Supporting Information

Strontium Isotopes Test Long-Term Zonal Isolation of Injected and Marcellus Formation Water after Hydraulic Fracturing

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Section S.1: Methods

Elemental Analysis. Concentrations of Sr and Ca were measured on a Spectroflame Modula ICP-AES following a modified version of EPA method 6010C. After filtration and acidification all produced water samples were diluted to 1:100 or 1:1000 (UD/LM samples and Marcellus shale samples respectively) with 2% HNO_3. Solutions were again spiked with ultrapure concentrated nitric acid to 4% HNO_3 by volume to ensure dissolution of any precipitates that may have formed over a two year storage time. Samples were spiked with ~1 ppm Sc internal standard to monitor instrument drift and matrix effects during elemental analysis. Further QA/QC analysis was carried out using matrix-matched calibration verifications throughout the analytical run as well as a certified standard solution (NIST 1640a) where Sr and Ca concentrations were measured to be within ± 10% of reported values.

Strontium Isotope Analysis. Sample preparation and analysis for Sr isotopes was carried out using the procedure of Wall et al.[36] A solution containing approximately 2 μg of Sr was aliquoted and evaporated to dryness. It was then redissolved in 8 N HNO_3 and separated from the other matrix elements using Sr Resin® (Eichrom) in a vacuum box. The separated Sr solution was analyzed for $^{87}Sr/^{86}Sr$ on a Thermo Neptune multicollector ICP-MS. Instrumental mass bias was corrected using an exponential law, assuming $^{86}Sr/^{88}Sr = 0.1194$. NIST Standard SRM 987 was run repeatedly with the unknown samples, and the final $^{87}Sr/^{86}Sr$ value of the sample reflects the offset from this standard, assuming a value for SRM 987 of 0.710240. Maximum total procedural blanks ranged from 40 to 320 pg Sr (n= 5), resulting in blank/sample ratios of ≤ 0.0002, which are negligible. Selected samples were replicated by taking additional aliquots and putting them through the full Sr separation and analysis procedure (**Table S2**).

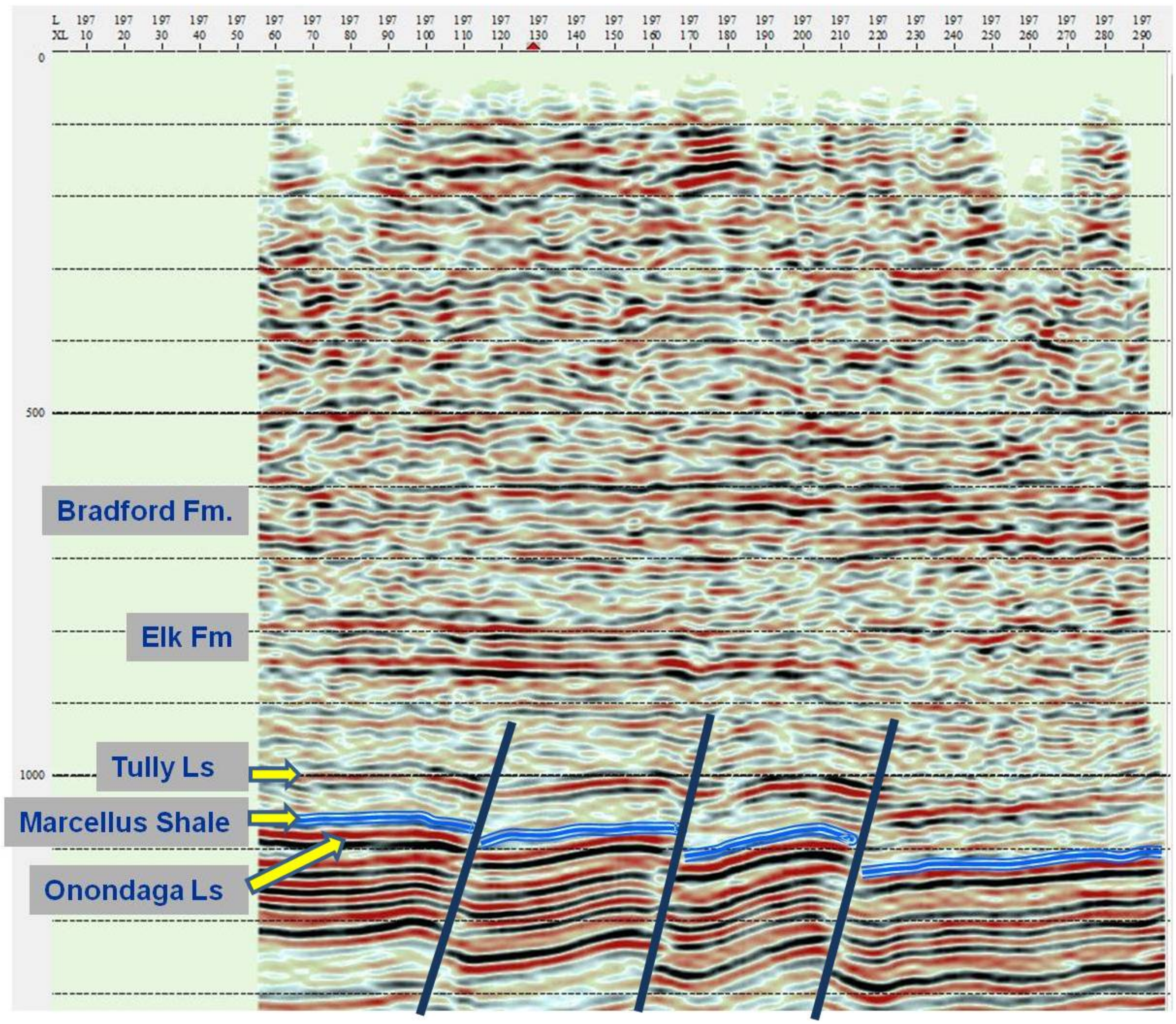

Figure S1. E-W seismic section at the Greene County site, with interpreted thrust faults. Note that the faults appear to die out shortly above the Tully Limestone, and do not extend into gas-producing Upper Devonian units. The ordinate is two-way travel time (ms) and the abscissa is distance in 1,000-ft increments. Figure from Hammack et al.[30]

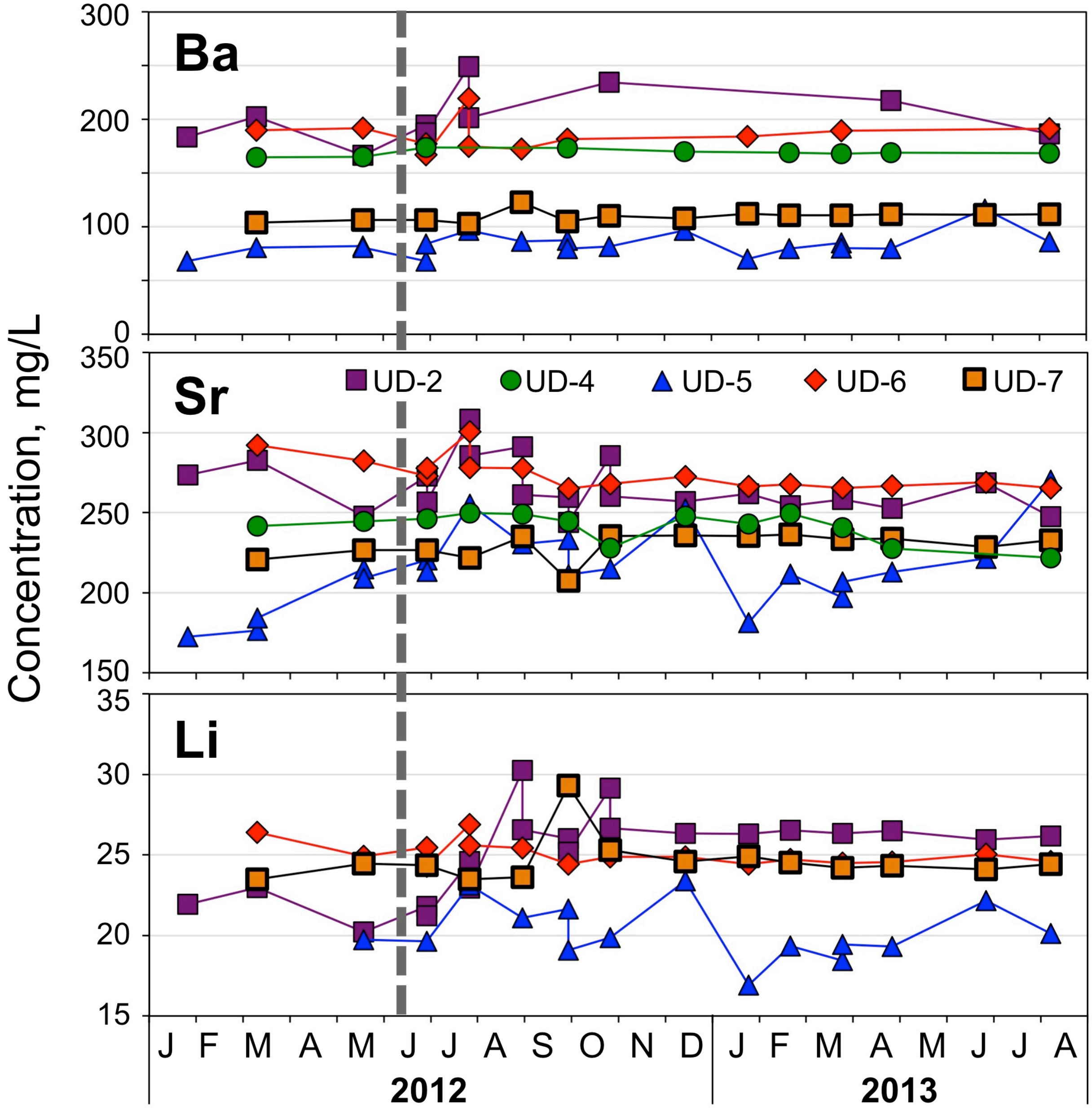

Figure S2. Selected element concentrations in Upper Devonian/Lower Mississippian conventional gas wells before and after hydraulic fracturing of the underlying Marcellus shale. The gray dashed line indicates the time of hydraulic fracturing.

Table S1. Sample information and elemental concentrations from the Greene County Site.

Sample Name	Date Collected	Sample Type	Specific Gravity	Li	Na	K	Mg	Ca	Sr	Ba	Fe
				mg/L							
Well UD-2: Upper Devonian/Lower Mississippian											
UD2-120125-T	1/25/12	Tank	1.091	21.9	34,300	183	1,910	14,800	274	184	177
UD2-120310-S	3/10/12	Separator	1.096	23.0	35,400	179	1,960	15,800	283	203	208
UD2-120518-S	5/18/12	Separator	1.100	20.2	33,200	176	1,860	14,200	248	167	259
UD2-120628-S	6/28/12	Separator	1.101	21.8	36,300	180	2,040	15,400	273	195	436
UD2-120628-T	6/28/12	Tank	1.096	21.2	34,300	164	1,910	14,300	256	188	78
UD2-120726-S	7/26/12	Separator	1.099	24.6	37,500	173	2,110	16,400	308	249	78
UD2-120726-T	7/26/12	Tank	1.110	22.9	36,500	178	2,040	15,500	286	202	118
UD2-120829-S	8/29/12	Separator	1.100	30.3	44,100	205	ND[a]	16,500	291	ND	96
UD2-120829-T	8/29/12	Tank	1.102	26.6	40,400	186	ND	14,400	261	ND	89
UD2-120928-S	9/28/12	Separator	1.099	26.0	39,900	177	ND	14,300	260	ND	106
UD2-120928-T	9/28/12	Tank	1.095	25.2	38,500	174	ND	13,600	244	ND	95
UD2-121025-S	10/25/12	Separator	1.115	29.1	43,400	198	ND	15,900	286	235	65
UD2-121025-T	10/25/12	Tank	1.101	26.7	40,500	187	ND	14,600	260	ND	73
UD2-121213-S	12/13/12	Separator	1.068	26.4	40,400	185	ND	14,700	257	ND	133
UD2-130123-T	1/23/13	Tank	1.090	26.3	40,300	184	ND	14,400	262	ND	79
UD2-130219-T	2/19/13	Tank	1.094	26.5	39,700	170	ND	10,600	254	ND	89
UD2-130325-T	3/25/13	Tank	1.091	26.3	39,300	177	ND	14,400	258	ND	85
UD2-130426-S	4/26/13	Separator	1.096	26.5	40,300	183	ND	13,900	253	218	76
UD2-130626-S	6/26/13	Separator	1.099	26.0	38,900	168	ND	15,200	269	ND	70
UD2-130807-S	8/7/13	Separator	1.093	26.2	40,600	191	ND	13,700	247	186	186
Well UD-4: Upper Devonian/Lower Mississippian											
UD4-120310-T	3/10/12	Tank	1.119	ND	38,000	195	1,960	15,200	242	165	ND
UD4-120518-T	5/18/12	Tank	1.125	ND	37,300	191	1,940	15,400	245	165	ND
UD4-120628-T	6/28/12	Tank	1.130	ND	39,700	190	2,060	15,700	246	174	ND
UD4-120726-T	7/26/12	Tank	1.124	ND	40,100	192	2,070	15,700	250	ND	ND
UD4-120829-T	8/29/12	Tank	1.123	ND	39,800	191	2,060	15,700	249	ND	ND
UD4-120928-T	9/28/12	Tank	1.124	ND	39,400	188	2,050	15,600	245	173	ND
UD4-121025-T	10/25/12	Tank	1.030	ND	36,600	176	1,920	14,400	228	ND	ND
UD4-121213-T	12/13/12	Tank	1.129	ND	39,800	192	2,100	15,700	248	170	ND
UD4-130123-T	1/23/13	Tank	1.108	ND	39,000	187	2,040	15,400	243	ND	ND
UD4-130219-T	2/19/13	Tank	1.128	ND	38,800	190	2,100	15,700	249	169	327
UD4-130325-T	3/25/13	Tank	1.131	ND	39,600	193	2,200	16,300	240	168	327
UD4-130426-T	4/26/13	Tank	1.118	ND	38,800	188	2,090	16,100	228	169	332
UD4-130807-T	8/7/13	Tank	1.103	ND	38,200	180	2,030	15,700	222	169	417
Well UD-5: Upper Devonian/Lower Mississippian											
UD5-120125-S	1/25/12	Separator	1.031	ND	ND	ND	ND	ND	ND	ND	ND
UD5-120125-T	1/25/12	Tank	1.078	ND	36,600	172	1,810	14,100	172	68	ND
UD5-120310-S	3/10/12	Separator	1.085	ND	37,300	171	1,840	14,300	176	81	ND
UD5-120310-T	3/10/12	Tank	1.100	ND	38,800	184	1,940	15,200	184	ND	ND
UD5-120518-S	5/18/12	Separator	1.117	19.7	37,900	185	1,960	15,200	215	82	234
UD5-120518-T	5/18/12	Tank	1.099	ND	ND	174	1,890	14,700	209	81	ND
UD5-120628-S	6/28/12	Separator	1.116	ND	ND	194	2,120	16,200	220	68	ND
UD5-120628-T	6/28/12	Tank	1.106	19.6	38,100	184	2,010	14,500	213	84	85
UD5-120726-S	7/26/12	Separator	1.084	23.1	42,600	220	2,290	17,700	255	97	81
UD5-120829-S	8/29/12	Separator	1.111	21.1	40,100	197	2,140	16,200	231	86	139
UD5-120928-S	9/28/12	Separator	1.074	21.7	40,600	205	2,170	16,500	233	87	118
UD5-120928-T	9/28/12	Tank	1.087	19.1	37,100	177	1,990	14,700	211	80	107
UD5-121025-T	10/25/12	Tank	1.106	19.8	38,300	184	2,060	15,300	215	82	95
UD5-121213-T	12/13/12	Tank	1.098	23.4	45,500	217	2,430	18,000	252	97	125

Sample Name	Date Collected	Sample Type	Specific Gravity	Li	Na	K	Mg	Ca	Sr	Ba	Fe
				mg/L							
UD5-130123-T	1/23/13	Tank	1.085	16.9	33,000	158	1,770	13,000	181	70	98
UD5-130219-T	2/19/13	Tank	1.071	19.3	37,400	180	1,980	14,700	212	80	127
UD5-130325-S	3/25/13	Separator	1.059	18.4	36,100	171	1,930	14,200	197	85	149
UD5-130325-T	3/25/13	Tank	1.090	19.4	37,600	180	2,040	14,800	207	80	147
UD5-130426-T	4/26/13	Tank	1.087	19.3	37,500	179	2,010	15,200	213	80	136
UD5-130626-T	6/26/13	Tank	1.116	22.2	41,500	202	2,260	15,800	221	116	248
UD5-130807-S	8/7/13	Separator	1.103	20.1	38,600	186	2,070	18,700	270	86	223
Well UD-6: Upper Devonian/Lower Mississippian											
UD6-120310-S	3/10/12	Separator	1.097	26.4	40,600	ND	2,060	16,600	292	190	89
UD6-120518-S	5/18/12	Separator	1.108	24.9	39,200	ND	1,950	15,700	282	192	85
UD6-120628-S	6/28/12	Separator	1.110	25.5	40,400	ND	2,050	15,800	273	177	68
UD6-120628-T	6/28/12	Tank	1.096	24.3	39,500	ND	1,970	16,200	278	167	56
UD6-120726-S	7/26/12	Separator	1.074	26.9	40,800	ND	2,070	16,400	301	220	63
UD6-120726-T	7/26/12	Tank	1.098	25.6	40,900	ND	2,070	16,300	278	175	50
UD6-120829-T	8/29/12	Tank	1.088	25.4	40,600	ND	2,030	16,200	278	173	64
UD6-120928-T	9/28/12	Tank	1.105	24.4	39,700	183	1,960	15,200	265	182	68
UD6-121025-T	10/25/12	Tank	1.081	24.9	39,800	187	2,010	15,700	268	ND	49
UD6-121213-T	12/13/12	Tank	1.097	24.9	40,500	190	2,020	16,000	273	ND	61
UD6-130123-T	1/23/13	Tank	1.094	24.4	39,800	186	2,020	15,800	266	184	72
UD6-130219-T	2/19/13	Tank	1.094	24.7	40,000	186	2,010	15,600	268	ND	72
UD6-130325-T	3/25/13	Tank	1.086	24.5	39,500	183	1,980	15,500	265	189	87
UD6-130426-T	4/26/13	Tank	1.094	24.6	39,900	186	2,020	15,600	267	ND	117
UD6-130626-T	6/26/13	Tank	1.110	25.0	40,500	186	2,060	16,000	269	ND	148
UD6-130807-T	8/7/13	Tank	1.102	24.6	40,300	187	2,070	15,900	266	191	147
Well UD-7: Upper Devonian/Lower Mississippian											
UD7-120310-T	3/10/12	Tank	1.080	23.5	37,000	198	1,970	15,400	221	104	329
UD7-120518-T	5/18/12	Tank	1.144	24.5	38,400	205	2,060	16,200	227	106	478
UD7-120628-T	6/28/12	Tank	1.119	24.4	39,500	198	2,110	16,100	227	107	430
UD7-120726-T	7/26/12	Tank	1.077	23.5	38,500	193	2,050	15,700	222	103	282
UD7-120829-T	8/29/12	Tank	1.117	23.6	39,300	197	2,120	16,200	235	123	349
UD7-120928-T	9/28/12	Tank	1.136	29.3	45,000	237	ND	16,100	207	105	454
UD7-121025-T	10/25/12	Tank	1.127	25.3	40,100	202	2,170	16,600	235	110	290
UD7-121213-T	12/13/12	Tank	1.136	24.6	40,200	201	2,150	16,400	236	108	296
UD7-130123-T	1/23/13	Tank	1.143	24.9	40,200	201	2,160	16,600	235	112	304
UD7-130219-T	2/19/13	Tank	1.129	24.5	39,700	196	2,130	16,400	237	111	308
UD7-130325-T	3/25/13	Tank	1.103	24.2	39,200	195	2,110	16,600	234	111	306
UD7-130426-T	4/26/13	Tank	1.136	24.3	39,700	196	2,140	16,500	234	112	318
UD7-130626-T	6/26/13	Tank	1.125	24.1	39,400	193	2,110	16,500	229	112	329
UD7-130807-T	8/7/13	Tank	1.139	24.4	39,900	197	2,150	16,900	233	112	401
Well MW-1: Middle Devonian, vertical, hydraulically fractured in 2006											
MW1-120310-T	3/10/12	Tank	1.076	ND	ND	ND	ND	14,900	1,830	ND	ND
MW1-120518-T	5/18/12	Tank	1.072	ND	ND	ND	ND	11,200	1,370	ND	ND
MW1-120628-T	6/28/12	Tank	1.093	78.2	39,500	169	1,480	12,900	1,650	1,568	23
MW1-120726-T	7/26/12	Tank	1.064	93.1	48,000	203	1,820	16,000	1,960	2,057	48
MW1-120829-T	8/29/12	Tank	1.097	71.4	35,100	150	1,350	12,100	1,400	1,586	82
MW1-120928-T	9/28/12	Tank	1.098	68.6	33,900	141	1,310	11,900	1,520	1,637	53
MW1-121025-T	10/25/12	Tank	1.067	69.5	33,400	150	1,310	11,700	1,460	1,649	89
MW1-121213-T	12/13/12	Tank	1.091	85.1	41,000	178	1,620	14,700	1,940	2,152	85
MW1-130123-T	1/23/13	Tank	1.089	84.5	40,200	177	1,590	14,500	1,950	2,146	106
MW1-130219-T	2/19/13	Tank	1.099	84.6	40,500	175	1,600	14,800	2,080	2,149	131
MW1-130325-T	3/25/13	Tank	1.091	85.7	39,300	175	ND	14,700	2,020	2,164	78

Sample Name	Date Collected	Sample Type	Specific Gravity	Li	Na	K	Mg	Ca	Sr	Ba	Fe
				mg/L							
MW1-130426-T	4/26/13	Tank	1.099	88.4	40,500	179	ND	17,500	2,070	2,256	88
MW1-130626-T	6/26/13	Tank	1.095	89.0	40,700	185	ND	15,900	2,190	2,326	140
MW1-130807-T	8/7/13	Tank	1.093	86.7	39,300	186	ND	15,200	2,330	2,305	173
Spring water: Shallow groundwater											
SPW-120518	5/18/12	Spring	ND	0.0170	5.86	0.60	13.9	50.6	0.161	0.076	0.038
SPW-120628	6/28/12	Spring	ND	0.0185	6.58	0.88	15.9	58.4	0.176	0.093	0.558
SPW-120726	7/26/12	Spring	ND	0.0193	6.63	1.67	16.4	61.0	0.190	0.126	1.561
SPW-120829	8/29/12	Spring	ND	0.0672	4.81	1.51	16.9	60.3	0.191	0.097	1.095
SPW-120928	9/28/12	Spring	ND	0.0214	7.23	1.30	18.0	64.6	0.196	0.125	3.024
SPW-121025	10/25/12	Spring	ND	0.0205	7.53	1.08	18.3	65.9	0.203	0.109	1.726
SPW-121213	12/13/12	Spring	ND	0.0177	6.13	0.83	14.3	53.7	0.162	0.080	0.089
SPW-130123	1/23/13	Spring	ND	0.0174	6.06	0.78	13.6	50.4	0.153	0.081	0.352
SPW-130219	2/19/13	Spring	ND	0.0172	5.92	0.78	13.8	51.7	0.153	0.077	0.129
SPW-130325	3/25/13	Spring	ND	0.0173	5.88	0.78	14.2	53.7	0.154	0.077	0.150
SPW-130426	4/26/13	Spring	ND	0.0186	6.38	0.81	16.1	57.7	0.175	0.082	0.288
SPW-130626	6/26/13	Spring	ND	0.0189	6.99	1.02	17.7	60.3	0.191	0.103	0.446
SPW-130807	8/7/13	Spring	ND	0.0196	7.80	0.98	17.5	64.0	0.193	0.096	0.174

[a]ND = not determined

Table S2. Strontium isotope compositions from the Greene County Site

Sample Name	Date Collected	Sample Type	$^{87}Sr/^{86}Sr^{a,b}$	ε_{Sr}^{c}
Well UD-2: Upper Devonian/Lower Mississippian				
UD2-120125-T	1/25/12	Tank	0.719902 ± 0.000015	151.39 ± 0.21
UD2-120310-S	3/10/12	Separator	0.719976 ± 0.000013	152.43 ± 0.19
(replicate)			0.720006 ± 0.000015	152.86 ± 0.21
UD2-120518-S	5/18/12	Separator	0.720076 ± 0.000016	153.84 ± 0.22
UD2-120628-S	6/28/12	Separator	0.720057 ± 0.000007	153.57 ± 0.10
UD2-120628-T	6/28/12	Tank	0.719941 ± 0.000007	151.94 ± 0.10
(replicate)			0.719954 ± 0.000007	152.12 ± 0.10
UD2-120726-S	7/26/12	Separator	0.719873 ± 0.000009	150.98 ± 0.13
UD2-120726-T	7/26/12	Tank	0.719937 ± 0.000007	151.88 ± 0.10
UD2-120829-S	8/29/12	Separator	0.719955 ± 0.000008	152.14 ± 0.11
UD2-120829-T	8/29/12	Tank	0.719934 ± 0.000006	151.84 ± 0.09
UD2-120928-S	9/28/12	Separator	0.719933 ± 0.000006	151.83 ± 0.09
UD2-120928-T	9/28/12	Tank	0.719914 ± 0.000007	151.56 ± 0.10
UD2-121025-S	10/25/12	Separator	0.719932 ± 0.000006	151.81 ± 0.09
(replicate)			0.719937 ± 0.000009	151.88 ± 0.12
UD2-121025-T	10/25/12	Tank	0.719930 ± 0.000008	151.78 ± 0.11
UD2-121213-S	12/13/12	Separator	0.720018 ± 0.000010	153.02 ± 0.15
UD2-130123-T	1/23/13	Tank	0.719945 ± 0.000010	152.00 ± 0.14
(replicate)			0.719941 ± 0.000009	151.94 ± 0.13
UD2-130219-T	2/19/13	Tank	0.719886 ± 0.000011	151.16 ± 0.16
UD2-130325-T	3/25/13	Tank	0.719902 ± 0.000011	151.39 ± 0.15
UD2-130426-S	4/26/13	Separator	0.719909 ± 0.000010	151.49 ± 0.14
UD2-130626-S	6/26/13	Separator	0.720026 ± 0.000010	153.14 ± 0.14
UD2-130807-S	8/7/13	Separator	0.720084 ± 0.000011	153.96 ± 0.16
Well UD-4: Upper Devonian/Lower Mississippian				
UD4-120310-T	3/10/12	Tank	0.720295 ± 0.000011	156.93 ± 0.16
UD4-120518-T	5/18/12	Tank	0.720267 ± 0.000012	156.54 ± 0.17
(replicate)			0.720304 ± 0.000009	157.06 ± 0.13
UD4-120628-T	6/28/12	Tank	0.720281 ± 0.000006	156.73 ± 0.09
UD4-120726-T	7/26/12	Tank	0.720284 ± 0.000007	156.78 ± 0.10
UD4-120829-T	8/29/12	Tank	0.720265 ± 0.000006	156.51 ± 0.08
UD4-120928-T	9/28/12	Tank	0.720264 ± 0.000006	156.49 ± 0.09
UD4-121025-T	10/25/12	Tank	0.720281 ± 0.000007	156.73 ± 0.10
(replicate)			0.720282 ± 0.000011	156.75 ± 0.16
UD4-121213-T	12/13/12	Tank	0.720275 ± 0.000010	156.65 ± 0.14
UD4-130123-T	1/23/13	Tank	0.720283 ± 0.000011	156.76 ± 0.15
UD4-130219-T	2/19/13	Tank	0.720278 ± 0.000010	156.69 ± 0.15
UD4-130325-T	3/25/13	Tank	0.720283 ± 0.000012	156.76 ± 0.16
UD4-130426-T	4/26/13	Tank	0.720280 ± 0.000011	156.72 ± 0.16
UD4-130807-T	8/7/13	Tank	0.720256 ± 0.000012	156.38 ± 0.16
			0.720249 ± 0.000010	156.28 ± 0.14
Well UD-5: Upper Devonian/Lower Mississippian				
UD5-120125-S	1/25/12	Separator	0.720875 ± 0.000012	165.11 ± 0.17
UD5-120125-T	1/25/12	Tank	0.720954 ± 0.000009	166.22 ± 0.13
UD5-120310-S	3/10/12	Separator	0.720949 ± 0.000011	166.15 ± 0.15
(replicate)			0.720981 ± 0.000013	166.60 ± 0.18
UD5-120310-T	3/10/12	Tank	0.720921 ± 0.000013	165.76 ± 0.18
(replicate)			0.720909 ± 0.000013	165.59 ± 0.19
UD5-120518-S	5/18/12	Separator	0.720853 ± 0.000013	164.80 ± 0.19
UD5-120518-T	5/18/12	Tank	0.720916 ± 0.000014	165.69 ± 0.19
UD5-120628-S	6/28/12	Separator	0.721120 ± 0.000006	168.56 ± 0.09
UD5-120628-T	6/28/12	Tank	0.720944 ± 0.000006	166.08 ± 0.09
UD5-120726-S	7/26/12	Separator	0.720934 ± 0.000008	165.94 ± 0.11
UD5-120829-S	8/29/12	Separator	0.720950 ± 0.000006	166.17 ± 0.09
UD5-120928-S	9/28/12	Separator	0.720955 ± 0.000007	166.24 ± 0.10
UD5-120928-T	9/28/12	Tank	0.720945 ± 0.000006	166.10 ± 0.09

Sample Name	Date Collected	Sample Type	$^{87}Sr/^{86}Sr^{a,b}$	ε_{Sr}^{c}
UD5-121025-T	10/25/12	Tank	0.720951 ± 0.000008	166.18 ± 0.11
UD5-121213-T	12/13/12	Tank	0.720948 ± 0.000012	166.14 ± 0.17
UD5-130123-T	1/23/13	Tank	0.720953 ± 0.000010	166.21 ± 0.14
UD5-130219-T	2/19/13	Tank	0.720944 ± 0.000014	166.08 ± 0.19
UD5-130325-S	3/25/13	Separator	0.720960 ± 0.000015	166.31 ± 0.22
UD5-130325-T	3/25/13	Tank	0.720954 ± 0.000009	166.22 ± 0.13
UD5-130426-T	4/26/13	Tank	0.720959 ± 0.000013	166.29 ± 0.18
UD5-130626-T	6/26/13	Tank	0.720865 ± 0.000011	164.97 ± 0.15
UD5-130807-S	8/7/13	Separator	0.720820 ± 0.000011	164.33 ± 0.16
Well UD-6: Upper Devonian/Lower Mississippian				
UD6-120310-S	3/10/12	Separator	0.720033 ± 0.000014	153.24 ± 0.19
UD6-120518-S	5/18/12	Separator	0.719918 ± 0.000014	151.61 ± 0.20
(replicate)			0.719944 ± 0.000015	151.98 ± 0.21
(replicate)			0.719951 ± 0.000020	152.08 ± 0.28
(replicate)			0.719969 ± 0.000016	152.33 ± 0.23
(replicate)			0.719966 ± 0.000018	152.29 ± 0.25
(replicate)			0.719977 ± 0.000015	152.45 ± 0.22
UD6-120628-S	6/28/12	Separator	0.720032 ± 0.000006	153.22 ± 0.08
UD6-120628-T	6/28/12	Tank	0.720102 ± 0.000007	154.21 ± 0.10
UD6-120726-S	7/26/12	Separator	0.719770 ± 0.000006	149.53 ± 0.08
UD6-120726-T	7/26/12	Tank	0.720097 ± 0.000007	154.14 ± 0.10
UD6-120829-T	8/29/12	Tank	0.720092 ± 0.000008	154.07 ± 0.11
UD6-120928-T	9/28/12	Tank	0.720091 ± 0.000008	154.05 ± 0.11
UD6-121025-T	10/25/12	Tank	0.720102 ± 0.000009	154.21 ± 0.12
(replicate)			0.720097 ± 0.000010	154.14 ± 0.14
UD6-121213-T	12/13/12	Tank	0.720081 ± 0.000010	153.91 ± 0.14
UD6-130123-T	1/23/13	Tank	0.720092 ± 0.000010	154.07 ± 0.15
UD6-130219-T	2/19/13	Tank	0.720089 ± 0.000009	154.03 ± 0.12
(replicate)			0.720097 ± 0.000011	154.14 ± 0.15
UD6-130325-T	3/25/13	Tank	0.720074 ± 0.000009	153.81 ± 0.13
UD6-130426-T	4/26/13	Tank	0.720083 ± 0.000010	153.94 ± 0.14
UD6-130626-T	6/26/13	Tank	0.720096 ± 0.000009	154.12 ± 0.13
UD6-130807-T	8/7/13	Tank	0.720087 ± 0.000008	154.00 ± 0.11
Well UD-7: Upper Devonian/Lower Mississippian				
UD7-120310-T	3/10/12	Tank	0.720222 ± 0.000014	155.90 ± 0.19
UD7-120518-T	5/18/12	Tank	0.720235 ± 0.000012	156.08 ± 0.17
(replicate)			0.720285 ± 0.000011	156.79 ± 0.16
UD7-120628-T	6/28/12	Tank	0.720280 ± 0.000005	156.72 ± 0.07
UD7-120726-T	7/26/12	Tank	0.720270 ± 0.000006	156.58 ± 0.09
(replicate)			0.720270 ± 0.000007	156.58 ± 0.10
UD7-120829-T	8/29/12	Tank	0.720285 ± 0.000004	156.79 ± 0.06
(replicate)			0.720283 ± 0.000005	156.76 ± 0.06
UD7-120928-T	9/28/12	Tank	0.720275 ± 0.000006	156.65 ± 0.09
UD7-121025-T	10/25/12	Tank	0.720286 ± 0.000006	156.80 ± 0.08
(replicate)			0.720294 ± 0.000010	156.92 ± 0.14
UD7-121213-T	12/13/12	Tank	0.720281 ± 0.000013	156.73 ± 0.18
UD7-130123-T	1/23/13	Tank	0.720255 ± 0.000009	156.37 ± 0.13
UD7-130219-T	2/19/13	Tank	0.720255 ± 0.000010	156.37 ± 0.14
UD7-130325-T	3/25/13	Tank	0.720254 ± 0.000012	156.35 ± 0.17
(replicate)			0.720238 ± 0.000010	156.13 ± 0.14
UD7-130426-T	4/26/13	Tank	0.720252 ± 0.000009	156.32 ± 0.13
UD7-130626-T	6/26/13	Tank	0.720252 ± 0.000011	156.32 ± 0.16
UD7-130807-T	8/7/13	Tank	0.720263 ± 0.000013	156.48 ± 0.19
Well MW-1: Middle Devonian, vertical, hydraulically fractured in 2006				
MW1-120310-T	3/10/12	Tank	0.711580 ± 0.000006	34.04 ± 0.09
MW1-120518-T	5/18/12	Tank	0.711541 ± 0.000016	33.49 ± 0.22
(replicate)			0.711570 ± 0.000013	33.90 ± 0.18
(replicate)			0.711576 ± 0.000006	33.98 ± 0.08
MW1-120628-T	6/28/12	Tank	0.711726 ± 0.000006	36.10 ± 0.09

Sample Name	Date Collected	Sample Type	$^{87}Sr/^{86}Sr$[a,b]	ε_{Sr}[c]
MW1-120726-T	7/26/12	Tank	0.711710 ± 0.000008	35.87 ± 0.11
(replicate)			0.711712 ± 0.000007	35.90 ± 0.10
MW1-120829-T	8/29/12	Tank	0.711729 ± 0.000007	36.14 ± 0.09
MW1-120928-T	9/28/12	Tank	0.711712 ± 0.000006	35.90 ± 0.09
(replicate)			0.711720 ± 0.000005	36.01 ± 0.08
MW1-121025-T	10/25/12	Tank	0.711710 ± 0.000006	35.87 ± 0.08
(replicate)			0.711705 ± 0.000007	35.80 ± 0.09
MW1-121213-T	12/13/12	Tank	0.711711 ± 0.000007	35.89 ± 0.10
MW1-130123-T	1/23/13	Tank	0.711698 ± 0.000007	35.70 ± 0.10
MW1-130219-T	2/19/13	Tank	0.711709 ± 0.000006	35.86 ± 0.08
MW1-130325-T	3/25/13	Tank	0.711703 ± 0.000007	35.77 ± 0.10
MW1-130426-T	4/26/13	Tank	0.711710 ± 0.000007	35.87 ± 0.10
MW1-130626-T	6/26/13	Tank	0.711692 ± 0.000008	35.62 ± 0.11
MW1-130807-T	8/7/13	Tank	0.711705 ± 0.000007	35.80 ± 0.10
Spring water: Shallow groundwater				
SPW-120518	5/18/12	Spring	0.713329 ± 0.000026	58.70 ± 0.37
(replicate)			0.713349 ± 0.000010	58.98 ± 0.15
SPW-120628	6/28/12	Spring	0.713353 ± 0.000006	59.04 ± 0.08
SPW-120726	7/26/12	Spring	0.713384 ± 0.000007	59.48 ± 0.10
SPW-120829	8/29/12	Spring	0.713361 ± 0.000005	59.15 ± 0.06
SPW-120928	9/28/12	Spring	0.713347 ± 0.000008	58.96 ± 0.11
SPW-121025	10/25/12	Spring	0.713357 ± 0.000008	59.10 ± 0.11
(replicate)			0.713352 ± 0.000009	59.03 ± 0.13
SPW-121213	12/13/12	Spring	0.713384 ± 0.000008	59.48 ± 0.11
SPW-130123	1/23/13	Spring	0.713434 ± 0.000010	60.18 ± 0.15
SPW-130219	2/19/13	Spring	0.713422 ± 0.000013	60.01 ± 0.18
SPW-130325	3/25/13	Spring	0.713353 ± 0.000010	59.04 ± 0.14
SPW-130426	4/26/13	Spring	0.713332 ± 0.000011	58.75 ± 0.16
SPW-130626	6/26/13	Spring	0.713363 ± 0.000012	59.18 ± 0.17
SPW-130807	8/7/13	Spring	0.713442 ± 0.000009	60.30 ± 0.13

[a]Normalized to SRM 987 Sr standard = 0.710240; 2s uncertainty based on in-run statistics.

[b]Reported replicates represent separate aliquots processed through columns and analyzed for $^{87}Sr/^{86}Sr$.

[c]ε_{Sr} defined as $(^{87}Sr/^{86}Sr_{sample}/^{87}Sr/^{86}Sr_{seawater} - 1)10^4$ where $^{87}Sr/^{86}Sr_{seawater} = 0.709166$.

Table S3. Marcellus horizontal well time series Sr isotope data. All data from Capo et al.[35] except where indicated.

Sample Name	Capo et al.[35] Sample Name	Date Collected	Days after Flowback	$^{87}Sr/^{86}Sr$[a,b]	ε_{Sr}[c]
MHD-120611	GRN-A1-0001	6/11/12	1	0.710785 ± 0.000006	22.83 ± 0.09
MHD-120612	GRN-A1-0002a	6/12/12	2	0.711099 ± 0.000005	27.26 ± 0.08
MHD-120612	GRN-A1-0002b	6/12/12	2	0.711178 ± 0.000007	28.37 ± 0.10
(replicate)	(replicate)			0.711166 ± 0.000006	28.20 ± 0.09
(replicate)[d]	n/a			0.711175 ± 0.000010	28.33 ± 0.14
MHD-120614	GRN-A1-0004	6/14/12	4	0.711149 ± 0.000007	27.96 ± 0.10
MHD-120615	GRN-A1-0005	6/15/12	5	0.711177 ± 0.000008	28.36 ± 0.11
MHD-120616	GRN-A1-0006a	6/16/12	6	0.711131 ± 0.000006	27.71 ± 0.08
MHD-120616	GRN-A1-0006b	6/16/12	6	0.711269 ± 0.000007	29.65 ± 0.10
MHD-120616	GRN-A1-0006c	6/16/12	6	0.711169 ± 0.000007	28.24 ± 0.10
MHD-120617	GRN-A1-0007	6/17/12	7	0.711165 ± 0.000007	28.19 ± 0.10
MHD-120618	GRN-A1-0008	6/18/12	8	0.711184 ± 0.000006	28.46 ± 0.08
(replicate)	(replicate)			0.711184 ± 0.000007	28.46 ± 0.10
MHD-120622	GRN-A1-0012	6/22/12	12	0.711241 ± 0.000010	29.26 ± 0.14
MHD-120727	GRN-A1-0047	7/27/12	47	0.711246 ± 0.000006	29.33 ± 0.08
MHD-120829	GRN-A1-0080	8/29/12	80	0.711267 ± 0.000007	29.63 ± 0.10
MHD-130320	GRN-A1-0283	3/20/13	283	0.711368 ± 0.000006	31.05 ± 0.09
MHD-130320[d]	n/a	4/26/13	320	0.711378 ± 0.000008	31.19 ± 0.12
(replicate)[d]	n/a			0.711378 ± 0.000007	31.19 ± 0.10
MHE-120611	GRN-A2-0001	6/11/12	1	0.710861 ± 0.000006	23.90 ± 0.09
MHE-120612	GRN-A2-0002a	6/12/12	2	0.711055 ± 0.000005	26.64 ± 0.07
MHE-120612	GRN-A2-0002b	6/12/12	2	0.711199 ± 0.000004	28.67 ± 0.06
MHE-120613	GRN-A2-0003a	6/13/12	3	0.711202 ± 0.000006	28.71 ± 0.09
MHE-120613	GRN-A2-0003b	6/13/12	3	0.711215 ± 0.000005	28.89 ± 0.07
(replicate)	(replicate)			0.711210 ± 0.000005	28.82 ± 0.07
MHE-120614	GRN-A2-0004	6/14/12	4	0.711220 ± 0.000006	28.96 ± 0.08
MHE-120616	GRN-A2-0006a	6/16/12	6	0.711251 ± 0.000008	29.40 ± 0.12
(replicate)	(replicate)			0.711255 ± 0.000008	29.46 ± 0.12
MHE-120616	GRN-A2-0006b	6/16/12	6	0.711259 ± 0.000008	29.51 ± 0.12
MHE-120616	GRN-A2-0006c	6/16/12	6	0.711250 ± 0.000008	29.39 ± 0.11
MHE-120617	GRN-A2-0007	6/17/12	7	0.711264 ± 0.000008	29.58 ± 0.11
MHE-120620	GRN-A2-0010	6/20/12	10	0.711257 ± 0.000014	29.49 ± 0.20
(replicate)	(replicate)			0.711285 ± 0.000016	29.88 ± 0.22
(replicate)	(replicate)			0.711286 ± 0.000007	29.89 ± 0.09
MHE-120622	GRN-A2-0012	6/22/12	12	0.711276 ± 0.000015	29.75 ± 0.21
(replicate)	(replicate)			0.711268 ± 0.000014	29.64 ± 0.19
MHE-120829	GRN-A2-0080	8/29/12	80	0.711341 ± 0.000006	30.67 ± 0.09
MHE-130320	GRN-A2-0283	3/20/13	283	0.711416 ± 0.000005	31.73 ± 0.07
MHE-130426[d]	n/a	4/26/13	320	0.711443 ± 0.000006	32.11 ± 0.08
MHF-120611	GRN-A3-0001	6/11/12	1	0.711074 ± 0.000006	26.90 ± 0.08
MHF-120613	GRN-A3-0003a	6/13/12	3	0.711192 ± 0.000007	28.57 ± 0.09
MHF-120613	GRN-A3-0003b	6/13/12	3	0.711225 ± 0.000005	29.03 ± 0.06
MHF-120614	GRN-A3-0004a	6/14/12	4	0.711225 ± 0.000006	29.03 ± 0.08
MHF-120614	GRN-A3-0004b	6/14/12	4	0.711240 ± 0.000008	29.25 ± 0.11
MHF-120615	GRN-A3-0005	6/15/12	5	0.711254 ± 0.000006	29.44 ± 0.08
MHF-130426[d]	n/a	4/26/13	320	0.711365 ± 0.000006	31.01 ± 0.08

[a]Normalized to SRM 987 Sr standard = 0.710240; 2σ uncertainty based on in-run statistics.

[b]Reported replicates represent separate aliquots processed through columns and analyzed for $^{87}Sr/^{86}Sr$.

[c]ε_{Sr} defined as $(^{87}Sr/^{86}Sr_{sample}/^{87}Sr/^{86}Sr_{seawater} - 1)10^4$ where $^{87}Sr/^{86}Sr_{seawater} = 0.709166$.

[d]New data (this study)

Table S4. Statistical analysis of change in Sr isotope composition (ε_{Sr}) after hydraulic fracturing using the Mann-Whitney U Test.

	Pre-Hydraulic Fracture			**Post-Hydraulic Fracture**				
Well	Sample size	Mean ε_{Sr}	Variance	Sample size	Mean ε_{Sr}	Variance	**Z**	**p-value**
UD-2	3	152.63	1.505	17	152.09	0.702	0.635	0.525
UD-4	2	156.86	0.009	11	156.65	0.021	2.171	0.030
UD-5	6	165.65	0.375	15	166.12	0.759	1.051	0.301
UD-6	2	152.68	0.618	14	153.67	1.479	1.747	0.081
UD-7	2	156.17	0.144	12	156.53	0.044	1.278	0.201
MW-1	2	33.92	0.031	12	35.87	0.022	2.191	0.028

Table S5. Averaged elemental concentration data used to model produced water-ground water mixing (manuscript Fig. 7).

	Na	Ca	Ba	Sr	Br	Cl	Total Ra activity[a]
	- mg L^{-1} -						pCi/L
Marcellus Produced Water[b]	22,240	9,700	2,150	2,750	450	22,200	2,460
Upper Devonian Produced Water[c]	35,510	14,180	520	840	780	84,280	910
Ground Water[d]	6.45	57.9	0.094	0.177	0.04	6.25	0.42

[b]Radium activity values of produced waters averaged from samples reported by Haluszczak et al.,[6] Rowan et al.,[8] and Dresel and Rose,[42] with total Ra from the latter estimated from ^{228}Ra values.

[b]Averaged from individual well samples reported by Hayes,[4] Chapman et al.,[5] Haluszczak et al.,[6] Warner et al.,[22] and Capo et al.[35]

[c]Averaged from individual well samples reported by Osborn and McIntosh[39] and Dresel and Rose.[42]

[d]Average of GCS spring water for Na, Ca, Ba and Sr, and of "Type A" groundwaters from Warner et al.[22] for Br, Cl and Ra.

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