

Supplement of Atmos. Chem. Phys., 19, 3779–3796, 2019  
<https://doi.org/10.5194/acp-19-3779-2019-supplement>  
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*Supplement of*

**Seasonality in the  $\Delta^{33}\text{S}$  measured in urban aerosols highlights an additional oxidation pathway for atmospheric  $\text{SO}_2$**

**David Au Yang et al.**

*Correspondence to:* David Au Yang (auyang@mail.gyig.ac.cn)

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1 **Calculation of the NSS-sulfates isotopic signatures**

2 The concentration of sea-salt sulfate (SS-s) present in aerosols is usually estimated using  
3 major ions elements according to the relation ( 1 ):

$$[\text{SO}_4^{2-}]_{\text{SS}} = 0.252[\text{Na}^+] \quad (1)$$

4 Quantity of non-sea-salt sulfate (NSS-s) is then determined using the relation ( 2 ):

$$[\text{SO}_4^{2-}]_{\text{NSS}} = [\text{SO}_4^{2-}]_{\text{T}} - [\text{SO}_4^{2-}]_{\text{SS}} \quad (2)$$

5 Where  $[\text{SO}_4^{2-}]_{\text{T}}$  is the total concentration of sulfate measured on the aerosols. The contribution  
6 of the SS-s is approximated using a mixing reaction that is expressed as:

$$\delta^{34}\text{S}_{\text{NSS}} = \frac{\delta^{34}\text{S}_{\text{T}} - (1 - X)\delta^{34}\text{S}_{\text{SS}}}{X} \quad (3)$$

7 With X the proportion of NSS defined as  $X = [\text{SO}_4^{2-}]_{\text{NSS}} / [\text{SO}_4^{2-}]_{\text{T}}$  and  $\delta^{34}\text{S}_{\text{SS}}$  is the average  
8 isotope composition of the ocean water sulfate (21‰; (Rees et al., 1978). The reaction ( 3 )  
9 can also be used to express the  $\delta^{33}\text{S}_{\text{NSS}}$ . Finally, the  $\Delta^{33}\text{S}_{\text{NSS}}$  is expressed according to the  
10 reaction ( 4 ):

$$\Delta^{33}\text{S}_{\text{NSS}} = \delta^{33}\text{S}_{\text{NSS}} - \left( \left( \frac{\delta^{34}\text{S}_{\text{NSS}}}{1000} + 1 \right)^{0.515} - 1 \right) \times 1000 \quad (4)$$

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14 Table S1 :  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ -values measured in  $\text{PM}_{10}$  aerosols from station 03 in Montréal  
 15 during 2013. *nd* (not determined) refers to samples for which the  $\Delta^{36}\text{S}$ -values could not be  
 16 properly measured due to low S concentrations (Au Yang et al., 2016)

Station 03				
Date	Day	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
		$\pm 0.1\text{‰} (1\sigma)$	$\pm 0.005\text{‰} (1\sigma)$	$\pm 0.1\text{‰} (1\sigma)$
10/01/13	10	4.465	0.074	-0.096
22/01/13	22	7.734	0.079	-0.060
03/02/13	34	6.332	0.182	0.121
15/02/13	46	4.385	0.107	0.392
21/02/13	52	6.790	0.027	0.417
05/03/13	64	7.804	0.167	-0.342
13/03/13	72	6.478	0.072	0.347
22/03/13	81	6.933	0.029	-0.306
04/04/13	94	7.709	0.075	-0.048
16/04/13	106	3.682	0.062	0.158
22/04/13	112	5.465	0.109	-0.673
04/05/13	124	8.060	0.102	-0.879
16/05/13	136	5.270	0.119	0.207
22/05/13	142	4.103	0.150	-0.512
03/06/13	154	8.234	0.072	0.196
15/06/13	166	5.458	0.031	0.978
21/06/13	172	3.809	0.164	-0.624
03/07/13	184	3.858	0.208	0.481
15/07/13	196	2.803	0.152	-0.388
14/08/13	226	4.939	0.115	0.166
07/09/13	250	4.891	0.208	-0.770
13/09/13	256	4.033	-0.006	0.017
19/09/13	262	5.413	0.136	-0.512
07/10/13	280	5.519	0.013	<i>nd</i>
13/10/13	286	3.670	0.133	-0.517
19/10/13	292	3.176	0.110	-0.363
06/11/13	310	6.150	0.061	0.005
06/12/13	340	6.464	0.007	<i>nd</i>
18/12/13	352	7.217	0.168	-0.188
24/12/13	358	4.728	0.108	<i>nd</i>

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19 Table S2 :  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ -values measured in  $\text{PM}_{10}$  aerosols from station 06 in Montréal  
 20 during 2013. *nd* (not determined) refers to samples for which the  $\Delta^{36}\text{S}$ -values could not be  
 21 properly measured due to low S concentrations (Au Yang et al., 2016)

		Station 06		
Date	Day	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
		$\pm 0.1\text{‰}$ ( $1\sigma$ )	$\pm 0.005\text{‰}$ ( $1\sigma$ )	$\pm 0.1\text{‰}$ ( $1\sigma$ )
10/01/13	10	6.948	0.019	-0.145
16/01/13	16	8.062	0.013	0.150
03/02/13	34	9.151	0.128	-0.396
15/02/13	46	7.455	0.060	0.077
21/02/13	52	6.615	-0.031	0.241
05/03/13	64	11.037	0.091	<i>nd</i>
17/03/13	76	11.292	0.003	-0.032
04/04/13	94	7.932	0.066	NM
16/04/13	106	7.581	0.053	0.002
22/04/13	112	7.542	0.083	-0.443
16/05/13	136	6.440	0.114	0.015
22/05/13	142	4.437	0.124	0.176
03/06/13	154	5.033	0.075	-0.188
15/06/13	166	6.370	0.046	0.497
21/06/13	172	5.798	0.194	-0.603
09/07/13	190	4.645	0.155	0.061
15/07/13	196	4.554	0.176	-0.249
21/07/13	202	5.896	-0.007	-0.079
08/08/13	220	5.066	0.070	-0.457
14/08/13	226	5.885	0.171	-0.234
20/08/13	232	3.654	0.319	-0.848
13/09/13	256	6.097	-0.068	0.276
19/09/13	262	6.271	0.175	-0.897
07/10/13	280	6.952	0.067	<i>nd</i>
13/10/13	286	2.005	0.174	-0.559
19/10/13	292	3.210	0.137	-0.257
06/11/13	310	8.361	0.028	0.149
18/11/13	322	6.122	0.001	0.718
24/11/13	328	8.720	-0.021	0.362
06/12/13	340	8.996	-0.075	-0.076
18/12/13	352	6.912	0.108	-0.339

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25 Table S3 :  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ -values measured in  $\text{PM}_{10}$  aerosols from station 13 in Montréal  
 26 during 2013. *nd* (not determined) refers to samples for which the  $\Delta^{36}\text{S}$ -values could not be  
 27 properly measured due to low S concentrations (Au Yang et al., 2016)

Station 13				
Date	Day	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
		$\pm 0.1\text{‰}$ ( $1\sigma$ )	$\pm 0.005\text{‰}$ ( $1\sigma$ )	$\pm 0.1\text{‰}$ ( $1\sigma$ )
10/01/13	10	5.753	0.055	0.681
16/01/13	16	8.595	-0.021	0.021
22/01/13	22	6.623	0.095	-0.092
03/02/13	34	4.996	0.155	-0.463
15/02/13	46	7.556	0.070	<i>nd</i>
05/03/13	64	10.563	0.060	<i>nd</i>
17/03/13	76	6.340	0.063	-0.335
04/04/13	94	8.084	0.073	0.480
16/04/13	106	6.554	0.067	0.309
04/05/13	124	6.953	0.019	<i>nd</i>
16/05/13	136	6.040	0.094	0.080
22/05/13	142	4.515	0.051	-0.484
03/06/13	154	5.527	0.063	-0.273
15/06/13	166	5.029	0.024	0.008
21/06/13	172	4.426	0.178	-0.820
03/07/13	184	3.397	0.209	-0.384
15/07/13	196	4.423	0.165	-0.359
08/08/13	220	4.843	0.054	<i>nd</i>
14/08/13	226	5.550	0.126	0.115
13/09/13	256	7.020	-0.020	0.437
19/09/13	262	6.203	0.138	-0.677
07/10/13	280	6.468	-0.022	-0.134
19/10/13	292	2.810	0.119	-0.411
06/11/13	310	8.607	0.003	0.036
18/11/13	322	6.655	-0.080	0.136
06/12/13	340	7.661	0.001	<i>nd</i>
18/12/13	352	7.927	0.148	-0.212

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30 Table S4 :  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ -values measured in  $\text{PM}_{10}$  aerosols from station 50 in Montréal  
 31 during 2013. *nd* (not determined) refers to samples for which the  $\Delta^{36}\text{S}$ -values could not be  
 32 properly measured due to low S concentrations (Au Yang et al., 2016)

Station 50				
Date	Day	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
		$\pm 0.1\text{‰}$ ( $1\sigma$ )	$\pm 0.005\text{‰}$ ( $1\sigma$ )	$\pm 0.1\text{‰}$ ( $1\sigma$ )
10/01/13	10	6.980	0.023	0.848
16/01/13	16	5.555	0.072	-0.316
22/01/13	22	5.005	0.123	-0.206
03/02/13	34	3.606	0.110	<i>nd</i>
15/02/13	46	5.488	0.027	-0.001
21/02/13	52	7.770	0.224	0.220
05/03/13	64	11.007	-0.018	0.046
23/03/13	81	6.885	0.052	0.168
16/04/13	106	8.560	0.062	-0.271
22/04/13	112	7.664	0.068	0.581
04/05/13	124	5.320	0.110	0.053
16/05/13	136	4.537	0.101	-0.365
22/05/13	142	3.959	0.072	0.160
03/06/13	154	6.329	0.019	0.080
15/06/13	166	3.658	0.197	-0.320
21/06/13	172	3.796	0.180	-0.383
03/07/13	184	5.528	0.168	-0.195
15/07/13	196	5.501	0.048	-0.010
21/07/13	202	8.152	0.058	0.101
08/08/13	220	5.775	0.160	0.217
14/08/13	226	3.605	0.316	-0.299
20/08/13	232	3.055	0.240	0.209
07/09/13	250	6.554	0.002	0.072
19/09/13	262	5.813	0.043	0.138
07/10/13	280	3.709	0.085	-0.293
13/10/13	286	3.272	0.129	-0.513
19/10/13	292	8.761	0.038	-0.326
06/11/13	310	5.159	-0.004	0.321
18/11/13	322	5.893	0.024	0.033
24/11/13	328	7.289	0.157	-0.422
06/12/13	340	3.720	0.086	-0.057
18/12/13	352	6.980	0.023	0.848
24/12/13	358	5.555	0.072	-0.316

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35 Table S5 :  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ -values measured in  $\text{PM}_{10}$  aerosols from station 98 in Montréal  
 36 during 2013. *nd* (not determined) refers to samples for which the  $\Delta^{36}\text{S}$ -values could not be  
 37 properly measured due to low S concentrations (Au Yang et al., 2016).

Station 98					
Date	Day	$[\text{SO}_4^{2-}]$	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
		$\pm 0.005 \mu\text{g}/\text{m}^3$	$\pm 0.1\text{‰} (1\sigma)$	$\pm 0.005\text{‰} (1\sigma)$	$\pm 0.1\text{‰} (1\sigma)$
10/01/13	10	0.533	6.469	0.041	0.782
16/01/13	16	0.842	4.425	0.068	<i>nd</i>
22/01/13	22	0.774	6.862	0.143	-0.135
03/02/13	34	2.043	3.223	0.216	0.029
15/02/13	46	1.282	4.211	0.096	-0.067
05/03/13	64	0.775	7.946	0.165	1.038
17/03/13	81	0.531	4.615	0.063	0.682
04/04/13	94	1.190	7.017	0.104	-0.770
16/04/13	106	1.376	5.043	0.073	0.189
22/04/13	112	1.349	4.067	0.170	-0.447
04/05/13	124	1.067	6.319	0.150	-0.520
16/05/13	136	0.801	4.966	0.175	-0.257
22/05/13	142	1.858	2.368	0.109	-0.294
03/06/13	154	0.891	5.856	0.115	1.317
15/06/13	166	0.896	6.302	0.043	0.528
21/06/13	172	1.355	3.480	0.295	-0.533
03/07/13	184	2.216	3.855	0.263	-0.277
15/07/13	196	1.774	3.007	0.250	-0.303
08/08/13	220	1.119	4.277	0.126	0.304
14/08/13	226	0.577	4.257	0.245	0.000
07/09/13	250	1.128	5.291	0.287	-0.027
13/09/13	256	0.171	4.387	0.076	1.751
19/09/13	262	1.344	4.712	0.218	-1.082
07/10/13	280	1.157	4.757	0.058	-0.038
13/10/13	286	1.990	3.773	0.144	-0.222
19/10/13	292	2.420	2.862	0.133	0.035
06/11/13	310	0.962	6.654	0.092	0.109
18/11/13	322	0.574	4.564	-0.022	0.048
24/11/13	328	0.046	6.361	-0.004	<i>nd</i>
06/12/13	340	1.175	2.473	0.020	-0.234
18/12/13	352	2.270	3.276	0.341	-0.462
24/12/13	358	0.130	5.270	0.120	0.336

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41 Table S6 : [Na] concentrations, calculated sea-sulfate and non-sea-sulfate concentrations, as  
 42 well as the corresponding S multi-isotope compositions in PM<sub>10</sub> aerosols from station 98 in  
 43 Montréal during 2013.

Station 98								
Date	[Na]	[SO <sub>4</sub> <sup>2-</sup> ] <sub>SS</sub>	[SO <sub>4</sub> <sup>2-</sup> ] <sub>NSS</sub>	[SO <sub>4</sub> <sup>2-</sup> ] <sub>NSS</sub>	δ <sup>34</sup> S <sub>NSS</sub>	δ <sup>33</sup> S <sub>T</sub>	δ <sup>33</sup> S <sub>NSS</sub>	Δ <sup>33</sup> S <sub>NSS</sub>
	μg/m <sup>3</sup>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	%	‰	‰	‰	‰
10/01/13	0.705	0.160	0.373	70	-0.202	3.369	0.170	0.274
16/01/13	0.955	0.223	0.618	73	-1.925	2.345	-0.715	0.277
22/01/13	2.345	0.574	0.200	25	-36.645	3.673	-16.854	2.197
03/02/13	1.418	0.340	1.703	83	-0.529	1.875	0.089	0.361
15/02/13	1.163	0.276	1.006	78	-0.664	2.263	-0.080	0.262
05/03/13	1.256	0.299	0.476	61	-0.903	4.251	0.118	0.583
17/03/13	0.943	0.220	0.311	58	-7.695	2.438	-3.493	0.479
04/04/13	1.195	0.284	0.906	76	2.319	3.713	1.486	0.292
16/04/13	1.045	0.246	1.130	82	1.350	2.668	0.894	0.199
22/04/13	1.008	0.237	1.112	82	0.248	2.263	0.442	0.314
04/05/13	1.013	0.238	0.829	77	1.819	3.401	1.273	0.336
16/05/13	0.780	0.179	0.621	77	0.056	2.730	0.400	0.371
22/05/13	0.909	0.212	1.646	88	-0.159	1.328	0.107	0.189
03/06/13	0.840	0.194	0.696	78	1.348	3.128	0.982	0.287
15/06/13	0.754	0.173	0.724	80	2.557	3.285	1.489	0.172
21/06/13	1.105	0.261	1.093	80	-0.941	2.086	0.002	0.487
03/07/13	1.729	0.419	1.797	81	-0.373	2.248	0.252	0.444
15/07/13	1.352	0.323	1.451	81	-1.225	1.798	-0.211	0.420
08/08/13	1.062	0.250	0.868	77	-0.833	2.328	-0.119	0.310
14/08/13	0.744	0.170	0.407	70	-3.157	2.436	-1.066	0.562
07/09/13	0.951	0.222	0.906	80	1.189	3.009	1.093	0.481
13/09/13	0.552	0.122	0.049	28	-39.185	2.334	-18.645	1.738
19/09/13	1.004	0.236	1.109	82	1.040	2.643	0.907	0.371
07/10/13	1.199	0.285	0.872	75	-0.873	2.506	-0.207	0.243
13/10/13	1.216	0.289	1.701	85	0.673	2.086	0.602	0.255
19/10/13	1.154	0.273	2.147	88	0.424	1.606	0.433	0.215
06/11/13	1.074	0.253	0.709	73	1.173	3.515	0.907	0.303
18/11/13	0.747	0.171	0.403	70	-2.828	2.327	-1.271	0.187
24/11/13	0.081	0.003	0.043	93	5.345	3.269	2.778	0.028
06/12/13	11.859	2.975	-1.800	-153	34.744	1.293	17.029	-0.723
18/12/13	1.837	0.446	1.824	80	-1.301	2.027	-0.121	0.550
24/12/13	0.149	0.038	0.152	80	1.135	2.832	0.858	0.274

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46 Tableau S7 : [Na] concentrations, calculated sea-sulfate and non-sea-sulfate concentrations , as  
 47 well as the corresponding S multi-isotope compositions in PM<sub>10</sub> aerosols from stations 03, 06,  
 48 13 and 50 in Montréal during 2013. *nm* (not measured) refers to samples which isotopic  
 49 compositions have not been measured for that day.

		[SO <sub>4</sub> <sup>2-</sup> ]	[Na]	[SO <sub>4</sub> <sup>2-</sup> ] <sub>SS</sub>	[SO <sub>4</sub> <sup>2-</sup> ] <sub>NSS</sub>	NSS	Δ <sup>33</sup> S <sub>NSS</sub>
		µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>	(%)	(%)
P03	16/01/2013	0.306	0.201	0.05	0.26	83	<i>nm</i>
	22/04/2013	0.316	0.175	0.04	0.27	86	0.088
	22/05/2013	0.413	0.301	0.08	0.34	82	0.120
	21/06/2013	0.288	0.162	0.04	0.25	86	0.089
	20/08/2013	0.802	0.271	0.07	0.73	91	<i>nm</i>
	13/09/2013	0.078	0.088	0.02	0.06	71	0.224
	13/10/2013	0.287	0.162	0.04	0.25	86	0.088
P06	22/04/2013	0.317	0.179	0.05	0.27	86	0.088
	21/06/2013	0.245	0.158	0.04	0.21	84	0.104
	21/07/2013	0.068	0.123	0.03	0.04	54	0.490
	20/08/2013	0.787	0.268	0.07	0.72	91	0.056
	13/09/2013	0.072	0.110	0.03	0.04	62	0.343
	13/10/2013	0.309	0.165	0.04	0.27	87	0.082
P13	22/05/2013	0.339	0.123	0.03	0.31	91	0.053
	21/06/2013	0.237	0.161	0.04	0.20	83	0.110
	21/07/2013	0.072	0.113	0.03	0.04	60	<i>nm</i>
	20/08/2013	0.732	0.229	0.06	0.67	92	<i>nm</i>
	13/09/2013	0.063	0.097	0.02	0.04	61	0.359
	19/10/2013	0.257	0.135	0.03	0.22	87	0.081
P50	22/04/2013	0.322	0.167	0.04	0.28	87	0.080
	22/05/2013	0.519	0.158	0.04	0.48	92	0.047
	21/06/2013	0.275	0.189	0.05	0.23	83	0.112
	21/07/2013	0.106	0.137	0.03	0.07	67	0.273
	20/08/2013	0.820	0.275	0.07	0.75	92	0.049
	19/09/2013	0.068	0.101	0.03	0.04	63	0.329
	13/10/2013	0.345	0.164	0.04	0.30	88	0.074
	24/11/2013	0.076	0.127	0.03	0.04	58	<i>nm</i>

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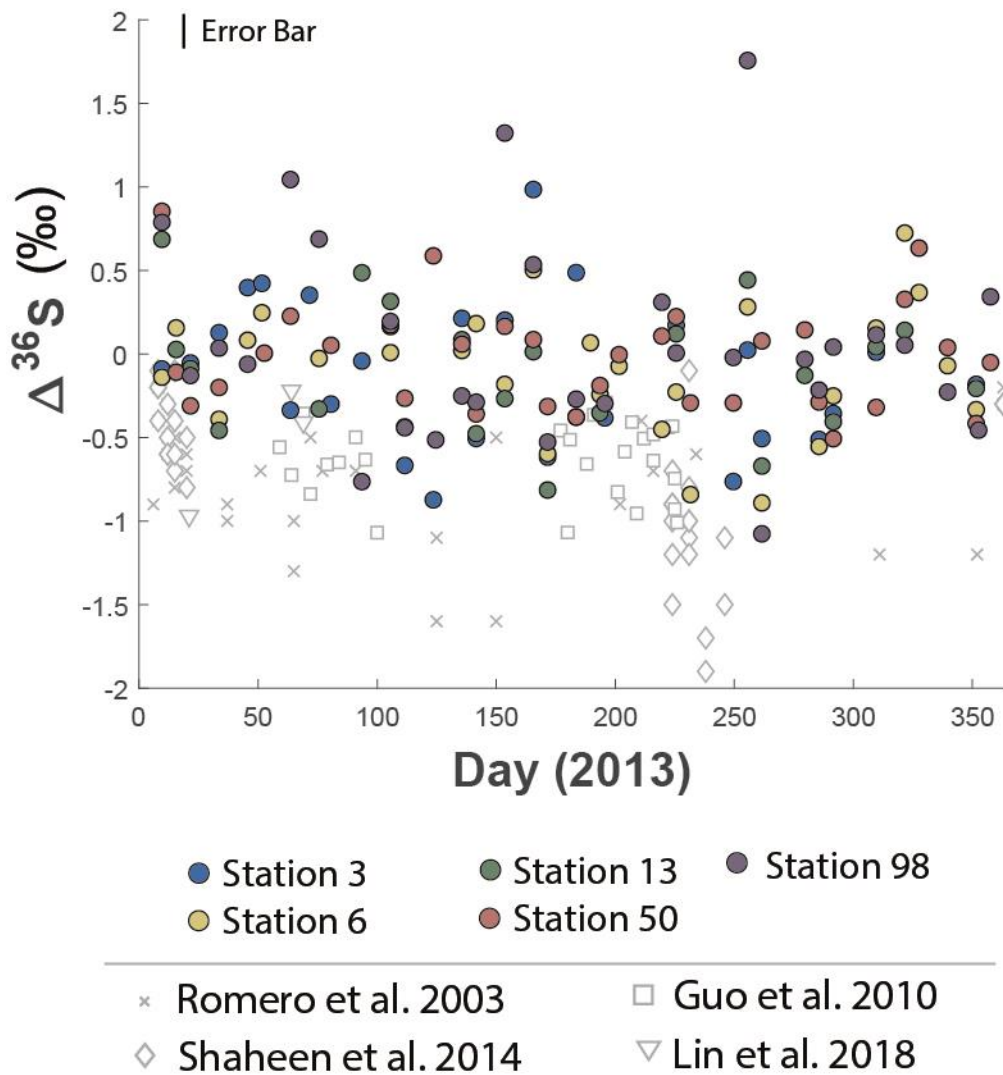
56

57 Table S8 :  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ -values measured in mineral dust samples collected at different  
 58 locations worldwide. *nd* (not determined) refers to samples for which the  $\Delta^{36}\text{S}$ -values could  
 59 not be properly measured due to low S concentrations (Au Yang et al., 2016)

Sample	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
	$\pm 0.1\text{‰}$ ( $1\sigma$ )	$\pm 0.005\text{‰}$ ( $1\sigma$ )	$\pm 0.1\text{‰}$ ( $1\sigma$ )
Douz (Tunisia)	9.052	0.028	0.462
Niger	7.770	0.035	<i>nd</i>
Jordan	6.905	-0.021	<i>nd</i>
Matmata (Tunisia)	6.322	0.045	<i>nd</i>
China	5.335	-0.009	<i>nd</i>
Morocco	13.692	-0.002	0.067

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Figure S1 : Sulfate  $\Delta^{36}\text{S}$  variations over time in Montréal  $\text{PM}_{10}$  aerosols.

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