Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Electronic supplementary information for the manuscript entitled

Water-rock interaction and the concentrations of major, trace, and rare earth elements in hydrocarbon-associated produced waters of the United States

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This PDF file includes:

Complete details on elemental and mineralogical analyses for bulk shale and leachate samples.

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S1. Supplementary Analytical Details

Shale elemental, mineralogical, and programmed pyrolysis analyses

Concentrations of 55 elements in the 12 shale samples were determined by SGS Mineral Services (Lakefield, Ontario, Canada). The powdered sample was decomposed using a sodium peroxide fusion followed by analysis using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass-spectrometry (ICP-MS). Total sulfur was determined by combustion followed by infrared detection on LECO instrumentation. Carbonate carbon was determined by coulometric titration.[1] A LECO C744 carbon analyzer was used to determine total carbon content by direct rock analysis and organic carbon content by analyzing samples following carbonate removal with 6 M HCl. Quantitative mineralogical analyses were conducted using a Panalytical X'Pert Pro X-ray diffractometer (XRD) and in-house U.S. Geological Survey (USGS) methods. Whole-pattern (2-70° 2θ, 0.02° step size) diffractograms were measured after samples were prepared by micronizing and mixed with an internal standard (20 wt. % corundum). Mineral phases were quantified using the Jade and ClaySim software packages (Material Data, Inc., Livermore, California). Whole-pattern fitting in Jade was used to estimate weight percentages for non-clay mineral major and minor phases in the whole rocks based on Rietveldt refinement, and ClaySim was then used to identify and quantify clay mineral phases present. Programmed pyrolysis parameters, which provide screening information related to organic matter type and thermal maturity, were determined using a Wildcat Hydrocarbon Analyzer with Kinetics (HAWK) following the manufacturer's instructions.[2] All data are available online.[3]

Water, acid, and brine leachate analyses

Analyses of water and HCl leaches for element concentrations were conducted at USGS research laboratories in Denver, Colorado using inductively coupled plasma-mass spectrometry (ICP-MS).[4] Concentrations for leachate duplicates were generally within 20% of each other for the water leaches and 10% for the HCl leaches. Standards analyzed as unknowns returned concentrations generally within 20% of expected concentrations. Artificial brine leachates were analyzed at the USGS Brine Research Instrumental and Experimental (BRInE) laboratory in Reston, Virginia for major cations and anions, trace elements, and total dissolved solids (TDS). Major cation and trace element concentrations were measured using a Horiba Ultima Expert inductively coupled plasma-optical emission spectrometer (ICP-OES) similar to other reports from the laboratory.[5-7] Standards were spiked with salts to approximate the composition of the artificial brine and analyzed as unknowns. Matrix spike recoveries for both major cations and trace elements were all within 30% of the expected values. Results for the leachate duplicates were generally within 30% of each other and standards were generally within 35% of expected concentrations. Concentrations of many trace elements were below detection limits in blanks or low relative to leachates, but blanks for Co Ni, Pb, and Sb overlapped with a substantial number of leachates. A recent interlaboratory comparison indicated that both ICP-MS and ICP-OES approaches may only be accurate to within 20% of the most probable values for trace element determinations within produced waters[5]; the element concentrations determined in this study on the leachate samples supports this finding. For the brine leachates, anions were measured using ion chromatography (IC) with a standard operating procedure modified from EPA Method 9056A.[8] TDS was measured by evaporation at 180°C following EPA Method 160.1.[9] It is important to note that the Na^{+}, Mg^{2+}, Ca^{2+}, Cl^{-} levels, and TDS determined in the brine leachates are almost entirely controlled by the initial artificial brine.

Table S1. Quartiles and numbers of samples for selected element concentrations (mg/L) in conventional and tight oil produced waters from the Bakken Formation, Niobrara Formation, and informal Wolfcamp shale[10] from the U.S. Geological Survey Produced Waters Geochemical Database (v2.3).[11] Data are plotted in Figure 1.

		Conventional				Tight Oil			
		Q1	Q2	Q3	n	Q1	Q2	Q3	n
Bakken	Cl	54,052	61,171	137,779	20	121,104	155,199	179,204	439
Bakken	Na	35,334	38,355	82,291	20	61,150	80,150	92,925	440
Bakken	Ca	2,303	2,987	3,899	20	7,894	12,698	17,030	439
Bakken	Mg	123	418	587	20	667	1,066	1,400	439
Bakken	K	2,255	3,150	3,350	4	2,460	4,070	5,320	385
Bakken	SO4	2,931	4,763	7,536	20	283	471	744	436
Bakken	Li	6	6	6	3	0	18	47	33
Niobrara	Cl	4,704	8,525	24,794	26	15,019	27,315	35,758	97
Niobrara	Na	3,252	5,720	15,837	26	9,269	17,275	22,998	96
Niobrara	Ca	51	153	615	26	86	383	605	96
Niobrara	Mg	16	31	185	26	24	49	84	95
Niobrara	K	18	41	122	12	58	87	104	9
Niobrara	SO4	18	38	129	16	15	25	49	45
Niobrara	Fe	5	7	10	2	8	10	11	62
Wolfcamp	Cl	36,026	60,802	99,999	473	63,050	69,550	75,375	14
Wolfcamp	Na	21,121	33,421	58,522	243	38,100	41,600	45,075	14
Wolfcamp	Ca	2,035	3,874	8,876	472	1,465	2,250	2,760	14
Wolfcamp	Mg	526	884	1,811	472	222	349	384	14
Wolfcamp	K	194	465	686	44	367	511	902	14
Wolfcamp	SO4	770	1,618	2,648	464	363	568	648	14
Wolfcamp	Sr	91	175	392	31	316	348	421	14
Wolfcamp	Fe	15	40	148	47	20	35	55	14
Wolfcamp	Mn	0.4	0.5	0.5	4	0.9	1.1	1.2	10

Table S2. Quartiles and numbers of samples for selected element concentrations (mg/L) in tight oil produced waters from the Bakken Formation, shale gas waters from the Marcellus Shale, and conventional waters from the Green River Formation from the U.S. Geological Survey Produced Waters Geochemical Database (v2.3).[11]. Data are plotted in Figure 2.

	Bakken - Tight Oil				Marcellus - Shale Gas				Green River - Conventional			
	Q1	Q2	Q3	n	Q1	Q2	Q3	n	Q1	Q2	Q3	n
Cl	121,104	155,199	179,204	439	33,258	67,200	98,825	302	2,560	6,050	13,625	412
Na	61,150	80,150	92,925	440	15,950	29,150	39,090	332	3,037	5,993	10,594	409
Ca	7,894	12,698	17,030	439	3,510	8,410	14,300	303	16	35	102	405
Mg	667	1,066	1,400	439	336	840	1,410	299	5	15	37	395
K	2,460	4,070	5,320	385	166	271	416	171	28	60	113	247
SO4	283	471	744	436	33	50	89	118	196	879	2,210	396
Sr	151	773	1,390	33	667	1,694	2,735	287	4	15	36	12
Li	0	18	47	33	40	69	95	257	2	3	5	94
Ba	12	19	32	291	194	1,250	2,640	301	0.1	0.1	0.5	5
Fe	13	68	128	388	20	47	110	290	0.1	0.2	1.6	7
Rb	10	14	19	13	0.6	0.8	0.9	21	0.2	0.2	0.3	5
Zn	4	13	15	9	0.1	0.2	0.5	150	0.08	0.18	0.35	6
Cu	0.02	0.04	0.06	11	0.06	0.25	0.25	113	0.06	0.10	0.20	7
Mn	0.004	0.008	0.011	11	2	4	8	235	0.03	0.07	0.78	6
Co	0.02	0.03	0.03	11	0.06	0.50	2.50	82				
Mo	0.009	0.012	0.018	11	0.02	0.05	0.40	94				
As	0.2	0.4	0.5	11	0.04	0.09	0.10	69				
Cd	0.02	0.05	0.06	5	0.00	0.03	0.05	70				
Cr	0.3	0.5	0.7	242	0.01	0.03	0.05	113				
Ni	0.24	0.26	0.34	11	0.03	0.11	0.40	118				
Pb	0.026	0.029	0.804	7	0.02	0.03	0.05	73				

Table S3. Median element concentrations (mg/L) in produced waters from conventional hydrocarbon wells in the U.S. Geological Survey (USGS) Produced Waters Geochemical Database v2.3 (PWGD)[11] split by basin. Empty cells indicate no data available.

	Alaska North Slope	Amarillo Arch	Anadarko	Appalachian	Arkla	Arkoma	Bend Arch	Big Horn
pH	7.2	7.0	6.8	5.7	6.3	6.9	6.4	7.8
TDS	23000	148675	85667	189820	96546	91485	130176	9184
Al		2.7	3.0	4.7				
As					5			
B	114	26	23	39	53	17	8	12
Ba	92	120	8	120	40	31	24	0
Br	54	38	336	745	900	242	231	27
Ca	224	5740	2260	12723	4839	4234	7992	454
Cd								
Cl	12860	87600	25467	76800	58884	51300	81153	1106
Co								
Cr								
Cs	1.1		0.05	0.6	2			
Cu		2	19	0.08	1			
F	1.1		47	1				
Fe	6	64	32	40	30	20	36	1
I	24	2	90	9	16	9	14	5
K	49	285	193	757	168	89	188	90
Li	3	33	3	45	23	36	6	3
Mg	66	1738	638	2083	924	1188	1816	122
Mn		0.7	10	34	9	10		
Mo								
Na	8055	50388	28934	37226	31955	27302	37213	2236
Ni								
P				0.07				
Pb			0.7	0.02	14			
Rb	0.3		0.35	39	4			
S			624	0.5	100	55		224
SO4	34	1800	490	140	174	182	233	3189
Sb								
Se			4					0.2
Si	23	93	44	15	8		25	25
Sr	26	80	163	589	370	137	481	8

U								
V								
Zn			5		5		2	2

	Central Kansas Uplift	Chadron Arch	Chautauqua Platform	Cherokee	Cook Inlet	Denver	Eagle	East Texas	Fort Worth
pH	7.1	7.7	6.3	7.0	7.9	7.9	7.9	7.3	5.8
TDS	57552	27896	180545	86652	19493	12275	11664	56523	163473
Al	120		0.3	86					
As									
B	8		6		7	18		72	6
Ba	4		29	42	3	2		17	53
Br	69	5	329	37	46	51		1130	646
Ca	2280	646	9768	4109	1549	57	95	1100	12733
Cd									
Cl	26994	8400	103196	51960	11224	4980	5098	33700	96620
Co									
Cr									
Cs			0.15		0.02				
Cu								1	
F									
Fe	12		33	12		2		17	160
I	9		9	2	12	3		28	17
K	114	70	223	132	73	50		74	385
Li	5	3	8		1	3		9	6
Mg	734	119	2030	1272	24	22	24	268	2227
Mn			8					17	35
Mo									
Na	14654	6116	53702	22632	5306	4139	4453	20372	45001
Ni									
P	1					0.7			
Pb									
Rb			1		0.16				
S			1						
SO_4	1317	3017	224	120	268	440	690	328	114
Sb									
Se									

Si	28		17	32		20		52	152
Sr	99		336	519	68	8		160	418
U									
V									
Zn								2	

	Great Basin	Green River	Gulf Coast	Illinois	Kansas Basins	Laramie	Las Animas Arch	Las Vegas - Raton	Llano Uplift	Los Angeles
pH	7.3	7.8	7.0	7.1	6.1	8.0	7.4	7.3	6.5	7.4
TDS	23112	13968	76111	93121	88523	9964	24544	22904	67958	30207
Al		1.0	0.1	28						0.01
As		0.03	0.002							
B	13	10	52	7.2						23
Ba		8	35	5					5	45
Br	76	17	134	121						19
Ca	708	156	1839	2399	2537	531	851	734	3140	473
Cd			0.0003							
Cl	10780	5050	44740	43364	26434	4050	8325	13176	40519	17587
Co			0.001							
Cr		0.03	0.1							
Cs	0.05		1.2	0.6						
Cu			0.0007							
F			2							2.01
Fe		8	25	6	135		64		16	3
I	5	3	18	6						64
K	253	95	220	90		50	110	90		66
Li	3	3	7	13		4	6			1
Mg	111	41	340	949	1043	98	172	111	972	321
Mn		21	3	0.9						1
Mo										
Na	6160	4304	25599	24225	23263	3796	6300	7497	20894	10431
Ni			0.004							
P	1.7		0.3							0.1
Pb		0.03	3							
Rb	0.2	0.8	0.6	4.2						
S			17							
SO4	1476	213	45	781	671	808	1850	1300	290	14
Sb										
Se		0.04								
Si		16	28	7						58
Sr	15	10	180	84			1		239	19
U										
V										
Zn		0.6	2							

	Michigan	Nemaha Uplift	North Park	Ouachita Thrust	Ozark Uplift	Pacific Coast	Palo Duro	Paradox	Permian
pH	5.9	6.6	8.2	6.7	8.1	7.9	6.7	7.1	6.9
TDS	285945	110952	12816	126421	6151	18137	171675	78526	85101
Al	1.3	292					19		9
As									
B	31					18	14	16	18
Ba	7	165		1.02		28	13	7	0.8
Br	1100	67					184	41	225
Ca	31000	3325	37	8200	8	141	8120	2087	2909
Cd									
Cl	174000	52453	850	68826	1778	9504	88591	31100	50504
Co									
Cr									
Cs	0.4							0.2	0.4
Cu	0.7						1	1	2
F	9								3
Fe	16	1	8	44	4	7	11	1	19
I	11	3		7		28	6	12	9
K	1814	196	117	170	3	88	477	445	389
Li	29		4	10			12	10	10
Mg	5962	1318	30	1646	3	50	2116	598	988
Mn	1						0.2	2	0.7
Mo									
Na	51000	28440	4675	28890	2089	6873	52613	19210	26919
Ni									
P									0.7
Pb	0.001								
Rb	3.3							2	3
S						6.54			202
SO4	276	283	860	427	258	72	877	1450	1528
Sb									
Se									
Si	3	25		91		67	28		20
Sr	629	478		180	1		214	93	62
U									
V									
Zn	0.0004						4	0.2	3

	Piceance	Powder River	Powder River - Wind River	Raton	Sacramento	Salina	San Joaquin	San Juan	Santa Maria
pH	7.5	7.7	8.0	7.3	7.4	6.8	7.2	7.6	7.8
TDS	19858	14583	17464	23558	15900	52740	25142	17756	18300
Al					0.03		3		
As		0.01							
B		11			28		45	3	26
Ba	43	11			6		1	1	5
Br		11			36	37	123		
Ca	292	120	56		182	1815	377	90	114
Cd		0.07							
Cl	8774	6754	1434		9200	27789	13450	1180	9570
Co									
Cr									
Cs					0.3				
Cu									
F					0.6		2		2
Fe	27	8			2	84	2	5	1
I		17			27		20	1	10
K	88	65	34		34	220	115	48	41
Li	4	4			0	1	2	5	
Mg	73	32	12		72	751	64	33	45
Mn		164			0.2			0.5	
Mo									
Na	6258	5183	5169		5280	12949	7845	3776	5345
Ni									
P		1.3					0.7		
Pb									
Rb					0.2		0.3		
S							31		21
SO4	408	554	149		5	1185	55	768	48
Sb									
Se		0.05							
Si					26		60	14	39
Sr	17	2			11	110	50	9	36
U									
V									
Zn		0.05							

	Sedgwick	Sierra Grande Uplift	Snake River	South Florida	Southern Oklahoma	Strawn	Sweetgrass Arch	Uinta	Ventura
pH	6.8	7.1	7.5	6.0	6.2	6.6	8.0	8.2	7.5
TDS	139693	18922	32214	245693	140859	50464	8073	17406	29717
Al	239								
As									
B	8			100	4			16	
Ba	9				60		4	0.6	8
Br	182			695	440			22	68
Ca	4553	608	441	23610	8320	2302	73	54	479
Cd									
Cl	60874	1975	14531	151851	85091	31145	3113	6645	15650
Co									
Cr									
Cs					0.05			0.1	
Cu								0.08	
F									
Fe	11			46	28		322	0	7
I	2				8			15	43
K	280	78	105	545	380	410	49	60	69
Li	14		3	12	17		2	3	2
Mg	1260	137	81	3426	2061	395	39	20	89
Mn					26			0.095	
Mo									
Na	34556	4968	11497	63376	40623	16182	2695	5796	7980
Ni									
P					4				
Pb									
Rb					0.2			0.17	
S									
SO4	420	8375	1641	314	84	34	76	905	23
Sb									
Se									
Si	18			35	42		25		65
Sr	183			14	425	224		12	21
U									
V									
Zn								0.3	

	Wasatch Uplift	Western Columbia	Williston	Wind River	Wisconsin Arch	Wyoming Thrust Belt	Yellowstone
pH	7.6	7.4	6.4	8.0		7.4	7.6
TDS	8694	24830	276832	9193	108373	28152	30153
Al			0.02				
As			0.2				
B			17	10			
Ba			2	3		12	
Br		36	346	251	489		
Ca	223	1889	8780	71	7916	570	3223
Cd			0.001				
Cl	1124	15788	167700	2696	66886	12240	18100
Co			0.006				
Cr			1				
Cs		0.04	0.08				
Cu			0.05				
F			6				
Fe			8	9		32	
I		16	10	16	3		
K	85	22	2700	52		548	28
Li	3		10	3			6
Mg	48	136	976	23	2355	60	178
Mn			0.1				
Mo			0.004				
Na	2388	5921	82934	2798		8267	7919
Ni			0.07	13			
P							
Pb			0.008				
Rb		0.05	1				
S				92			
SO4	2945	40	905	560	747	1260	10
Sb			0.001				
Se			0.08	0.3			
Si			57	34			
Sr		12	312	5			
U			0.009				
V			0.4				
Zn			0.04				

Table S4. Sample counts for the median element concentrations in Table S3 for produced waters from conventional hydrocarbon wells.

	Alaska North Slope	Amarillo Arch	Anadarko	Appalachian	Arkla	Arkoma	Bend Arch	Big Horn
pH	31	223	4510	353	2145	136	185	1201
TDS	31	442	4800	1668	2324	224	214	1389
Al	0	14	6	113	0	0	0	0
As	0	0	0	0	2	0	0	0
B	8	1	87	75	105	7	4	13
Ba	25	11	409	552	740	65	11	14
Br	8	22	113	1230	122	7	10	7
Ca	31	442	6125	1564	2321	224	214	1378
Cd	0	0	0	0	0	0	0	0
Cl	30	441	6206	1581	2324	224	214	1387
Co	0	0	0	0	0	0	0	0
Cr	0	0	0	0	0	0	0	0
Cs	9	0	50	5	9	0	0	0
Cu	0	20	2	49	67	0	0	0
F	9	0	1	28	0	0	0	0
Fe	25	46	617	741	741	37	38	45
I	8	23	126	770	120	9	10	12
K	11	33	299	1365	274	36	18	426
Li	9	27	247	406	114	20	13	115
Mg	31	441	6068	1527	2319	224	213	1359
Mn	0	14	11	391	51	1	0	0
Mo	0	0	0	0	0	0	0	0
Na	24	273	3133	1553	2189	223	183	1351
Ni	0	0	0	0	0	0	0	0
P	0	0	0	6	0	0	0	0
Pb	0	0	1	16	1	0	0	0
Rb	9	0	63	29	9	0	0	0
S	0	0	1	22	1	1	0	1
SO4	22	426	5754	955	1778	172	190	1333
Sb	0	0	0	0	0	0	0	0
Se	0	0	1	0	0	0	0	4
Si	7	5	12	274	18	0	18	3
Sr	21	20	432	983	255	37	24	3
U	0	0	0	0	0	0	0	0
V	0	0	0	0	0	0	0	0
Zn	0	19	3	221	52	0	0	0

	Central Kansas Uplift	Chadron Arch	Chautauqua Platform	Cherokee	Cook Inlet	Denver	Eagle	East Texas	Fort Worth
pH	699	53	1322	152	63	1064	7	1699	89
TDS	3018	60	5566	356	63	1117	7	1764	114
Al	19	0	18	7	0	0	0	0	0
As	0	0	0	0	0	0	0	0	0
B	1	0	41	0	5	31	0	9	2
Ba	15	0	930	75	9	4	0	240	30
Br	78	3	70	22	14	2	0	15	5
Ca	3009	60	5547	356	63	1097	7	1756	114
Cd	0	0	0	0	0	0	0	0	0
Cl	3008	60	5566	355	61	1117	7	1762	114
Co	0	0	0	0	0	0	0	0	0
Cr	0	0	0	0	0	0	0	0	0
Cs	0	0	8	0	1	0	0	0	0
Cu	0	0	0	0	0	0	0	5	0
F	0	0	0	0	0	0	0	0	0
Fe	150	0	581	17	0	20	0	250	23
I	34	0	60	11	8	24	0	13	5
K	48	21	238	3	16	444	0	208	13
Li	8	19	100	0	3	100	0	22	5
Mg	3011	60	5562	356	62	1076	7	1760	114
Mn	0	0	10	0	0	0	0	5	1
Mo	0	0	0	0	0	0	0	0	0
Na	2773	59	4850	170	62	1088	7	1717	111
Ni	0	0	0	0	0	0	0	0	0
P	1	0	0	0	0	1	0	0	0
Pb	0	0	0	0	0	0	0	0	0
Rb	0	0	8	0	1	0	0	0	0
S	0	0	17	0	0	0	0	0	0
SO4	2843	58	4778	326	59	1075	7	1653	86
Sb	0	0	0	0	0	0	0	0	0
Se	0	0	0	0	0	0	0	0	0
Si	16	0	70	51	0	11	0	21	24
Sr	25	0	315	16	10	21	0	184	12
U	0	0	0	0	0	0	0	0	0
V	0	0	0	0	0	0	0	0	0
Zn	0	0	0	0	0	0	0	5	0

	Great Basin	Green River	Gulf Coast	Illinois	Kansas Basins	Laramie	Las Animas Arch	Las Vegas - Raton	Llano Uplift	Los Angeles
pH	31	2822	12170	1001	3	15	81	8	34	285
TDS	33	3140	14578	2598	37	16	99	9	37	297
Al	0	3	37	3	0	0	0	0	0	3
As	0	1	30	0	0	0	0	0	0	0
B	2	35	651	80	0	0	0	0	0	9
Ba	0	112	2792	79	0	0	0	0	7	233
Br	3	7	905	318	0	0	0	0	0	8
Ca	33	3124	14499	2266	37	14	99	9	37	297
Cd	0	0	49	0	0	0	0	0	0	0
Cl	33	3175	14616	2338	37	15	98	9	37	296
Co	0	0	38	0	0	0	0	0	0	0
Cr	0	1	2	0	0	0	0	0	0	0
Cs	1	0	82	3	0	0	0	0	0	0
Cu	0	0	50	0	0	0	0	0	0	0
F	0	0	248	0	0	0	0	0	0	8
Fe	0	305	4468	660	2	0	1	0	5	172
I	3	23	681	62	0	0	0	0	0	163
K	11	1285	1566	362	0	6	55	4	0	15
Li	3	373	757	25	0	1	14	0	0	3
Mg	32	3038	14368	2262	37	14	98	9	37	296
Mn	0	4	226	344	0	0	0	0	0	7
Mo	0	0	0	0	0	0	0	0	0	0
Na	33	3089	14212	2190	37	15	97	9	36	295
Ni	0	0	40	0	0	0	0	0	0	0
P	1	0	2	0	0	0	0	0	0	5
Pb	0	1	113	0	0	0	0	0	0	0
Rb	2	2	165	3	0	0	0	0	0	0
S	0	0	50	0	0	0	0	0	0	0
SO4	32	2816	10454	2093	32	13	99	9	37	161
Sb	0	0	0	0	0	0	0	0	0	0
Se	0	11	0	0	0	0	0	0	0	0
Si	0	2	1010	589	0	0	0	0	0	172
Sr	4	21	1371	307	0	0	1	0	1	18
U	0	0	0	0	0	0	0	0	0	0
V	0	0	0	0	0	0	0	0	0	0
Zn	0	4	208	0	0	0	0	0	0	0

	Michigan	Nemaha Uplift	North Park	Ouachita Thrust	Ozark Uplift	Pacific Coast	Palo Duro	Paradox	Permian
pH	255	101	42	17	2	25	162	572	8972
TDS	835	490	47	24	2	27	331	600	15069
Al	1	8	0	0	0	0	1	0	4
As	0	0	0	0	0	0	0	0	0
B	24	0	0	0	0	1	3	9	413
Ba	63	50	0	1	0	3	13	10	674
Br	375	47	0	0	0	0	4	11	380
Ca	835	490	42	24	2	27	331	597	11792
Cd	0	0	0	0	0	0	0	0	0
Cl	835	489	47	24	2	27	331	600	11803
Co	0	0	0	0	0	0	0	0	0
Cr	0	0	0	0	0	0	0	0	0
Cs	64	0	0	0	0	0	0	4	3
Cu	6	0	0	0	0	0	1	8	2
F	53	0	0	0	0	0	0	0	15
Fe	89	78	6	8	1	8	18	9	1483
I	135	23	0	1	0	10	4	10	312
K	375	22	26	8	2	2	28	116	1484
Li	90	0	6	9	0	0	10	40	378
Mg	831	490	46	24	2	27	331	598	11718
Mn	31	0	0	0	0	0	1	8	57
Mo	0	0	0	0	0	0	0	0	0
Na	793	450	46	22	2	26	306	597	8033
Ni	0	0	0	0	0	0	0	0	0
P	0	0	0	0	0	0	0	0	2
Pb	5	0	0	0	0	0	0	0	0
Rb	36	0	0	0	0	0	0	5	3
S	0	0	0	0	0	1	0	0	10
SO4	765	398	43	20	2	22	324	595	11566
Sb	0	0	0	0	0	0	0	0	0
Se	0	0	0	0	0	0	0	0	0
Si	33	9	0	1	0	14	6	0	244
Sr	331	66	0	10	1	0	12	17	1110
U	0	0	0	0	0	0	0	0	0
V	0	0	0	0	0	0	0	0	0
Zn	19	0	0	0	0	0	1	4	2

	Piceance	Powder River	Powder River - Wind River	Raton	Sacramento	Salina	San Joaquin	San Juan	Santa Maria
pH	364	3407	5	4	51	20	308	2066	29
TDS	397	3562	9	4	61	53	328	2274	31
Al	0	0	0	0	2	0	6	0	0
As	0	3	0	0	0	0	0	0	0
B	0	18	0	0	47	0	189	4	6
Ba	14	249	0	0	61	0	144	60	7
Br	0	1	0	0	59	1	106	0	0
Ca	395	3544	9	0	61	53	328	1505	30
Cd	0	1	0	0	0	0	0	0	0
Cl	400	3590	9	0	61	53	328	1637	31
Co	0	0	0	0	0	0	0	0	0
Cr	0	0	0	0	0	0	0	0	0
Cs	0	0	0	0	39	0	0	0	0
Cu	0	0	0	0	0	0	0	0	0
F	0	0	0	0	46	0	67	0	1
Fe	24	575	0	0	43	5	114	134	11
I	0	11	0	0	58	0	149	68	1
K	164	2128	1	0	58	2	150	240	6
Li	41	358	0	0	49	1	104	6	0
Mg	383	3460	9	0	61	53	327	1501	30
Mn	0	1	0	0	43	0	0	29	0
Mo	0	0	0	0	0	0	0	0	0
Na	383	3476	7	0	61	53	273	1636	30
Ni	0	0	0	0	0	0	0	0	0
P	0	1	0	0	0	0	1	0	0
Pb	0	0	0	0	0	0	0	0	0
Rb	0	0	0	0	47	0	84	0	0
S	0	0	0	0	0	0	2	0	4
SO4	374	3081	4	0	40	51	303	1017	27
Sb	0	0	0	0	0	0	0	0	0
Se	0	34	0	0	0	0	0	0	0
Si	0	0	0	0	49	0	134	1	10
Sr	7	29	0	0	59	1	131	128	2
U	0	0	0	0	0	0	0	0	0
V	0	0	0	0	0	0	0	0	0
Zn	0	8	0	0	0	0	0	0	0

	Sedgwick	Sierra Grande Uplift	Snake River	South Florida	Southern Oklahoma	Strawn	Sweetgrass Arch	Uinta	Ventura
pH	149	8	6	51	683	2	147	582	15
TDS	1002	8	6	56	1260	2	222	602	30
Al	19	0	0	0	0	0	0	0	0
As	0	0	0	0	0	0	0	0	0
B	2	0	0	1	65	0	0	34	0
Ba	6	0	0	0	305	0	3	17	24
Br	69	0	0	1	66	0	0	48	15
Ca	1002	8	6	56	1259	2	221	592	30
Cd	0	0	0	0	0	0	0	0	0
Cl	1001	8	6	56	1258	2	222	600	30
Co	0	0	0	0	0	0	0	0	0
Cr	0	0	0	0	0	0	0	0	0
Cs	0	0	0	0	1	0	0	8	0
Cu	0	0	0	0	0	0	0	24	0
F	0	0	0	0	0	0	0	0	0
Fe	43	0	0	17	126	0	2	28	11
I	15	0	0	0	67	0	0	47	21
K	18	5	1	5	149	1	38	377	17
Li	5	0	1	1	112	0	8	147	12
Mg	1002	8	6	56	1261	2	220	577	30
Mn	0	0	0	0	4	0	0	24	0
Mo	0	0	0	0	0	0	0	0	0
Na	987	8	6	56	1196	2	194	597	29
Ni	0	0	0	0	0	0	0	0	0
P	0	0	0	0	6	0	0	0	0
Pb	0	0	0	0	0	0	0	0	0
Rb	0	0	0	0	1	0	0	8	0
S	0	0	0	0	0	0	0	0	0
SO4	809	8	6	55	926	2	184	582	22
Sb	0	0	0	0	0	0	0	0	0
Se	0	0	0	0	0	0	0	0	0
Si	8	0	0	1	21	0	4	0	10
Sr	12	0	0	5	175	1	0	46	13
U	0	0	0	0	0	0	0	0	0
V	0	0	0	0	0	0	0	0	0
Zn	0	0	0	0	0	0	0	27	0

	Wasatch Uplift	Western Columbia	Williston	Wind River	Wisconsin Arch	Wyoming Thrust Belt	Yellowstone
pH	26	5	9313	1579	0	55	6
TDS	31	5	9428	1764	2	59	6
Al	0	0	1	0	0	0	0
As	0	0	12	0	0	0	0
B	0	0	38	29	0	0	0
Ba	0	0	66	9	0	1	0
Br	0	5	161	2	1	0	0
Ca	31	5	9423	1759	2	59	6
Cd	0	0	2	0	0	0	0
Cl	31	5	9443	1762	2	59	6
Co	0	0	2	0	0	0	0
Cr	0	0	1374	0	0	0	0
Cs	0	1	41	0	0	0	0
Cu	0	0	12	0	0	0	0
F	0	0	35	0	0	0	0
Fe	0	0	3629	64	0	16	0
I	0	5	154	11	1	0	0
K	5	1	3992	752	0	43	6
Li	2	0	471	229	0	0	5
Mg	31	5	9251	1686	2	54	6
Mn	0	0	35	0	0	0	0
Mo	0	0	11	0	0	0	0
Na	31	5	9372	1734	0	59	6
Ni	0	0	3	1	0	0	0
P	0	0	0	0	0	0	0
Pb	0	0	1	0	0	0	0
Rb	0	1	41	0	0	0	0
S	0	0	0	2	0	0	0
SO4	30	2	9366	1634	2	57	6
Sb	0	0	2	0	0	0	0
Se	0	0	34	2	0	0	0
Si	0	0	24	1	0	0	0
Sr	0	2	162	11	0	0	0
U	0	0	1	0	0	0	0
V	0	0	3	0	0	0	0
Zn	0	0	4	0	0	0	0

Table S5. Median element concentrations (mg/L) in produced waters from shale gas wells in the USGS Produced Waters Geochemical Database (v2.3)[11] split by basin. Empty cells indicate no data available.

	Anadarko - Southern Oklahoma	Appalachian	Green River	Illinois	Michigan
pH	7.7	6.5	7.0	6.8	6.6
TDS	15695	112500	21450	67458	112642
Al		0.3			
As		0.08			
B		14.55			6
Ba	4	1219	31		58
Br		650			157
Ca	119	8390	347	1130	25250
Cd		0.03			
Cl	6957	66900	10120	42000	71995
Co		0.5			
Cr		0.03			
Cs		0.3			0.088
Cu		0.3			
F		3			
Fe	20	47	11	24	76
I		27			2
K	190	271	95	263	400
Li		69	0.8		12
Mg	15	834	38	1060	2350
Mn		4			0.9
Mo		0.05			
Na	5851	28850	5502	19700	36875
Ni		0.1			
P		0.07			
Pb		0.03			
Rb		0.8			
S		3			
SO4	170	50	39	159	19
Sb		0.1			
Se		0.05			
Si					6
Sr		1627			275
Ti		0.2			
Tl		0.1			
U					
V					
Zn		0.2			

Table S6. Sample counts for the median element concentrations in Table S5 for produced waters from shale gas wells.

	Anadarko - Southern Oklahoma	Appalachian	Green River	Illinois	Michigan
pH	2526	109	38	8	214
TDS	989	320	40	9	100
Al	0	142	0	0	0
As	0	70	0	0	0
B	0	122	0	0	51
Ba	472	308	14	0	60
Br	0	267	0	0	192
Ca	2515	310	39	9	201
Cd	0	71	0	0	0
Cl	2513	310	39	9	100
Co	0	83	0	0	0
Cr	0	114	0	0	0
Cs	0	21	0	0	1
Cu	0	114	0	0	0
F	0	67	0	0	0
Fe	999	298	38	4	56
I	0	5	0	0	1
K	19	174	27	4	67
Li	0	260	7	0	53
Mg	987	306	39	9	66
Mn	0	240	0	0	51
Mo	0	96	0	0	0
Na	989	340	39	9	234
Ni	0	118	0	0	0
P	0	79	0	0	0
Pb	0	73	0	0	0
Rb	0	21	0	0	0
S	0	84	0	0	0
SO4	2432	124	30	5	34
Sb	0	67	0	0	0
Se	0	67	0	0	0
Si	0	0	0	0	51
Sr	0	294	0	0	60
Ti	0	67	0	0	0
Tl	0	68	0	0	0
U	0	0	0	0	0
V	0	0	0	0	0
Zn	0	152	0	0	0

Table S7. Median element concentrations (mg/L) in produced waters from tight oil wells in the USGS Produced Waters Geochemical Database v2.3[11] divided by basin. Empty cells indicate no data available.

	Anadarko - Southern Oklahoma	Atlantic Coastal Plain	Denver	East Texas	Green River	Gulf Coast	Permian	Powder River	Williston
pH	7.7	6.9	7.2	7.2	7.4		7.5	6.9	6.0
TDS	16762	78039	46631	89180	27571	139798	106000	24400	254534
Al									0.09
As									0.4
B							35		0.3
Ba	4			20			81	63	19
Br		12					578		610
Ca	155	3911	352	1933	331	7000	1970	331	12698
Cd									0.05
Cl	4974	46431	28529	54141	18800	86000	63200	14556	155199
Co									0.03
Cr									0.5
Cs									0.004
Cu									0.04
F									8
Fe	19		9	9	39		53	24	68
I		1.4					80		48
K	152	648	56		58		374	315	4070
Li									18
Mg	19	264	49	415	98	1050	334	38	1066
Mn							1.2		0.008
Mo									0.01
Na	6309	24715	18099	32083	11081	45600	38400	8927	80150
Ni									0.3
P									
Pb									0.03
Rb									13.8
S									
SO4	240	769	25	17	64	67	547	17	471
Se									1.5
Si							14		
Sr							345		773
U									0.003
V									0.9
Zn									13

Table S8. Sample counts for the median element concentrations in Table S7 for produced waters from tight oil wells.

	Anadarko - Southern Oklahoma	Atlantic Coastal Plain	Denver	East Texas	Green River	Gulf Coast	Permian	Powder River	Williston
pH	296	8	90	32	8	0	22	10	431
TDS	90	11	91	32	6	9	22	10	439
Al	0	0	0	0	0	0	0	0	1
As	0	0	0	0	0	0	0	0	11
B	0	0	0	0	0	0	22	0	13
Ba	37	0	0	2	0	0	1	1	291
Br	0	2	0	0	0	0	22	0	30
Ca	290	11	91	32	5	9	22	10	439
Cd	0	0	0	0	0	0	0	0	5
Cl	297	11	91	32	7	9	22	10	439
Co	0	0	0	0	0	0	0	0	11
Cr	0	0	0	0	0	0	0	0	242
Cs	0	0	0	0	0	0	0	0	13
Cu	0	0	0	0	0	0	0	0	11
F	0	0	0	0	0	0	0	0	13
Fe	111	0	55	7	5	0	22	8	388
I	0	2	0	0	0	0	22	0	19
K	2	2	3	0	3	0	22	9	385
Li	0	0	0	0	0	0	0	0	33
Mg	90	11	90	32	5	9	22	10	439
Mn	0	0	0	0	0	0	18	0	11
Mo	0	0	0	0	0	0	0	0	11
Na	90	11	91	31	6	9	22	10	440
Ni	0	0	0	0	0	0	0	0	11
P	0	0	0	0	0	0	0	0	0
Pb	0	0	0	0	0	0	0	0	7
Rb	0	0	0	0	0	0	0	0	13
S	0	0	0	0	0	0	0	0	0
SO4	286	8	36	26	7	5	15	6	436
Se	0	0	0	0	0	0	0	0	2
Si	0	0	0	0	0	0	22	0	0
Sr	0	0	0	0	0	0	22	0	33
U	0	0	0	0	0	0	0	0	1
V	0	0	0	0	0	0	0	0	2
Zn	0	0	0	0	0	0	0	0	9

Table S9. Organic carbon and carbonate carbon in shale samples along with relative categorization. More information on programmed pyrolysis parameters used in assessing organic matter types and thermal maturity can be found in the method reference[2] (HC = hydrocarbon; TOC = total organic carbon).

Shale Sample	Category	Org. C (wt%)	Carbonate C (wt%)	Hydrogen index (mg-HC/g-TOC)	Tmax (°C)	Production Index
1_Uteland Butte mem. (inf.[12-14]	Intermediate	2.4	12.04	280	441	0.61
2_Marcellus Shale of Hamilton Group	Intermediate	3.95	0.11	5	591	0.11
3_Marcellus Shale of Hamilton Group	Intermediate	2.48	1.91	269	444	0.20
4_Barnett Formation	Intermediate	3.08	2.07	12	590	0.23
5_Bakken Formation	High organic	11.765	0.37	149	451	0.20
6_Niobrara Formation	Intermediate	4.43	8.62	402	439	0.17
7_Parachute Creek Member of Green River Formation	High organic	14.175	4.94	905	442	0.03
8_Garden Gulch Member of Green River Formation	High organic	12.935	2.4	888	442	0.05
9_Cow Ridge Member of Green River Formation	Low carbonate	8.67	0.01	724	435	0.02
10_Boquillas Formation	Intermediate	1.95	9.85	547	433	0.11
11_Mancos Shale	Low carbonate	2.95	0.01	255	423	0.05
12_Woodford Shale	High organic	12.295	2.18	664	430	0.03

Table S10. Quantitative mineralogical composition of shale samples as assessed by X-ray diffraction (XRD). GRF = Green River Formation. Blank cells indicate absence or quantification at <1 wt. %.

Shale Sample	XRD Quartz (wt%)	XRD Albite (wt%)	XRD K-spar (wt%)	XRD Analcime (wt%)	XRD Calcite (wt%)	XRD Dolomite (wt%)	XRD Pyrite (wt%)	XRD Fluor-apatite (wt%)	XRD Chlorite (wt%)	XRD Illite (wt%)	XRD Kaolinite (wt%)	XRD Amorph. (wt%)
1_Uteland Butte member	1				12	87						
2_Marcellus Shale of the Hamilton Group	40	10			4		4		3	33	7	
3_Marcellus Shale of the Hamilton Group	37	6			15		2		4	25	7	6
4_Barnett Formation	55	8			7	10	2	3		14		2
5_Bakken Formation	47	14			2	4	5		2	25		1
6_Niobrara Formation	8				85		3			4		
7_Parachute Creek Member of the Green River Formation	15	12	18	1	10	44						
8_Garden Gulch Member of the Green River Formation	36	14		1		18	2			26		3
9_Cow Ridge Member of the Green River Formation	43	10		1					4	25	7	11
10_Boquillas Formation	14				77	7					2	
11_Mancos Shale	36	13			3				4	32	8	4
12_Woodford Shale	60	5				16	2		1	10	1	5

Table S11. Metrics for assessing the degree to which elements are labile in the different leachates and how lability may relate to pH. The fraction extracted is the mass of element in leachate divided by mass associated with the shale leached and median values are presented. NSD indicates no Si data were available for the shale. Asterisks indicate the median may be unduly influenced by few samples above reporting limits. The Pearson correlation coefficient is that for leachate pH compared against leachate element concentration. Only coefficients >0.4 or <−0.4 are presented, otherwise, cells are left blank. ND indicates no leachate data above the reporting limit. AB indicates element included in artificial brine prior to shale leaching.

Element	Median fraction extracted			Coefficient of correlation with pH		
	H_2O	HCl	Brine	H_2O	HCl	Brine
Al	0.01%	0.3%	0.01%	-0.9		-0.8
As	3%	5%	3%		-0.4	
Ba	0.1%	6%	4%	0.4		
Ca	1%	42%	AB	0.5	0.8	ND
Cd	3%	17%	9%	-0.8		-0.8
Co	11%	9%	2%	-0.9	-0.4	-0.9
Cr	0.2%	5%	0.05%	-0.9		-0.9
Cu	1%	3%	27%*	-0.8		-1.0
Fe	0.001%	4%	1%	-1.0		-0.6
K	0.5%	0.4%	2%		-0.6	
Li	2%	5%	6%	-0.9		-0.9
Mg	1%	29%	AB	-1.0	0.5	ND
Mn	14%	31%	1%	-0.9		-0.9
Mo	17%	6%	20%			
Ni	6%	6%	1%	-0.9	-0.4	-0.9
P	7%*	33%		-0.6		ND
Pb		10%	5%	ND		
Rb	0.1%	0.3%		-0.9	-0.5	ND
S	4%	0.03%	6%	-0.9		-0.9
Si	NSD	NSD	NSD	-0.8		-0.8
Sb		7%	18%	ND		
Sr	1%	35%	6%	0.4	0.7	0.4
Ti	0.002%	0.1%		-0.9		ND
Y	1%	25%		-0.8	-0.4	ND
Zn	7%	5%	3%	-0.9		-0.9

Figure S1. Basin-median concentrations of total dissolved solids (TDS) and values of pH for produced waters types and brine leachates. Values for seawater provided for comparison.[15]

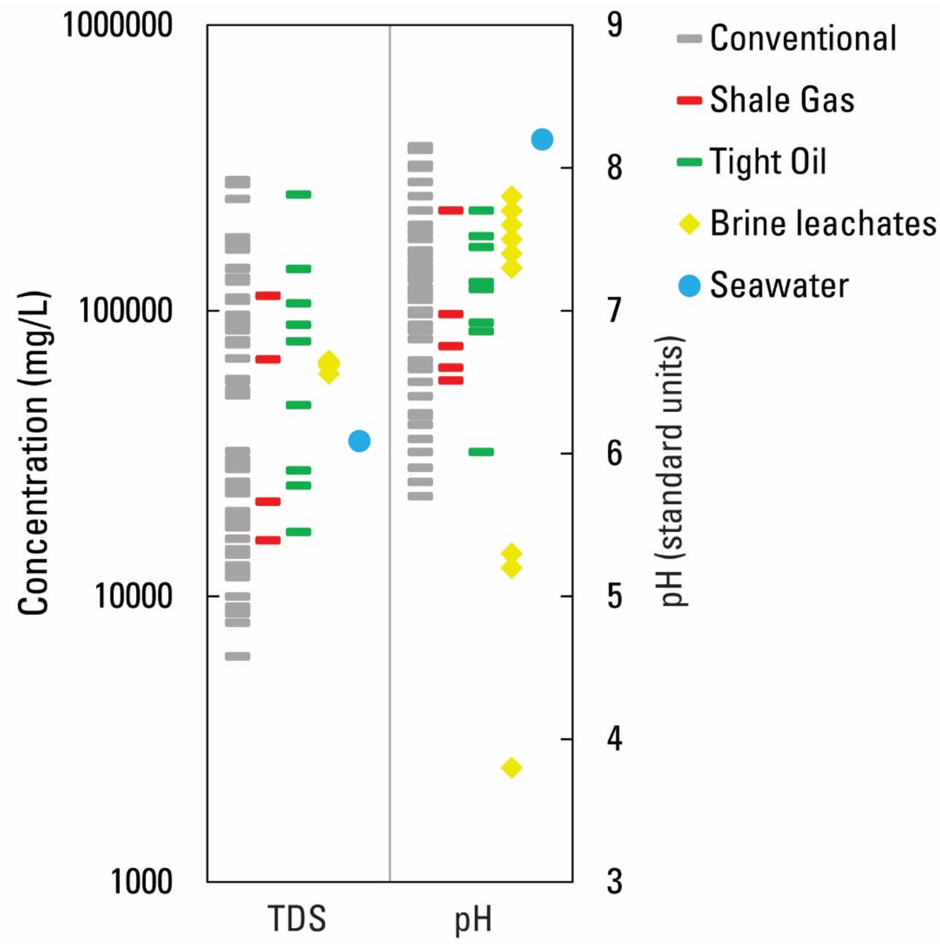


Figure S2. Basin median concentrations of Na and Cl in produced waters types from the U.S. Geological Survey Produced Waters Geochemical Database (v2.3)[11] compared to concentrations in modern seawater.

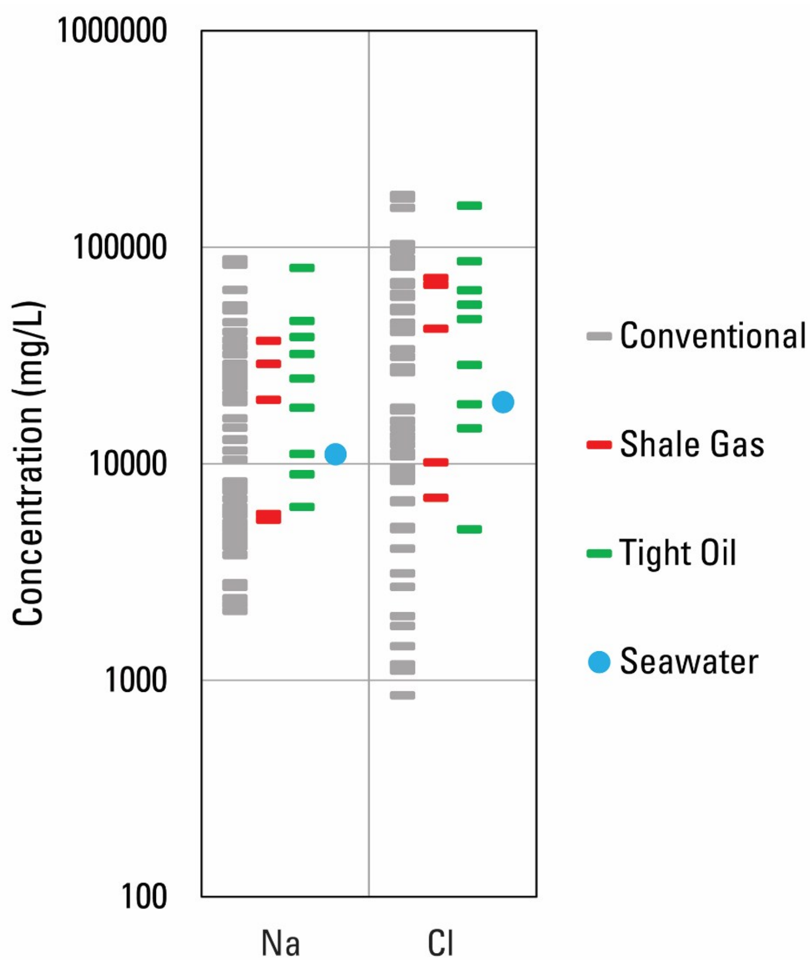


Figure S3. Scatterplots comparing log molar concentrations of chloride in produced waters types and brine and HCl leachates to log molar concentrations of Na (a), K (b), Mg (c), and Ca (d) for individual samples from the U.S. Geological Survey Produced Waters Geochemical Database (v2.3).[11] For reference, concentrations in seawater are plotted[15] along with a light blue line indicating an evaporation/dilution trend for seawater that does not account for halite or other mineral saturation. Also, for reference, darker blue lines indicate the 1:1 slopes in (a) and (b), and 2:1 slopes in (c) and (d) as in Hanor (2001)[16].

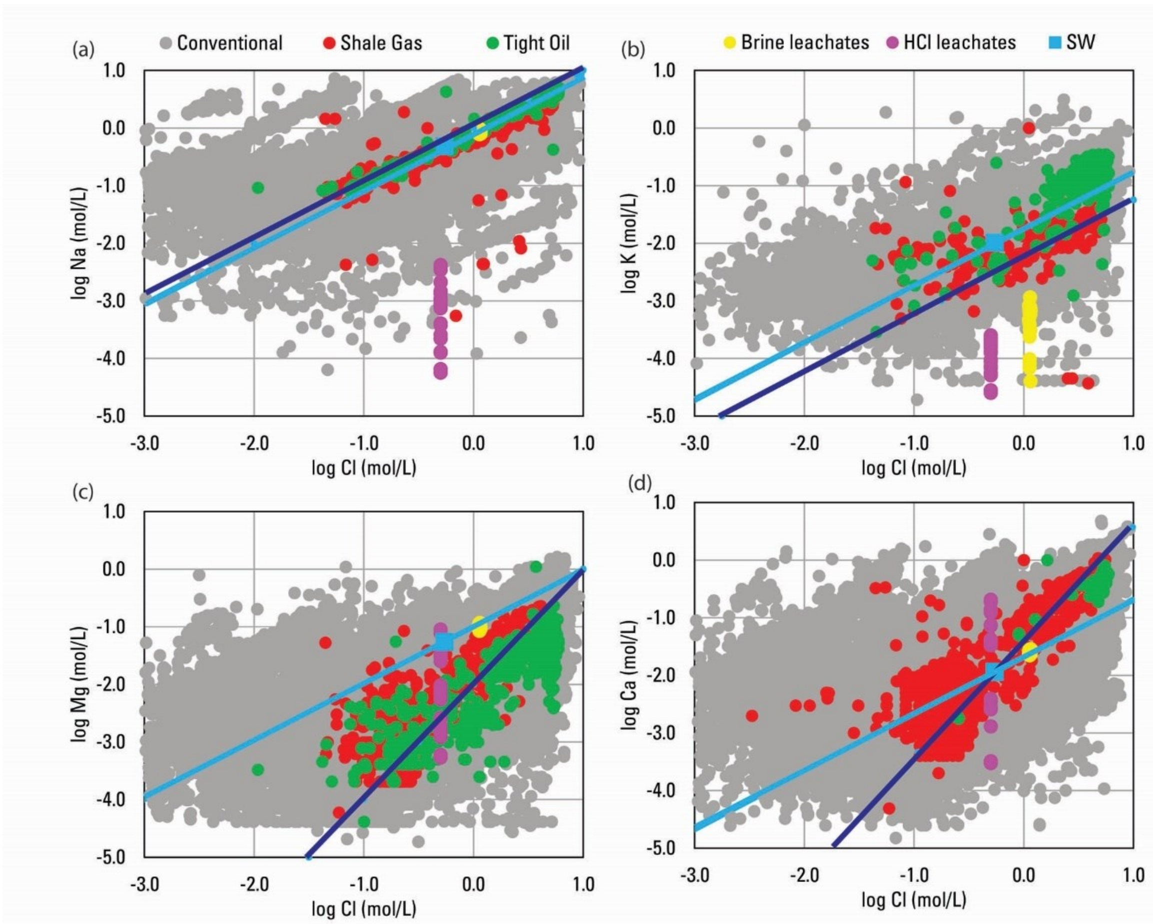


Figure S4. Scatterplots of pH in individual samples of produced waters and water, HCl, and brine leachates versus log molar concentrations of Na (a), K (b), Ca (c), and Mg (d).

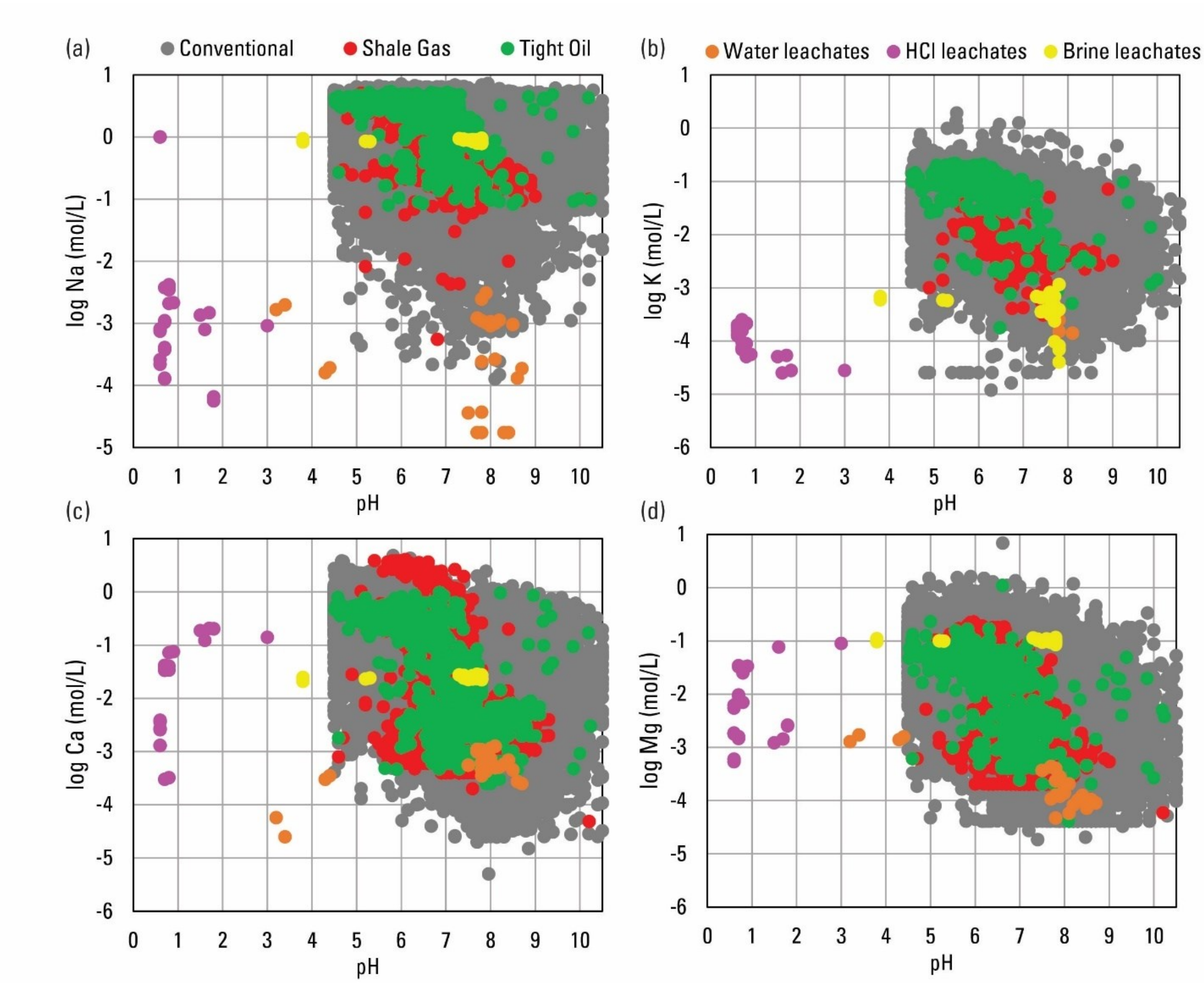


Figure S5. Ratio of element concentration in the 12 shales used in the leaching experiments to concentrations in shale reference compositions. For the major elements (Al, Ca, Fe, K, Mg, Mn, P, and Ti) the reference is the North American shale composite (NASC)[17]. For the trace elements (As, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Rb, Sr, Sb, Zn, the reference is an average composition for world black shales[18]. For S, the reference is an average for gas shales in the United States[19]. Concentrations of As and Cd were below reporting limits for several shales. Concentrations of Cr, Cu, Mo, Ni, Pb, S, Sb, Ti, and Zn were below reporting limits for Shale-1. Cow Ridge, Uteland Butte (informal[12-14]), Garden Gulch, and Parachute Creek are members of the Green River Formation.

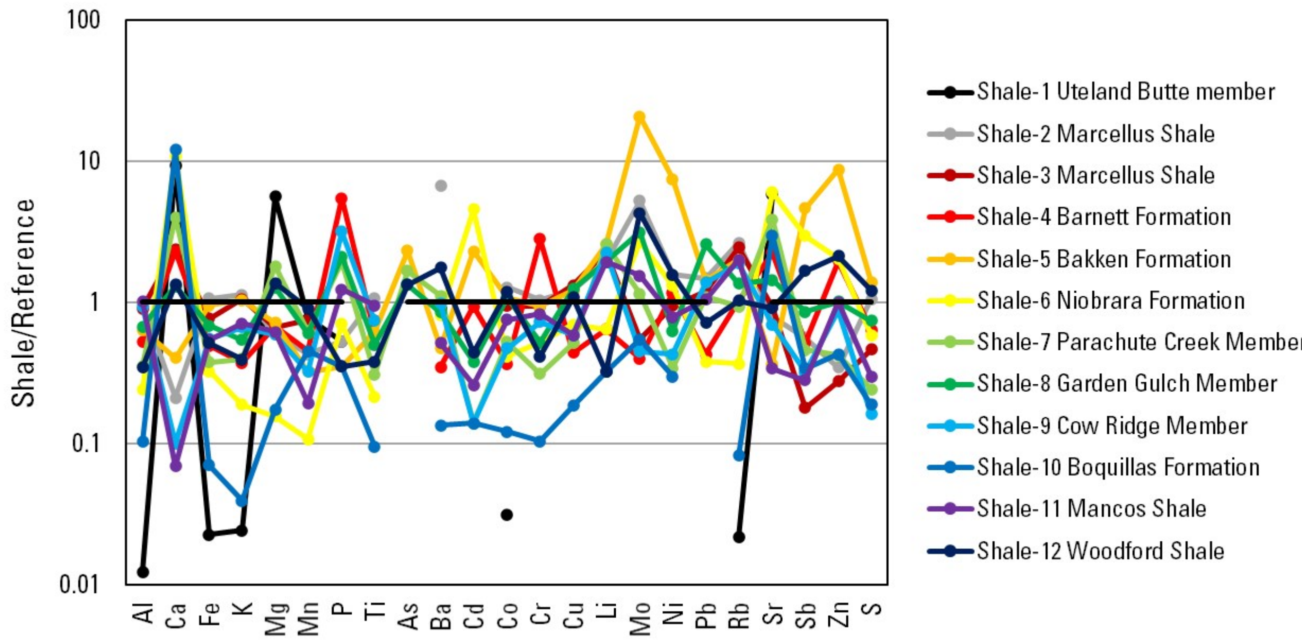


Figure S6. Scatterplots showing relations between the Nd and K (a), Gd and K (b), Nd and Rb (c), Gd and Rb (d), Nd and P (e), and Gd and P (f) in the HCl leachates. Concentrations have been centered log ratio transformed to place them in a compositional data analysis framework and prevent spurious correlations. Neodymium is a light rare earth element (LREE) and Gd is a middle rare earth element (MREE). Values of R^2 and p-values are provided for reference, with black text indicating values for all samples and values in red omitting the carbonate-dominated Shale 1 (informal Uteland Butte member[12-14] of the Green River Formation) samples. Note that mobilization of the MREE element is significantly positively correlated with illite-associated elements K and Rb, but not P, as from a phosphate mineral. In contrast, the LREE element is not significantly correlated with K or Rb and not quite correlated with P at the p = 0.05 threshold.

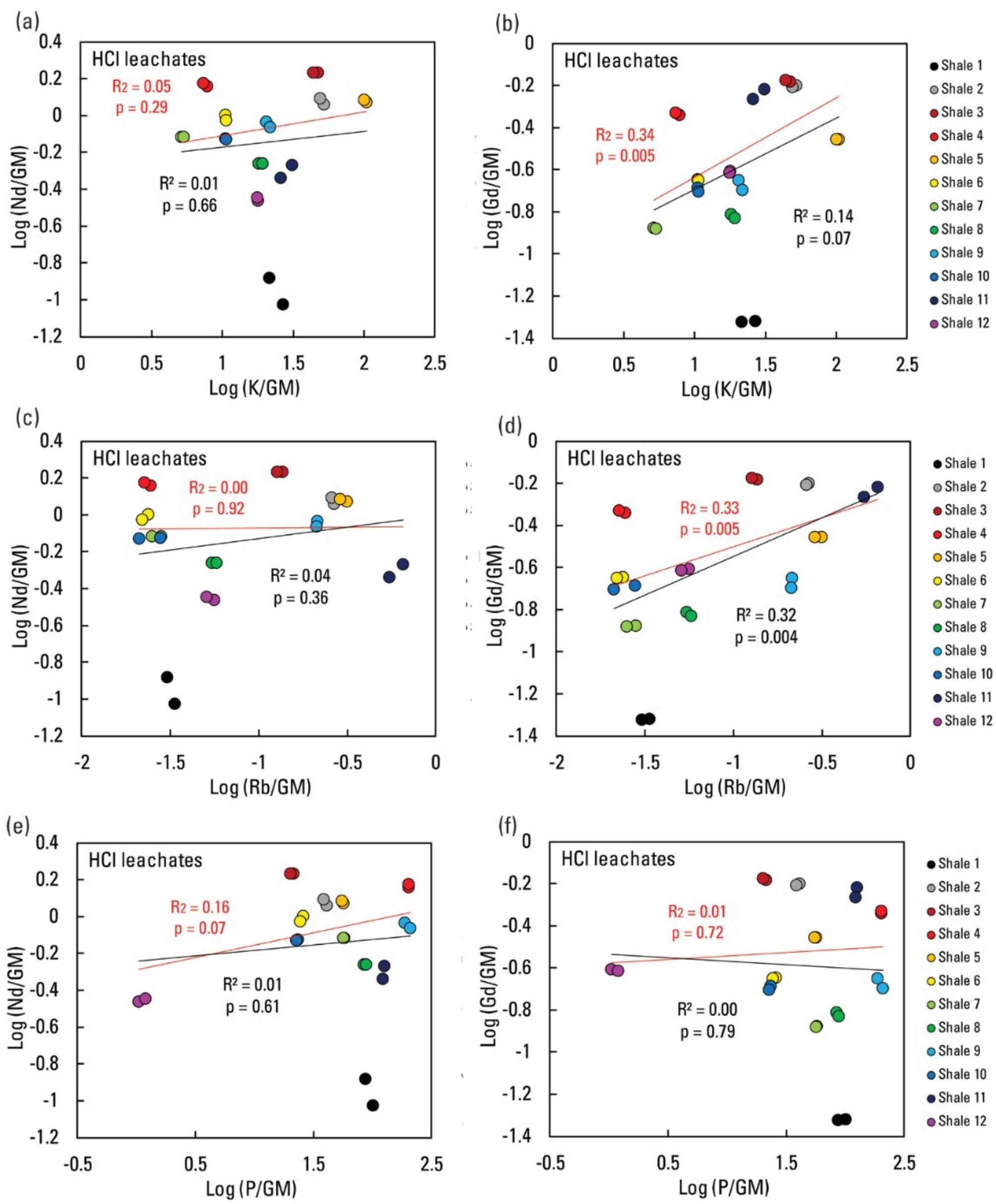


Figure S7. Scatterplots showing relations between illite abundance in shale samples assessed by x-ray diffraction (XRD) and concentrations of the LREE Nd and the MREE Gd in the HCl leachates. Values of R^2 and p-values are provided for reference, with black text indicating values for all samples and values in blue omitting the fluorapatite-bearing Shale 4 (Barnett Formation) samples. Apatite minerals are substantial hosts for REEs. Note that the MREE element correlates significantly positively with illite but the LREE does not.

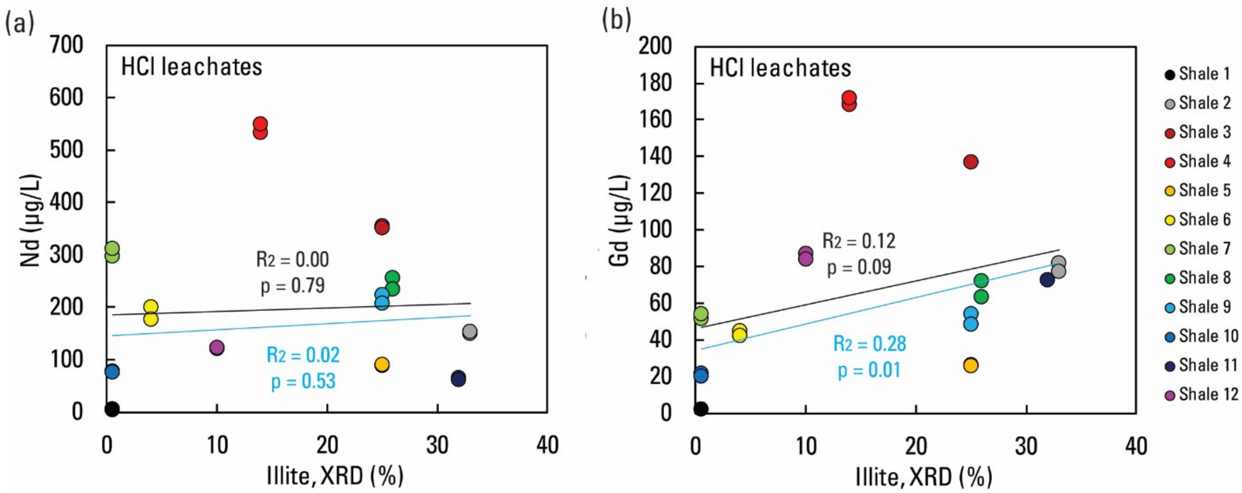
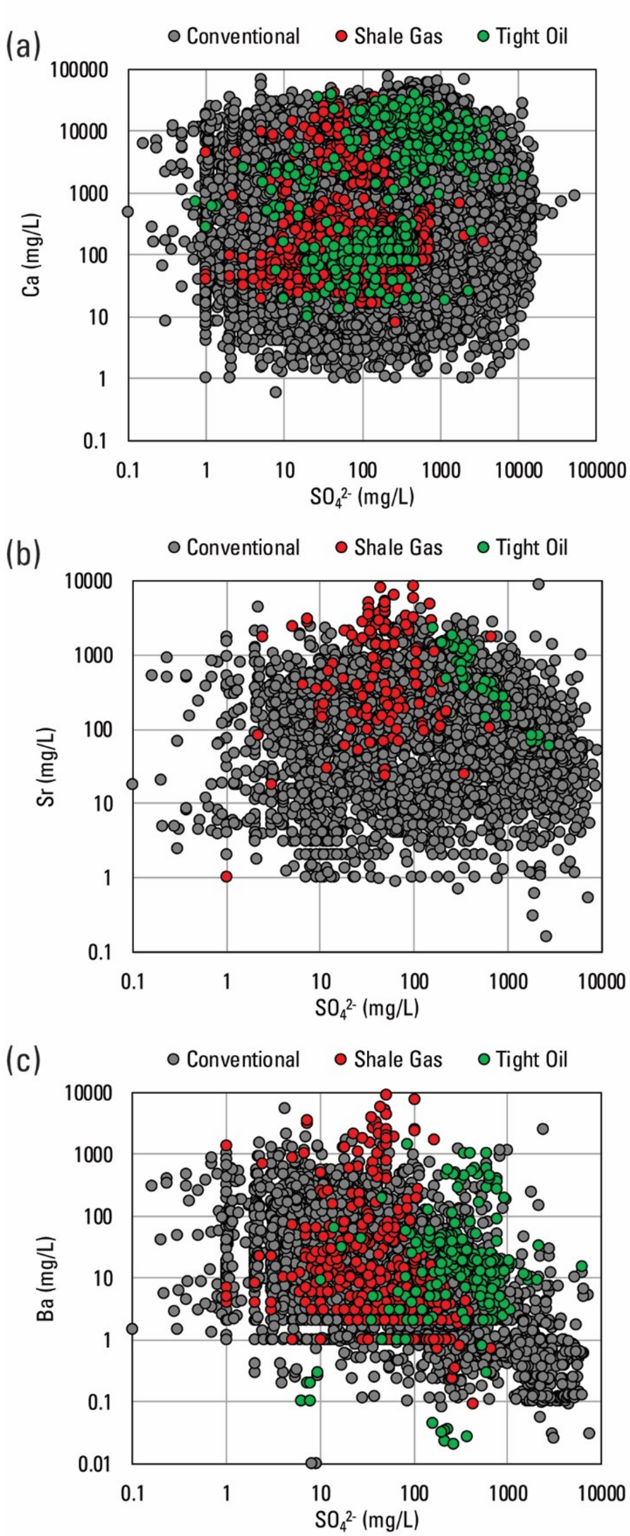


Figure S8. Scatterplots of concentrations of Ca (a), Sr (b), and Ba (c) versus SO_4^{2-} in produced waters using data from the U.S. Geological Survey Produced Waters Database (v2.3).[11]



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