waters of that particular general composition show saturation with respect to fluorite in that aquifer.

The content of F in seawater varies, but based on a salinity of 35,000 mg/l Turekian (1969) selected a representative value of 1.3 mg/l. For formation waters with salinity several times that of seawater, contents of F similar to those found in the Alberta Basin (Fig. 6) could have originated from the initial seawater. However, water-rock reactions cannot be ruled out. Formation waters with salinity less than seawater and F contents >~1.3 mg/l suggest water-

Table 4. Example of distribution of F complexes in formation water adjusted for calcite, quartz and illite saturation at formation temperature (73°C)

F complex	Percent of total F (5.5 mg/l)		
	Unadjusted (25°C)	Calcite saturation (73°C)	Calcite, quartz, illite saturation (73°C)
F ⁻	49.72	24.56	24.40
AlF ²⁺	—	—	0.03
AlF ₂ ⁺	—	—	0.37
AlF ₃ ⁰	—	—	0.18
AlF ₄ ⁻	—	—	0.01
HF ⁰	<0.01	0.11	0.11
MgF ⁺	38.69	63.37	62.97
NaF ⁰	4.00	4.37	4.34
AlF ₅ ²⁻	—	—	<0.01
AlF ₆ ³⁻	—	—	<0.01
VO ₂ F ⁰	7.59	7.59	7.59
VO ₂ F ₂ ⁻	<0.01	<0.01	<0.01
VOF ⁺	*	*	*
VOF ₂	*	*	*
FeF ₂ ⁺	*	*	*
SiF ₆ ²⁻	<0.01	<0.01	<0.01
Total	100.00	100.00	100.00
pH	6.94	5.50	5.50
ΔG _{diff} fluorite	2.62	1.33	1.33

— = not determined (Al not included in input data).

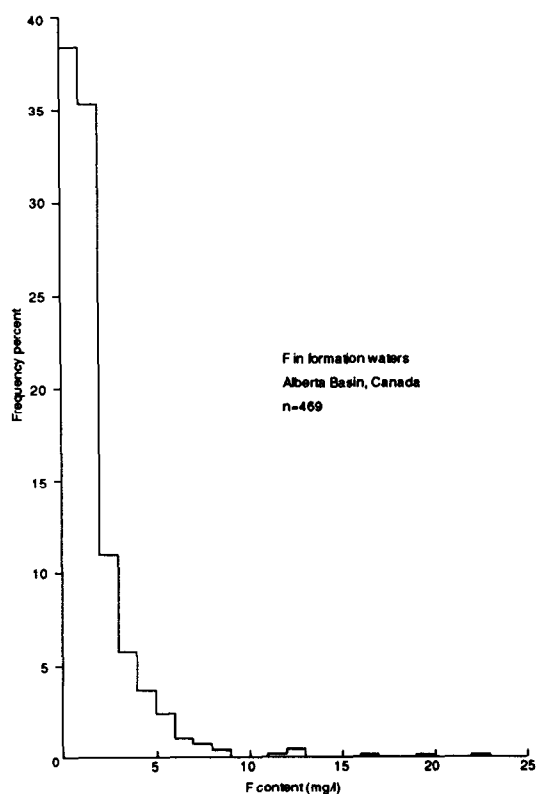
* = not reported by SOLMINEQ.88 (value <10⁻³⁵).

Fig. 6. Frequency percent distribution of F in formation waters from the Alberta Basin.

rock reactions with adjacent shales (as a general observation, the F content of sedimentary rocks is shales > carbonates = arenites). But of the data reported by Koritnig (1971), the rocks which have some of the highest F contents and which are also common in some of the uppermost Cretaceous and Tertiary sections of the Alberta Basin are volcanic ash and bentonite. The degree to which bentonite or bentonitic shales may have contributed to some of the very high F contents of formation waters in the post-Colorado aquifer-aquitard system remains speculative.

Fluorite is seldom reported in the sedimentary rocks of the Alberta Basin, in part because it is seldom sought. Based on the saturation data in Table 1, the most likely aquifers in which to find fluorite would be the Winnipegosis and Basal aquifers, where the majority of the formation waters show over-saturation with respect to fluorite. Other aquifers cannot be ruled out however; indeed, fluorite has been reported from the Triassic Baldonnel Formation in the subsurface of British Columbia (Reed, 1959). The Winnipegosis aquifer in northwestern Alberta contains fluorite which has been the subject of a fluid inclusion study (Aulstead and Spencer, 1985). In correlative strata at the Zn-Pb ore occurrence at Pine Point in the adjacent Northwest Territories, fluorite is present but is "extremely rare" (Jackson and Beales, 1967). As far as the author can determine, fluorite has not been reported from Cretaceous sedimentary rocks in the Alberta Basin. These findings are consistent with the fluorite satura-

tion data for formation waters in the Alberta Basin and suggest that fluorite may be of more widespread occurrence in pre-Prairie aquifers than so far indicated from the literature.

CONCLUSIONS

Fluorine was determined in 469 formation waters from the Alberta Basin. Contents range up to 22 mg/l, with a mean of 1.83 mg/l and a median value of 1.20 mg/l. The less saline formation waters from shallower, cooler aquifers are dominantly undersaturated with respect to fluorite, and there is a gradual change to saturation with increasing salinity and formation temperature. This trend is accompanied by a change from F present as F^- to F occurring mainly as MgF^+ . Complexes of Al and F, and VO and F account for only a minor proportion of F held in complexes. Although the source of the F is not generally known, it is speculated that some of the very high contents in the formation waters from non-marine parts of the Upper Cretaceous post-Colorado aquifer could originate from local bentonite and bentonitic shales. Reports of fluorite in the sedimentary rocks of the Alberta Basin are generally consistent with the saturation trends for fluorite in the formation waters.

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John Hem died 27 December 1994, and this paper was probably one of the last he reviewed. He was a long-time friend of the author and this paper is dedicated to his memory.

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APPENDIX

Vanadium was determined by ICP methods in 554 formation water samples from the Alberta Basin, of which 469 also were analyzed for F (see main paper). Vanadium was below detection (0.01 mg/l) in 59% of the samples, and ranged up to 3.5 mg/l in the remainder. Statistics of the minimum, mean, median and maximum content of V for those samples in which it was above detection are given in Table A1 by basin-wide hydrostratigraphic units for direct comparison with the F data in Table 1. Increased temperature and salinity are accompanied by increased mean, median and maximum contents of V. For samples reporting V, the mean for the basin is 0.51 mg/l. Using a best-case scenario, with 325 samples having 0.01 mg/l (detection limit), the mean for the Alberta Basin is <0.22 mg/l ($325 \times 0.01 + 229 \times 0.51$ divided by 554).

Table A1. Summary of V (mg/l) in formation waters, Alberta Basin, Canada, by basin-scale hydrostratigraphic units

Hydrostratigraphic unit	No.	Below detection	V (mg/l)			
			Min.	Mean	Median	Max.
post-Colorado aquifer-aquitard system	33	24 (73%)	0.01	0.03	0.01	0.10
Colorado aquitard system	131	88 (67%)	0.01	0.16	0.14	0.50
U. Mannville aquifer	61	32 (52%)	0.04	0.25	0.20	0.68
Clearwater aquitard	—					
L. Mannville aquifer	88	53 (60%)	0.02	0.20	0.17	0.62
Jurassic aquitard	—					
Mississippian-Jurassic aquifer system	103	75 (73%)	0.05	0.40	0.21	1.6
Exshaw-Banff aquitard	—					
U. Devonian aquifer system	59	26 (44%)	0.10	0.64	0.35	2.9
Ireton aquitard	—					
Middle-upper Devonian aquifer system	48	19 (40%)	0.13	1.04	0.90	2.7
Prairie aquiclude-aquitard system	10	1 (10%)	0.50	1.27	0.96	3.5
Winnipegosis aquifer	13	4 (31%)	0.57	1.26	1.20	2.0
Elk Point aquiclude system	—					
Cambrian aquitard system	1	1 (100%)				
Basal aquifer	7	2 (29%)	1.1	1.94	1.60	3.0
ALBERTA BASIN	554	325 (59%)	0.01	0.51	0.23	3.5