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REGIONAL AND ISOTOPIC HYDROGEOCHEMISTRY: DEEP-BASIN BRINE AQUIFER PALO DURO BASIN, TEXAS PANHANDLE

by

R. Stephen Fisher

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Bureau of Economic Geology
W.L. Fisher, Director
The University of Texas at Austin
University Station, P.O. Box X
Austin, Texas 78713

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In the second half of 1983 and the first quarter of 1984, brines from the sub-salt, deep-basin aquifer were collected at the DOE-SWEC #1 J. Friemel well site, Deaf Smith County, Texas. Seven zones were sampled, bringing the total number of samples from permeable units below the Evaporite Aquitard in the Palo Duro Basin to seventeen. The locations of all DOE wells from which deep-basin brines have been collected are shown in figure 1. The zones sampled are identified in Table 1, and the results of analyses for major and minor aqueous species and stable isotopes are presented in Table 2.

This report presents the data for samples collected from the #1 J. Friemel well, and a preliminary comparison of compositions of brines from the J. Friemel well with brines collected from the other DOE test wells. Results of a detailed study integrating all available hydrologic and geochemical data from the Palo Duro Basin will be the subject of a later report.

Chemical Composition of J. Friemel Fluids

Samples from the J. Friemel well are Na-Cl type brines, with chlorinities ranging from about 130 to 178 g/l, and salinities ranging from about 215 to 290 g/l (Table 2). Field measurements of pH yield values from 4.2 to 6.4, with a mean of 5.7 (Table 2). The major cation composition of the brines is summarized in figure 2; Na is the dominant cation; Ca and Mg are present in minor but important amounts. Cl comprises more than 99% of the anionic species of each zone sampled.

Palo Duro Basin brines are generally considered to have derived high salinities and chlorinities by halite dissolution (Bassett and Bentley, 1983). The Cl:Br ratios of J. Friemel brines range from 581 to 1,053 (mg/l ratio). Cl:Br ratios of brines that have acquired all chlorinity by dissolving primary halite are about 10,000 (Holser, 1979), whereas Cl:Br ratios of deep-basin brines from the #1 Sawyer and #1 Zeeck wells are about 200 (BEG, 1983). The ratios observed at the J. Friemel well suggest that these fluids have acquired chlorinity by halite dissolution and have then mixed with deep-basin fluids such as those present at the Sawyer and Zeeck sites. The Na:Cl ratio of a brine which derived all its Na and Cl from halite is 0.65 (mg/l ratio). Measured Na:Cl ratios from brines at the J. Friemel site are generally less than 0.56, indicating that Na has been removed from solution since halite dissolution.

Oxygen and Hydrogen Isotopic Composition of J. Friemel Fluids

Samples from all zones of the J. Friemel well are isotopically depleted in both ^{18}O and ^{2}H relative to standard mean ocean water (SMOW) (Table 2, figure 3). The depleted isotopic compositions indicate that although the J. Friemel well site (northeast Deaf Smith County, figure 1) is not in a known major recharge area, a significant fraction of the fluid now present at depths as great as 8,100 ft and temperatures as high as 55°C is isotopically similar to local meteoric water. The deep-basin brine apparently has not been present under formation conditions long enough for oxygen isotopic equilibration.

Dissolved Gases in J. Friemel Fluids

Results of dissolved gas analyses are shown in Table 3. Nitrogen and methane are the principal components of the gas; however, small but significant amounts of free hydrogen are present in most samples. This information has been interpreted previously as indicating highly reducing in situ conditions at or near the water-hydrogen stability boundary (BEG, 1983).

REGIONAL AND ISOTOPIC GEOCHEMISTRY OF THE DEEP-BASIN BRINE AQUIFER

Oxygen and Hydrogen Isotopic Compositions

Figure 4 shows the oxygen isotopic composition of brines plotted versus depth and temperature. The regional geothermal gradient (15.4^{o}C/km) was established from the linear regression equation relating sample depth and temperature; mean annual surface temperature was assumed to be 17^{o}C.

The state of oxygen isotopic equilibrium between water and host rock was determined as follows. Dolomite was assumed to be the primary isotopic buffer in the system, because of its abundance relative to the other minerals present. The oxygen isotopic composition of dolomite was taken to be -3 +/- 1 o/oo PDB (about +28 o/oo SMOW). The fractionation factor for dolomite-water is 3 o/oo greater than that for calcite-water (Land, 1983) and the calcite-water fractionation factor thus modified from Friedman and O'Neil (1977) was used to calculate the equilibrium oxygen isotopic composition of formation water as a function of temperature and burial depth. Figure 4 shows that only samples from the Zeeck and Sawyer wells approach oxygen isotopic equilibrium with dolomite host rock at sample depth and temperature.

Given the suggested age of the fluids (Ziakowski, Kosanke and Hubbard, in press), the long residence times within the basin (Bassett and Bentley, 1983;

Wirojanagud and others, in press), and the general state of chemical equilibrium of brines with respect to carbonate minerals (Bassett and Bentley, 1983), the lack of oxygen isotopic equilibrium is unexpected.

The kinetics of isotopic exchange do not appear to be an important factor controlling isotopic equilibration. Exchange kinetics are primarily dependent on temperature (Hoefs, 1980). The range of Palo Duro deep-basin brine temperatures (32^{o} to 55^{o}C, Table 2) is not large enough to result in significantly different exchange rates between warmer and cooler samples. More importantly, several of the brines at lower formation temperatures (#1 Zeeck, zones 2 and 3, Table 2, and figure 4) are in or near isotopic equilibrium with dolomite, whereas some samples at higher temperatures (J. Friemel zones 1 and 2) are not. It may be that oxygen isotopic exchange between the oxygen of water and that of carbonate minerals occurs via dissolved carbonate molecules, and that exchange rates are hindered by low dissolved carbonate concentrations in the deep-basin brines. However, the data do not support this view. Brine samples with depleted oxygen isotopic compositions include fluids with relatively high dissolved carbonate concentrations at higher temperatures (e.g., #1 Mansfield zones 1 and 2, Table 2), and brines with enriched oxygen isotopic compositions include samples with low carbonate concentrations at lower temperatures (e.g., #1 Zeeck, zone 3, Table 2).

A more likely explanation for the lack of isotopic equilibration is that the deep-basin brines contain a significant component of relatively young, isotopically depleted fluid. Flow times through the basin may be as long as suggested by Bassett and Bentley (1983) and Wirojanagud and others (in press), but the age of the fluid calculated from flow times and position in the basin is a misleading number if the fluid is a mixture of basinal brine that has moved along a regional flow path, and younger water recharged from a different source. The volume percent of isotopically nonequilibrated fluid can be estimated from the oxygen isotopic mass balance. For the case of J. Friemel zone 6, Pennsylvanian Carbonate, the oxygen isotopic composition measured is about -3 o/oo (SMOW). The composition predicted for dolomite equilibrium at formation temperature is about 0 o/oo. Assuming that the depleted fluid had an oxygen isotopic composition similar to that of modern meteoric water in the area (about -5 o/oo) and that the basinal fluid had reached isotopic equilibrium with dolomite, the zone 6 J. Friemel brine consists of approximately 50% depleted, unequilibrated water. If some isotopic enrichment of the younger water occurred prior to mixing with deep basinal fluids, the estimated contribution of young fluid to the deep-basin brine aquifer would be proportionately greater. In either case, the isotopic composition of deep-basin fluids records a significant contribution of younger water that has not equilibrated with the host rock.

Date plotted in figure 5 support this interpretation. Deep-basin brine samples with low Cl:Br ratios generally have enriched oxygen isotopic compositions. Brines that have depleted isotopic compositions generally have higher Cl:Br ratios. The higher ratios resulted from mixing of deep-basinal brine (low Cl:Br ratio) and fluid which has dissolved halite earlier along its flow path (high Cl:Br ratio).

Chemical Compositions

Figure 6 presents the Na + K, Ca, and Mg compositions of all deep-basin brines on a trilinear diagram grouped by the lithology of the aquifer. Two linear arrays are apparent: one group is composed of all samples from Wolfcamp zones and the second is composed of all non-Wolfcamp samples (brines from both Pennsylvanian carbonates and Pennsylvanian-Permian Granite Wash; see also Bassett and Bentley, 1983). Both lines have in common a sodium-rich end-member, but have different Ca:Mg ratios. The Ca:Mg activity ratio of brines from Wolfcamp zones is in reasonable agreement with values controlled by calcite-dolomite equilibrium (Land, 1983), whereas the higher ratios of brines from non-Wolfcamp zones indicate that other processes must be in effect.

If the predominance of Na in these brines were due solely to the amount of halite dissolved, samples falling nearest the Na vertex should also have the highest chlorinities and salinities. However, samples with the highest chlorinities (more than 150 g/l, Zeeck zone 1, J. Friemel zones 4, 5 and 6) plot in the center of the array (figure 6). It is clear that Na is being selectively removed from brines more effectively in some zones than in others. The processes controlling the major ion ratios in these samples is the subject of continuing work.

CONCLUSIONS

To date there have been four tests wells drilled, sampling 17 permeable zones beneath the candidate host rock in a basin of approximatey 12,500 square miles. Investigations of the geochemical environment and hydrologic history of deep-basin brines are based on the compositions of these fluids.

The #1 Mansfield well is actually not within the Palo Duro Basin (figure 1) and brines sampled at the #1 Mansfield well are not normal deep-basinal fluids (BEG, 1983). Data from samples at the Sawyer, Zeeck, and J. Friemel wells indicate a significant mixing of fluids in the sub-salt aquifer. One fluid is a normal deep-basinal brine. The other is younger, isotopically similar to local meteoric water, and has had significant contact with halite. This younger fluid has probably entered the deep aquifer system via cross-formational flow from overlying units (BEG, 1983).

The Palo Duro Basin is not a simple hydrogeochemical system. It is unlikely that the processes controlling the isotopic and major chemical compositions of brines beneath the candidate host rock can be unequivocally identified without additional wells and sampling intervals.

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FIGURE CAPTIONS

Figure 1. Location map of study area showing well locations and major structural elements of the Palo Duro Basin. Well designations are Z = #1 Zeeck; S = #1 Sawyer; M = #1 Mansfield; F = #1 J. Friemel.

Figure 2. Plot of cationic composition for samples from the #1 J. Friemel well. See Table 1 for zone identifications.

Figure 3. Plot of oxygen and hydrogen isotopic composition of samples from J. Friemel well in relation to Meteoric Water Line.

Figure 4. Plot of oxygen and hydrogen isotopic composition of all deep-basin brine samples. Solid line indicates composition of water in equilibrium with dolomite at burial temperature. Temperatures determined from the local geothermal gradient.

Figure 5. Plot of Cl:Br ratio versus oxygen isotopic composition.

Figure 6. Plot of cationic composition of all deep-basin brine samples. See Table 1 for zone identifications.

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Table 2. Summary of chemical and stable isotopic compositions of deep-basin brine samples.

Table 3. Dissolved gas compositions of J. Friemel brines (analyses by Glenn Thompson, University of Arizona).

WELL	ZONE	FORMATION	TEST INTERVAL (ft)	I.D.#
Sawyer #1	1	Ellenberger sandstone	4716-4727	S-1
			4732-4746	
Sawyer #1	2	Upper Ellenberger	4604-4620	S-2
			4632-4640	
Sawyer #1	3	Mississippian limestone	4500-4510	S-3
			4520-4535	
Sawyer #1	4	Pennsylvanian granite wash	4258-4270	S-4
			4280-4290	
			4300-4312	
			4325-4342	
Sawyer #1	5	Permian Wolfcamp	3172-3189	S-5
Mansfield #1	1	Permian Wolfcamp	4818-4890	M-1
Mansfield #1	2	Permian Wolfcamp	4638-4514	M-2
Zeeck #1	1	Pennsylvanian carbonate	7140-7152	Z-1
			7172-7230	
Zeeck #1	2	Permian Wolfcamp	5603-5640	Z-2
Zeeck #1	3	Permian Wolfcamp	5476-5550	Z-3
J. Friemel #1	1	Granite wash	8168-8204	F-1
J. Friemel #1	2	Granite wash	8122-8132	F-2
J. Friemel #1	3	Granite wash	8040-8050	F-3
J. Friemel #1	4	Granite wash	7895-7904	F-4
J. Friemel #1	5	Granite wash	7707-7711	F-5
J. Friemel #1	6	Pennsylvanian carbonate	7300-7326	F-6
J. Friemel #1	7	Permian Wolfcamp	5825-5926	F-7

Table 1. List of wells from which deep-basin brines were collected. I.D. numbers are used to identify wells and zones in data plots.

Table 2. Summary of chemical and stable isotopic compositions of deep-basin brine samples.

Well	Sawyer #1	Sawyer #1	Sawyer #1	Sawyer #1	Sawyer #1	Mansfield #1
Zone	Ellenburger Carbonate-Sand.	U. Ellenburger Carbonate	Mississippian Limestone	Pennsylvanian Granite Wash	Permian Wolfcamp	Permian Wolfcamp
Depth (ft)	4,716	4,604	4,500	4,228	3,172	4,818
T (°C)	39.0	39.0	39.0	39.0	35.0	38.0
pH	5.35	7.5	5.4	4.4	6.1	5.6
Ca	22,900.0	21,600.0	19,400.0	18,300.0	6,760.0	5,960.0
Mg	2,600.0	2,810.0	2,310.0	2,180.0	2,490.0	1,320.0
Na	60,200.0	64,000.0	61,000.0	63,400.0	43,450.0	78,400.0
K	459.0	420.0	337.0	332.0	118.0	369.0
Sr	660.0	710.0	574.0	563.0	113.0	99.5
HCO_3	560.0	40.2	106.0	26.0	144.0	131.0
SO_4	169.0	230.0	237.0	336.0	2,010.0	1,220.0
Cl	139,000.0	133,000.0	132,000.0	136,000.0	86,300.0	138,000.0
Cl/Br	296.0	271.0	227.0	237.0	261.0	1,290.0
$\delta^{18}O$	-1.73	-0.83	-0.61	-1.19	+0.72	-5.78
δD	-27.0	-13.0	-18.0	-15.0	-23.0	-43.0
$\delta^{34}S$			+12.86	+13.77	+10.37	+17.35
$\delta^{13}C$	+5.14	-2.25	+3.42	+0.12	+1.83	+2.63

Table 2. (continued)

Well Zone	Mansfield #1 Permian Wolfcamp	Zeeck #1 Pennsylvanian Carbonate	Zeeck #1 Permian Wolfcamp	Zeeck #1 Permian Wolfcamp	J. Friemel #1 Granite Wash	J. Friemel #1 Granite Wash
Depth (ft)	4,514	7,140	5,603	5,474	8,168	8,122
T(°C)	41.0	56.0	38.0	41.0	55.0	55.0
pH	4.8	5.8	6.9	6.25	5.9	5.9
Ca	6,020.0	11,950.0	6,780.0	6,240.0	15,700.0	15,400.0
Mg	1,600.0	1,550.0	1,290.0	1,820.0	2,110.0	2,130.0
Na	76,100.0	76,350.0	61,700.0	69,300.0	77,930.0	78,230.0
K	380.0	197.0	314.0	339.0	620.0	610.0
Sr	89.9	1,380.0	250.0	110.0	444.0	420.0
HCO_3	161.0	30.9	113.0	94.4	35.0	69.0
SO_4	1,320.0	81.1	977.0	1,650.0	440.0	487.0
Cl	131,000.0	151,500.0	105,000.0	120,000.0	148,500.0	148,100.0
Cl/Br	1,110.0	188.0	231.0	234.0	922.0	1,028.0
$\delta^{18}O$	-5.12	+0.73	+0.80	+2.17	-2.88	-3.53
δD	-42.0	-14.0	-23.0	-23.0	-28.0	-35.0
$\delta^{34}S$	+16.6	+12.58		+13.3	+9.76	+9.77
$\delta^{13}C$	+1.83	+3.31		+2.76		-6.82

Table 2. (continued)

Well Zone	J. Friemel #1 Granite Wash	J. Friemel #1 Granite Wash	J. Friemel #1 Granite Wash	J. Friemel #1 Pennsylvanian Carbonate	J. Friemel #1 Wolfcamp
Depth (ft)	8,040	7,895	7,707	7,300	5,825
T(°C)	55.0	55.0	53.0	52.0	38.0
pH	6.0	6.2	5.2	6.4	4.2
Ca	15,050.0	17,120.0	19,330.0	12,790.0	8,390.0
Mg	2,180.0	2,560.0	3,020.0	2,560.0	2,160.0
Na	77,300.0	77,670.0	87,580.0	78,460.0	72,470.0
K	636.0	578.0	551.0	530.0	589.0
Sr	410.0	451.0	571.0	363.0	150.0
HCO_3	71.0	21.0	43.0	73.0	205.0
SO_4	492.0	519.0	378.0	631.0	1,373.0
Cl	147,420.0	156,900.0	178,500.0	150,800.0	129,770.0
Cl/Br	1,053.0	581.0	649.0	973.0	881.6
$\delta^{18}O$	-3.46	-5.41		-2.7	-3.7
δD	-34.0	-26.0		-31.0	-36.0
$\delta^{34}S$	+9.86	+10.12			
$\delta^{13}C$	-6.51	-6.65			

GAS CONCENTRATIONS IN SAMPLE WATER IN MG/LITER

	J. FRIEMEL NO. 1 ZONE 4		J. FRIEMEL NO. 1 ZONE 6		J. FRIEMEL NO. 1 ZONE 7	
CYLINDER #	810600	810641	810600	810641	810600	810641
HYDROGEN	0.06[a]	0.04	0.05	0.03	0.09	0.10
ARGON	1.3	1.5	1.2	0.91	0.93	0.91
OXYGEN	0.037	<0.01 ND	0.29	<0.01 ND	<0.01 ND	<0.01 ND
NITROGEN	129	128	141	95.7	78.6	77.3
METHANE	42.7	46.0	40.3	31.4	35.1	34.7
CARBON MONOXIDE	<0.05 ND	<0.05 ND	<0.05 ND	<0.05 ND	~0.05[c]	~0.05[c]
CARBON DIOXIDE	<0.01 ND	0.013	<0.01 ND	0.032	0.071	0.051
ETHYLENE	<0.01 ND	<0.01 ND	<0.01 ND	<0.01 ND	0.016	0.016
ETHANE	0.76	0.84	1.5	1.1	3.4	3.4
% OF TOTAL[b] GAS PRESSURE ACCOUNTED FOR	99.9	98.4	101.1	96.6	95.4	95.9

[a] Values represent gas concentrations in the liquid phase determined by the McAullife method, R. McAullife, Chem. Tech. Jan., 46-51 (1971). Analytical precision based on replicate analysis of a given sample is typically ±5% or better. Calibration is based primarily on Scott Speciality Gas Standards with a stated accuracy of ±2%. Systematic errors which include effects due to contamination, container leakage, chemical reactions during sample transfer, storage and handling can be qualitatively assessed by comparing the results of the duplicate samples for a given zone.

[b] Individual gas component pressures measured by gas chromatography will equal the tota gas pressure measured by pressure transducer if all the components have been measured.

[c] Gas concentration only slightly above detection limit, quantitation approximate.

Table 3. Dissolved gas compositions of J. Friemel brines (analyses by Glenn Thompson, University of Arizona).

	J. FRIEMEL NO. 1 ZONE 1	
CYLINDER #	810600	810641
HYDROGEN	0.002	0.004
ARGON	1.3	1.6
OXYGEN	ND <0.002	ND <0.002
NITROGEN	100	130
METHANE	47	55
CARBON DIOXIDE	0.09	0.07
CARBON MONOXIDE	ND <0.05	ND <0.05
ETHYLENE	ND <0.005	ND <0.005
ETHANE	0.52	0.62
% OF TOTAL[b] GAS PRESSURE ACCOUNTED FOR	98.0	93.3

[a] Values represent gas concentrations in the liquid phase determined by the McAullife method, R. McAullife, Chem. Tech., Jan., 46-51 (1971). Analytical precision based on replicate analysis of a given sample is typically ±5% or better. Calibration is based primarily on Scott Speciality Gas Standards with a stated accuracy of ±2%. Systematic errors which include effects due to contamination, container leakage, chemical reactions during sample transfer, storage and handling can be qualitatively assessed by comparing the results of the duplicate samples for a given zone.

[b] Individual gas component pressures measured by gas chromatography will equal the total gas pressure measured by pressure transducer if all the components have been have been measured.

Dr. Glenn M. Thompson
GMT Tracer Research
Department of Hydrology & Water Resour
University of Arizona - Tucson

Table 3. Continued.

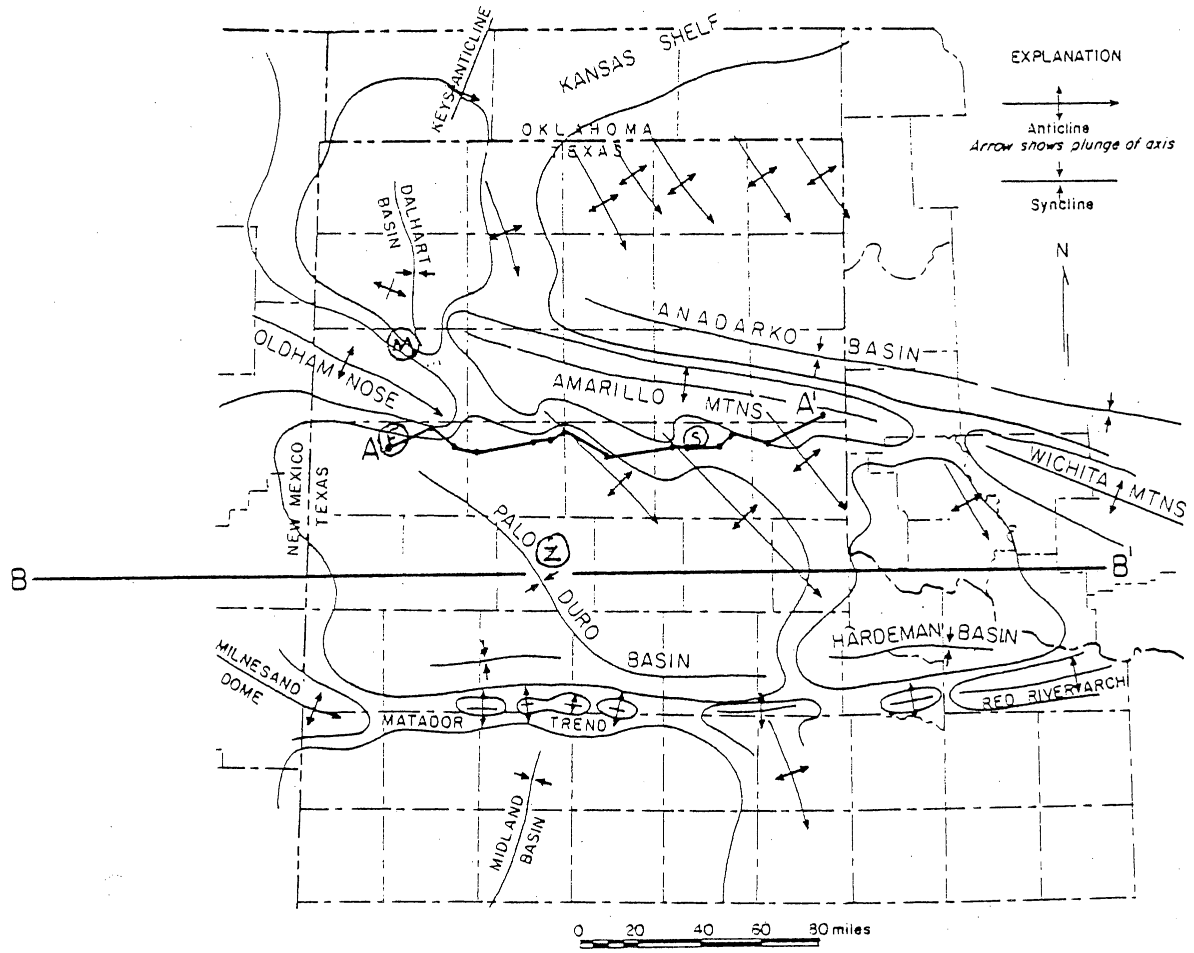
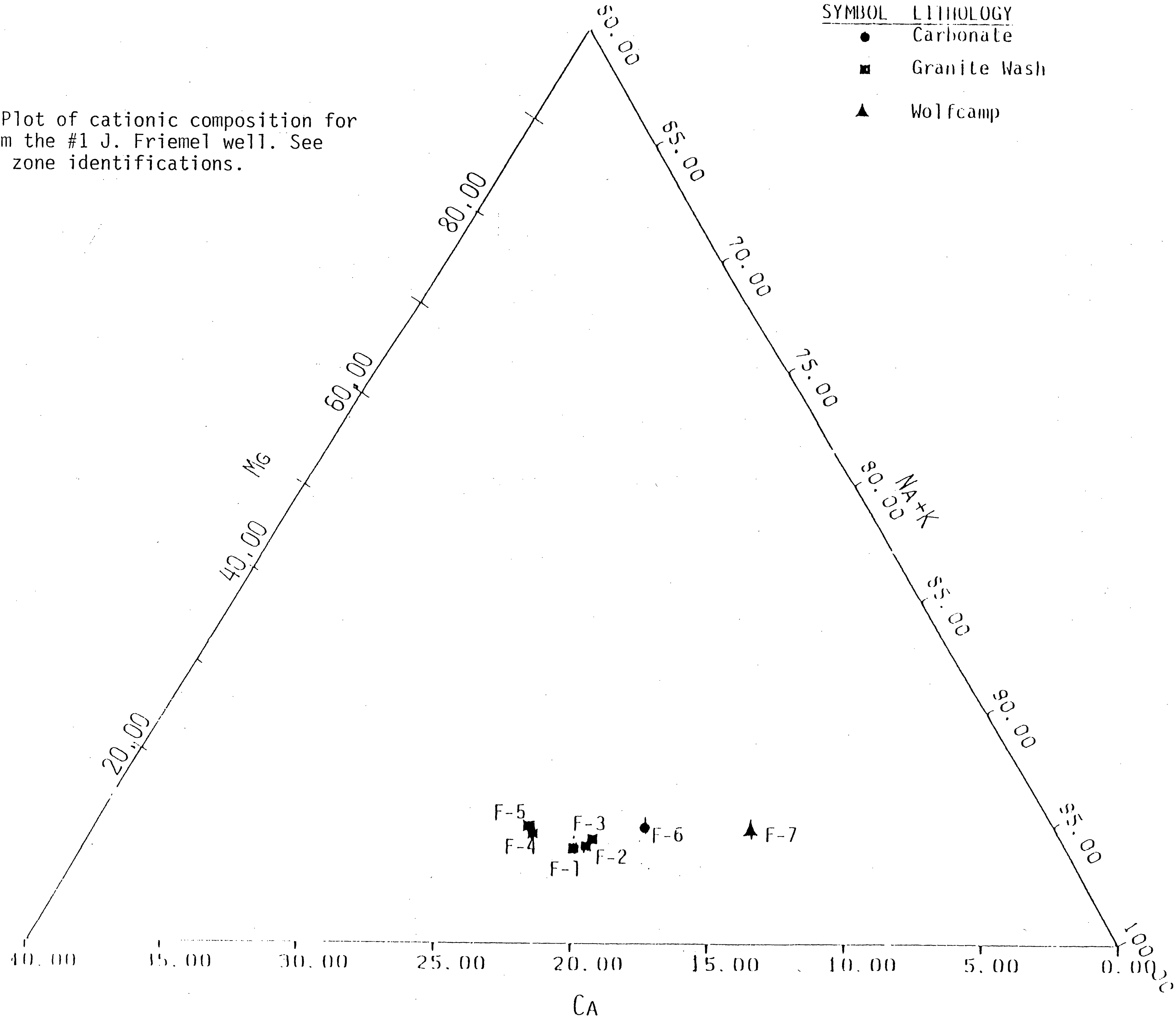


Figure 1. Location map of study area showing well locations and major structural elements of the Palo Duro Basin. Well designations are Z:#1 Zeeck, S:#1 Sawyer, M:#1 Mansfield, F: #1 J. Friemel.

Figure 2. Plot of cationic composition for samples from the #1 J. Friemel well. See Table 1 for zone identifications.



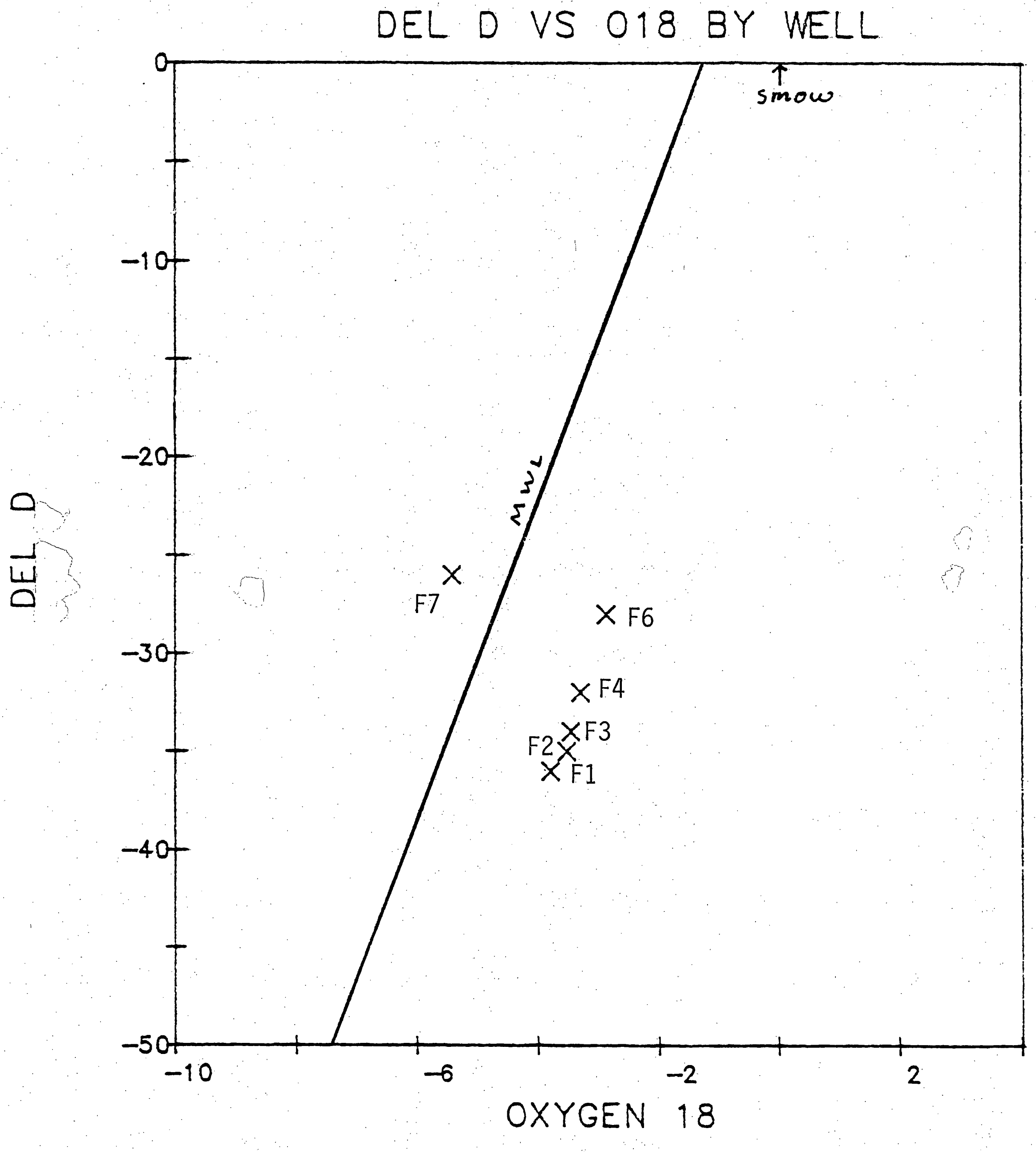
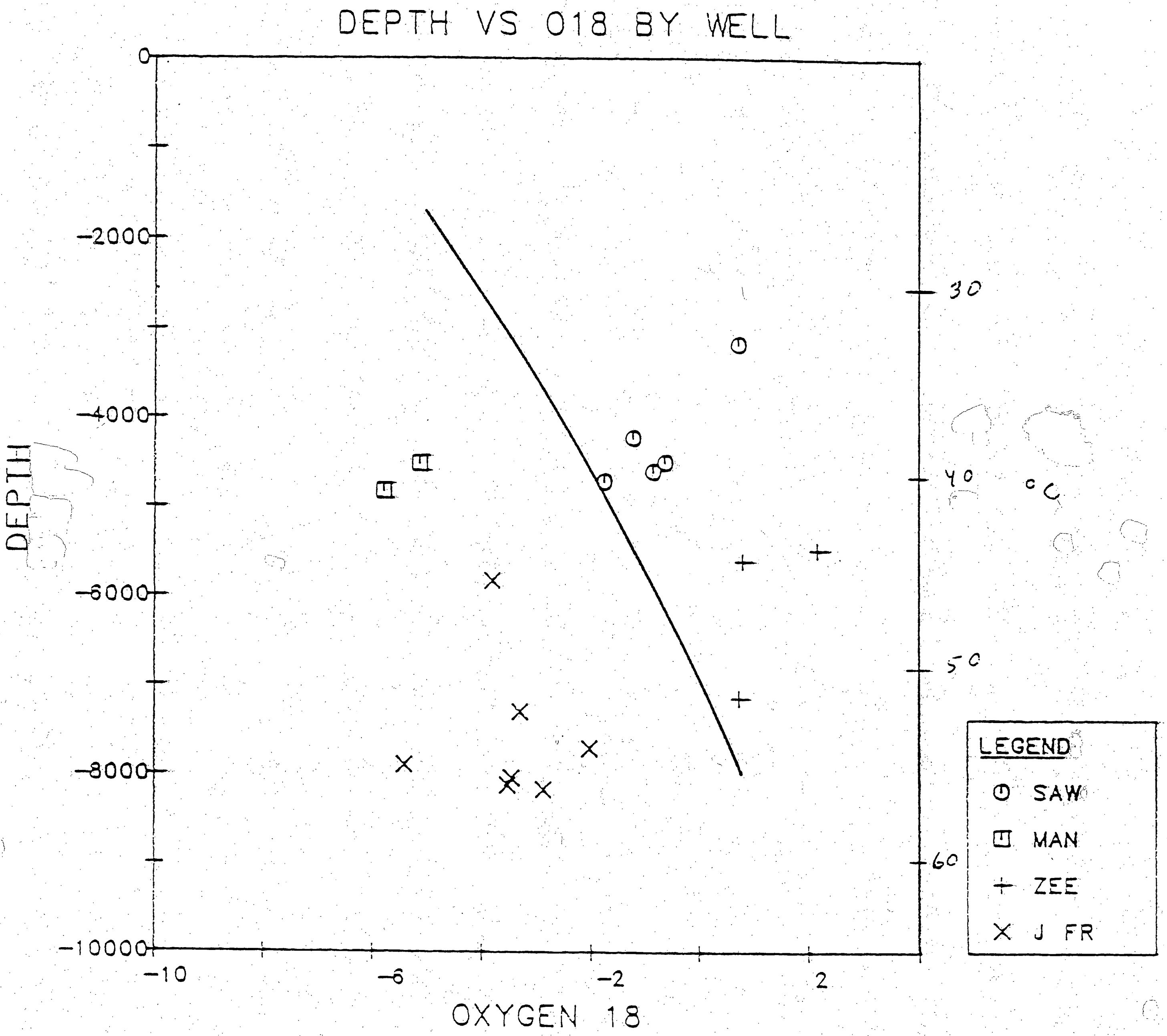


Figure 3. Plot of oxygen and hydrogen isotopic composition of samples from J. Friemel well in relation to Meteoric Water Line.



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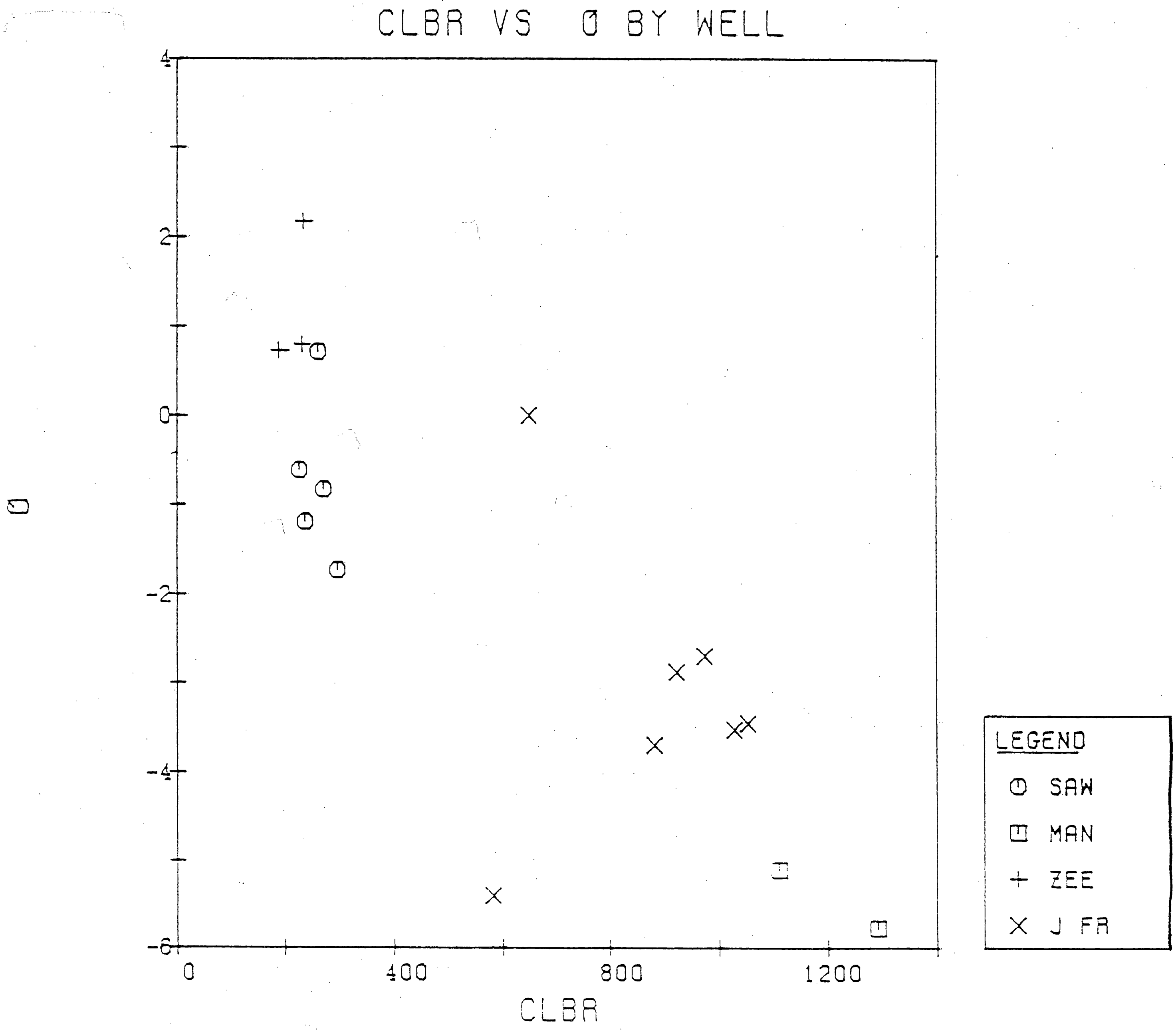

Figure 5. Plot of Cl:Br ratio versus oxygen isotopic composition.

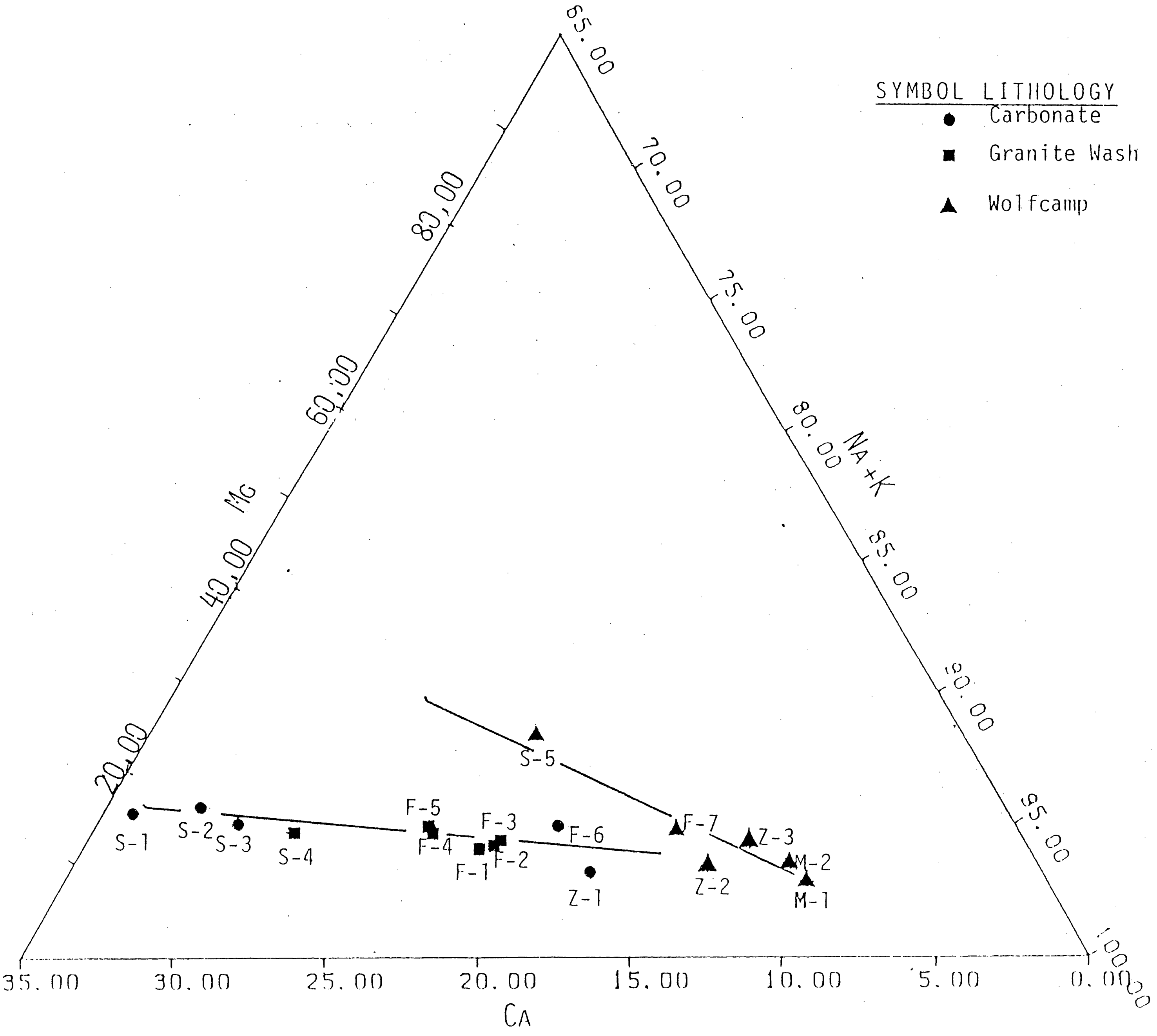

Figure 6. Plot of cationic compositions of all deep-basin brine samples. See Table 1 for zone identifications.