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Evolution of formation waters in the Permian Basin, United States: Late Permian evaporated seawater to Neogene meteoric water

Arthur H. Saller and Alan M. Stueber

ABSTRACT

Understanding subsurface waters is important for hydrocarbon exploration and development. Waters from the Permian Basin were collected and analyzed for stable isotopes, ionic concentrations, and strontium isotopes to determine their origin. Three main geochemical groups of waters are present. Group 1 has high $\delta^{18}\text{O}$ and δD values with high total dissolved solids (TDS; 100–240 g/L), including high concentrations of Na^+ , Cl^- , and Br^- . Group 1 waters contain distinctly less sodium (Na^+) than chlorine (Cl^-) on a molar basis, similar to modern seawater. Group 2 and 3 waters have low $\delta^{18}\text{O}$ and δD values. Group 2 waters have relatively low TDS (4–75 g/L). Group 3 waters have high TDS (170–225 g/L), Na^+ and Cl^- in approximately equal molar amounts, and low Br^- concentrations. Group 1 waters are interpreted as forming from highly evaporated seawater during precipitation of uppermost Permian salts. Because of their high density, those waters displaced preexisting formation waters throughout the Permian Basin during the latest Permian. Waters in groups 2 and 3 came mainly from precipitation in the mountains of southeast New Mexico. Those mountains formed during Neogene tectonic uplifts. Group 3 waters acquired their Na^+ and Cl^- by dissolution of upper Permian salt. Many group 2 and 3 waters acquired their Ca^{2+} and SO_4^{2-} by dissolution of Permian anhydrite or gypsum. Some waters contain a mixture of these groups. Understanding the origin of subsurface waters helps predict subsurface salinity, aquifer drive, sulfate reduction, chemical reactions during water injection, and chemistry of diagenetic waters.

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Alan M. Stueber received B.S. and M.A. degrees from Washington University (St. Louis) and a Ph.D. from the University of California, San Diego. He held academic positions at Miami University (Ohio), Louisiana State University, and Southern Illinois University (Edwardsville). He died October 29, 2009. Alan Stueber was an excellent teacher, superb geochemist, and wonderful person. He is missed.

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INTRODUCTION

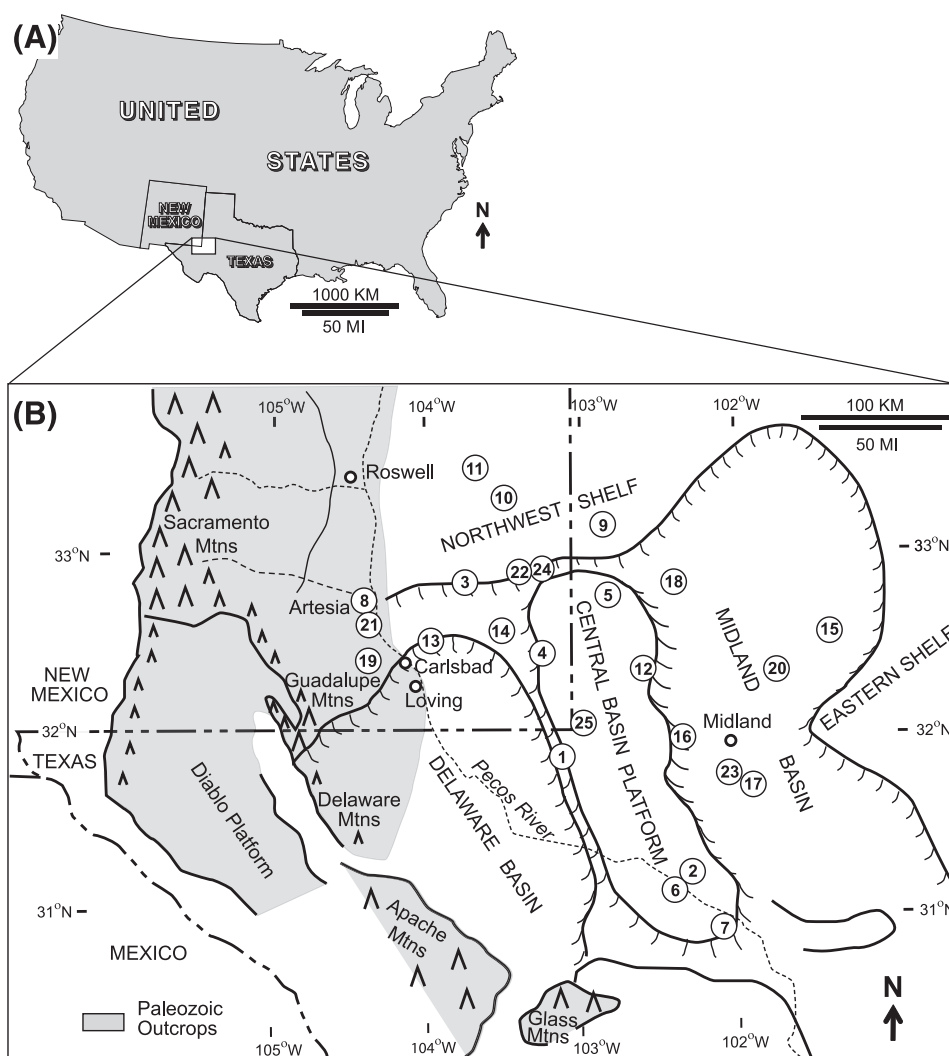
Understanding subsurface waters is important for many facets of hydrocarbon exploration and production. Knowledge of the salinity of formation waters is critical for the accurate interpretation of hydrocarbon saturations in resistivity logs. The hydrology of subsurface waters may determine whether an aquifer can supply sustained reservoir pressure. Waters circulating at oil–water contacts can sweep oil out of reservoirs or facilitate in the degradation of oil. Burial diagenesis can greatly alter the reservoir quality of carbonate rocks, and the geochemistry of diagenetic components is impacted by the water involved in the alteration; hence, insight into the geochemistry of subsurface waters will help in the accurate interpretation of diagenetic environments. The elemental composition of brines determines whether

scaling will be a significant issue during production, especially when waters are mixed.

Oil has been produced from the Permian Basin (Figure 1) for over 90 yr, and approximately 584,000 oil and gas wells have been drilled in the basin (C. R. Lemons, 2017, personal communication). As a result, the Permian Basin has a very large geologic database and acts as a natural geologic laboratory. Determining the origin and distribution of subsurface waters has been complicated by the long history of oil production and injection of water and CO₂ into the subsurface, and care must be taken to ensure that formation waters collected have not been contaminated by injected fluids.

Permian Basin waters have been studied by several different groups including McNeal (1965), Dutton (1987), Senger et al. (1987), Bein and Dutton (1993), Stueber et al. (1998), Barnaby et al. (2004),

Figure 1. (A) Map showing location of study area in the southwestern United States. (B) Map of the Permian Basin and mountainous areas to the west. The Permian Basin is generally considered to be the Midland Basin, Delaware Basin, and adjacent shelfal areas. Numbers show location of wells sampled. Multiple wells were sampled at some locations. See Table 1 for details of wells sampled at each location. Waters from the Cline and Wolfcamp shale were sampled and analyzed from the areas shown by Engle et al. (2016). Barnaby et al. (2004) sampled waters in Indian Basin and Dagger Draw fields that are approximately at location 19. Part of those results are shown and discussed in this paper. The town of Artesia coincides approximately with sample location 8. Mtns = Mountains.



and Engle et al. (2016). McNeal (1965) shows regional patterns in pressure and chemistry of Permian Basin waters. Most other studies have examined the geochemistry of specific parts of the Permian Basin. The purposes of this study are to (1) document the geochemical characteristics of the Permian Basin waters on a regional basis, (2) determine the origin of those waters, (3) relate characteristics of the subsurface waters to hydrocarbon production, and (4) provide insight into the evolution of waters in other basins.

GEOLOGICAL SETTING AND STRATIGRAPHY

During the early Paleozoic, the Permian Basin was a part of the passive southwest margin of North America. Sedimentation started in the Cambrian with deposition of sand and then Ordovician carbonates of the Ellenburger Group (Figure 2; Adams, 1965). Carbonate and shale deposition continued until the Mississippian when proto-South America (part of Gondwana) collided with proto-North America (part of Laurasia), and the Permian Basin area changed from the broad Tobosa Basin to the Delaware and Midland Basins separated by the Central Basin platform (Figure 1; Galley, 1958; Adams, 1965; Hills, 1984; Horak, 1985). Following Mississippian and Early Pennsylvanian tectonic deformation, the Permian Basin was dominated by regional subsidence from the middle Pennsylvanian to the late Permian. Carbonate platforms were built on the margins of the Midland and Delaware Basins from the middle Pennsylvanian to the late Permian (Adams, 1965). Both basins were largely filled by the late Permian, and then the basins and adjacent shelves and platforms were covered by evaporites of the Salado Formation in the latest Permian (Adams, 1965).

The Permian Basin area was relatively stable during the Mesozoic (Horak, 1985). Minor subsidence allowed deposition of some Triassic siliciclastics and Cretaceous carbonates. During the Laramide tectonic event (latest Cretaceous and early Neogene), the Permian Basin and especially areas to the west were thrust and uplifted (Horak, 1985). Basin and range tectonics have been uplifting the western margin of the Permian Basin for the last 24

NEOGENE		OGALLALA AQUIFER			
		PLATFORM SHELF	DELAWARE BASIN	MIDLAND BASIN	
252	PERMIAN	OCHOAN	SALADO	SALADO	SALADO
		GUADALUPIAN	DELAWARE Mtn GP	CASTILE	
				TANSILL	TANSILL
				YATES	YATES
				BELL CANYON	SEVEN RIVERS
				CHERRY CANYON	QUEEN
				GRAYBURG	GRAYBURG
				SAN ANDRES	SAN ANDRES
		LEONARDIAN	YESO GLORIETA CLEAR FORK ABO	BRUSHY CANYON	BRUSHY CANYON
				CUTOFF	
				BONE SPRING	SPRABERRY (Informal)
		WOLFCAMPIAN	WOLFCAMPIAN	WOLFCAMPIAN	WOLFCAMPIAN
299	PENNSYLVANIAN	VIRGILIAN	CISCO	CISCO	CISCO
		MISSOURIAN	CANYON	CANYON	CANYON
		DESMOINESIAN	STRAWN	STRAWN	STRAWN
		ATOKAN	ATOKA	ATOKA	ATOKA
		MORROWAN	MORROW	MORROW	
323	MISSISSIPPIAN	CHESTERIAN	MISSISSIPPIAN		
		MERAMECIAN			
		OSAGEAN			
		KINDERHOOKIAN			
359	DEVONIAN	FAMENNIAN	WOODFORD		
		FRASNIAN			
		GIVETIAN			
		EIFELIAN			
		EMSIAN	THIRTYONE		
		PRAGIAN			
		LOCHKOVIAN			
		PRIDOLI			
419	SILURIAN	LUDLOW	WRISTEN GROUP		
		WENLOCK			
		LLANDOVERY			
		ASHGILLIAN			
		CARADOCIAN	FUSSELMAN		
		LLANDEILIAN			
		LLANVIRNIAN			
		ARENIGIAN			
444	ORDOVICIAN	TREMADOCIAN	ELLENBURGER		
485	CAMBRIAN		BLISS		
					CAMBRIAN

Figure 2. Generalized Permian Basin stratigraphy showing intervals sampled in this study. Modified extensively from Dutton et al. (2005) and Matchus and Jones (1984). Age dates at left are from The Geological Society of America (2017).

m.y. (Horak, 1985). During the Pliocene and Pleistocene, fluvial sands, gravels, and muds of the Ogallala Formation (Figure 2) were deposited as sediments were eroded from mountains uplifted to the west.

PREVIOUS STUDIES

Formation waters in and near the Permian Basin have been studied geochemically in the Midland, Palo Duro (e.g., Bassett and Bentley, 1982; Dutton, 1987; Fisher and Kreitler, 1987; Knauth, 1988), and Delaware Basins (e.g., Stein and Krumhansl, 1988; Lambert, 1992; Siegel and Anderholm, 1994) as evaluations for potential nuclear waste storage. Bein and Dutton (1993) formulated a regional model for the origin, distribution, and movement of brines in the Palo Duro, Anadarko, and northern Midland Basins. This model has a diagenetically modified Permian brine of evaporitic origin currently mixing with and being displaced by a more dilute brine derived from meteoric water as young as 5–10 Ma. The process is taking place in a deep-basin brine aquifer system in Paleozoic strata with intrusion of meteoric water being initiated from highlands created by recent Basin and Range uplift (Trimble, 1980; Senger, 1991).

Stueber et al. (1998) studied formation waters in the Southwest Andrews area on the eastern side of the Central Basin platform. They focused on the Pennsylvanian and lower Permian carbonate reservoir section. In the Southwest Andrews area, meteoric waters interpreted as coming from southeast New Mexico were mixing with highly saline formation waters. Stable isotopes and elemental ratios indicated that the highly saline waters came from highly evaporated seawater that had precipitated halite. Widespread halite deposition occurred in the latest Permian, and the highly saline formation water apparently formed during uppermost Permian salt deposition and descended deeply into the basin because of its very high density.

Barnaby et al. (2004) collected 71 water samples from the Upper Pennsylvanian reservoir in the Indian Basin and Dagger Draw field complex on the northwestern side of the Delaware Basin (approximately location 19 on Figure 1B). Although they focused on strontium isotopes, they also analyzed stable oxygen and hydrogen isotopes as well as dissolved elemental

concentrations. They found that waters within the field were heterogeneous and used strontium isotopes to determine reservoir connectivity and paths of fluid flow. The waters in the Indian Basin and Dagger Draw field complex were generally derived from precipitation (rain and snow) in highlands to the west. The waters acquired modest salinity by dissolution of upper Permian salts, then flowed through a variety of Paleozoic carbonates while moving down and into the subsurface.

Engle et al. (2016) focused on formation waters produced from the “Wolfcamp shale” and “Cline shale” in the Midland Basin (Figure 1B) and put those data into a regional context. Wolfcamp shale is an informal unit that Engle et al. (2016) use for basinal shales that are Wolfcampian. Similarly, Cline shale is an informal term for Virgilian basinal shales that correlate with the Cisco (Figure 2). Engle et al. (2016) also recognized saline late Permian waters as well as young meteoric waters. They postulated a deep basin meteoric aquifer system in the middle and lower Paleozoic of the Permian Basin (Devonian to Ordovician). Engle et al. (2016) also used data from Stueber et al. (1998) and many additional samples collected from different intervals and various areas in the Permian Basin to understand the evolution of formation waters in the Permian Basin on a regional basis.

METHODS

Chemical and isotopic data for this study were obtained through analyses of 90 water samples. Most samples were formation water from wells scattered across the Permian Basin (Figure 1; Table 1), and productive intervals ranged from the Lower Ordovician (Ellenburger) to upper Permian (Capitan). Waters from the Ogallala aquifer and Pecos River were also acquired and analyzed. The samples were collected between 1994 and 1999 from intervals not subjected to water injection in the immediate vicinity of the well. These data include samples from the Southwest Andrews area previously presented in Stueber et al. (1998), as well as many additional samples that allow a regional distribution of water characteristics. Production fluids were generally obtained from the bleeder valve on the well head. Formation water was then separated from the oil–

Table 1. Composition of Permian Basin Waters

Sample, Location	Formation	Field	Well	Interval, ft	Interval, m	Na, mg/L	Ca, mg/L	Mg, mg/L	K, mg/L	Sr, mg/L	Cl, mg/L	Br, mg/L	SO ₄ , mg/L	TDS, g/L	δ ¹⁸ O*, ‰ SMOW	δD*, ‰ SMOW	⁸⁷ Sr/ ⁸⁶ Sr [†]
1, 1	Capitan	Hendricks reef	Crane County Water			900	782	247	21	13	1480	4.9	2250	5.7	-7.3	-54	0.70761
2, 2	Grayburg	McCamey	3648	2500	762	5290	579	259	140	23	7810	9.4	1590	15.7	-7.2	-50	
3, 2	Grayburg	McCamey	3501	2500	762	7190	535	290	171	23	10,600	18.1	1250	20.1	-6.3	-43	0.70781
4, 3	Grayburg	Maljamar	Maljamar APB	4131-4252	1259-1296	67,430	11,000	4580	2160	222	139,300	356	1120	226.2	3.2	-15	0.70723
			State 1														
5, 4	Grayburg	Euine-Monument S	Chevron EMSU 290	4500-5000	1372-1524	4170	813	325	137	17	6910	15.8	1150	13.5	-7.4	-52	0.70852
6, 4	Grayburg	Euine-Monument S	Chevron EMSU B 920	4500-5000	1372-1524	6040	945	512	263	20	10,820	32.3	1130	19.8	-7.3	-47	
7, 4	San Andres	Euine-Monument S	Chevron WSW 459	4000-4500	1219-1372	5480	1160	373	120	22	9120	16.1	2660	19	-7.6	-52	0.70792
8, 5	San Andres	Blackwatch	Montrose 1	4553-4644	1388-1415	6300	1160	315	221	27	10,270	na	1550	20.1	-8.9	-48	
9, 5	San Andres	Blackwatch	Somerled 1	4525-4590	1379-1399	6300	690	289	218	34	9750	na	701	18.3	-9.1	-49	
10, 5	San Andres	Blackwatch	Braemar 3	4540-4644	1384-1415	6400	1260	333	230	26	9690	7	3490	21.4	-9.1	-47	
11, 5	San Andres	Blackwatch	Calodonia 3	4549-4636	1387-1413	6240	1260	270	225	25	9520	6.9	3230	20.8	-9.1	-49	0.70732
12, 5	San Andres	Blackwatch	Montrose 1	4539-4654	1383-1419	6300	827	287	217	31	9620	8.1	1950	19.2	-8.7	-50	
13, 5	San Andres	Texland-Rector	Donna Holler 1	4739-4825	1444-1471	2920	1100	328	150	23	4650	5.5	2660	11.8	-8.1	-55	0.70746
14, 6	San Andres	Chenot-Putham	Woodward 33	1585-1645	483-501	1310	216	197	53	11	2120	4.8	11	3.9	-7.9	-56	0.70798
15, 7	San Andres	Yates	Station 25	1500	457	1960	392	262	56	16	3030	5.8	800	6.5	-7.7	-60	
16, 7	San Andres	Yates	Station 73	1500	457	2300	345	223	73	16	3490	6.3	314	6.8	-7.7	-57	0.70819
17, 7	San Andres	Yates	Station 46	1500	457	2390	387	233	77	33	3670	6	74	6.9	-7.7	-56	
18, 8	San Andres	Atoka	Dayton FI 1 Fee	1553-1651	473-503	69,130	2120	546	568	47	108,400	30.6	4380	185.2	-5.3	-41	
19, 8	San Andres	Atoka	Dayton ER 1 Fee	1577-1642	481-500	72,050	1920	506	281	43	112,700	28.1	4800	192.3	-7	-49	0.70752
20, 9	San Andres	Plains	Read & Stevens	5255-5290	1602-1612	81,340	2050	622	352	57	130,700	49.5	2830	218	-7.6	-56	0.70777
			Truett-Jones 2														
21, 8	San Andres	Eagle Creek	Mitchell SWD			83,460	1840	477	513	33	131,400	24.2	3990	221.7	-6.3	-33	
22, 8	San Andres	Eagle Creek	Yates Morris Est CC 3	1324-1441	404-439	81,340	2100	535	674	40	130,600	36.8	3560	218.9	-5.8	-31	0.70755
23, 10	San Andres	Baum	Dwight A Tipton			77,570	1950	583	302	50	123,600	47.8	3220	207.3	-7	-57	0.70758
			sunray A 6822 1														
24, 11	San Andres	Paul Lease	Tank battery	3996-4066	1218-1239	37,290	25,970	8720	4300	662	128,900	1083	432	207.4	3.8	-30	0.70707

(continued)

Table 1. Continued

Sample, Location	Formation	Field	Well	Interval, ft	Interval, m	Na, mg/L	Ca, mg/L	Mg, mg/L	K, mg/L	Sr, mg/L	Cl, mg/L	Br, mg/L	SO ₄ , mg/L	TDS, g/L	$\delta^{18}\text{O}^*$, ‰ SMOW	δD^* , ‰ SMOW	$^{87}\text{Sr}/$ $^{86}\text{Sr}^\dagger$
25, 4	San Andres	Arrowhead	Chevron WSW 600	4000-4500	1219-1372	3440	1020	325	71	20	5700	10.7	2310	12.9	-7.7	-53	
26, 12	San Andres	SW Andrews	Parker Q 4	4632-4738	1412-1444	13,100	1670	483	395	40	21,800	39	3520	41.1	-7	-40	0.70732
27, 12	San Andres	SW Andrews	Parker X 12	4658-4717	1420-1438	15,400	1880	523	408	45	25,200	37	4090	47.6	-7.6	-44	0.70723
28, 12	San Andres	SW Andrews	Parker N 2	4616-4664	1407-1422	14,700	2310	932	458	43	26,000	42	3350	47.9	-6.8	-40	0.70729
29, 12	San Andres	SW Andrews	Parker F 2	4624-4684	1409-1428	15,800	1730	536	433	41	26,300	30	3980	48.9	-6.9	-43	0.70737
30, 12	San Andres	SW Andrews	Parker X 11	4646-4686	1416-1428	18,500	2660	1130	475	55	33,200	60	2440	58.6	-5.9	-39	0.70741
31, 12	San Andres	SW Andrews	Parker State 4	5000-5500	1524-1676	8380	985	345	262	26	13,400	17	2840	26.3	-6.6	-43	0.707861
32, 13	Delaware	Scanlon	Zinnia Fed Unit 1	3900-3905	1189-1190	44,090	14,930	3050	512	340	100,100	652	1070	164.7	-1.2	-28	
33, 14	Brushy Canyon	North Lea	Truman Fed 6	8052-8216	2454-2504	69,990	15,590	2770	1240	522	144,100	1346	556	236.1	3.5	-15	
34, 14	Cherry Canyon	North Lea	Read & Stevens Mark Fed 8	5548-5572	1691-1698	55,150	20,630	5910	1060	557	137,900	834	584	222.6	2.9	-13	
35, 8	Yeso	Atoka	Boykin ACV Com 1	2782-3623	848-1104	63,590	3380	719	580	65	103,000	76.3	3170	174.6	-4.9	-45	
36, 8	Yeso	Penasco	Yates Babcock IR 1	2141-2327	653-709	46,770	7680	1900	932	148	88,950	222	1680	148.3	-2.2	-34	
37, 14	Bone Spring	Quail Ridge	Pipeline 16-1	10,133-10,149	3089-3093	47,300	3170	691	977	63	79,200	654	2890	134.9	4	-22	
38, 15	Leonard	Reinecke	Miller-Conrad 1	5452-5458	1662-1664	21,270	2620	1030	352	51	39,400	142	2190	67.1	-3.4	-34	
39, 16	Spraberry	Odessa	Texland Exxon Barrow 16-1	5642-5653	1720-1723	23,330	1580	686	310	65	40,890	83.8	543	67.5	-4.6	-37	
40, 17	Spraberry	Spraberry Trend	Midland AF Fee 1	7825-8610	2385-2624	45,370	3920	547	467	907	79,030	717	281	131.2	4.4	-20	
41, 17	Spraberry	Spraberry Trend	Midland AV Fee 3	7680-9117	2341-2779	51,870	4270	629	508	1010	90,130	818	223	149.5	3.8	-19	
42, 6	Wolfcamp	Chenot- Putnam	Cabeen 3	4427-4706	1349-1434	15,220	2100	1090	176	46	27,600	69.2	2430	48.7	-2.5	-26	
43, 12	Wolfcamp	SW Andrews	Deford 2	8559-8983	2609-2738	55,850	8550	1975	763	395	97,600	461	914	166.6	3	-23	0.70875
44, 12	Wolfcamp	SW Andrews	Parker H 27	8607-8822	2623-2689	53,000	8100	1420	480	590	103,000	588	455	167.6	5.9	-15	0.70856
45, 12	Wolfcamp	SW Andrews	Parker AB 1	8648-8678	2636-2645	59,300	11,000	1950	661	550	121,700	627	570	196.4	4.1	-17	0.70889
46, 12	Wolfcamp	SW Andrews	Ford 3	8575-8649	2614-2636	64,500	9800	2220	845	497	132,000	821	501	211.2	4.9	-17	0.70878
47, 12	Wolfcamp	SW Andrews	Parker P 16	8660-8664	2640-2641	68,950	10,150	2265	933	515	131,100	788	487	215.2	4.7	-15	0.70873
48, 18	Wolfcamp	NE Adair	Texland - McIntyre 1	8862-8868	2701-2703	67,210	7630	1240	344	872	121,400	1014	356	200.1	5.5	-13	

(continued)

Table 1. Continued

Sample, Location	Formation	Field	Well	Interval, ft	Interval, m	Na, mg/L	Ca, mg/L	Mg, mg/L	K, mg/L	Sr, mg/L	Cl, mg/L	Br, mg/L	SO ₄ , mg/L	TDS, g/L	$\delta^{18}\text{O}^*$, ‰ SMOW	δD^* , ‰ SMOW	$^{87}\text{Sr}/^{86}\text{Sr}^\dagger$
49, 12	Wolfcamp- Canyon	SW Andrews	Parker H 20	8817–9365	2687–2854	55,950	11,300	2085	720	565	103,200	524	477	174.9	4.5	–15	0.70891
50, 19	Cisco	Indian Basin	Chevron 11	7500	2286	2910	433	111	78	11	3520	13.6	2630	9.7	–7.6	–51	
51, 12	Cisco- Canyon	SW Andrews	B.O. Parker 11 1	9092–9188	2771–2801	31,250	4375	915	553	132	61,100	213	2760	101.3	–2	–33	0.70886
52, 12	Cisco- Canyon	SW Andrews	Parker AA 1	9012–9166	2747–2794	33,800	4970	962	554	144	63,700	199	2320	106.7	–0.7	–25	0.70882
53, 12	Cisco- Canyon	SW Andrews	Parker D 31	8965–9134	2733–2784	45,700	7100	1215	647	285	83,100	355	943	139.4	2.7	–21	0.70876
54, 12	Cisco- Canyon	SW Andrews	Parker N 3	8920–9431	2719–2875	46,250	7050	1270	601	256	86,300	365	1480	143.6	2.2	–19	0.70874
55, 12	Cisco- Canyon	SW Andrews	Parker Z 1	9012–9204	2747–2805	50,200	8290	1520	981	500	96,800	421	597	159.4	4.6	–15	0.70888
56, 12	Wolfcamp to Strawn	SW Andrews	Crosby State 3	8601–9506	2622–2897	50,000	8400	1590	780	450	97,700	423	557	159.9	4.9	–20	0.70883
57, 12	Cisco- Canyon	SW Andrews	Parker AB 2	8802–9168	2683–2794	46,900	10,500	1750	420	520	103,100	555	465	164.3	4	–17	0.70891
58, 12	Cisco- Canyon- Strawn	SW Andrews	Ford 18	9072–9732	2765–2966	51,850	8100	1580	999	449	105,400	497	524	169.5	4.9	–17	0.70881
59, 12	Cisco- Canyon- Strawn	SW Andrews	University GG 2	9069–9770	2764–2978	52,200	8150	1565	1017	451	105,800	487	511	170.2	5.3	–15	0.70881
60, 12	Wolfcamp to Strawn	SW Andrews	Grafta Deep 3	8601–9424	2622–2872	56,400	8600	1845	675	475	112,400	680	575	181.7	4.5	–15	0.70868
61, 12	Wolfcamp to Strawn	SW Andrews	Iverson Deep 1	8365–9390	2550–2862	63,800	9950	1960	616	660	155,700	763	457	194	5.2	–14	0.70864
62, 12	Cisco- Canyon	SW Andrews	Halliday 3A	9047–9161	2758–2792	65,700	9600	2140	862	492	121,300	699	452	201.3	4.7	–17	0.70881
63, 15	Cisco- Canyon	Reinecke	Miller-Conrad 1	6867–6871	2093–2094	25,300	2600	641	581	103	43,200	80.1	1046	73.6	–5.3	–46	0.71254
64, 12	Cisco- Canyon- Strawn	SW Andrews	Parker C 16	8993–9596	2741–2925	23,000	3205	720	473	124	39,700	142	2320	69.7	–3.3	–36	0.70929

(continued)

Table 1. Continued

Sample, Location	Formation	Field	Well	Interval, ft	Interval, m	Na, mg/L	Ca, mg/L	Mg, mg/L	K, mg/L	Sr, mg/L	Cl, mg/L	Br, mg/L	SO ₄ , mg/L	TDS, g/L	$\delta^{18}\text{O}^*$, ‰ SMOW	δD^* , ‰ SMOW	$^{87}\text{Sr}/^{86}\text{Sr}$
65, 12	Cisco-Canyon-Strawn	SW Andrews	Parker D 1	8992-9784	2741-2982	31,050	4225	925	626	163	55,200	182	2930	95.3	-2.5	-37	0.70869
66, 12	Cisco-Canyon-Strawn	SW Andrews	Parker P 3	9074-9780	2766-2981	56,550	8300	1650	959	371	111,100	482	825	180.3	4.3	-17	0.70869
67, 12	Lower Canyon	SW Andrews	Parker H 23	9352-9390	2850-2862	59,000	8500	1670	1060	281	114,000	508	889	185.9	6.1	-18	
68, 20	Canyon	BC Canyon	E.M. Long 1	9055-9060	2760-2761	55,900	7080	1170	656	1190	101,700	719	110	168.6	6	-19	
69, 21	Canyon	McMillan	Eastern Shore TL Fed 1	7648-7741	2331-2359	3760	675	109	54	16	4350	10.5	2850	11.8	-7.7	-57	0.70897
70, 9	Strawn	Plains	Read & Stevens Truett-Jones 1	12,406-12,496	3781-3809	20,860	2650	463	467	72	37,680	32.5	1650	63.9	-7.9	-56	
71, 12	Strawn	SW Andrews	Parker 68-30E	9487-9579	2892-2920	54,000	10,100	1730	1330	425	114,200	453	850	183.2	5	-17	0.70881
72, 12	Strawn	SW Andrews	Ant. University 3	9747-9933	2971-3028	59,000	9100	1940	630	460	120,000	600	520	192.3	4.7	-18	0.70881
73, 13	Strawn	Burton Flat	Eland AFC Fed. Com. 1	10,898-11,076	3322-3376	29,600	8010	1230	110	1440	61,000	485	198	102.1	8.1	-19	
74, 22	Strawn	Lovington	Chesapeake Little 6 1			24,410	2920	728	66	439	46,910	400	321	76.2	7.1	-8	
75, 14	Morrow	North Lea	Read & Stevens N Lea Fed 1-Y	12,994-13,225	3961-4031	13,990	963	193	186	58	23,460	170	503	39.5	3	-16	
76, 12	Devonian	Southwest Andrews	Parker H 1	10,465-10,485	3190-3196	11,500	1460	364	343	39	19,500	28	3980	37.2	-7.9	-55	0.71454
77, 12	Devonian	SW Andrews	Parker State 7	10,485-10,523	3196-3207	16,200	1750	428	389	77	27,000	49	1950	47.9	-6.6	-49	0.71097
78, 23	Devonian	Bryant G	Texas Ten NCT 1 3H	12,000-12,119	3658-3694	38,200	6660	913	1260	632	73,030	368	90	121.3	8.6	-18	
79, 23	Devonian	Bryant G	Bryant G Devonian Unit 29H	11,846-11,905	3611-3629	32,030	5910	822	913	569	61,790	299	125	102.5	8.8	-15	
80, 24	Devonian	Dean	Kochia AAM State 1	13,594-13,598	4143-4145	37,880	1670	409	270	48	59,100	30.9	2260	101.7	-8.3	-65	0.71389
81, 12	Ellenburger	SW Andrews	Perkins 1	12,294-12,324	3747-3756	16,800	1930	433	441	70	28,500	34.4	1150	49.4	-6.3	-45	
82, 12	Ellenburger	SW Andrews	Perkins 2	12,236-12,293	3730-3747	16,370	1900	460	424	64	27,900	45.6	2330	49.5	-5.6	-45	
83, 12	Ellenburger	SW Andrews	Perkins 3	12,242-12,320	3731-3755	16,170	1860	437	411	64	27,900	47.6	2230	49.1	-5.7	-45	0.71349

(continued)

Table 1. Continued

Sample, Location	Formation	Field	Well	Interval, ft	Interval, m	Na, mg/L	Ca, mg/L	Mg, mg/L	K, mg/L	Sr, mg/L	Cl, mg/L	Br, mg/L	SO ₄ , mg/L	TDS, g/L	δ ¹⁸ O*, ‰ SMOW	δD*, ‰ SMOW	⁸⁷ Sr/ ⁸⁶ Sr†
84, 15	Ellenburger	Reinecke	W. Wolf 1	8612-8629	2625-2630	13,930	1750	374	333	46	24,000	26.2	1900	42.4	-8.3	-62	0.71926
85, 25	Ellenburger	SE Dollarhide	E.P. Cowden 1	12,816-12,832	3906-3911	46,420	10,430	1660	987	375	93,500	422	695	154.5	0.8	-18	0.71504
86	Pecos River	At Artesia				1060	539	185	14	9	1750	0.46	893	4.5	-6.1	-50	
87	Pecos River	At Loving				568	444	173	12	7	926	0.49	772	2.9	-5.3	-46	
88	Salt Lake	Near Loving				95,700	265	12,600	41,500	10	202,000	113	13,600	365.8	3	-25	
89	Ogallala	At Lovington	Collier Residence	100	30	100	102	13	2.1	0.7	63	0.42	101	0.3	-6.4	-44	0.70848
90	Ogallala	At Maljamar				23	63	11	2.5	0.6	31	0.22	32	0.2	-6.5	-46	

Depths are in feet below surface. Locations for samples are shown in Figure 1B. Precisions are given in the Methods section.

Abbreviations: Ah = Arrowhead; Ant. = antelope; Fed = Federal; na = not available; SMOW = standard mean ocean water; SWD = salt water disposal; TDS = total dissolved solids.

*δ¹⁸O and δD are relative to SMOW.

†⁸⁷Sr/⁸⁶Sr are relative to National Bureau of Standards 987 value of 0.71014.

water emulsion and passed through a 0.45-μm filter, acidified to pH < 2 with Ultrex concentrated nitric acid (HNO₃), and stored in polyethylene bottles. The filtrate was then split into subsamples for different types of analyses.

Concentrations of major and minor cations and anions as well as selected trace elements were determined at the University of Michigan by inductively coupled plasma emission spectroscopy (ICP) and ion chromatography (Walter et al., 1990). Precision of analyses ranges from ±1% for Sr²⁺ to ±7% for K⁺, based upon replicate analyses. Chloride, bromide, and SO₄ concentrations were measured on a Dionex 4000i series ion chromatograph with AS2 and AS5 columns and suppressed conductivity detection. Precision of anion analyses was ±1% for Cl⁻ and SO₄²⁻ and ±3% for Br⁻. Analyses of some subsamples that had not been treated with HNO₃ yielded results identical to those for acidified samples.

Subsamples were analyzed at Chempet Research Corporation for stable oxygen isotope ratios using the standard CO₂ equilibration method (Epstein and Mayeda, 1953) and for stable hydrogen isotope ratios after liberation of hydrogen gas through reaction with hot metallic uranium (Godfrey, 1962). Oxygen isotopic analyses have been corrected for the effects of brine chemistry using the equation of Sofer and Gat (1972) and are reported as per mil (‰) deviations from the standard mean ocean water (SMOW; Craig, 1961). Precision (two standard deviations [2σ]) for δ¹⁸O is ±0.2‰. Precision (2σ) for δD is ±2‰. After separation of strontium by ion chromatography, ⁸⁷Sr/⁸⁶Sr ratios were determined at Washington University according to procedures described in Podosek et al. (1991). Measured strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) were adjusted to a value of 0.710140 for National Bureau of Standards (NBS) 987. Precision (2σ) for ⁸⁷Sr/⁸⁶Sr was ±0.00002. Values from other studies shown on figures have also been adjusted to an NBS 987 ratio of 0.710140.

RESULTS

Results for geochemical analyses of waters are in Table 1. Stable isotopes and elemental concentrations show distinct patterns, some of which are correlated to geographic location and stratigraphic position.

Isotope ratios, $\delta^{18}\text{O}$ and δD , cluster at two end members. The light (low) end member has $\delta^{18}\text{O}$ values of -9.2‰ to -5‰ SMOW and δD of -30‰ to -65‰ SMOW (Figure 3A). Those data cluster along the meteoric line of Craig (1961). The heavy (high) end member has $\delta^{18}\text{O}$ values of $+2\text{‰}$ to $+9\text{‰}$ SMOW and δD of -22‰ to -12‰ SMOW as is apparent on Figure 3A. Most of the remaining data are mixtures between the two end members. Samples belonging to the low $\delta^{18}\text{O}$ and δD end member include most of the formation waters collected from the Grayburg, San Andres, and Capitan Formations as well as waters from the Pecos River and Ogallala aquifer, and some formation waters from the Devonian, Ordovician, and Pennsylvanian carbonates (Figure 3A). Samples with high $\delta^{18}\text{O}$ and δD include many waters from Pennsylvanian and Wolfcampian shelfal carbonates as well as basinal sandstones and carbonates of the Leonardian and Guadalupian. Mixtures of the two end members occur in waters from Pennsylvanian, Wolfcampian, and Leonardian shelf carbonates (Figure 3A).

Concentrations of dissolved solids are highly variable in Permian Basin formation waters. The distribution of total dissolved solids (TDS) and stable isotopic compositions show distinct patterns relative to stratigraphy but not depth (Figures 3B, 4). Concentrations of TDS range from 3.9 g/L (3900 mg/L) to 240 g/L (240,000 mg/L; Figure 3B). In saline formation waters, sodium (Na^+) is the dominant cation (900–83,460 mg/L), and chloride (Cl^-) is the dominant anion (1480–155,700 mg/L; Figure 5; Table 1). Dissolved calcium is variable, from 216 to 25,970 mg/L (Figure 6A), magnesium varies from 109 to 8720 mg/L (Figure 6B; Table 1), and potassium varies from 21 to 4300 mg/L (Table 1). Dissolved sulfate (SO_4^{2-}) varies from 11 to 4800 mg/L (Figure 6A). Bromine varies from less than 1 to 1346 mg/L in subsurface brines (Figure 7) (Ogallala waters have <1 mg/L Br^-).

Isotope ratios of dissolved strontium are variable (Figure 8). Most San Andres waters have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are similar to mid to late Permian seawater (Burke et al., 1982). Most waters from Pennsylvanian and Wolfcampian carbonates are in a fairly narrow field of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.7086 and 0.7090 (Figure 8). Waters from Devonian and Ordovician strata are much more radiogenic than other waters collected with values of 0.71097

to 0.71926 (Figure 8; Table 1) that are far above contemporaneous (Paleozoic) seawater (Burke et al., 1982; Veizer et al., 1999).

INTERPRETATION

The stable oxygen and hydrogen isotopes in water ($\delta^{18}\text{O}$ and δD) give great insight into their origin. Low $\delta^{18}\text{O}$ and δD values near the “meteoric line” of Craig (1961) are generally associated with rainwater, whereas high $\delta^{18}\text{O}$ and δD values are commonly associated with trajectories of evaporated seawater (Craig, 1961; Craig et al., 1963; Holser, 1979). Waters with $\delta^{18}\text{O}$ of $+2\text{‰}$ to $+9\text{‰}$ SMOW and δD of -24‰ to -8‰ SMOW (Figure 3A) can form when seawater undergoes extreme evaporation and prolonged halite precipitation. As seawater evaporates, both $\delta^{18}\text{O}$ and δD initially increase (Holser, 1979; Gat, 1996), but when seawater evaporation is extreme, the trajectory of the $\delta^{18}\text{O}$ and δD composition of seawater “hooks” around at approximately four times seawater concentration (Figure 3A; Holser, 1979). With continued evaporation, $\delta^{18}\text{O}$ and δD of evaporated seawater decrease so that a field of $\delta^{18}\text{O}$ of $+3\text{‰}$ to $+5\text{‰}$ SMOW and δD of -22‰ to -12‰ SMOW corresponds to an evaporative concentration of approximately 10 times seawater, which would also be associated with the precipitation of a large amounts of halite (Holser, 1979). Interaction between marine carbonates with high $\delta^{18}\text{O}$ values ($+20\text{‰}$ to $+30\text{‰}$ SMOW) can also increase $\delta^{18}\text{O}$ values in formation waters (Land and Prezbindowski, 1981), however, the correlation of high $\delta^{18}\text{O}$ with high Br^- , TDS, δD , and lack of increase of $\delta^{18}\text{O}$ with depth in our samples suggest evaporation of seawater is main cause of high $\delta^{18}\text{O}$, rather than rock–water interaction. Engle et al. (2016) made similar conclusions. Interactions between lower Paleozoic carbonates and evaporated seawater may be responsible for a few of the extremely high $\delta^{18}\text{O}$ values ($+8\text{‰}$ to $+9\text{‰}$ SMOW ; Figure 3A).

Bromine concentrations and other ion relationships with Na^+ and Cl^- provide additional insights into the origins of subsurface waters. Bromine is preferentially excluded from halite and most other minerals precipitated from evaporating seawater (Herrmann, 1972). As a result, waters precipitating halite should have progressively increasing Br^- in the

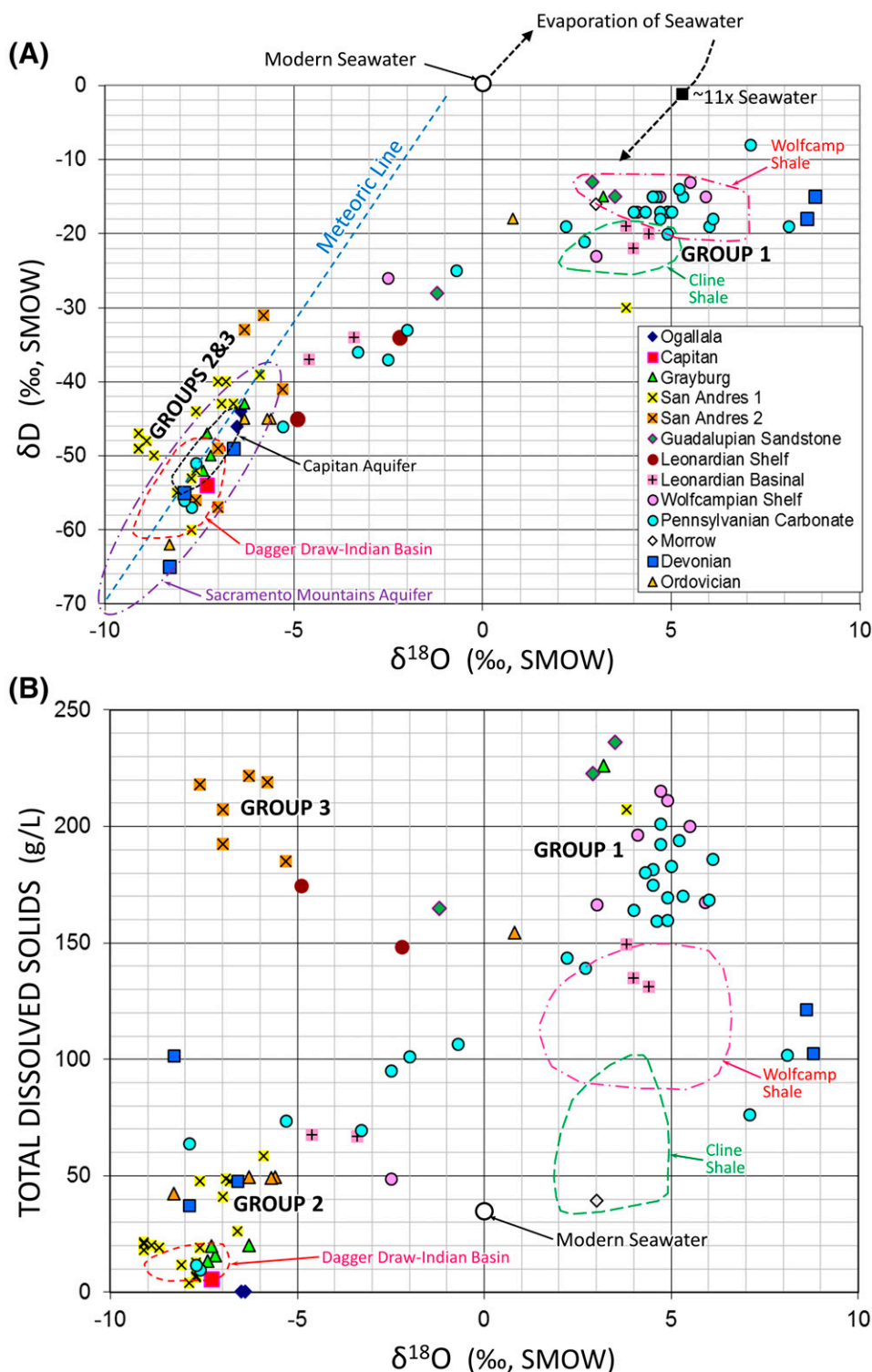
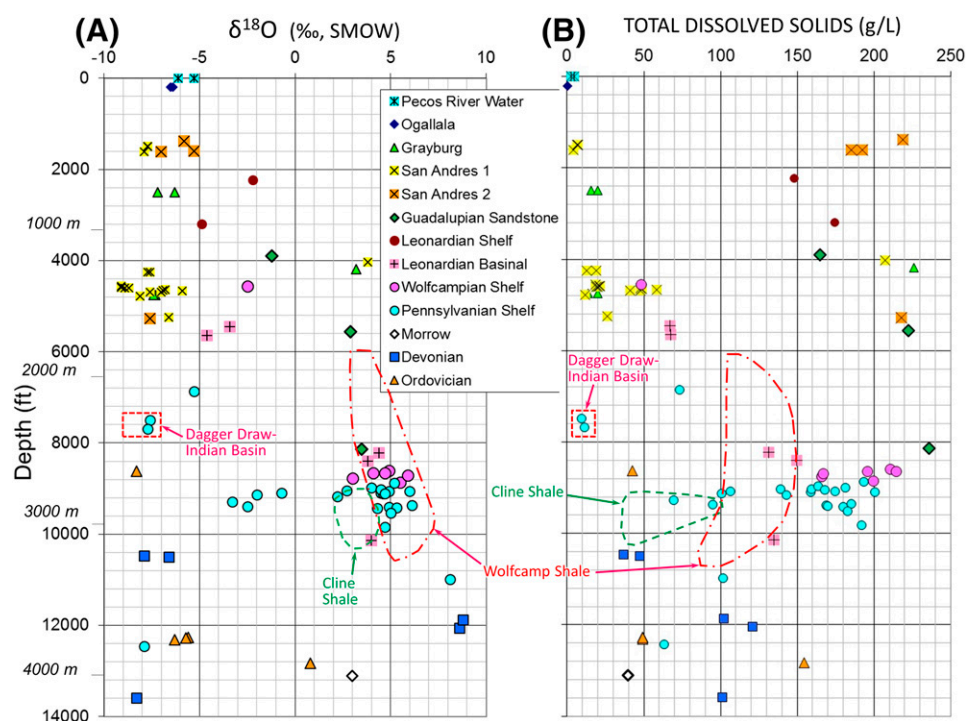


Figure 3. (A) Plot of $\delta^{18}\text{O}$ versus δD for water samples. Blue dashed line is the meteoric precipitation line from Craig (1961). Data for meteoric waters from the Sacramento Mountains aquifer are from Eastoe and Rodney (2014). Black dashed line and arrows show the trajectory of highly evaporated seawater from Holser (1979). Data for waters from the Wolfcamp and Cline shales are from Engle et al. (2016). Dagger Draw and Indian Basin water data are from Pennsylvanian carbonates reported by Barnaby et al. (2004). Capitan aquifer data are from Lambert and Harvey (1987). Group 1 waters have $\delta^{18}\text{O}$ values that cluster from +2‰ to +9‰ SMOW (standard mean ocean water), and δD values cluster from -12‰ to -24‰ SMOW. Groups 2 and 3 have $\delta^{18}\text{O}$ values of -5‰ to -10‰ SMOW, and δD values of -30‰ to -70‰ SMOW. San Andres 2 samples have high salinity (>150 g/L) and low $\delta^{18}\text{O}$. San Andres 1 samples represent the remainder of the San Andres samples. (B) Plot of $\delta^{18}\text{O}$ versus total dissolved solids (TDS). Group 1 waters generally have $\delta^{18}\text{O}$ values of +2‰ to +9‰ SMOW and TDS of 100–240 g/L. Group 2 waters have $\delta^{18}\text{O}$ values of -5‰ to -10‰ SMOW, and low TDS (4–70 g/L). Group 3 waters have $\delta^{18}\text{O}$ values of -5‰ to -10‰ SMOW, and high TDS (180–230 g/L).

residual waters. Halite precipitated from the evaporated seawater should have low Br^- relative to the precipitating waters (i.e., seawater) because Br^- is preferentially excluded from halite. Hence, waters that gained their salinity by dissolving halite should also have low Br^- . Bromine in subsurface waters can

also come from organic material (Engle et al., 2016) complicating its interpretation. When Br^- is plotted against $\delta^{18}\text{O}$ (Figure 7), Permian Basin waters with $\delta^{18}\text{O}$ greater than seawater generally have high Br^- concentrations, and waters with $\delta^{18}\text{O}$ less than seawater generally have low Br^- concentrations. Hence,

Figure 4. (A) Plot of $\delta^{18}\text{O}$ for Permian Basin waters versus depth. (B) Plot of total dissolved solids for Permian Basin waters versus depth. Data for waters from the Wolfcamp and Cline shales are from Engle et al. (2016). Dagger Draw and Indian Basin water data are from Pennsylvanian carbonates reported by Barnaby et al. (2004). San Andres 2 samples have high salinity (>150 g/L) and low $\delta^{18}\text{O}$. San Andres 1 samples represent the remainder of the San Andres samples. SMOW = standard mean ocean water.



the waters with low $\delta^{18}\text{O}$ values and low Br^- concentrations (below seawater) are interpreted as meteoric waters that gained most of their salinity by dissolution of halite. Permian Basin waters with high $\delta^{18}\text{O}$ ratios and high Br^- concentrations (above seawater) are interpreted as seawater that was intensely evaporated and precipitated halite (similar to Bein and Dutton, 1993; Stueber et al., 1998). Waters with Br^- concentrations of 400–1000 mg/L (Figure 7) correspond to 6–20 times seawater concentration (McCaffrey et al., 1987).

Permian Basin waters can be divided into three groups based on $\delta^{18}\text{O}$ and concentrations of Br^- , TDS, Na^+ , and Cl^- (Table 2). The geochemistry of these groups is related to evaporation of seawater or influx of meteoric (fresh) water. In the Permian Basin, significant amounts of halite were only deposited in the upper Permian (interval from San Andres [Guadalupian] to Salado [Ochoan]). Hence, highly saline waters that precipitated halite came from that period of time, and waters that dissolved halite, must have dissolved halite from those stratigraphic intervals (Figure 9). Analyses of halite from the Castile and Salado Formations in the Permian Basin have Br^- concentrations similar to group 3 water that dissolved halite (calculated from data in table 10 of Moore, 1960; Raup and Hite, 1978). Group 1 waters have high $\delta^{18}\text{O}$, high TDS, relatively high Br^- , and high Na^+

and Cl^- concentrations with Cl^- in distinctly higher molar amounts than Na^+ . Group 1 waters are interpreted to be highly evaporated late Permian seawater (Figure 9A). Group 2 waters with low $\delta^{18}\text{O}$, low TDS, and relatively low Br^- , are interpreted as Neogene meteoric water (rainwater) entering the Permian Basin from mountains to the northwest (Figures 1, 9B). Group 3 waters have low $\delta^{18}\text{O}$, high TDS, relatively low Br^- , and high Na^+ and Cl^- present in approximately equal molar amounts. Group 3 waters are interpreted as Neogene meteoric water that dissolved significant amounts of upper Permian halite as they entered the subsurface (Table 2). A number of other formation waters appear to be mixtures of those three groups.

Group 2 and 3 waters have Mg^{2+} and Ca^{2+} concentrations that are different from group 1 waters. Most group 2 and 3 waters have Ca^{2+} and SO_4^{2-} (Figure 6A) in similar molar amounts, and hence were likely the result of meteoric waters dissolving anhydrite or gypsum. Magnesium concentrations in group 2 and 3 waters are generally low (<8000 mg/L) and are not proportional to Cl^- (Table 1).

Group 1 waters generally have high Ca^{2+} , low SO_4^{2-} , and low Mg^{2+} concentrations (Figure 6A, B). Group 1 waters have distinctly more Ca^{2+} and distinctly less Mg^{2+} than would be expected for evaporated seawater (Figure 6B), suggesting that group 1

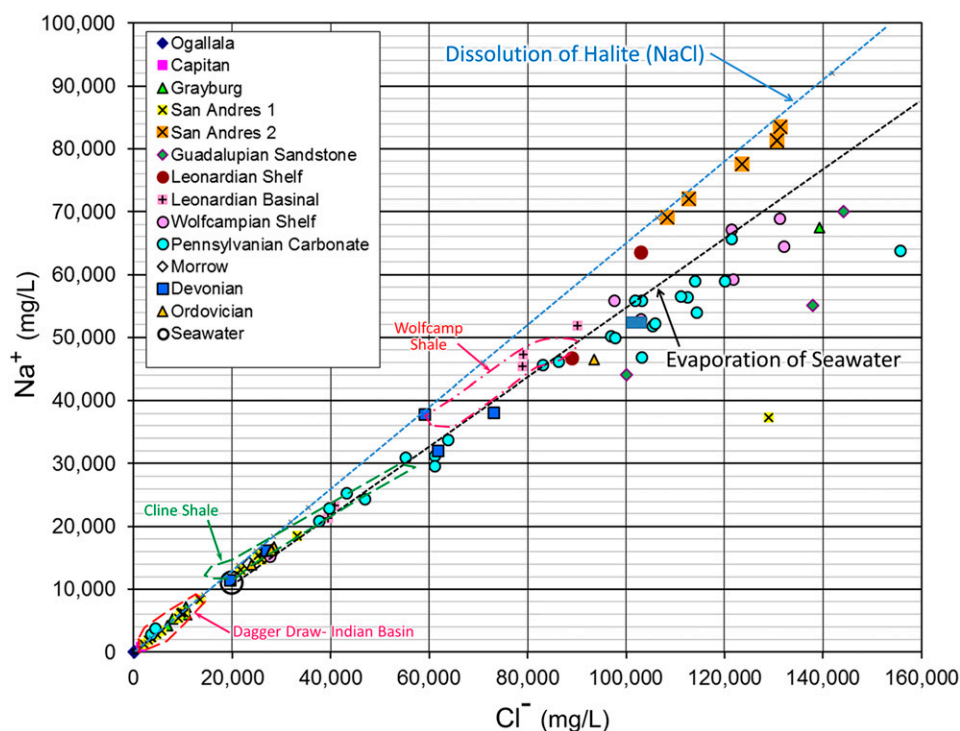


Figure 5. Plot of Na^+ versus Cl^- for Permian Basin water data. Black dashed line for evaporation of modern seawater is from data in McCaffrey et al. (1987). Blue dashed line for dissolution of halite assumes equal molar amounts of Na^+ and Cl^- . Data for waters from the Wolfcamp and Cline shales are from Engle et al. (2016). Dagger Draw and Indian Basin water data are from Pennsylvanian carbonates reported by Barnaby et al. (2004). San Andres 2 samples have high salinity (>150 g/L) and low $\delta^{18}\text{O}$. San Andres 1 samples represent the remainder of the San Andres samples.

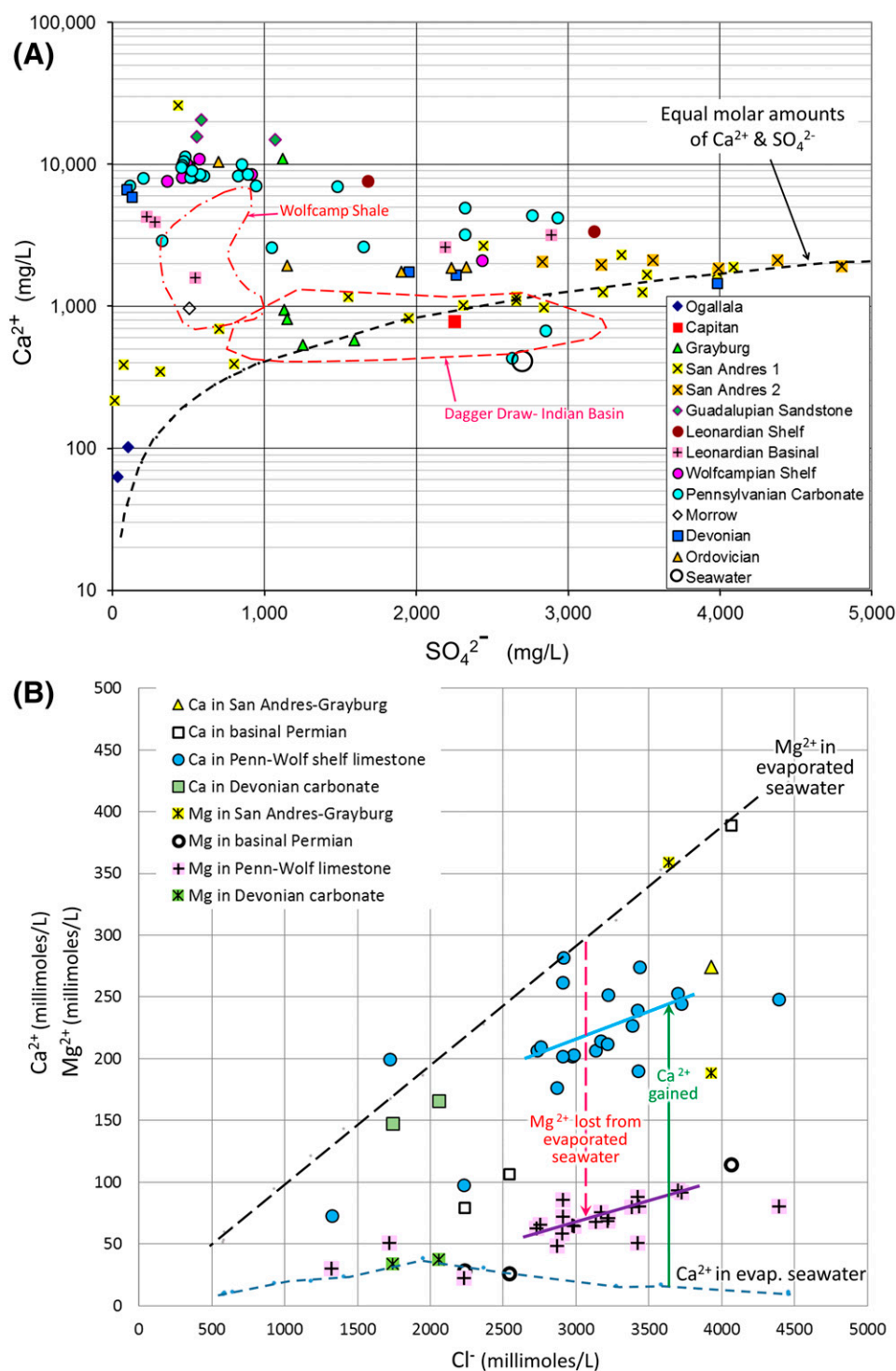
waters have been involved in dolomitization. Relative to evaporated seawater, the excess Ca^{2+} in many group 1 waters is approximately equal on a molar basis to the deficit of Mg^{2+} (Figure 6B), supporting significant dolomitization by group 1 waters.

The San Andres and Grayburg Formations are dominated by group 2 and 3 waters (Figure 10A). Some San Andres and Grayburg waters from the Northern and Northwest Shelves have high salinities (>180 g/L) and are group 1 and 3 waters, whereas San Andres and Grayburg waters on the Central Basin platform have low salinities (<50 g/L) making them group 2 waters (Figure 10A). San Andres and Grayburg water $^{87}\text{Sr}/^{88}\text{Sr}$ ratios are generally consistent and low (0.70707–0.70852) with the two high $\delta^{18}\text{O}$ samples having very low $^{87}\text{Sr}/^{88}\text{Sr}$ ratios (Table 1). The group 2 and 3 waters in the San Andres and Grayburg Formations have consistent $^{87}\text{Sr}/^{88}\text{Sr}$ ratios (most 0.70723–0.70819) that are similar to seawater during deposition of the San Andres and Grayburg Formations (Figure 8), and hence could have come from dissolution of parts of those formations. The lowest $^{87}\text{Sr}/^{88}\text{Sr}$ ratios in waters (0.70707 and 0.70723) are observed in San Andres and Grayburg waters with high $\delta^{18}\text{O}$ values, which is consistent with derivation from latest Permian (Ochoan) seawater (Figure 9A). The other San Andres and

Grayburg waters probably derived much of their strontium from dissolution of anhydrites in the San Andres and Grayburg Formations that would have had $^{87}\text{Sr}/^{88}\text{Sr}$ that were similar to seawater at their time of deposition (0.7070). Group 3 waters have distinctly higher Sr concentrations (40–70 mg/L) than San Andres group 2 waters (3–20 mg/L; Figure 8).

Formation waters in shallow marine Pennsylvanian and lower Wolfcampian carbonates on the eastern Central Basin platform and Midland Basin are generally group 1 waters (high $\delta^{18}\text{O}$ values, high TDS, and high Br^- concentrations; Figure 10B). However, waters in similar shallow marine Pennsylvanian and lower Wolfcampian carbonates on the western side of the Delaware Basin are group 2 waters (low $\delta^{18}\text{O}$ values, low TDS, and low Br^- ; Table 1; Barnaby et al., 2004). The strontium isotopic composition of waters from shallow marine Pennsylvanian and lower Wolfcampian carbonates are relatively consistent with most $^{87}\text{Sr}/^{88}\text{Sr}$ ratios between 0.70856 and 0.70929 in formation waters with both high and low $\delta^{18}\text{O}$ values (groups 1 and 2; Figure 8). These $^{87}\text{Sr}/^{88}\text{Sr}$ ratios are higher than seawater from the Mississippian to the Eocene (Burke et al., 1982; Veizer et al., 1999); however, most are slightly below the $^{87}\text{Sr}/^{88}\text{Sr}$ ratio that Register and Brookins (1980) derived for waters precipitating Salado halite,

Figure 6. (A) Plot of Ca^{2+} versus sulfate (SO_4^{2-}) for Permian Basin waters. Black dashed curve shows trend produced by dissolution of CaSO_4 and assumes equal molar amounts of Ca^{2+} and SO_4^{2-} . Field of waters from the Wolfcamp shale is from Engle et al. (2016). Dagger Draw and Indian Basin water data are from Pennsylvanian carbonates reported by Barnaby et al. (2004). San Andres 2 samples have high salinity (>150 g/L) and low $\delta^{18}\text{O}$. San Andres 1 samples represent the remainder of the San Andres samples. (B) Plot of Ca^{2+} and Mg^{2+} versus Cl^- for data with $\delta^{18}\text{O} > 3.0\text{‰}$ SMOW (standard mean ocean water) (group 1). Data are shown relative to curves of Ca^{2+} and Mg^{2+} in evaporated seawater from McCaffrey et al. (1987). Most of these data show an increase in Ca^{2+} and decrease in Mg^{2+} relative to the precursor evaporated seawater. On a molar basis, the increase in Ca^{2+} is very similar to the decrease in Mg^{2+} , suggesting that change in the water chemistry was caused by dolomitization. The change is approximately 200–250 mmol/L for saline waters with >2500 mmol/L of chloride.



suggesting substantial input of strontium from the highly evaporated seawater that precipitated the Salado salts. The waters precipitating the Salado salt apparently had $^{87}\text{Sr}/^{88}\text{Sr}$ ratios higher than late Permian seawater because of input radiogenic strontium from siliciclastic sands, silts, and clay

carried by wind and streams flowing into the Salado evaporative basin (Engle et al., 2016). Dolomitization of Pennsylvanian and Wolfcampian limestones by the group 1 waters probably exchanged strontium with the host limestone causing formation waters to have $^{87}\text{Sr}/^{88}\text{Sr}$ ratios between the original Salado derived

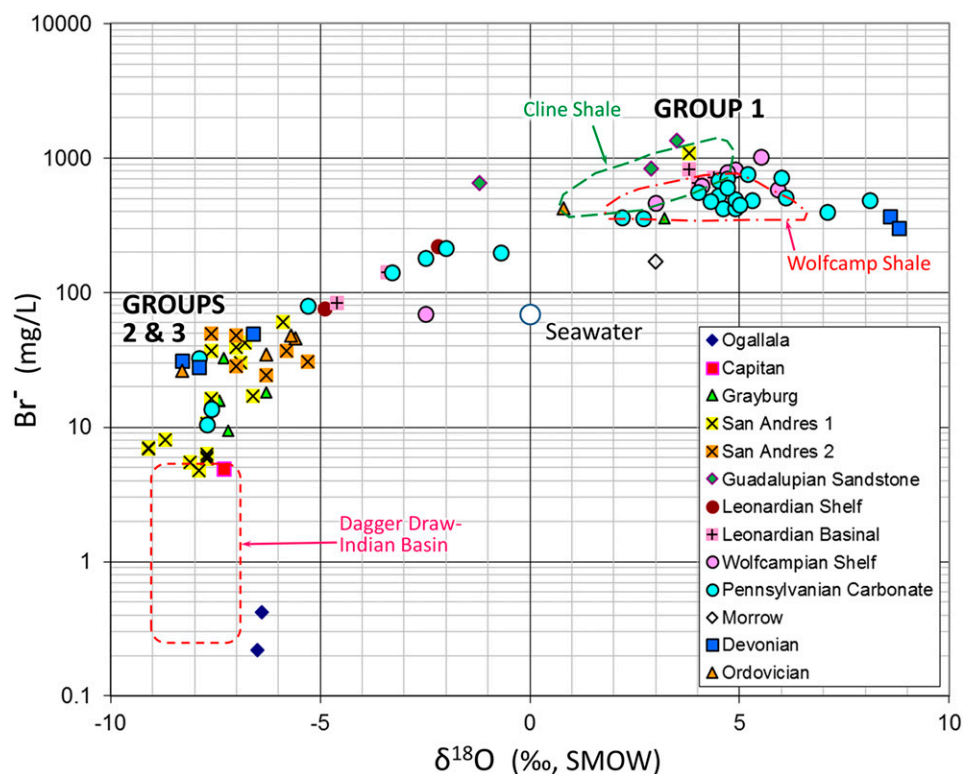


Figure 7. Plot of Br^- versus $\delta^{18}\text{O}$. Group 1 waters have high $\delta^{18}\text{O}$ and high Br^- concentrations that are associated with evaporated seawater. Group 2 and 3 waters have low $\delta^{18}\text{O}$ and low Br^- (less than seawater) that are associated with meteoric water that may have dissolved halite. Data for waters from the Wolfcamp and Cline shales are from Engle et al. (2016). Dagger Draw and Indian Basin water data are from Pennsylvanian carbonates reported by Barnaby et al. (2004). San Andres 2 samples have high salinity (>150 g/L) and low $\delta^{18}\text{O}$. San Andres 1 samples represent the remainder of the San Andres samples. SMOW = standard mean ocean water.

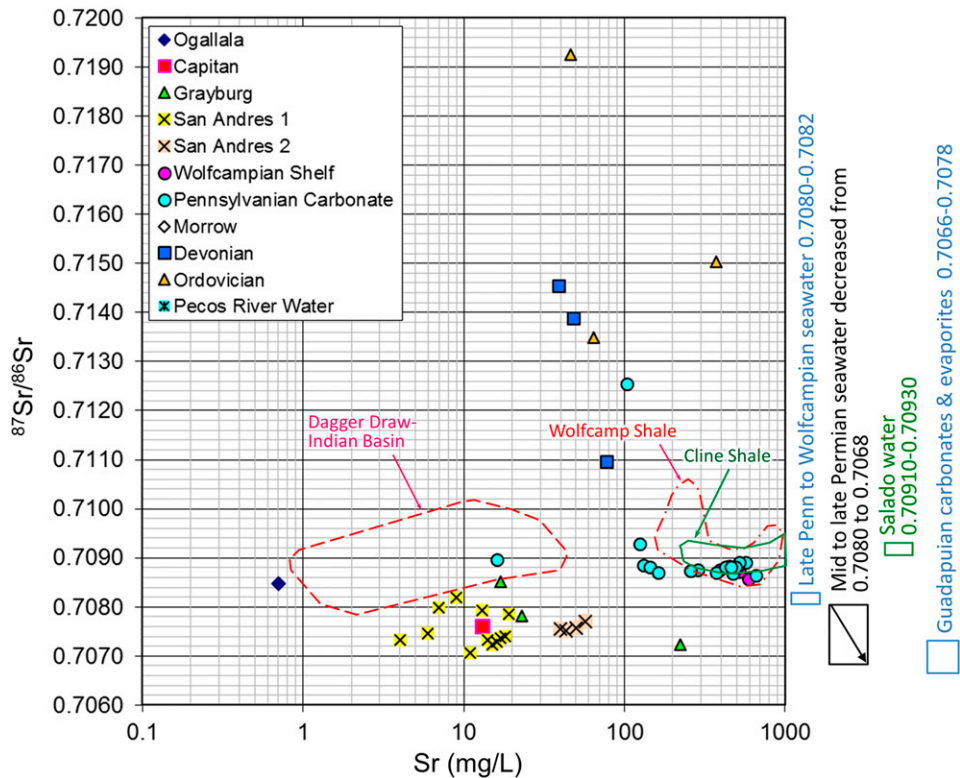
water and Pennsylvanian–Wolfcampian seawater (Figure 8).

Waters in Ordovician (Ellenburger) and Devonian carbonates have variable TDS, $\delta^{18}\text{O}$ values, and Br^- concentrations. We do not have enough data from those intervals to show geographic patterns. Several formation waters from Ordovician and Devonian carbonates have low TDS, low $\delta^{18}\text{O}$ values, and low Br^- concentrations (group 2) suggesting waters that were originally meteoric. Two waters from the Devonian of Bryant G Field have moderate salinity, high $\delta^{18}\text{O}$ values, and high Br^- concentrations (group 1) suggesting they came from highly evaporated late Permian seawater. Their $\delta^{18}\text{O}$ values (+8 to +9) are higher than any other samples and might have been increased by rock–water interaction (similar to Land and Prezbindowski, 1981). Unfortunately, those Devonian group 1 samples were not analyzed for strontium isotopes (Table 1). Group 2 water $^{87}\text{Sr}/^{88}\text{Sr}$ ratios in Ordovician and Devonian strata (0.71097–0.71454; Figure 8) are higher than observed in seawater during the entire Phanerozoic (Veizer et al. 1999), suggesting strontium input from a radiogenic source. The waters with high $^{87}\text{Sr}/^{88}\text{Sr}$ ratios have meteoric characteristics (low $\delta^{18}\text{O}$ values, low TDS, and low Br^- ; group

2). The high $^{87}\text{Sr}/^{88}\text{Sr}$ ratios may indicate that these meteoric waters flowed through the radiogenic basement before entering the Ellenburger and Devonian carbonate intervals and acquired radiogenic strontium from those rocks.

Several samples in this study were collected from basal Permian sandstone and carbonates. Most basal samples (“Leonardian Basinal” and “Guadalupian Sandstone”) have relatively high $\delta^{18}\text{O}$ values, moderate to high salinities (131–236 g/L), and high Br^- concentrations (group 1), suggesting the waters were derived from brines associated with evaporation of late Permian seawater and halite precipitation. Some of the most saline (highest TDS) water samples come from Permian sandstones in the northeastern Delaware Basin (samples 33, 34 with TDS of 236 and 223 g/L, respectively). McNeal (1965) also shows very high salinities in the Permian basinal sands in the eastern part of the Delaware Basin. The reason for the higher salinity (TDS) in waters in Permian sands in the eastern part of the basin is not geochemically obvious. It is possible that eastward tilting of the Delaware Basin caused eastward infiltration of denser water to the more deeply buried Delaware sandstones. A Grayburg

Figure 8. Plot of strontium isotope ratios versus strontium concentration for Permian Basin waters. Fields for Pennsylvanian (Penn) and Permian seawater are from curves in Veizer et al. (1999). Strontium isotope values for Pennsylvanian and Wolfcampian shelfal carbonates are above contemporaneous and late Permian seawater, but are slightly less than values derived for waters precipitating Salado halite (Register and Brookins, 1980). Data for waters from the Wolfcamp and Cline shales as well as Guadalupian carbonates and evaporites are from Engle et al. (2016). Dagger Draw and Indian Basin water data are from Pennsylvanian carbonates reported by Barnaby et al. (2004). Data from the literature are adjusted to a National Bureau of Standards 987 standard $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.71014. San Andres 2 samples have high salinity (>150 g/L) and low $\delta^{18}\text{O}$. San Andres 1 samples represent the remainder of the San Andres samples.



sample (no. 4) as well as those Delaware sandstone waters (sample nos. 33 and 34 in Table 1) have very high TDS with $\delta^{18}\text{O}$ and δD values characteristic of group 1 waters. Extreme evaporation of seawater can cause a similar trend (Holser, 1979; McCaffrey et al., 1987). A few samples from basinal intervals have moderate to low $\delta^{18}\text{O}$ values, moderate to low TDS (60–70 g/L), and moderate Br^- concentrations, and hence are hybrid waters or mixtures of our three groups of waters.

Waters from the Cline (Cisco) and Wolfcamp shales in the Midland Basin have high $\delta^{18}\text{O}$, δD , and high Br^- values like our group 1 waters, but have moderate to low TDS, Cl^- , and Na^+ concentrations (Figures 3–5, 7; Engle et al., 2016). Engle et al. (2016) interpret waters in the Cline and Wolfcamp shales as coming from evaporated late Permian seawater, similar to our group 1 waters, but with clays acting as semipermeable membranes preventing complete diffusion of ions into those shales.

Table 2. Geochemical Characteristics of Groups of Permian Basin Waters

Group	$\delta^{18}\text{O}$, ‰ SMOW	δD , ‰ SMOW	TDS, g/L	NaCl Concentration	Br Concentration	Main Intervals
1	+2 to +9	–25 to –8	100–240	High; molar Cl more than molar Na	Greater than seawater	Wolfcamp and Pennsylvanian carbonate shelf; Pennsylvanian and Permian basinal sands and shales
2	–9.5 to –4.5	–65 to –30	5–75	Low	Less than seawater	Grayburg, San Andres, Devonian, Ellenburger
3	–8 to –4.5	–55 to –30	170–235	High; molar amounts of Cl and Na are similar	Greater than seawater	San Andres

Abbreviations: $\delta^{18}\text{O}$ = stable oxygen; δD = stable deuterium; SMOW = standard mean ocean water; TDS = total dissolved solids.

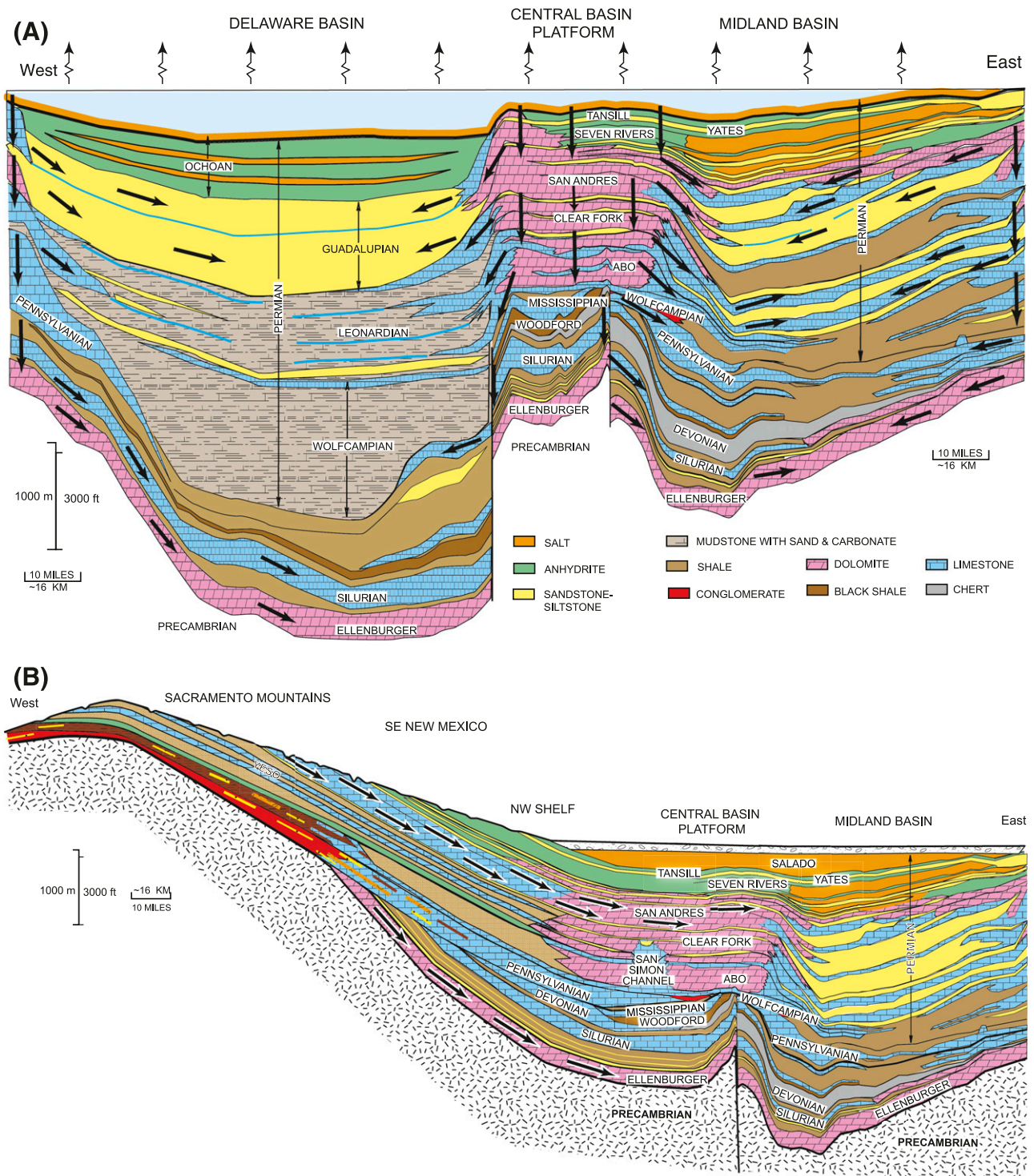
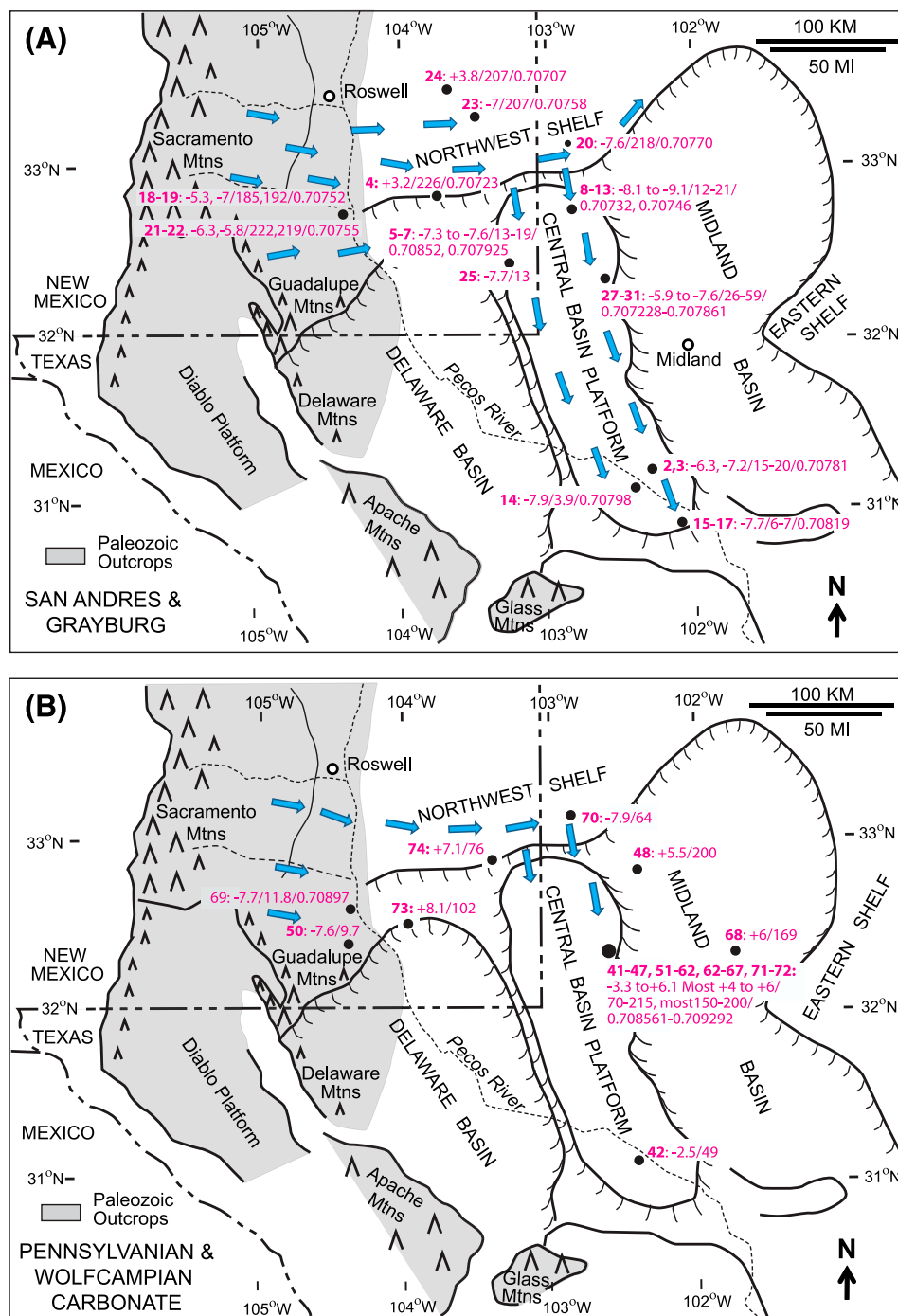


Figure 9. (A) Schematic cross section across the Permian Basin showing stratigraphy near the end of the Permian. Highly saline waters (group 1) were generated by evaporation of seawater during halite precipitation and deposition near the end of the Permian, and those very dense waters (black arrows) descended into Paleozoic strata displacing most of the preexisting formation waters in the Permian Basin. Base cross section is modified from data in Matchus and Jones (1984). (B) Schematic cross section from the Sacramento Mountains in southeast New Mexico (left) across the Permian Basin (to right) showing current structure and stratigraphy. Meteoric waters (groups 2 and 3; arrows) started in the Sacramento Mountains and descended into the San Andres Formation across the northern shelf and Central Basin platform. Meteoric waters also descended into the Ellenburger, though the connection to surface charging is not obvious in this section. Eastern (right) part of the base cross section is modified from Matchus and Jones (1984).

Figure 10. (A) Map showing data for the San Andres and Grayburg intervals in the Permian Basin and adjacent areas. Four numbers are shown at most locations: Sample number(s)/ $\delta^{18}\text{O}$ (‰)/total dissolved solids (grams per liter)/ $^{87}\text{Sr}/^{86}\text{Sr}$ values. Some locations do not have $^{87}\text{Sr}/^{86}\text{Sr}$ values. Sample numbers and additional data at those locations are shown in Table 1. Blue arrows show probable directions of Neogene meteoric water flow. (B) Map of the Permian Basin and adjacent areas showing water data for upper Pennsylvanian and Wolfcampian shelfal carbonate strata. Blue arrows show possible directions of Neogene meteoric water flow. Mtns = Mountains.



HISTORY OF FORMATION WATERS IN THE PERMIAN BASIN

Most strata in the Permian Basin were deposited in seawater. Although many stratigraphic intervals experienced repeated subaerial exposure and infiltration by freshwater, upon subsequent transgressions, seawater would have displaced the freshwater because of its greater density. This displacement by marine

waters is observed in all major modern carbonate provinces, for example the Bahamas (Swart et al., 2001) and Pacific atolls (Schlanger, 1963).

The group 1 brines with high $\delta^{18}\text{O}$ and δD values (+3‰ to +9‰ SMOW and δD of -22‰ to -12‰ SMOW, respectively) apparently entered the subsurface in the late Permian when halite deposition was widespread (Figure 9A). Those hypersaline Permian waters appear to occur now wherever

Neogene meteoric water is not present. From that distribution and other factors, we postulate that prior to the infiltration of Neogene meteoric waters, those highly saline late Permian waters (group 1) filled most of the Permian Basin. The halite-rich strata of the uppermost Guadalupian and Ochoan were deposited over almost the entire Permian Basin, hence dense brines that formed during deposition of those formations could infiltrate the Permian Basin's entire Paleozoic section from many different entry points (probably broad areas) across the Permian Basin. These brines have a density $>1.15 \text{ g/cm}^3$, which gives them substantial gravitational energy to move down and displace all previous, less dense formation waters.

The pervasive replacement of most Permian Basin formation waters by group 1 waters (Figure 9A) is supported by the apparent presence of these brines in some of the stratigraphically oldest (deepest) and youngest intervals as well as low-permeability basinal sandstones and shale (Table 1; Engle et al., 2016). Group 1 waters came from the Devonian in two wells. One sample from the Ellenburger (sample no. 85) appears to contain a slightly altered (diluted) group 1 water. Areas of very high-salinity water occur elsewhere in Ordovician and Devonian strata (McNeal, 1965), suggesting that many group 1 waters are present in the deep Ordovician as well as the Devonian in the Permian Basin. A group 1 water was also recovered from the Grayburg (sample no. 4, Figure 10A; Table 1), one of the shallowest reservoir intervals in the Permian Basin.

The late meteoric waters (groups 2 and 3) probably entered the Permian Basin from the west and northwest. Potentiometric maps indicate that recent flow in most Permian Basin formations has been mainly from west to east (McNeal, 1965; Figure 9B). Modern rainwater in the Guadalupe Mountains and Carlsbad area varies in $\delta^{18}\text{O}$ from -2.3‰ to -14.1‰ SMOW (Hill, 1996, appendix 4). Spring waters from McKittrick Canyon in the Guadalupe Mountains have $\delta^{18}\text{O}$ values of -8.1‰ SMOW. Our samples from the Pecos River have $\delta^{18}\text{O}$ values of -6.1‰ and -5.3‰ SMOW at Artesia and Loving (Figure 1), respectively. Our samples of the Ogallala aquifer have $\delta^{18}\text{O}$ values of -6.4‰ and -6.5‰ SMOW. Eastoe and Rodney (2014) sampled waters in Sacramento Mountains and found $\delta^{18}\text{O}$ values from -7.9‰ to -10.2‰ SMOW. Hence, meteoric waters from the Sacramento Mountains and Pecos River

drainage have $\delta^{18}\text{O}$ values in the range of -5.3‰ to -10.2‰ SMOW, which is very similar to the group 2 and 3 meteoric waters ($\delta^{18}\text{O}$ of -9.2‰ to -5‰ SMOW).

That source of water is also consistent with hydrogen isotope (δD) data. Modern rainwater in the Guadalupe Mountains and Carlsbad area varies in δD from -19‰ to -97‰ SMOW (Hill, 1996, appendix 4). Spring waters in McKittrick Canyon have δD of -50‰ SMOW. Our samples of the Pecos River have δD values of -50‰ and -46‰ SMOW at Artesia and Loving, respectively. Our samples of the Ogallala aquifer have δD of -44‰ and -46‰ SMOW. Eastoe and Rodney (2014) found δD of waters in Sacramento Mountains to range from -53‰ to -71‰ SMOW. Hence, meteoric waters from the Guadalupe Mountains and Pecos River drainage have δD in the range of -44‰ to -50‰ SMOW, which is similar to the water compositions in the group 2 and 3 waters (δD of -30‰ to -56‰ SMOW). Therefore, hydrogen isotope data (δD) also support meteoric waters in the Permian Basin (group 2 and 3) coming from the Guadalupe and Sacramento Mountains on the west side of the Permian Basin (Figures 1, 9B).

The basin was originally overlain by the salts of the Salado Formation. After uplift, the initial meteoric waters would have dissolved halite before entering the deeper subsurface. Hence, the saline meteoric waters (group 3) may represent some of the earlier Neogene meteoric waters entering the Permian Basin, however, dissolution of halite in the Salado and Castile continues through the present, and hence saline meteoric waters continue to form and descend into the basin.

San Andres and Grayburg

After entering the Grayburg and San Andres Formations in southwest New Mexico, Neogene meteoric waters probably flowed laterally to the east and south (Figures 9B, 10A) through higher permeability conduits along the margin of the northern shelf and Central Basin platform. This is a corridor of low-salinity San Andres waters shown in McNeal (1965), and this flow route is consistent with a potentiometric map in McNeal (1965). This is similar to the model in Trentham et al. (2012). The waters have hydraulic head established by relatively high elevations of the San Andres Formation on the eastern flank of the Sacramento Mountains and start in a confined

artesian aquifer on the northwest side of the Delaware Basin (Land and Newton, 2007). Those waters flowed to the southernmost part of the Central Basin platform. The distance from the eastern edge of the mountains in New Mexico to the southern Permian Basin is approximately 300 km (185 mi) (Figure 1B). Uplift started circa 24 Ma (Horak, 1985). Waters traveling 185 mi (300 km) in 24 m.y. would require a flow rate of only 0.4 ft (12.5 cm)/yr, which is reasonable for active aquifer systems (Alley et al., 1999).

In a few areas near the northern, updip limits of permeable dolomites, flow in San Andres and Grayburg Formations was apparently protected from the Neogene meteoric waters, and the saline Permian water (group 1) remains (sample no. 4, Grayburg; no. 24, San Andres; Figure 9A). Note that the lateral facies change from permeable dolomites to low-permeability anhydritic rock is much further south in the Grayburg Formation than in the San Andres Formation (Ramondetta, 1982; Kerans and Kempter, 2002). Most of the San Andres waters have relatively low salinity, except for some waters in the north and west (group 3 waters) that have high Na^+ and Cl^- concentrations in similar molar concentrations suggesting that they dissolved halite. The upper San Andres Formation contains halite in the northwest part of the Permian Basin (Ramondetta, 1982), therefore, the salt could also have been dissolved from the San Andres, though much of it may have come from dissolution of the Salado Formation.

Basinal Sandstones and Carbonates

Our water samples from Permian basinal sandstones and carbonates generally have moderate to high salinity with intermediate to high $\delta^{18}\text{O}$ values (Figure 3). Similar characteristics were observed by Engle et al. (2016) for lower Permian basinal shales in the Midland Basin (TDS of 36,000–125,000 mg/L and $\delta^{18}\text{O}$ of +1‰ to +7‰ SMOW for Cline and Wolfcamp shales). Waters derived from late Permian evaporated seawater moved down because of their high density and filled the Permian Basin including basinal sandstones, carbonates and shales (Figure 9A). These evaporated late Permian waters were modified as they entered the shale decreasing TDS (Engle et al., 2016). The basinal strata, especially shale and most of the Permian basinal sandstone-siltstone intervals,

have limited regional permeability, which probably limited the intrusion of Neogene meteoric waters from the mountains of southeast New Mexico into those basinal strata during the last 24 m.y. Salinity data from McNeal (1965) show a trend of low salinity in updip Delaware sandstones in the west part of the Delaware Basin. Those sandstones outcrop in the Delaware and Guadalupe Mountains and, hence, meteoric water is probably entering Delaware sandstones there and flowing down dip (to the east); however, the permeability and amount of water going into the Delaware sandstones has apparently not been sufficient to replace all of the saline group 1 waters in those basinal sandstones.

Pennsylvanian and Wolfcampian Shelf and Platform Carbonates

The Pennsylvanian and Wolfcampian shelf and platform carbonate interval is dominated by the saline latest Permian evaporated seawater (group 1), however, Neogene (group 2) waters occur in some parts of the basin in this interval (Figures 9B, 10B). Our data set from the Pennsylvanian and Wolfcampian shelf section is not robust regionally, and hence does not show a continuous flow path for the meteoric waters that occur in that interval. Data in Bein and Dutton (1993) suggest low-salinity waters along the southern margin of the northern shelf in the Pennsylvanian and that corresponds to a low-salinity area in maps of the Strawn and Wolfcampian by McNeal (1965). Therefore, the low-salinity group 2 waters in the Pennsylvanian and Wolfcampian section were originally probably derived from meteoric waters in southeast New Mexico, and then came through narrow corridors in Pennsylvanian and lower Wolfcampian strata from the west (Figures 9B, 10B).

Devonian and Ellenburger

Waters from Devonian and Ellenburger (Ordovician) strata vary geographically in the Permian Basin and include saline brines in some fields, but low-salinity meteoric waters in many other fields. McNeal (1965) shows very high-salinity waters in the Devonian and Ellenburger in southeastern Delaware Basin and southern Central Basin platform and low-salinity waters at many other places in the Permian Basin,

especially along a northwest–southeast trend emanating from the eastern Sacramento Mountains area and Artesia area of New Mexico. Engle et al. (2016) also observed meteoric waters in Ordovician and Devonian strata and postulated a “Deep Basin Meteoric Aquifer System” in the Permian Basin with low-salinity and low $\delta^{18}\text{O}$ values. Evaporated late Permian seawater descending into the Ellenburger and Devonian across the entire basin during the late Permian is suggested by (1) a few group 1 waters and mixtures with group 1 in this study, and (2) very high salinities noted in those intervals in other areas by McNeal (1965).

Our group 2 waters as well as low-salinity water described by McNeal (1965) and meteoric waters described in these intervals by Engle et al. (2016) suggest meteoric waters from the mountains of southeast New Mexico also reached Ellenburger and Devonian strata in many parts of the basin during the Neogene. The exact path that those waters flowed is not clear because Ordovician and Devonian strata do not outcrop on the eastern side of the Sacramento Mountains (Figure 9B). The radiogenic strontium isotope ratios in these formation waters suggest that the meteoric waters may have flowed through the radiogenic basement. However, those meteoric waters have not reached all parts of the Permian Basin. Flow rates required to get group 2 meteoric waters to Devonian and Ordovician strata in the southern Permian Basin would be similar to the calculation for group 2 waters in the San Andres. Uplift started circa 24 Ma (Horak, 1985). Waters traveling 185 mi (300 km) in 24 m.y. would only require a flow rate of 0.4 ft (12.5 cm)/yr, which is reasonable for active aquifer systems (Alley et al., 1999).

DISCUSSION

A few ideas presented here deserve further discussion.

Volumetrics for Group 1 Water

Could enough water have been produced during deposition of the Salado to fill all the pores in the subsurface of the Permian Basin? Below are some simple calculations. The Salado Formation is commonly 1000–2000 ft (300–600 m) thick (Matchus

and Jones, 1984; Hill, 1996). Approximately 240 ft (73 m) of seawater will evaporate to form 3 ft (1 m) of halite (Dean, 1978). Approximately 1500 ft (457 m) of Salado salt required approximately 109,500 ft (33,375 m; 1500×73 ft [457×73 m]) of cumulative seawater (across the basin) to come into the Permian Basin to form the Salado salts. Assuming the average thickness of Permian Basin strata is approximately 12,000 ft (3658 m; estimate from cross sections by Matchus and Jones, 1984; Figure 9A) and assuming 10% average porosity, 1200 ft (366 m) of water would be required across the basin to fill the pores. This is only 1/90 of the minimum water required to precipitate the Salado. Hence, plenty of water could be produced during Salado deposition to infiltrate and fill pores in the Permian Basin.

Salinities of Group 1 Waters Are Lower Than Expected for Seawater Evaporated to Halite Saturation

Although group 1 waters are highly evaporated seawater that precipitated halite, the waters are not as saline as would be expected for evaporated Permian seawater that precipitated halite. Engle and Blondes (2014) and Engle et al. (2016) indicate that evaporated Permian seawater that precipitated halite should have a salinity of 311 g/L, which is above most of our group 1 waters that are commonly 100–240 g/L (Figure 3B). Mixtures of variable stages of evaporated seawater could produce the observed $\delta^{18}\text{O}$, δD , and TDS concentrations observed in our group 1 waters. For example, when seawater concentrated by a factor of 4 is mixed with seawater concentrated by a factor of 45, the resulting brine has a salinity of 220 g/L with $\delta^{18}\text{O}$ and δD similar to our group 1 waters (Engle et al., 2016). Hence, group 1 waters likely represent a mixture of Permian seawater at various stages of evaporation.

Rock–Water Interaction Altering Stable Oxygen Isotopic Composition of Subsurface Waters

Rock–water interactions have altered the stable oxygen isotopic composition of many limestones during subaerial exposure (Allan and Matthews, 1982, among others). This is expected when meteoric

waters dissolve and reprecipitate carbonate because the amount of oxygen in water far exceeds the amount of oxygen in dissolved carbonate; hence the reprecipitated carbonate largely equilibrates with the water in systems with active water circulation. In relatively closed systems, rock–water interactions have been proposed to alter the composition of the waters (Land and Prezbindowski, 1981) because the volume of oxygen in the carbonate rock is large relative to the formation waters. The $\delta^{18}\text{O}$ of carbonate rocks is very high (+20‰ to +30‰ SMOW) relative to most surface waters, and, hence, interaction with carbonate rocks could increase the $\delta^{18}\text{O}$ of the waters. Although possible, we do not think that rock–water interactions have significantly affected most Permian Basin waters for several reasons. First, there is no petrographic or isotopic evidence that such a process is widespread in carbonate rocks of the Permian Basin. Such a process, if widespread, should homogenize the $\delta^{18}\text{O}$ of the rock and that is not observed in studies of geochemical components of Permian Basin carbonates (Dickson and Saller, 1995; Dickson et al., 2001). Second, high $\delta^{18}\text{O}$ values occur in samples with high salinity. Interactions of carbonate rocks with water will not significantly increase salinity (especially Na^+ and Cl^-), however, evaporation of seawater increases both. Third, widespread alteration of the isotopic composition of Permian Basin water by rock–water interaction was also discounted by Engle et al. (2016). It is possible that in the two Devonian waters with very high $\delta^{18}\text{O}$ values (+8‰ to +9‰ SMOW) (Figure 3A), the $\delta^{18}\text{O}$ compositions that started high (+3‰ to +6‰) were increased by rock–water interactions.

Water in Other Basins

Some other basins in the world may have waters that formed by processes similar to those observed in the Permian Basin. The Alberta Basin has (1) evaporitic waters that are geochemically similar to our group 1 water that could have formed from evaporated seawater during salt deposition in the Devonian, and (2) meteoric waters similar to our group 2 and 3 waters that are entering the Alberta Basin from the modern Rocky Mountains to the west (Hitchon and Friedman, 1969; Hitchon et al., 1971; Connolly et al., 1990a, b; Michael and Bachu, 2001). Wilson and

Long (1993) interpret highly saline waters in the Michigan Basin as being derived from highly evaporated seawater based on isotope and ion concentration data similar to ours. Evaporitic basins along the south Atlantic, the Middle East, and other parts of the world might have waters with origins similar to those in the Permian Basin.

IMPLICATIONS TO DEVELOPING RESERVOIRS

Information discerned from formation waters can have many implications for developing reservoirs. First, understanding salinities and variations in salinities of formation waters can have a significant impact on calculations of water and oil saturations from resistivity logs. It is important to know or predict where low-salinity meteoric waters might be replacing or mixing with high-salinity waters. Group 1 waters commonly have salinities (TDS) of 150–200 g/L, which would give a water resistivity (R_w) of approximately 0.059–0.049 ohm m (Crain, 2017). In contrast, group 2 waters commonly have salinities of 10–50 g/L, which would give an R_w of 0.57–0.14 ohm m at 75°F (24°C; Crain, 2017). If low-resistivity meteoric waters (group 2) were in a formation, and water saturation calculations were based on high-salinity formation waters, oil could be calculated in a formation filled with water and vice versa.

Below is a simple example of how different water resistivities would affect calculations of water and hydrocarbon saturations in a reservoir. Water saturation (S_w) can be calculated from the Archie equation:

$$S_w = [(1/\Phi^m) * (R_w/R_t)]^{(1/n)}$$

(Asquith and Gibson, 1982; derived from Archie, 1942), where S_w = water saturation, Φ = porosity, m = cementation exponent, R_w = resistivity of the water, R_t = formation resistivity, and n = saturation exponent.

For our calculation, relatively common parameters are assumed: $\Phi = 0.15$, $m = 2.5$, $n = 2$ (Asquith and Gibson, 1982). An R_w of 0.05 ohm m (typical group 1 water) would give an R_t of 5.7 ohm m at a S_w of 1. An R_w of 0.35 ohm m (typical group 2 waters) would give an R_t of 40 ohm m at an S_w of 1. If an R_w of 0.05 ohm m (group 1) was assumed, but the rock was filled with group 2 water (R_w of 0.35 ohm m), an

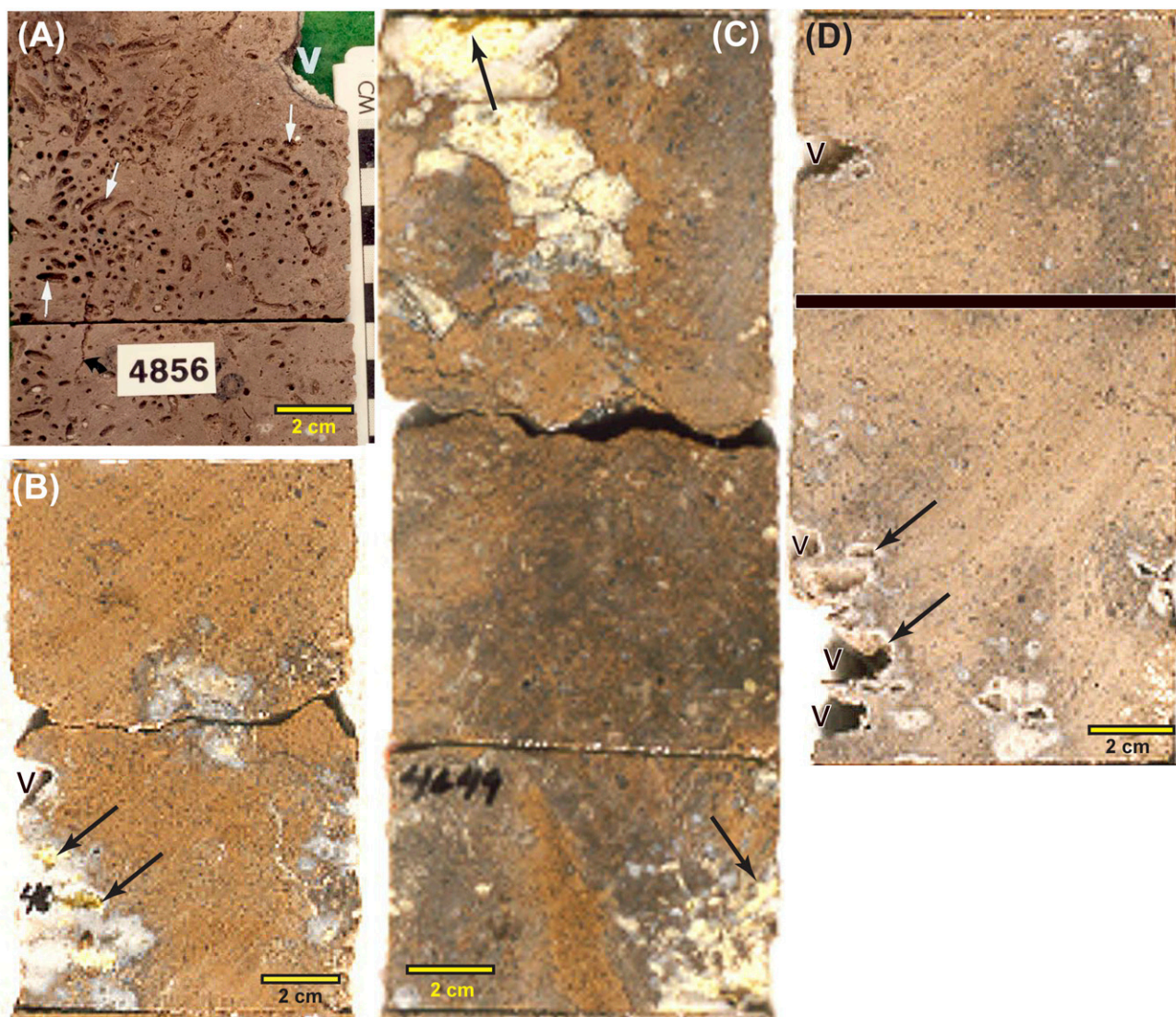


Figure 11. Core photographs showing alteration near oil–water contacts. (A) Burrowed dolomitized fusulinid wackestone-packstone at South Cowden field (Grayburg Formation) with molds of fusulinids (arrows) and a vug (V) formed by dissolution of an anhydrite nodule by late meteoric waters flowing through the Grayburg aquifer. (B–D) Burrowed dolomitized fusulinid wackestone-packstones near the oil–water contact in the San Andres Formation at Blackwatch field (location 5 on Figure 1). Photos from Renee Robertson. (B, C) Anhydrite nodules were partially converted to calcite (white), sulfur (arrows; yellow) and open pore space (V). (D) Dissolved anhydrite nodules resulted in V lined by white calcite cement (arrows). Small molds of fusulinids are common.

R_t of 40 ohm m would result, and an S_w of 0.38 is calculated. This would be incorrectly interpreted as a formation with a hydrocarbon saturation of 0.62 (62%).

Active flow of meteoric water from the surface can affect oil production. For example, active water circulation of meteoric waters in an aquifer adjacent to the reservoir might provide a natural water drive. Many Ellenburger reservoirs and Devonian reservoirs have natural water drives (Galloway et al., 1983) that are apparently associated with the

group 2 meteoric water. A few San Andres and Grayburg reservoirs adjacent to a shelf or platform margin aquifer have a partial water drive (Means, Midland Farms; Galloway et al., 1983), but most platform interior reservoirs do not. Hence, knowledge of the source of the waters can help identify potential water drive early in the appraisal and development of a field.

Relatively cool waters flowing through aquifers can cause flushing, tilting of the oil–water contact, and alteration (bacterial sulfate reduction) of the lowest oil

in some reservoirs especially in San Andres and Grayburg reservoirs (Brown, 2001; Lindsay, 2001; Trentham et al., 2012; Harouaka et al., 2014). This circulation of group 2 meteoric waters has apparently contributed to significant residual oil zones in San Andres reservoirs (Seminole, Wasson, Vacuum fields) that are now the target of CO₂ floods (Koperma et al., 2006; Trentham et al., 2012; Wachtman et al., 2012; Harouaka et al., 2014).

In addition to altering hydrocarbons, these meteoric waters have caused anhydrite dissolution and precipitation of alteration minerals, calcite and sulfur at oil–water contacts (Figure 11). The calcite cements associated with anhydrite alteration at the oil–water contact at Blackwatch field (location 5 on Figure 1) have $\delta^{18}\text{O}$ values of -9.9‰ to -11.8‰ PDB , and $\delta^{13}\text{C}$ values of -23.4‰ to -32.3‰ PDB . The very low $\delta^{13}\text{C}$ values require an organic source (probably oil) for much of the carbon. The $\delta^{18}\text{O}$ values of the calcite cements could be derived from precipitation from meteoric water with $\delta^{18}\text{O}$ of approximately -5.5‰ SMOW at the current formation temperature of 40°C (104°F), assuming equilibrium precipitation (Friedman and O'Neil, 1977). Hence, the isotope data support calcite precipitation by bacterial sulfate reduction at the existing oil–water contact. Because $\delta^{18}\text{O}$ of approximately -5.5‰ SMOW is higher than the current formation waters at Blackwatch field (-9‰ SMOW), waters associated with sulfate reduction and calcite precipitation were probably heavier either because of a difference in the composition of the meteoric waters circulating through the San Andres at time of alteration or because of a mixing of light water ($\delta^{18}\text{O}$ values of -7‰ to -9‰ SMOW) with heavier water in the formation prior to more widespread invasion by the current freshwater.

Water injection for pressure maintenance and water flooding are common in Permian Basin oil reservoirs. Precipitation of carbonate or sulfate crystals in injection and producing wells and in the adjacent formations can cause significant problems for flow of water and oil. Precipitation of anhydrite or gypsum in the well bore or the adjacent formation during water injection is an especially common problem (Allen and Roberts, 1978; Moghadasi et al., 2003). Knowledge of the ionic composition of the formation waters can give insights and potentially predict mineral precipitation related to mixing of waters.

The following is an example of how mixing two formation waters result in a water with a much higher ion product capable of gypsum precipitation. Saline Permian Basin waters (group 1) commonly have high Ca^{2+} concentrations (10,000 mg/L; 250 millimoles/L) and low SO_4^{2-} concentrations (500 mg/L; 5.2 mmol/L; Figure 6A) giving an ion product of 1302 millimoles²/L² for $\text{Ca}^{2+} \times \text{SO}_4^{2-}$. In contrast, meteoric (group 2) formation waters can have low Ca^{2+} (1800 mg/L; 45 mmol/L) and high SO_4^{2-} concentrations (4000 mg/L; 41.7 mmol/L; Figure 6A) giving an ion product of 1875 mmol²/kg². A mixing of those two waters at a 1/1 ratio results in a solution with Ca^{2+} of 5900 mg/L (147 mmol/L) and SO_4^{2-} of 2250 mg/L (23.4 mmol/L) resulting in an ion product of 3457 mmol²/L², which is much more supersaturated with respect to gypsum than either of the precursors. That mixture is similar to the ionic product (3479 mmol²/L²) of seawater concentrated by evaporation by a factor of four that McCaffrey et al. (1987) found precipitating gypsum.

The geochemical characterization of formation waters will obviously help in interpreting the burial diagenesis of rocks in the Permian Basin. Clearly, radically different waters can be encountered during burial that would affect the geochemistry of carbonates precipitated. The interpretation of stable oxygen isotopes ($\delta^{18}\text{O}$) is probably the most affected with the potential for variations of more than 15‰ in the deep host waters. Knowledge of the geochemistry of the formation waters in the basin during burial would also help with the interpretation of trace elements, strontium isotopes, and fluid inclusions in diagenetic carbonates.

CONCLUSIONS

Formation waters in a basin can vary greatly through time. In the Permian Basin during the latest Permian, very saline, dense, evaporated seawater associated with salt precipitation (group 1 waters) displaced most of the formation waters previously present in the basin. Their high density made those highly saline waters gravitationally stable in the basin and difficult to displace until Neogene tectonics created mountains in southeast New Mexico. Fresh waters from those highlands (groups 2 and 3)

have been displacing the dense evaporated seawater in the basin because of the hydraulic head created by high elevation (>8000 ft [2500 m] above sea level). The distribution of those meteoric waters has been determined by permeability networks in Paleozoic strata that created aquifers of meteoric water (groups 2 and 3) above and below older waters (group 1). In some areas, meteoric waters became very saline when they dissolved upper Permian salts forming group 3 waters. As a result, three groups of waters are present in the Permian Basin. (1) Late Permian evaporated seawater commonly has very high salinities (100–240 g/L), heavy stable oxygen isotopes ($\delta^{18}\text{O}$ of +2‰ to +9‰ SMOW), high bromine concentrations (substantially greater than seawater), and Cl^- concentrations that are distinctly greater than Na^+ on a molar basis (similar to seawater). (2) Low-salinity, meteoric waters from mountains in southeast New Mexico have light stable oxygen isotopes ($\delta^{18}\text{O}$ of –5‰ to –10‰ SMOW) and low bromine concentrations (substantially less than seawater). (3) Some meteoric waters from mountains in southeast New Mexico became saline by dissolving salt and, as a result, have low $\delta^{18}\text{O}$ values (–5‰ to –10‰ SMOW), low bromine concentrations (substantially less than seawater), but high TDS and molar chlorine (Cl^-) concentrations that are similar to Na^+ . Mixtures of these three groups of waters are also present.

The origin of the waters gives geoscientists and engineers insights into (1) water salinities for determining hydrocarbon saturations from resistivity logs, (2) the possibility of a natural water drive, (3) ionic concentrations that might cause scaling in producers and precipitation of carbonates and sulfates in the reservoir around injectors, (4) geochemistry of waters affecting rocks and possible reactions (dolomitization) occurring during burial diagenesis, and (5) the possibility of alteration of oil at the oil–water contact. Other basins in the world may have similar formation waters. This geochemical information can be derived from ionic concentrations from routine subsurface water analyses and relatively inexpensive stable isotope analyses ($\delta^{18}\text{O}$ and δD) of the waters. Strontium isotope analyses give additional insight, but they are generally more expensive, and may be more complicated to interpret.

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