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Supplement of

Lignin oxidation products as a potential proxy for vegetation and environmental changes in speleothems and cave drip water – a first record from the Herbstlabyrinth, central Germany

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S1 Acid-to-aldehyde ratios in the drip water samples

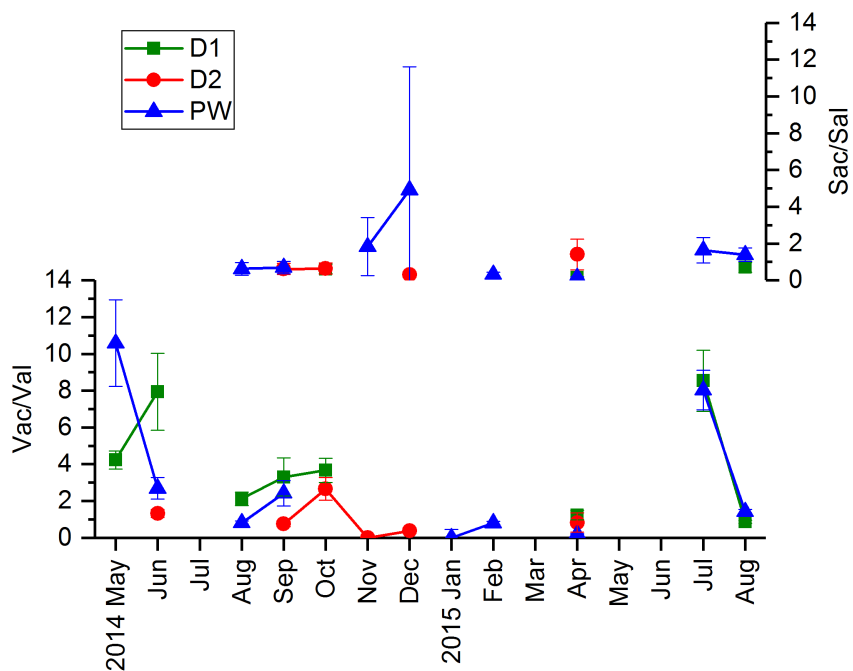


Figure S1. Vac/Val and Sac/Sal ratios in the drip water.

For the fast drip site *D1*, the values range from 0.9–8.5 for Vac/Val and 0.2–0.7 for Sac/Sal. For the slow drip site *D2*, the values are 0.0–2.7 for Vac/Val and 0.3–0.6 (1.4 with high uncertainty) for Sac/Sal, and for the pool water *PW*, 0.0–10.6 for Vac/Val and 0.2–1.8 (4.9 with high uncertainty) for Sac/Sal.

S2 Acid-to-aldehyde ratios in the stalagmite samples

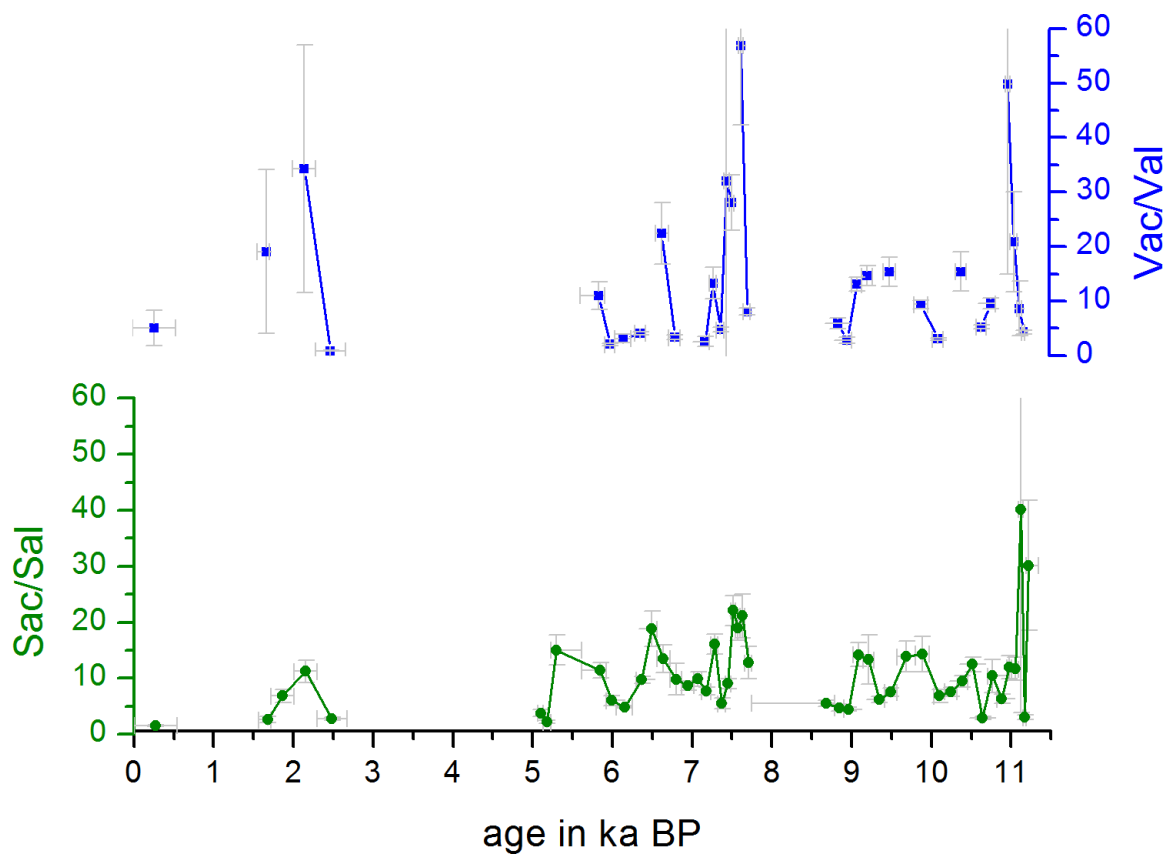


Figure S2. Ratios of syringic acid to syringaldehyde (Sac/Sal) and vanillic acid to vanillin (Vac/Val) in plotted against the age of the stalagmite.

The ratio of Vac/Val in the stalagmite samples ranges from 0.9 to 57, and the ratio of Sac/Sal ranges from 1.6 to 40.

S3 Correlation coefficients for the stalagmite samples

Table S1. Pearson's correlation coefficients r (with $p < 0.05$) of the middle and older part of the stalagmite

Pearson's r	C/V	S/V	$\Sigma 8$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mg	P	Sr	Ba	U	growth rate
C/V	-	0.88	-0.44	-	-0.34	-	-	-0.68	-	-	-
S/V	0.88	-	-0.42	0.41	-	-	-	-0.65	-	-	-
$\Sigma 8$	-0.44	-0.42	-	-	-	-	0.40	-	-	-	0.58
$\delta^{13}\text{C}$	-	0.41	-	-	0.43	-0.33	-	-	-	-	-
$\delta^{18}\text{O}$	-0.34	-	-	0.43	-	-0.32	-	-	0.45	-	-
Mg	-	-	-	-0.33	-0.32	-	-0.49	0.53	-0.71	-0.56	-
P	-	-	0.40	-	-	-0.49	-	-0.38	0.49	0.78	0.43
Sr	-0.68	-0.65	-	-	-	0.53	-0.38	-	-	-0.63	-0.32
Ba	-	-	-	-	0.45	-0.71	0.49	-	-	0.55	-
U	-	-	-	-	-	-0.56	0.78	-0.63	0.55	-	-
growth rate	-	-	0.58	-	-	-	0.43	-0.32	-	-	-

Table S2. Spearman's correlation coefficients ρ (with $p < 0.05$) of the middle and older part of the stalagmite.

Spearman's ρ	C/V	S/V	$\Sigma 8$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mg	P	Sr	Ba	U	growth rate
C/V	-	0.84	-0.46	-	-0.37	-	-	-0.82	-	0.45	-
S/V	0.84	-	-0.33	0.35	-	-	-	-0.70	-	0.38	-
$\Sigma 8$	-0.46	-0.33	-	-	-	-	-	0.35	0.35	-	-
$\delta^{13}\text{C}$	-	0.35	-	-	0.43	-	-0.34	-	-	-	-0.32
$\delta^{18}\text{O}$	-0.37	-	-	0.43	-	-	-	0.34	0.43	-	-
Mg	-	-	-	-	-	-	-	-	-0.74	-0.58	0.41
P	-	-	-	-0.34	-	-	-	-	0.45	0.76	0.35
Sr	-0.82	-0.70	0.35	-	0.34	-	-	-	-	-0.51	-
Ba	-	-	0.35	-	0.43	-0.74	0.45	-	-	0.56	-0.31
U	0.45	0.38	-	-	-	-0.58	0.76	-0.51	0.56	-	-
growth rate	-	-	-	-0.32	-	0.41	0.35	-	-0.31	-	-

Table S3. Pearson's correlation coefficients r (with $p < 0.05$) of the middle part of the stalagmite

Pearson's r	C/V	S/V	$\Sigma 8$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mg	P	Sr	Ba	U	growth rate
C/V	-	0.82	-0.51	-	-	-	-0.48	-	-0.56	-	-
S/V	0.82	-	-0.54	-	-	-	-0.53	-	-0.57	-	-0.45
$\Sigma 8$	-0.51	-0.54	-	-	-	-	0.66	-	0.60	-	0.79
$\delta^{13}\text{C}$	-	-	-	-	0.53	0.69	-0.65	-	-	-0.59	-
$\delta^{18}\text{O}$	-	-	-	0.53	-	0.50	-	-	-	-0.64	-
Mg	-	-	-	0.69	0.50	-	-	-	-	-0.55	-
P	-0.48	-0.53	0.66	-0.65	-	-	-	-	0.73	0.80	0.56
Sr	-	-	-	-	-	-	-	-	0.67	-	-
Ba	-0.56	-0.57	0.60	-	-	-	0.73	0.67	-	0.78	-
U	-	-	-	-0.59	-0.64	-0.55	0.80	-	0.78	-	-
growth rate	-	-0.45	0.79	-	-	-	0.56	-	-	-	-

Table S4. Spearman's correlation coefficients ρ (with $p < 0.05$) of the middle part of the stalagmite

Spearman's ρ	C/V	S/V	$\Sigma 8$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mg	P	Sr	Ba	U	growth rate
C/V	-	0.80	-0.53	-	-	-	-	-	-0.57	-	-
S/V	0.80	-	-	-	-	-	-0.45	-	-0.53	-	-
$\Sigma 8$	-0.53	-	-	-	-	-	0.52	-	0.63	-	-
$\delta^{13}\text{C}$	-	-	-	-	0.61	0.56	-0.64	-	-	-0.63	-
$\delta^{18}\text{O}$	-	-	-	0.61	-	0.60	-	-	-	-0.55	-
Mg	-	-	-	0.56	0.60	-	-	-	-	-0.54	-
P	-	-0.45	0.52	-0.64	-	-	-	-	0.60	0.75	-
Sr	-	-	-	-	-	-	-	-	0.73	-	-
Ba	-0.57	-0.53	0.63	-	-	-	0.60	0.73	-	0.76	-
U	-	-	-	-0.63	-0.55	-0.54	0.75	-	0.76	-	-
growth rate	-	-	-	-	-	-	-	-	-	-	-

Table S5. Pearson's correlation coefficients r (with $p < 0.05$) of the older part of the stalagmite

Pearson's r	C/V	S/V	$\Sigma 8$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mg	P	Sr	Ba	U	growth rate
C/V	-	0.70	-	-	-	-0.52	-	-0.77	0.62	0.61	-
S/V	0.70	-	-	0.52	0.56	-0.54	-	-0.71	0.72	0.58	-
$\Sigma 8$	-	-	-	-	-	-	-	-	-	-	-
$\delta^{13}\text{C}$	-	0.52	-	-	0.67	-0.57	-	-	0.53	-	-0.60
$\delta^{18}\text{O}$	-	0.56	-	0.67	-	-0.56	-	-	0.65	-	-0.65
Mg	-0.52	-0.54	-	-0.57	-0.56	-	-0.59	0.85	-0.92	-0.79	-
P	-	-	-	-	-	-0.59	-	-0.59	-	0.83	-
Sr	-0.77	-0.71	-	-	-	0.85	-0.59	-	-0.89	-0.89	-
Ba	0.62	0.72	-	0.53	0.65	-0.92	-	-0.89	-	0.81	-
U	0.61	0.58	-	-	-	-0.79	0.83	-0.89	0.81	-	-
growth rate	-	-	-	-0.60	-0.65	-	-	-	-	-	-

Table S6. Spearman's correlation coefficients ρ (with $p < 0.05$) of the older part of the stalagmite

Spearman's ρ	C/V	S/V	$\Sigma 8$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mg	P	Sr	Ba	U	growth rate
C/V	-	0.76	-	-	-	-0.71	-	-0.77	0.66	0.71	-
S/V	0.76	-	-	0.45	-	-0.68	-	-0.77	0.71	0.67	-
$\Sigma 8$	-	-	-	-	-	-	-	-	-	-	-
$\delta^{13}\text{C}$	-	0.45	-	-	0.58	-	-	-	0.49	-	-0.75
$\delta^{18}\text{O}$	-	-	-	0.58	-	-0.49	-	-	0.65	-	-0.78
Mg	-0.71	-0.68	-	-	-0.49	-	-0.45	0.93	-0.88	-0.88	-
P	-	-	-	-	-	-0.45	-	-0.48	-	0.72	-
Sr	-0.77	-0.77	-	-	-	0.93	-0.48	-	-0.85	-0.88	-
Ba	0.66	0.71	-	0.49	0.65	-0.88	-	-0.85	-	0.85	-0.62
U	0.71	0.67	-	-	-	-0.88	0.72	-0.88	0.85	-	-
growth rate	-	-	-	-0.75	-0.78	-	-	-	-0.62	-	-

S4 Principal component analysis of the stalagmite samples

Table S7. Coefficients of the principal component analysis of the stalagmite

Coefficients of	middle and older part				middle part				older part			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
C/V	0.31	-0.42	-0.10	0.08	-0.31	-0.26	-0.21	0.46	0.30	0.23	-0.38	0.34
S/V	0.29	-0.44	-0.01	0.13	-0.33	-0.23	-0.08	0.40	0.33	-0.06	-0.19	0.54
S8	-0.01	0.44	-0.14	0.44	0.32	0.30	-0.11	0.22	-0.04	-0.09	0.72	0.61
d13C	0.15	-0.20	0.45	0.44	-0.30	0.26	0.39	0.35	0.25	-0.42	0.02	0.08
d18O	-0.08	0.14	0.59	0.22	-0.14	0.53	0.12	-0.25	0.26	-0.43	-0.07	-0.07
Mg	-0.40	-0.13	-0.35	0.15	-0.23	0.40	-0.03	0.37	-0.39	0.02	-0.18	0.21
P	0.34	0.35	-0.18	-0.15	0.40	-0.01	-0.27	0.17	0.23	0.38	0.45	-0.27
Sr	-0.48	0.15	0.09	-0.13	0.20	-0.07	0.70	0.14	-0.39	-0.19	0.08	0.03
Ba	0.25	0.36	0.36	-0.13	0.39	0.03	0.29	0.33	0.41	-0.05	-0.01	-0.09
U	0.45	0.18	-0.13	-0.26	0.36	-0.28	0.00	0.22	0.36	0.27	0.18	-0.10
growth rate	0.15	0.23	-0.33	0.62	0.22	0.44	-0.35	0.23	-0.12	0.56	-0.15	0.26

Table S8. Eigenvalues and explained variance of the principal component analysis of the stalagmite

	middle and older part			middle part			older part		
	Eigen-value	Percentage of Variance	Cumulative	Eigen-value	Percentage of Variance	Cumulative	Eigen-value	Percentage of Variance	Cumulative
1	3.47	31.55%	31.55%	4.95	44.99%	44.99%	5.63	51.14%	51.14%
2	2.96	26.88%	58.42%	2.45	22.27%	67.26%	2.24	20.36%	71.50%
3	2.07	18.81%	77.23%	1.39	12.64%	79.90%	1.26	11.44%	82.95%
4	1.12	10.21%	87.44%	0.95	8.67%	88.57%	0.82	7.41%	90.36%
5	0.36	3.29%	90.73%	0.54	4.92%	93.49%	0.36	3.27%	93.63%
6	0.31	2.83%	93.56%	0.28	2.54%	96.03%	0.28	2.55%	96.19%
7	0.25	2.26%	95.82%	0.17	1.51%	97.54%	0.20	1.80%	97.98%
8	0.21	1.92%	97.73%	0.14	1.30%	98.85%	0.15	1.37%	99.36%
9	0.13	1.16%	98.90%	0.06	0.53%	99.38%	0.04	0.34%	99.70%
10	0.08	0.77%	99.66%	0.05	0.44%	99.81%	0.02	0.22%	99.92%
11	0.04	0.34%	100.00%	0.02	0.19%	100.00%	0.01	0.08%	100.00%