Supplementary Materials For:

Stable bromine isotopic composition of Coal Bed Methane (CBM) produced water, the occurrence of enriched ^{81}Br, and implications for fluid flow in the Midcontinent, USA

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Citation: Stotler, R. L., Kirk, M.F., Newell, K.D., Goldstein, R.H., Frape, S.K., Gwynne, R. Stable bromine isotopic composition of Coal Bed Methane (CBM) produced water, the occurrence of enriched ^{81}Br, and implications for fluid flow in the Midcontinent USA. *Minerals* **2021**, *11*, 358. https://doi.org/10.3390/min11040358

Table S1: Pearson R correlations for various bivariate datasets. R correlations in red and in shaded tabs are not significant (p-values are available in Table S2). Unless noted otherwise in parentheses, n = 15.

R	$\delta^{2}H$	$\delta^{18}O$	$\delta^{37}Cl$	$\delta^{81}Br$	$^{87}Sr/^{86}Sr$	$\delta^{2}H$-C1	$\delta^{13}C$-C1	$\delta^{13}C$-CO_2
Temp	-0.72 (13)	-0.70(13)	-0.22(14)	-0.78(14)	0.88(13)	0.09(13)	0.20(13)	0.01(13)
$\delta^{2}H$		0.91	-0.01	0.88	-0.93	0.08	-0.22	-0.01
$\delta^{18}O$			-0.21	0.73	-0.87	0.01	0.09	0.16
$\delta^{37}Cl$				0.25(17)	-0.20(17)	0.34	-0.48	-0.25
$\delta^{81}Br$					-0.88(17)	0.04	-0.46	-0.22
$^{87}Sr/^{86}Sr$						-0.02	0.24	0.03
$\delta^{2}H$-C1							0.03	0.01
$\delta^{13}C$-C1								0.80

Table S2: The p-values for Pearson R correlations for various bivariate datasets (R-correlations are available in Table S1). The p-values in red are not significant. The n values are noted in Table S1.

p-value	$\delta^{2}H$	$\delta^{18}O$	$\delta^{37}Cl$	$\delta^{81}Br$	$^{87}Sr/^{86}Sr$	$\delta^{2}H$-C1	$\delta^{13}C$-C1	$\delta^{13}C$-CO_2
Temperature	<0.01	<0.01	0.46	<0.01	<0.01	0.77	0.50	0.97
$\delta^{2}H$		<0.01	0.97	<0.01	<0.01	0.76	0.43	0.98
$\delta^{18}O$			0.46	<0.01	<0.01	0.96	0.74	0.57
$\delta^{37}Cl$				0.34	0.45	0.22	0.07	0.36
$\delta^{81}Br$					<0.01	0.89	0.08	0.43
$^{87}Sr/^{86}Sr$						0.97	0.38	0.91
$\delta^{2}H$-C1							0.90	0.98
$\delta^{13}C$-C1								<0.01

Table S3: Summary of geochemical characteristics of Group A and B fluids.

	Group A[1]			Group B[2]		
	Min	Mean ± 1 St.Dev.	Max	Min	Mean ± 1 St.Dev.	Max
End of Hole Depth (m)	246	319±43	388	298	346±35	346
End of Hole Elevation (m)[3]	-113	-35±37	24	-111	-48±39	-4
Top Perforation Elevation (m)[4]	23	103±53	178	50	112±37	141
Lowest Perforation Elevation (m)[4]	-76	-9±37	28	-68	49±82	137
Temperature (°C)	15.2	17.1±0.8	17.7	19.3	23.4±3.6	28.2
TDS (g/L)	37.7	55.3±16.6	91.3	34.7	50.7±10.8	63.4
Na/Cl (molar ratio)	0.70	0.78±0.04	0.83	0.77	0.81±0.03	0.86
K/Br (molar ratio)	0.81	1.19±0.29	1.70	2.30	2.62±0.20	2.85
Ca/Mg (molar ratio)	0.42	0.79±0.19	1.08	1.24	1.37±0.07	1.43
Br/Cl*1000 (molar ratio)	1.709	1.987±0.255	2.655	1.432	1.482±0.036	1.528
SO_4/Cl (molar ratio)	0.045	0.061±0.018	0.097	0.036	0.056±0.020	0.089
SO_4/Br (molar ratio)	21.455	31.005±9.078	50.471	24.365	37.977±13.077	59.341
δ^2H ‰ (SMOW)	-42.5	-39.2±1.8	-35.8	-50.6	-48.9±1.0	-47.9
δ^{18}O ‰ (SMOW)	-6.42	-6.00±0.32	-5.37	-7.39	-7.12±0.20	-6.83
δ^{37}Cl ‰ (SMOC)	-0.81	0.04±0.40	0.68	-0.30	-0.12±0.13	0.04
δ^{81}Br ‰ (SMOB)	1.1	2.27±0.43	3.17	-0.63	0.40±0.34	0.75
^{87}Sr/^{86}Sr	0.708797	0.70892±0.00008	0.709055	0.710477	0.71071±0.00024	0.711091
He (mol %)	n.d.	0.0139±0.0106[5]	0.0311	0.0361	0.0568±0.0261	0.1010
δ^{13}C-CO_2 ‰ (VPDB)	-5.36	4.12±4.26	9.24	2.87	4.91±1.35	6.67
δ^{13}C-C1 ‰ (VPDB)	-69.95	-61.51±4.06	-57.03	-62.75	-59.04±2.35	-56.50
δ^2H-C1 ‰ (VSMOW)	-224.9	-222.1±2.1	-218.2	-228.2	-222.5±4.3	-217.2

[1]Group A wells include (n = 11): 1, 2, 3, 5, 8, 9, 10, 12, 13, 15, 16
[2]Group B wells include (n = 4): 4, 6, 7, 11
[3] Elevations are relative to mean sea level
[4] Perforation information was available from eleven wells (1, 4, 5, 6, 7, 8, 10, 11, 12, 14, 15). Wells were perforated between one and nine times, for a maximum of 2.4 and a minimum of 0.6 m, for an average of 0.9 m. The "Top Perforation Elevation" refers to the elevation of the uppermost part of the highest elevation perforation, and the "Lowest Perforation Elevation" refers to the elevation of the lowermost part of the deepest elevation perforation.
[5]Non-detect values were treated as "0" for mean and standard deviation calculations.

Table S4: Number and percentage of samples with $\delta^{81}Br$ > 2.00 ‰ (SMOB).

	n >2.00 ‰	**n**	**%**
Bohemian Massif[1]	3	23	13%
Canadian Shield[2]	0	44	0%
China Quaternary aquifers[3]	0	17	0%
Egypt coastal aquifers[4]	0	23	0%
Fennoscandian Shield[2]	1	18	6%
Illinois Basin[5]	0	10	0%
Kagan Gas Field[6]	0	4	0%
Mexico Geothermal Fields[7]	0	71	0%
North China Plain[8]	0	10	0%
Northern Apennine Foredeep Basin[9]	0	23	0%
Osberg Field & Paris Basin[10,11]	0	33	0%
S. Ontario sedimentary[12,13]	6	209	4%
Saudi Arabia sabkhas[15]	0	7	0%
Siberian Platform[16]	2	34	6%
South China Sea sedimentary basins[17]	0	9	0%
Williston Basin[12]	6	94	6%
Total Previous Studies	**18**	**629**	**3%**
Cherokee Basin (this study)	**11**	**17**	**65%**

References: [1][11], [2][13], [3][17], [4][18], [5][22], [6][15], [7][20], [8][16], [9][14], [10][10], [11][70], [12][71], [13][72], [14][21], [15][12], [16][19]

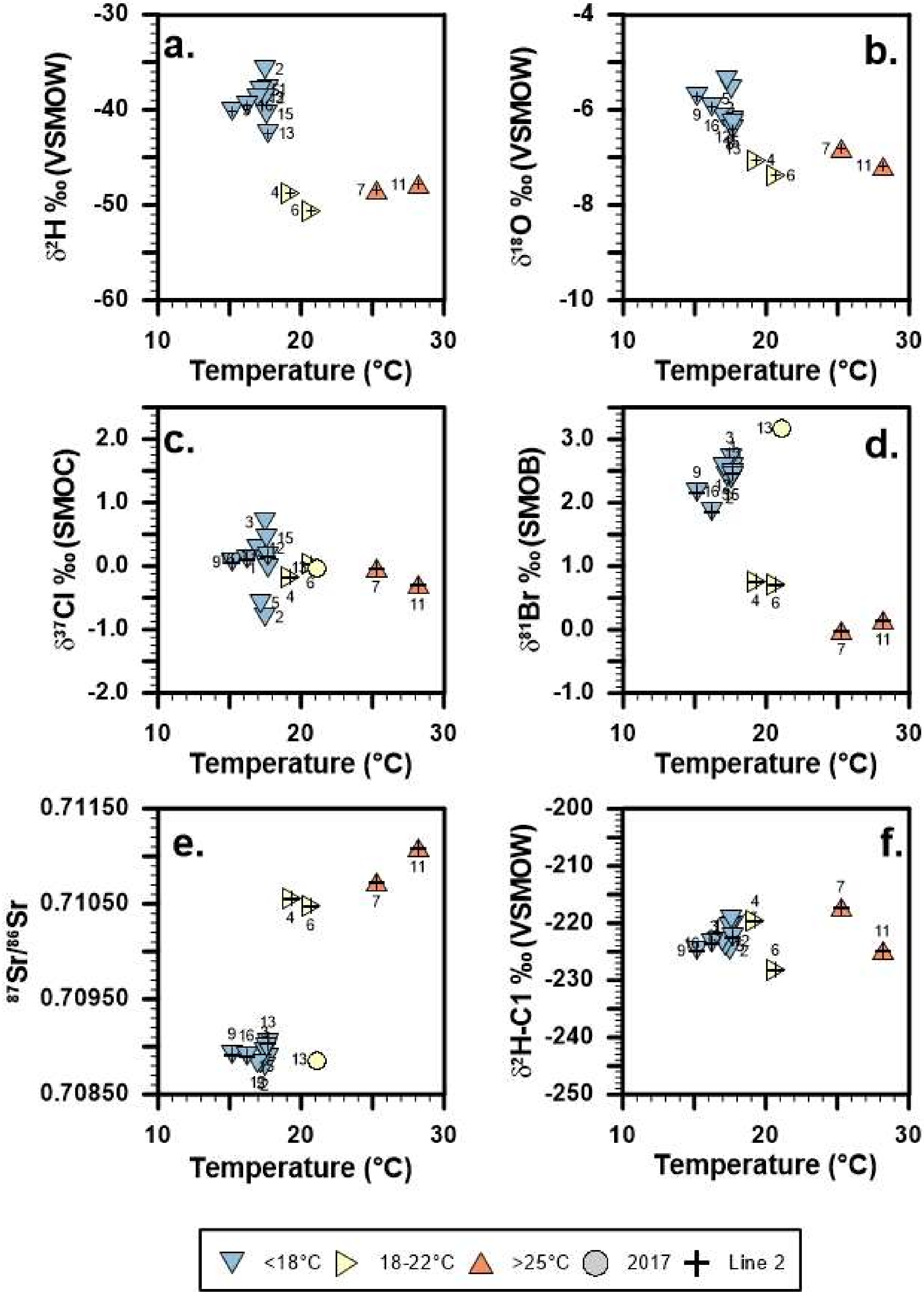

Figure S1. Comparisons of temperature with (a) δ^2H-H_2O, (b) $\delta^{18}O$, (c) $\delta^{37}Cl$, (d) $\delta^{81}Br$, (e) $^{87}Sr/^{86}Sr$, (f) δ^2H-C1

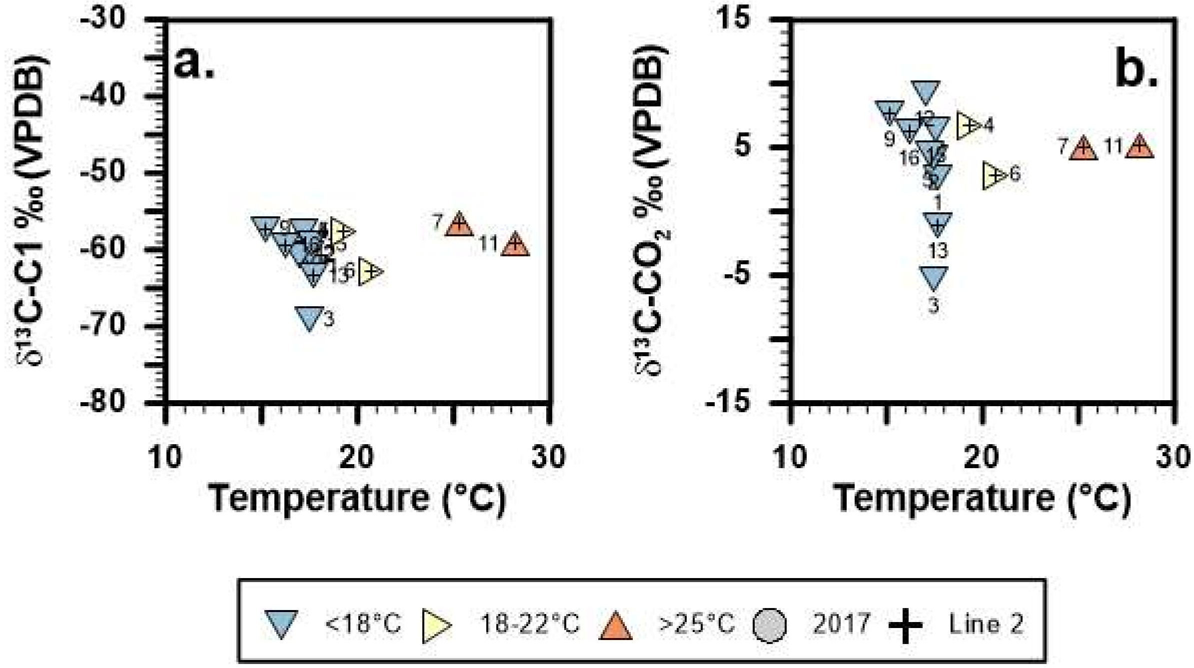

Figure S2. Temperature vs. (a) δ^{13}C-C1, (b) δ^{13}C-CO_2.

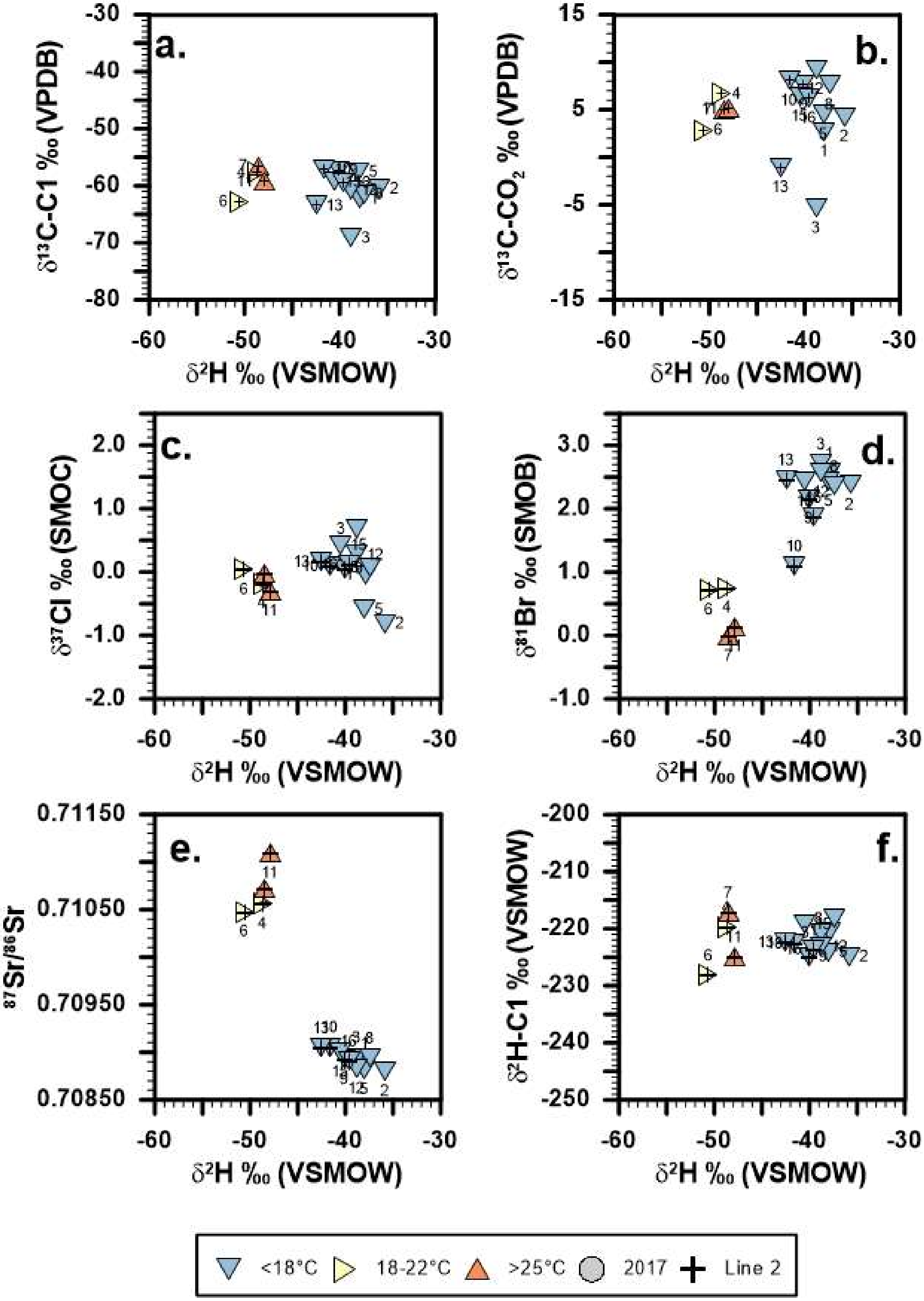

Figure S3: δ^2H-H_2O vs. (a) $\delta^{13}C$-C1, (b) $\delta^{13}C$-CO_2, (c) $\delta^{37}Cl$, (d) $\delta^{81}Br$, (e) $^{87}Sr/^{86}Sr$, (f) δ^2H-C1.

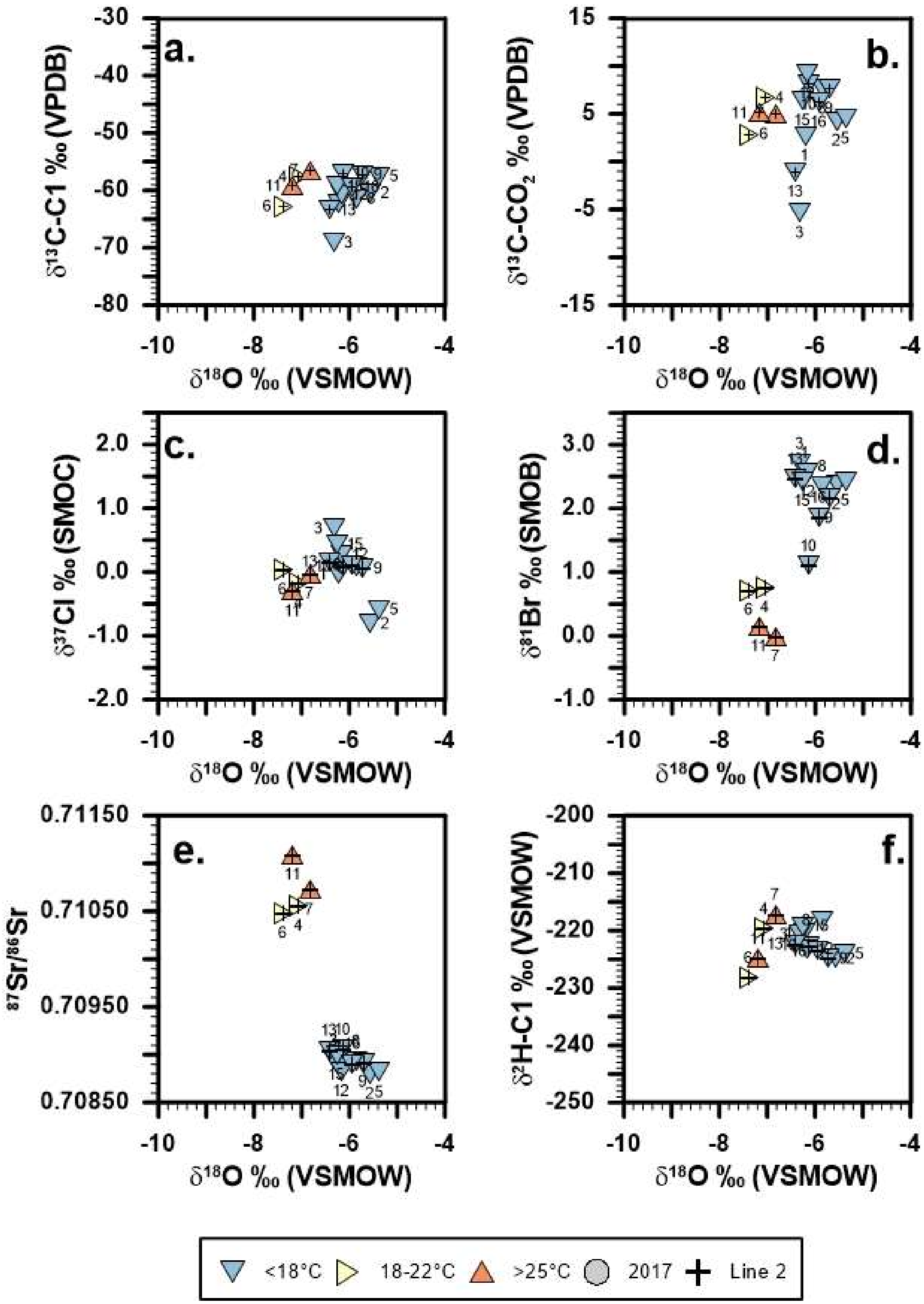

Figure S4. $\delta^{18}O$ vs. (a) $\delta^{13}C$-C1, (b) $\delta^{13}C$-CO_2, (c) $\delta^{37}Cl$, (d) $\delta^{81}Br$, (e) $^{87}Sr/^{86}Sr$, (f) $\delta^{2}H$-C1

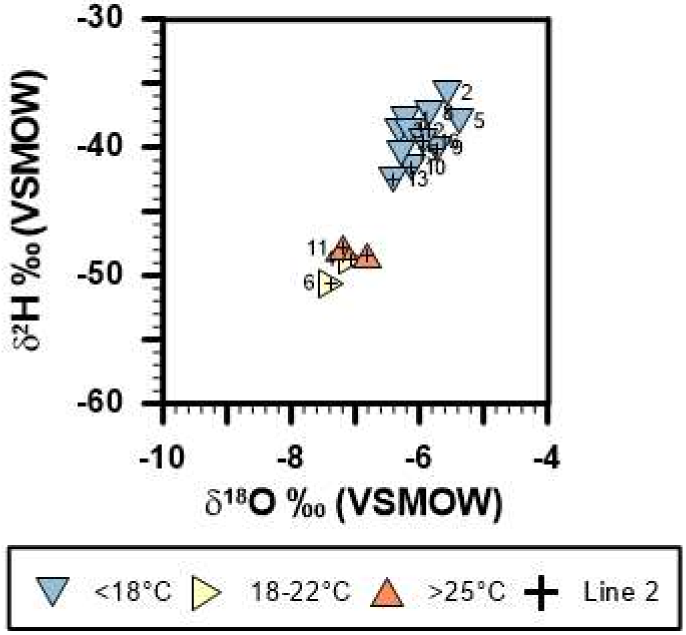

Figure S5: δ^2H-H_2O vs. $\delta^{18}O$.

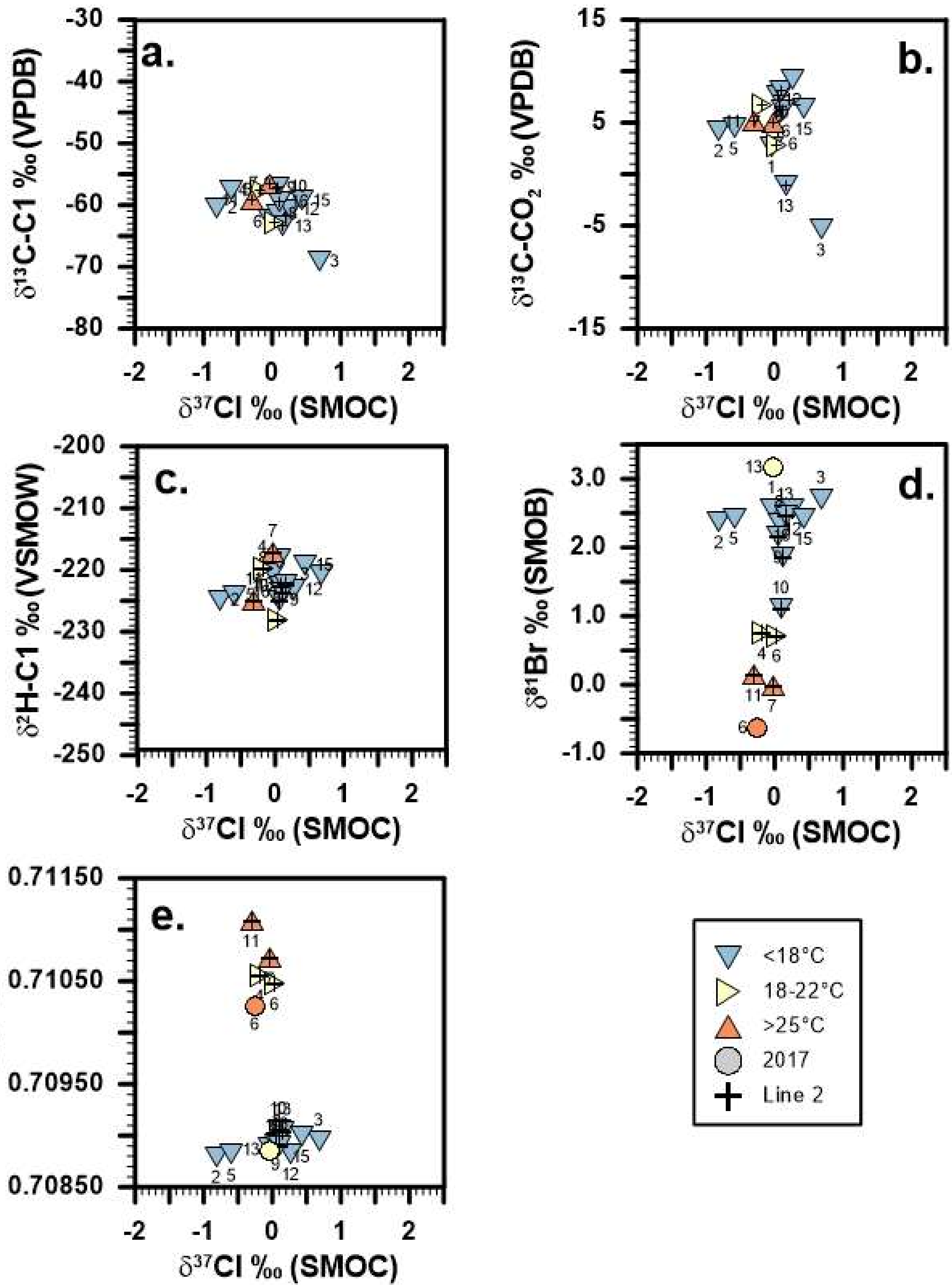

Figure S6: δ^{37}Cl vs. (a) δ^{13}C-C1, (b) δ^{13}C-CO_2, (c) δ^{2}H-C1, (d) δ^{81}Br, (e) ^{87}Sr/^{86}Sr.

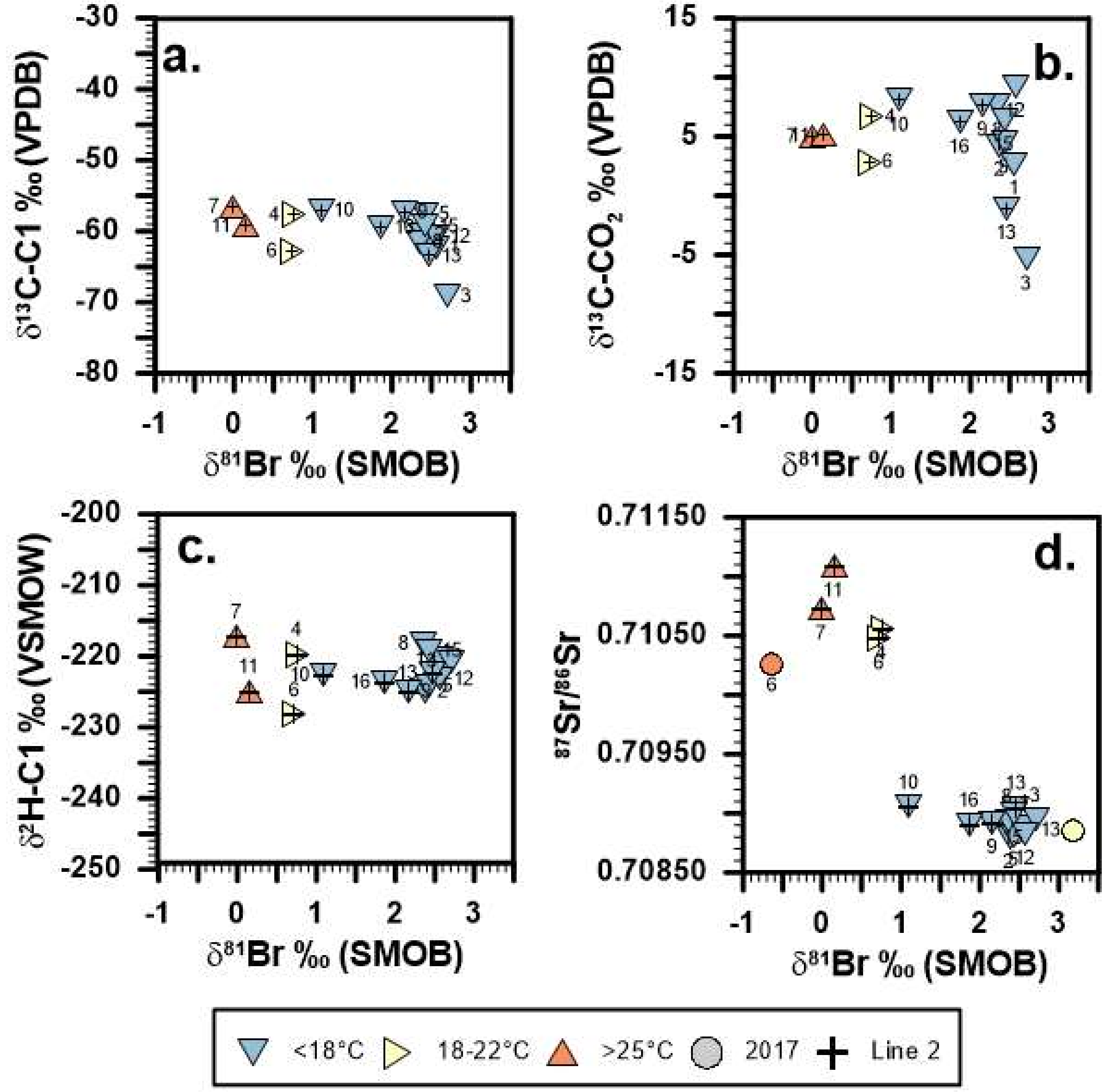

Figure S7: δ^{81}Br vs. (a) δ^{13}C-C1, (b) δ^{13}C-CO_2, (c) δ^{2}H-C1, (e) ^{87}Sr/^{86}Sr.

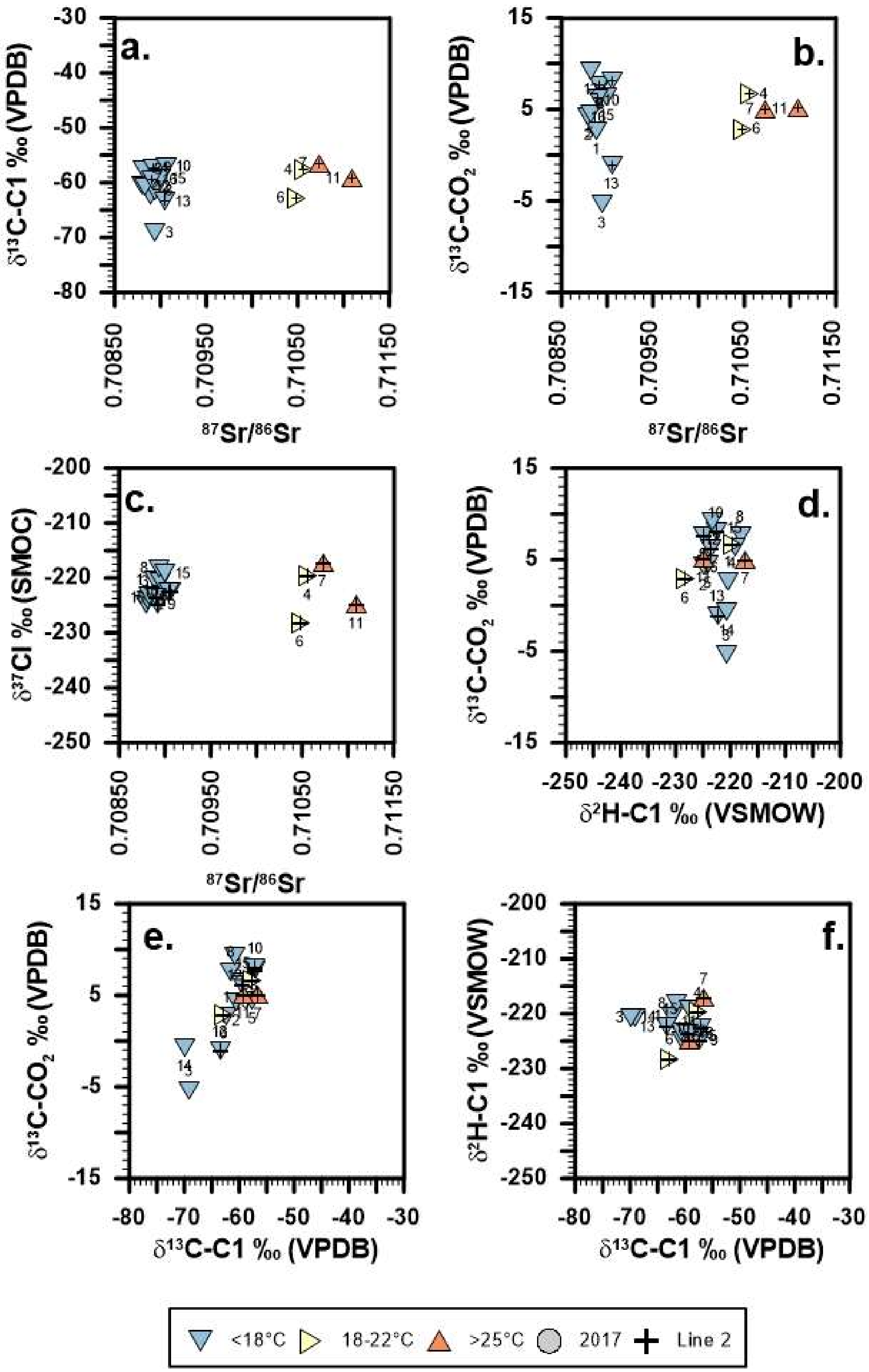

Figure S8: $^{87}Sr/^{86}Sr$ vs. (a) $\delta^{13}C$-C1, (b) $\delta^{13}C$-CO_2, (c) $\delta^{2}H$-C1; (d) $\delta^{2}H$-C1 vs $\delta^{13}C$-CO_2; and $\delta^{13}C$-C1 vs. (e) $\delta^{13}C$-CO_2, (f) $\delta^{2}H$-C1.

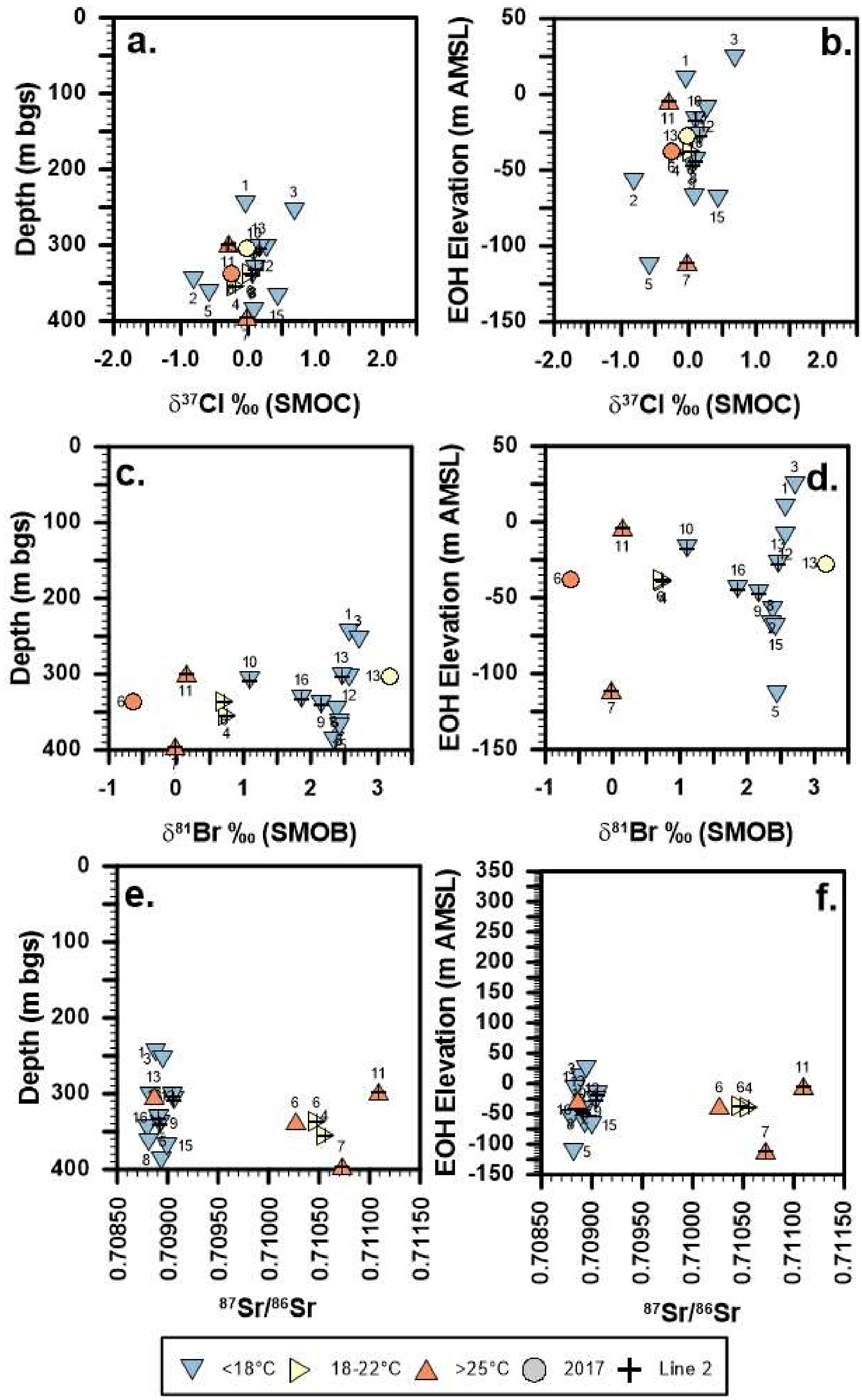

Figure S9. δ^{37}Cl vs. (a) depth (bgs = below ground surface) and (b) end of hole (EOH) elevation (AMSL = above mean sea level); δ^{81}Br vs. (c) depth and (d) EOH elevation; and ^{87}Sr/^{86}Sr vs. (e) depth and (f) EOH elevation.