Supplementary Information

Geochemical conditions conducive for retention of trace elements and radionuclide during shale-fracturing fluid interactions

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1. The whole rock digestion procedure

Approximately 10 mg of sample in a microwave vessel was pre-treated with 2 ml of 50% v/v H_2O_2 to decompose organics and sulfide minerals prior to digestion. Peroxide solution was added dropwise to prevent any fumes. After the initial reaction stopped (~1 hr), 9 ml concentrated HNO_3 (70% w/v), 4 ml HF (48% w/v) and 2 ml HCl (37% w/v) were added slowly to the vessel. The vessels were capped and heated at 180 ^oC in a CEM Microwave Digestor. After the digestion, 20 ml of de-ionized water (18 MΩ) water was added to the mixtures. The solutions were centrifuged at 3000 rpm for 35 min, and the supernatant was filtered in acid washed falcon tube. The solid residue was black in color, indicating that organic and other sulfide minerals were not fully decomposed. Therefore, to achieve total digestion, the residue was further digested with 10 ml of 50% w/v H_2O_2 and 1 ml of conc. HNO_3 and evaporated to dryness at 85 ^oC. Second aliquot of 12 ml 50% w/v H_2O_2 was added to the residue and heated at 85 ^oC. After 6 hr of heating, solutions turned transparent and no residue was left. The solution was filtered and combined with the first supernatant. The digestion was performed on triplicates and 3 control blanks were included. Simultaneous digestion of certified reference material, SBC-1 was also performed to assess the accuracy of the digestion procedure.

2. Sequential Extractions:

S1: 1.0 gram composite shale sample was shaken with 16 ml of 1 M $MgCl_2$ (pH 7) on a rotary shaker for 1 h at room temperature. Thereafter, the sample was centrifuged at 6000 rpm for 15 min and the supernatant was filtered. The solid residue was rinsed with 10 ml of de-ionized

water (18 MΩ), which after centrifugation was collected and added to the reagent solution to be analyzed.

S2: The residue was shaken with 25 ml of 1M sodium acetate (pH 5) for 5 h at room temperature, centrifuged, and the supernatant filtered. The residue was rinsed with de-ionized water as in step S1 and added to reagent solution to be analyzed.

S3: The residue was extracted further with 40 ml of H_2O_2 (30% w/v) at pH 2 adjusted by HNO_3. The addition of peroxide took place in two stages. The first aliquot of 20 ml was slowly added to the residue and allowed to react for ~1h at room temperature. Then, the solution was gently heated at 50 ^oC in a water bath for 1 hr. The temperature was slowly increased to 85^oC to reduce the volume to about 3 ml. After cooling, the second aliquot of 20 ml of H_2O_2 (30% w/v) was added stepwise at 85^oC until no more bubbling was observed. At this point, solid residues turned grey. After cooling, 20 ml of 0.01 N HNO_3 was added to desorb any metals. The supernatant was separated as described for previous fractions above.

S4: The shale residue after the oxidized extraction step (S4) primarily contains silicate minerals; residue composition was estimated from the difference between the whole-rock digestions and the sum of the sequential fractions (S1-S3).

Table S1: ICP-MS Method detection limit and element concentration in controls associated with extractions, treatments and digestion

	Cr µg/L	Mn µg/L	Fe µg/L	Co µg/L	Ni µg/L	Cu µg/L	As µg/L	Se µg/L	Sr µg/L	Cd µg/L	Ba µg/L	Pb µg/L	U µg/L
ICP-MS detection Limit	**0.48**	**0.29**	**1.11**	**0.04**	**0.16**	**0.24**	**0.04**	**1.01**	**0.16**	**0.05**	**0.11**	**1.16**	**0.01**
Blank Concentration in each treatment													
E1-ox-DI-ph7	BDL	BDL	BDL	BDL	BDL	25.6	0.7	BDL	9.6	BDL	6.6	BDL	BDL
E1-ox-Sal-ph7	3.1	BDL	164.1	0.3	BDL	BDL	0.1	5.9	13.4	0.1	5.5	16.8	BDL
E2-ox-DI-ph4	BDL	11.4	14.5	0.1	BDL	BDL	0.5	BDL	190.9	BDL	427.2	BDL	BDL
E2-ox-Sal-ph4	BDL	BDL	BDL	BDL	BDL	14.3	1.4	9.9	67.6	BDL	167.7	BDL	BDL
E3-anox-DI-ph7	BDL	BDL	BDL	0.7	BDL	8.3	0.2	BDL	2.0	0.2	BDL	3.7	0.1
E3-anox-Sal-ph7	BDL	BDL	BDL	0.0	BDL	0.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL
E4-anox-DI-ph4	BDL	BDL	BDL	2.4	BDL	18.4	BDL	BDL	1.4	0.6	BDL	7.2	0.1
E4-anox-Sal-ph4	BDL	BDL	BDL	0.1	46.7	80.4	0.3	BDL	11.5	0.2	BDL	1.6	BDL
E5-anox-Sal-ph4	20.6	2.3	214.9	1.3	91.4	6.0	1.6	4.7	6.0	BDL	BDL	7.8	BDL
Blank Digestion	5.3	0.4	94.1	0.1	6.7	BDL	3.0	BDL	BDL	BDL	BDL	BDL	0.1
S1-blank-Exchangeable	9.3	52.3	BDL	0.1	8.4	BDL	2.0	26.0	BDL	3.8	BDL	BDL	BDL
S2-blank-Acid-Parallel	BDL	BDL	100.0	0.2	BDL	BDL	0.6	1.3	BDL	1.0	BDL	2.9	BDL
S4-blank-Oxidized SQ	BDL	2.0	149.2	0.2	BDL	4.9	BDL	BDL	2.6	0.5	3.9	1.9	3.9

Table S2: Concentration of elements extracted in batch treatments

	E1-ox-DI-pH7	E2-ox-DI-pH4	E3-anox-DI-pH7	E4-anox-DI-pH4	E5-anox-DI-pH4
	µg g-1	µg g-1	µg g-1	µg g-1	µg g-1
Cr	ND	ND	0.00 ± 0.03	0.44 ± 0.03	12.98 ± 0.86
Mn	0.64 ± 0.05	0.75 ± 0.40	2.07 ± 0.06	50.86 ± 3.41	113.60 ± 24.95
Co	4.96 ± 0.84	22.35 ± 5.28	15.69 ± 4.29	126.97 ± 26.11	317.32 ± 9.70
Ni	0.17 ± 0.02	0.85 ± 0.14	0.09 ± 0.05	4.83 ± 0.60	108.70 ± 3.50
Cu	0.04 ± 0.07	ND	0.26 ± 0.05	0.72 ± 0.13	118.88 ± 3.60
As	0.04 ± 0.01	0.07 ± 0.01	0.02 ± 0.0023	0.07 ± 0.01	19.48 ± 0.77
Se	0.26 ± 0.08	0.24 ± 0.17	0.17 ± 0.02	0.55 ± 0.04	6.28 ± 0.41
Sr	27.92 ± 1.02	41.93 ± 1.28	36.67 ± 0.29	74.29 ± 1.81	56.23 ± 1.40
Cd	0.01 ± 0.01	0.02 ± 0.00	0.01 ± 0.01	0.05 ± 0.01	0.35 ± 0.01
Ba	1.00 ± 0.14	2.09 ± 1.31	1.16 ± 0.05	2.16 ± 0.05	0.80 ± 0.13
U	0.57 ± 0.06	0.86 ± 0.13	0.73 ± 0.03	0.78 ± 0.01	7.83 ± 0.29
Fe	ND	ND	ND	481 ± 66	26542 ± 1009

	E1-ox-Sal-pH7	E2-ox-Sal-pH4	E3-anox-Sal-pH7	E4-anox-Sal-pH4	E5-anox-Sal-pH4
	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
Cr	0.03 ± 0.04	0.04 ± 0.02	ND	0.24 ± 0.02	9.39 ± 2.27
Mn	0.91 ± 0.04	1.99 ± 1.18	1.00 ± 0.02	48.81 ± 0.35	54.95 ± 7.58
Co	4.61 ± 0.52	20.43 ± 6.77	5.47 ± 0.66	114.45 ± 3.83	337.09 ± 16.76
Ni	0.26 ± 0.03	0.76 ± 0.08	0.01 ± 0.01	4.32 ± 0.02	118.89 ± 7.57
Cu	0.05 ± 0.08	0.04 ± 0.05	0.47 ± 0.23	0.61 ± 0.09	131.03 ± 8.07
As	0.03 ± 0.0033	0.09 ± 0.01	0.03 ± 0.0031	0.07 ± 0.0014	21.11 ± 2.36
Se	0.17 ± 0.11	0.56 ± 0.11	0.18 ± 0.01	0.52 ± 0.02	7.20 ± 0.78
Sr	49.90 ± 1.03	55.63 ± 0.42	49.55 ± 0.26	81.20 ± 1.08	62.01 ± 3.74
Cd	0.02 ± 0.03	0.06 ± 0.08	0.01 ± 0.00	0.07 ± 0.01	0.38 ± 0.02
Ba	5.18 ± 0.23	5.63 ± 0.26	4.86 ± 0.02	5.99 ± 0.06	1.22 ± 0.10
U	0.80 ± 0.02	0.78 ± 0.06	0.63 ± 0.00	0.80 ± 0.01	8.85 ± 1.00
Fe	ND	ND	0.52 ± 0.73	372 ± 23	30047 ± 2593

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