

Supplementary Material for

**(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> exchange reaction and double-spike MC-ICP-MS  
method for gypsum U-Th dating**

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**Table S1**

Certified mass fractions of six gypsum standards in this study

	GBW03109	GBW03110	GBW03111a	GYP-C	TIG-1	FGD-1
SiO <sub>2</sub> (%)	0.27	7.21	0.63	3.50	0.11	0.13
Al <sub>2</sub> O <sub>3</sub> (%)	0.02	1.92	0.14	0.79	0.57	0.02
Fe <sub>2</sub> O <sub>3</sub> (%)	0.02	0.63	0.11	0.40	0.26	0.01
CaO(%)	40.70	28.50	32.30	30.40	32.30	32.70
MgO(%)	1.02	4.92	2.47	5.35	0.12	0.01
K <sub>2</sub> O(%)	0.02	0.38	0.03	0.36	0.01	0.01
Na <sub>2</sub> O(%)	0.02	0.02	0.01	0.02	0.04	0.01
TiO <sub>2</sub> (%)	0.00	0.10	0.01	0.04	0.82	0.01
SO <sub>3</sub> (%)	55.63	32.55	40.72	33.00	43.40	46.40
H <sub>2</sub> O(%)	0.17	14.27	17.95	14.37	20.30	20.70
CO <sub>2</sub> (%)	2.17	8.63	5.44	11.20	1.41	0.02
L.O.I(%)	2.30	23.55	23.60	25.93	22.03	21.04
Th( $\mu\text{g g}^{-1}$ )				0.52	2.14	0.03
U( $\mu\text{g g}^{-1}$ )				0.72	2.50	

**Table S2**

Measurement of gypsum/carbonate reaction efficiency ( $F_{[Ca]D}$  value) using different chemical processes

condition	medium	Ca (theoretical)	Ca(measured)	$F_{[Ca]D}(\%)$
R = 1:4, T = 1.5 h	Na <sub>2</sub> CO <sub>3</sub>	0.0234	0.0197	84.38
	duplicate 1	0.0234	0.0202	86.19
	duplicate 2	<b>0.0234</b>	<b>0.0199</b>	84.99
	<b>average</b>			<b>85.19</b>
	K <sub>2</sub> CO <sub>3</sub>	0.0237	0.0203	85.68
	duplicate 1	0.0234	0.0200	85.40
	duplicate 2	<b>0.0235</b>	<b>0.0201</b>	85.38
	<b>average</b>			<b>85.49</b>
	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	0.0235	0.0212	90.11
	duplicate 1	0.0235	0.0207	88.18
	duplicate 2	<b>0.0235</b>	<b>0.0209</b>	88.82
	<b>average</b>			<b>89.04</b>
M = (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , T = 1.5 h	<b>molar ratio</b>	Ca (theoretical)	Ca(measured)	$F_{[Ca]D}(\%)$
	<b>1:1.1</b>	0.0235	0.0172	73.43
	duplicate 1	0.0235	0.0171	72.88
	duplicate 2	0.0235	0.0169	72.07
	<b>average</b>			<b>72.79</b>
	<b>1:2</b>	0.0235	0.0185	78.97
	duplicate 1	0.0235	0.0190	80.65
	duplicate 2	0.0235	0.0181	77.18
	<b>average</b>			<b>78.94</b>
	<b>1:3</b>	0.0234	0.0189	80.55
	duplicate 1	0.0234	0.0186	79.43
	duplicate 2	0.0234	0.0191	81.61
	<b>average</b>			<b>80.53</b>
	<b>1:4</b>	0.0233	0.0203	87.13
	duplicate 1	0.0235	0.0203	86.35
	duplicate 2	0.0234	0.0201	85.88
	<b>average</b>			<b>86.46</b>
	<b>1:5</b>	0.0233	0.0199	85.71
	duplicate 1	0.0235	0.0202	85.97
	duplicate 2	0.0234	0.0205	87.59
	<b>average</b>			<b>86.42</b>
R = 1:4, M = (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	<b>time (h)</b>	Ca (theoretical)	Ca(measured)	$F_{[Ca]D}(\%)$
	<b>0.5</b>	0.0232	0.0171	73.71
	duplicate 1	0.0236	0.0165	70.06
	<b>average</b>			<b>71.88</b>
	<b>1</b>	0.0232	0.0183	79.07
	duplicate 1	0.0235	0.0184	78.41
<b>average</b>			<b>78.74</b>	

<b>1.5</b>	0.0235	0.0205	87.07
duplicate 1	0.0235	0.0210	89.55
<b>average</b>			<b>88.31</b>
<b>2</b>	0.0236	0.0220	93.18
duplicate 1	0.0236	0.0229	97.30
<b>average</b>			<b>95.24</b>
<b>4</b>	0.0235	0.0224	95.52
duplicate 1	0.0235	0.0228	97.23
<b>average</b>			<b>96.37</b>
<b>8</b>	0.0232	0.0220	94.85
duplicate 1	0.0234	0.0228	97.42
<b>average</b>			<b>96.14</b>

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R is the molar ratio of gypsum/carbonate

T is the reaction time

M is the carbonate medium

Table S3 The U-Th content,  $\delta^{234}\text{U}$ , and  $^{230}\text{Th}/^{238}\text{U}$  activity ratio values of FGD-1 gypsum standards using two different digestion processes.

No	Sample	$^{238}\text{U}$ (ng g <sup>-1</sup> )	$^{232}\text{Th}$ (ng g <sup>-1</sup> )	$\delta^{234}\text{U}$ (measured)	$^{230}\text{Th} / ^{238}\text{U}$ (activity)
1	FGD-1*	40.9 ±0.1	19.3 ±0.4	-14.4 ±2.2	4.398 ±0.028
2	duplicate* 1	41.3 ±0.1	20.0 ±0.4	-11.4 ±1.9	4.337 ±0.027
3	duplicate* 2	42.9 ±0.1	19.8 ±0.4	-12.9 ±2.1	4.293 ±0.029
4	duplicate* 3	42.2 ±0.1	19.9 ±0.4	-11.3 ±2.4	4.350 ±0.031
5	duplicate* 4	42.6 ±0.1	19.9 ±0.4	-11.8 ±2.4	4.273 ±0.029
6	duplicate* 5	43.1 ±0.1	20.1 ±0.4	-11.7 ±2.1	4.270 ±0.027
1	FGD-1#	41.0 ±0.1	19.6 ±0.4	-13.5 ±2.9	4.360 ±0.021
2	duplicate# 1	43.0 ±0.1	20.3 ±0.4	-12.5 ±2.1	4.242 ±0.038
3	duplicate# 2	41.7 ±0.1	20.0 ±0.5	-15.1 ±2.1	4.384 ±0.034
4	duplicate# 3	41.9 ±0.1	20.4 ±0.4	-14.3 ±2.0	4.383 ±0.038
5	duplicate# 4	43.0 ±0.1	20.0 ±0.4	-12.1 ±2.2	<i>4.213 ±0.034</i>
6	duplicate# 5	42.6 ±0.1	20.0 ±0.4	-11.8 ±4.5	4.270 ±0.024
7	duplicate# 6	41.2 ±0.0	19.3 ±0.4	-11.7 ±1.6	4.360 ±0.021
8	duplicate# 7	41.2 ±0.0	19.2 ±0.4	-11.7 ±1.6	4.359 ±0.020
9	duplicate# 8	42.3 ±0.1	20.3 ±0.5	-10.5 ±2.5	4.291 ±0.025
10	duplicate# 9	41.8 ±0.1	19.6 ±0.4	-13.9 ±2.7	4.369 ±0.027
11	duplicate# 10	40.4 ±0.1	19.3 ±0.5	-10.8 ±2.7	4.379 ±0.034
12	duplicate# 11	42.4 ±0.1	19.8 ±0.4	-13.0 ±2.8	4.339 ±0.033
13	duplicate# 12	41.6 ±0.1	19.7 ±0.4	-15.2 ±2.7	4.302 ±0.038
14	duplicate# 13	41.5 ±0.1	19.7 ±0.4	-14.9 ±2.8	4.344 ±0.035
15	duplicate# 14	41.3 ±0.1	19.6 ±0.4	-12.3 ±3.1	4.315 ±0.041
16	duplicate# 15	41.7 ±0.1	19.6 ±0.4	-12.5 ±2.9	4.309 ±0.034
17	duplicate# 16	41.6 ±0.1	19.4 ±0.4	-11.1 ±3.1	4.328 ±0.034
18	duplicate# 17	40.4 ±0.1	19.3 ±0.4	-10.4 ±3.0	4.350 ±0.034
19	duplicate# 18	41.5 ±0.1	19.5 ±0.4	-10.4 ±3.1	4.361 ±0.036
20	duplicate# 19	41.7 ±0.1	19.4 ±0.5	-13.9 ±2.9	4.381 ±0.035
21	duplicate# 20	40.7 ±0.1	20.1 ±0.5	-11.6 ±3.7	4.393 ±0.024
22	duplicate# 21	40.0 ±0.1	19.4 ±0.4	-13.1 ±3.6	4.364 ±0.023
23	duplicate# 22	41.9 ±0.1	20.5 ±0.5	-10.2 ±2.1	4.395 ±0.031
24	duplicate# 23	42.1 ±0.1	20.2 ±0.5	-11.6 ±2.6	4.276 ±0.034
25	duplicate# 24	40.8 ±0.1	20.0 ±0.6	-10.5 ±2.4	4.313 ±0.022
26	duplicate# 25	41.9 ±0.1	19.3 ±0.6	-12.8 ±2.6	<i>4.229 ±0.022</i>
27	duplicate# 26	41.3 ±0.1	20.2 ±0.6	-15.0 ±3.0	4.293 ±0.028
28	duplicate# 27	42.6 ±0.1	19.8 ±0.6	-11.8 ±2.6	4.342 ±0.023
29	duplicate# 28	40.2 ±0.1	19.7 ±0.6	-11.6 ±2.5	4.372 ±0.022
30	duplicate# 29	40.2 ±0.1	19.8 ±0.5	-14.9 ±3.4	4.353 ±0.026
31	duplicate# 30	40.1 ±0.1	19.8 ±0.4	-12.3 ±3.2	4.375 ±0.029
32	duplicate# 31	41.5 ±0.1	20.4 ±0.4	-13.0 ±3.2	4.338 ±0.026
33	duplicate# 32	41.3 ±0.2	20.3 ±0.4	-10.6 ±4.0	4.315 ±0.030

34	duplicate# 33	40.4 ±0.1	20.0 ±0.4	-14.5 ±3.3	4.334 ±0.028
35	duplicate# 34	40.6 ±0.1	20.1 ±0.4	-12.0 ±4.7	4.375 ±0.033
36	duplicate# 35	41.4 ±0.1	20.1 ±0.4	-11.8 ±4.0	4.267 ±0.030
37	duplicate# 36	40.0 ±0.1	19.5 ±0.4	-10.4 ±3.4	4.326 ±0.028
38	duplicate# 37	39.9 ±0.1	19.5 ±0.4	-11.8 ±3.1	4.299 ±0.029
39	duplicate# 38	39.5 ±0.2	19.6 ±0.4	-14.2 ±4.7	4.282 ±0.032
40	duplicate# 39	40.3 ±0.1	19.3 ±0.4	-14.6 ±3.6	4.291 ±0.033
41	duplicate# 40	40.8 ±0.1	19.9 ±0.4	-12.7 ±3.5	4.324 ±0.028
42	duplicate# 41	39.6 ±0.1	19.4 ±0.4	-15.5 ±3.5	4.276 ±0.027
43	duplicate# 42	40.4 ±0.1	19.1 ±0.4	-14.1 ±3.0	4.263 ±0.030

FGD-1\* and duplicates\* are the gypsum samples treated with the dilute HCl digestion method.

FGD-1# and duplicates# are the gypsum samples treated with the (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> exchange reaction method.

The <sup>230</sup>Th/<sup>238</sup>U activity ratio in grey italic font represents the outliers, which were not used in the calculation of the average value.