Widespread shoaling of sulfidic waters linked to the end-Guadalupian (Permian) mass extinction

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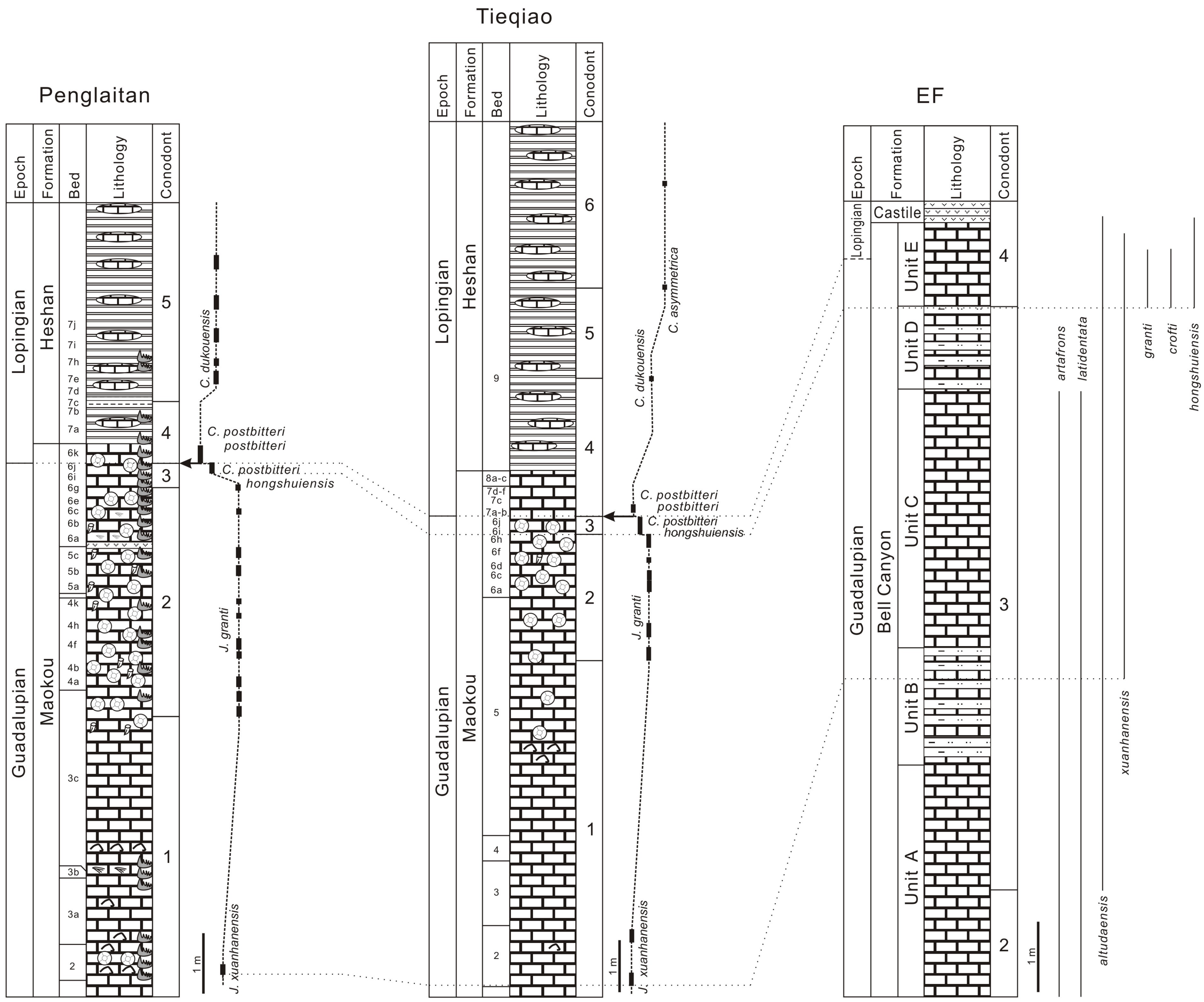

Fig. DR1: The biostratigraphic correlation between the Penglaitan, Tieqiao and EF sections. The conodont biostraigraphy in South China is after Jin et al. (2006) and Mei et al. (1998) and the conodont biostratigraphy of the EF section is after Wardlaw and Nestell (2010). For both the Penglaitan and Tieqiao sections, five conodont zones of J. xuanhanensis, J. granti, C. p. hongshuiensis, C. p. postbitteri, and C. dukouensis were defined and the two sections are correlated based on conodont zonation. The correlation between the EF section and the Penglaitan section is based on the conodont zone of J. xuanhanensis at each section, the conodont zone of C. p. hongshuiensis at each section, and the Guadalupian-Lopingian boundary identified at each section.

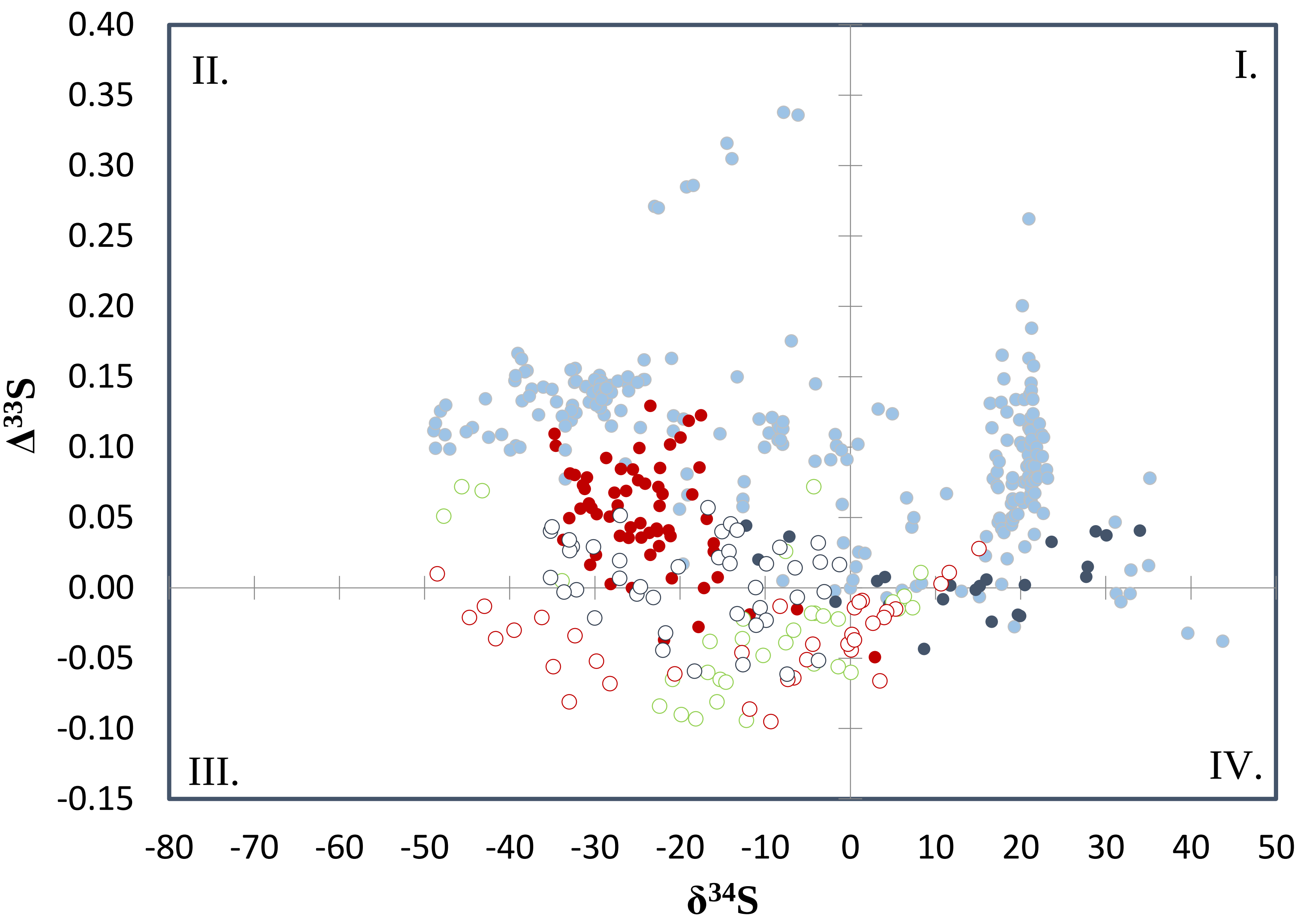

Fig. DR2: Published multiple S-isotopic data for reduced sulfur species in modern sediments and the Phanerozoic sedimentary rocks.

1: Filled grey circle – Farquhar et al., 2000; Johnston et al., 2008; Canfield et al., 2010; Zerkle et al., 2010; Scheiderich et al., 2010; Li et al., 2010; Strauss et al., 2012.

2: Filled red circle – Shen et al., 2011.

3: Filled blue circle – Sim et al., 2015.

4: Unfilled red circle - Tieqiao section; unfilled green circle – Penglaitan section; unfilled circle – EF section (this study)

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Analytical method of multiple S-isotopes for pyrite:

In this study, pyrite sulfur from rock samples was extracted using chromium reduction and converted to silver sulfide (Canfield et al., 2010). During this procedure, the product H_2S was carried by nitrogen gas through a condenser and a bubbler filled with milli-Q water, and collected as silver sulfide by reacting with silver nitrate solution.

Silver sulfide (Ag_2S) was converted to SF_6 by fluorination by reaction with a 5-fold excess of F_2 at 250°C for 8 h in a Ni reaction vessel. After the reaction, product SF_6 was condensed from the residual F_2 into a liquid-nitrogen cooled trap (-177°C). The F_2 was removed to another part of the manifold where it was passivated by reaction with hot KBr. The SF_6 was subsequently thawed to room temperature, and then cooled to -111°C to condense contaminants such as trace HF, before it was transferred to the injection loop of a gas chromatograph (GC) which was cooled to -177°C. GC purification of SF_6 was undertaken using a composite column consisting of a 1/8 in. diameter, six foot lead column of 5A molecular sieve, followed by a 1/8 inch diameter, 12 foot long Haysep-Q™ column. The He carrier flow was set at 20 mL/min. The SF_6 peak was registered on a TCD and then isolated by freezing into a liquid-nitrogen cooled trap. The isotopic composition of the purified SF_6 was determined by dual-inlet gas-source mass spectrometry monitoring ion beams at *m*/*e* of 127, 128, 129, and 131 using a Thermo Finnigan MAT 253 gas source mass spectrometer.

One sigma uncertainties on mass-dependent reference materials are better than ±0.2‰, ±0.01‰, and ±0.2‰ in $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$, respectively. Uncertainties on the measurements reported here are estimated to be better than ±0.2‰, ±0.01‰, and ±0.2‰. The results of our measurements are presented in Tables DR1-3.

Table DR1: Multiple S-isotopic data of the Penglaitan section

Formation	Sample	$\delta^{33}S$	$\delta^{34}S$	$\delta^{36}S$	$\Delta^{33}S$	$\Delta^{36}S$
Heshan	PLT7-12	3.74	7.30	13.95	-0.014	0.031
Heshan	PLT7-11	-8.73	-16.76	-31.52	-0.060	0.081
Heshan	PLT7-9	-10.88	-20.89	-39.48	-0.065	-0.169
Heshan	PLT7-7	-6.39	-12.19	-22.59	-0.094	0.446
Heshan	A9-2	-3.89	-7.59	-14.73	0.026	-0.358
Heshan	PLT7-2	-6.53	-12.60	*	-0.022	*
Heshan	PLT7-1	-6.58	-12.66	-23.89	-0.036	0.030
Heshan	A4	-11.69	-22.41	-42.00	-0.084	0.145
Heshan	A1	-24.83	-47.75	-89.82	0.051	-1.053
Maokou	6k	-23.71	-45.65	-86.38	0.072	-1.426
Maokou	6j	-17.58	-33.87	-63.98	0.005	-0.609
Maokou	6i	-22.43	-43.22	-81.63	0.069	-1.109
Maokou	6h	-2.17	-4.17	-8.01	-0.018	-0.095
Maokou	6(f-g)	-2.37	-4.57	-8.72	-0.018	-0.064
Maokou	6c	-1.66	-3.18	-6.13	-0.020	-0.086
Maokou	6b	-3.47	-6.66	-12.57	-0.030	0.040
Maokou	6a	-8.56	-16.48	-31.08	-0.038	0.002
Maokou	5c	-2.15	-4.30	-8.84	0.072	-0.678
Maokou	5b	-2.25	-4.25	-8.05	-0.054	0.011
Maokou	4k	-10.36	-19.84	-37.05	-0.090	0.307
Maokou	4g	-9.47	-18.14	-33.91	-0.093	0.271
Maokou	4f	-0.02	0.07	0.33	-0.060	0.191
Maokou	4b	-7.96	-15.27	-28.70	-0.065	0.111
Maokou	PLT3-7	-7.62	-14.62	-27.34	-0.067	0.253
Maokou	PLT3-6	4.27	8.29	*	0.011	*
Maokou	PLT3-5	2.87	5.62	10.75	-0.015	0.053
Maokou	PLT3-4	-0.78	-1.41	-2.64	-0.056	0.040
Maokou	PLT3-3	3.25	6.33	11.66	-0.006	-0.402
Maokou	3c base 20cm	2.56	4.99	9.52	-0.010	0.018
Maokou	3a top 20cm	-3.95	-7.58	*	-0.039	*
Maokou	2c	-5.33	-10.23	-19.41	-0.048	-0.049
Maokou	2b	-0.75	-1.42	-2.87	-0.022	-0.186
Maokou	2a	-8.17	-15.66	-29.34	-0.081	0.192

* denotes samples with contaminant at 131 daltons.

Table DR2: Multiple S-isotopic data of the Tieqiao section

Formation	Sample	$\delta^{33}S$	$\delta^{34}S$	$\delta^{36}S$	$\Delta^{33}S$	$\Delta^{36}S$
Heshan	TQ-S-A29	0.00	0.09	0.36	-0.044	0.175
Heshan	TQ-S-A28	7.78	15.10	28.99	0.028	0.097
Heshan	TQ-S-A21	2.72	5.32	10.48	-0.015	0.342
Heshan	TQ-S-A19	2.18	4.27	7.98	-0.017	-0.147
Heshan	TQ-S-A17	0.71	1.39	2.85	-0.009	0.207
Heshan	TQ-S-A16	-3.49	-6.64	-12.46	-0.064	0.118
Heshan	TQ-S-A15	-10.73	-20.60	-38.93	-0.061	-0.146
Heshan	TQ-S-A14	0.24	0.49	0.79	-0.014	-0.134
Heshan	TQ-S-A13	-17.22	-33.01	-62.00	-0.081	-0.214
Maokou	TQ-S-A12	-25.27	-48.50	-91.03	0.010	-0.896
Maokou	TQ-S-A11	-20.56	-39.49	-74.21	-0.030	-0.522
Maokou	TQ-S-A10	-23.31	-44.72	-84.02	-0.021	-0.769
Maokou	TQ-S-A9	-22.37	-42.96	-80.59	-0.013	-0.551
Maokou	TQ-S-A8	-18.18	-34.88	-65.43	-0.056	-0.191
Maokou	TQ-S-A7	-16.82	-32.34	-61.12	-0.034	-0.571
Maokou	TQ-S-A6	-15.52	-29.81	-56.31	-0.052	-0.432
Maokou	TQ-S-A5	-21.72	-41.66	-78.40	-0.036	-0.721
Maokou	TQ-S-A4	-18.85	-36.23	-68.32	-0.021	-0.604
Maokou	TQ-S-A3	-14.70	-28.22	-53.05	-0.068	-0.112
Maokou	TQ-S-A2	-3.85	-7.34	-13.90	-0.065	-0.001
Maokou	TQ-S-A1	-2.68	-5.10	-9.69	-0.051	-0.015
Maokou	TQ-S-B1	-6.62	-12.72	-24.23	-0.046	-0.193
Maokou	TQ-S-B2	-0.18	-0.28	0.15	-0.040	0.682
Maokou	TQ-S-B3	0.07	0.19	0.34	-0.033	-0.022
Maokou	TQ-S-B4	-2.31	-4.40	-8.44	-0.040	-0.093
Maokou	TQ-S-B5	-4.26	-8.24	-15.90	-0.013	-0.313
Maokou	TQ-S-B6	-6.18	-11.81	-21.89	-0.086	0.425
Maokou	TQ-S-B7	2.02	3.97	7.95	-0.021	0.392
Maokou	TQ-S-B8	0.52	1.03	2.10	-0.010	0.140
Maokou	TQ-S-B9	1.34	2.64	5.84	-0.025	0.811
Maokou	TQ-S-B10	0.21	0.48	1.03	-0.037	0.120
Maokou	TQ-S-B11	5.47	10.65	20.63	0.003	0.298
Maokou	TQ-S-B12	1.72	3.47	7.51	-0.066	0.904
Maokou	TQ-S-B13	-4.91	-9.33	-17.45	-0.095	0.207
Maokou	TQ-S-B14	5.99	11.63	22.16	0.011	-0.063

Table DR3: Multiple S-isotopic data of the EF section

Formation	Sample	$\delta^{33}S$	$\delta^{34}S$	$\delta^{36}S$	$\Delta^{33}S$	$\Delta^{36}S$
Bell Canyon	EF11	-8.59	-16.72	-32.24	0.057	-0.709
Bell Canyon	EF10	-7.97	-15.46	-29.55	0.022	-0.374
Bell Canyon	EF8.1	-13.96	-27.02	-51.51	0.052	-0.793
Bell Canyon	EF7.8	-18.28	-35.20	-66.90	0.007	-1.076
Bell Canyon	EF7.57-7.62	-15.60	-30.02	-57.34	-0.021	-1.062
Bell Canyon	EF7.54-7.57	-18.25	-35.20	-66.95	0.040	-1.128
Bell Canyon	EF7.52-7.54	-16.70	-32.17	-61.37	-0.001	-1.138
Bell Canyon	EF7.47-7.52	-17.47	-33.63	-64.30	-0.003	-1.372
Bell Canyon	EF7.39-7.46	-11.27	-21.71	-41.79	-0.032	-0.939
Bell Canyon	EF7.26-7.34	-10.43	-20.19	-38.83	0.015	-0.819
Bell Canyon	EF7.16-7.29	-5.75	-11.13	-21.37	0.000	-0.318
Bell Canyon	EF7.0	-3.89	-7.43	*	-0.061	*
Bell Canyon	EF6.8	-7.34	-14.24	-26.93	0.026	-0.040
Bell Canyon	EF6.4	-5.48	-10.59	-20.31	-0.014	-0.289
Bell Canyon	EF6.3	-5.13	-9.90	-18.94	-0.023	-0.215
Bell Canyon	EF6.15	-7.29	-14.14	-27.35	0.017	-0.652
Bell Canyon	EF5.8	-3.22	-6.22	-11.83	-0.007	-0.035
Bell Canyon	EF5.5	-7.76	-15.08	-29.17	0.040	-0.706
Bell Canyon	EF5.3	-5.08	-9.87	-19.23	0.017	-0.549
Bell Canyon	EF4.9	-4.25	-8.28	-16.24	0.029	-0.567
Bell Canyon	EF4.5	-3.34	-6.50	-12.76	0.014	-0.440
Bell Canyon	EF4.1	-7.21	-14.04	-27.26	0.045	-0.745
Bell Canyon	EF3.5	-1.92	-3.78	-7.17	0.032	0.002
Bell Canyon	EF3.0	-1.80	-3.53	-7.12	0.018	-0.416
Bell Canyon	EF2.5	-1.58	-3.06	-6.20	-0.003	-0.397
Bell Canyon	EF2.1	-0.64	-1.28	-2.85	0.017	-0.417
Bell Canyon	EF1.8	-6.82	-13.28	-25.68	0.041	-0.591
Bell Canyon	EF1.6	-1.97	-3.73	-7.05	-0.052	0.019
Bell Canyon	EF1.3	-9.53	-18.31	*	-0.059	*
Bell Canyon	EF1.0	-5.74	-11.07	*	-0.027	*
Bell Canyon	EF0.7	-6.89	-13.30	-25.17	-0.018	-0.060
Bell Canyon	EF0.4	-6.57	-12.62	-23.71	-0.055	0.123
Bell Canyon	EF0.0	-11.45	-22.02	-41.98	-0.044	-0.548
Bell Canyon	EF-0.2	-18.15	-35.02	-66.24	0.043	-0.742
Bell Canyon	EF-0.5	-16.93	-32.66	-61.86	0.029	-0.713
Bell Canyon	EF-1.0	-17.07	-32.94	-62.34	0.027	-0.682
Bell Canyon	EF-1.5	-13.00	-25.08	-47.83	-0.004	-0.718
Bell Canyon	EF-2.0	-11.99	-23.14	-44.21	-0.007	-0.704
Bell Canyon	EF-2.2	-14.03	-27.08	-51.50	0.007	-0.679
Bell Canyon	EF-2.5	-14.02	-27.09	-51.40	0.019	-0.571
Bell Canyon	EF-2.8	-17.11	-33.02	-62.45	0.034	-0.645
Bell Canyon	EF-3.1	-15.63	-30.17	-57.19	0.029	-0.639
Bell Canyon	EF-3.4	-12.78	-24.66	-46.69	0.001	-0.360

* denotes samples with contaminant at 131 daltons.

Table DR4: Fractionations used in modeling calculations in Figure 3

Source	Fractionations		Averages		Fractionation for SDP w/ Reox		
	alpha 34	alpha 33	alpha 34	alpha 33	alpha 34	alpha 33	F
Sulfite	0.969598	0.984177	0.970091	0.984443	1.007534	1.003904	0.75
Sulfite	0.970583	0.984708					
Sulfite	0.946291	0.971996	0.950992	0.974468	1.012404	1.006424	0.75
Sulfite	0.955693	0.976941					
Elemental S	0.975442	0.987184	0.973296	0.986081	1.020437	1.01055	0.25
Elemental S	0.97115	0.984977					

Source: Johnston et al., 2005 modified in Johnston et al., 2007.

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Table DR5: The equations and calculations for generation of mixing arrays in Figure 3

The mixing is calculated between two end members. The abundance of a specific isotope in the mixing reservoir can be expressed as:

$$^{3i}S_{mixing} = f \cdot {}^{3i}S_A + (1-f) \cdot {}^{3i}S_B \quad (1)$$

Where, for example, ^{3i}S represents the amount (e.g., atoms) of sulfur isotope ^{32}S, ^{33}S, ^{34}S or ^{36}S in each reservoir (A, B, and mixing). A, and B are the two end members (i.e. sulfate and sulfide). f represents the fraction of A reservoir compared to the total mixing sulfur amount.

The S-isotopic composition of sulfate was estimated by a study of Wu et al. (2010), and S-isotopic values of sulfide were measured by this study. Thus, using:

$$\delta^{34}S = 1000 \cdot \left[\frac{\left({}^{34}S / {}^{32}S \right)_{sample}}{\left({}^{34}S / {}^{32}S \right)_{reference}} - 1 \right] \quad (2)$$

Rearranging (2) to get $\left({}^{34}S / {}^{32}S \right)_{sample}$ and $^{34}S_{sample}$:

$$^{34}R = \left({}^{34}S / {}^{32}S \right)_{sample} = \left(\frac{\delta^{34}S}{1000} + 1\right) \cdot \left({}^{34}S / {}^{32}S \right)_{reference} \quad (3)$$

$$^{34}S_{sample} = \left(\frac{\delta^{34}S}{1000} + 1\right) \cdot \left({}^{34}S / {}^{32}S \right)_{reference} \cdot {}^{32}S_{sample} \quad (4)$$

$$^{34}S_{sample} = {}^{34}R \cdot {}^{32}S_{sample} \quad (5)$$

Where ^{3i}R is the isotope ratio $^{3i}S / {}^{32}S$.

And, using:

$$\Delta^{33}S = \delta^{33}S - 1000 \cdot \left[\left(\frac{\delta^{34}S}{1000} + 1 \right)^{0.515} - 1 \right] \quad (6)$$

$$= 1000 \cdot \left[\frac{\left({}^{33}S / {}^{32}S \right)_{sample}}{\left({}^{33}S / {}^{32}S \right)_{reference}} - 1 \right] - 1000 \cdot \left[\left(\frac{\delta^{34}S}{1000} + 1 \right)^{0.515} - 1 \right]$$

Therefore:

$$\Delta^{33}S = 1000\cdot\left[\frac{\left({}^{33}S/{}^{32}S\right)_{sample}}{\left({}^{33}S/{}^{32}S\right)_{reference}} - \left(\frac{\delta^{34}S}{1000}+1\right)^{0.515}\right] \quad (7)$$

Rearranging (7) to get $\left({}^{33}S/{}^{32}S\right)_{sample}$ and ${}^{33}S_{sample}$:

$${}^{33}R=\left({}^{33}S/{}^{32}S\right)_{sample} =[\frac{\Delta^{33}S}{1000}+\left(\frac{\delta^{34}S}{1000}+1\right)^{0.515}]\cdot\left({}^{33}S/{}^{32}S\right)_{reference} \quad (8)$$

$${}^{33}S_{sample} = [\frac{\Delta^{33}S}{1000}+\left(\frac{\delta^{34}S}{1000}+1\right)^{0.515}]\cdot\left({}^{33}S/{}^{32}S\right)_{reference}\cdot {}^{32}S_{sample} \quad (9)$$

$${}^{33}S_{sample} = {}^{33}R\cdot{}^{32}S_{sample} \quad (10)$$

Similar to ${}^{33}S_{sample}$, ${}^{36}S_{sample}$ can be expressed as:

$${}^{36}R = \left({}^{36}S/{}^{32}S\right)_{sample} = [\frac{\Delta^{36}S}{1000}+\left(\frac{\delta^{34}S}{1000}+1\right)^{1.9}]\cdot\left({}^{36}S/{}^{32}S\right)_{reference} \quad (11)$$

$${}^{36}S_{sample} = [\frac{\Delta^{36}S}{1000}+\left(\frac{\delta^{34}S}{1000}+1\right)^{1.9}]\cdot\left({}^{36}S/{}^{32}S\right)_{reference}\cdot {}^{32}S_{sample} \quad (12)$$

$${}^{36}S_{sample} = {}^{36}R\cdot{}^{32}S_{sample} \quad (13)$$

Furthermore, considering $^{32}S + {}^{33}S + {}^{34}S + {}^{36}S=1$:

$$\left({}^{33}S/{}^{32}S\right)_{sample} + \left({}^{34}S/{}^{32}S\right)_{sample} + \left({}^{36}S/{}^{32}S\right)_{sample} = \left(\frac{{}^{33}S + {}^{34}S + {}^{36}S}{{}^{32}S}\right)_{sample}$$

$$= \left(\frac{1 - {}^{32}S}{{}^{32}S}\right)_{sample}$$

$$= \left(\frac{1}{{}^{32}S} - 1\right)_{sample} \tag{14}$$

Thus:

$$^{32}S_{sample} = \frac{1}{1 + \left({}^{33}S/{}^{32}S\right)_{sample} + \left({}^{34}S/{}^{32}S\right)_{sample} + \left({}^{36}S/{}^{32}S\right)_{sample}}$$

$$= \frac{1}{1 + {}^{33}R + {}^{34}R + {}^{36}R} \tag{15}$$

Applying (15) to (5), (10), (13):

$$^{34}S_{sample} = \frac{{}^{34}R}{1 + {}^{33}R + {}^{34}R + {}^{36}R} \tag{16}$$

$$^{33}S_{sample} = \frac{{}^{33}R}{1 + {}^{33}R + {}^{34}R + {}^{36}R} \tag{17}$$

$$^{36}S_{sample} = \frac{{}^{36}R}{1 + {}^{33}R + {}^{34}R + {}^{36}R} \tag{18}$$

Depending on (1) and (15), (16), (17), (18):

$$^{32}S_{mixing} = f \cdot {}^{32}S_A + (1 - f) \cdot {}^{32}S_B$$

$$= f \cdot \frac{1}{1 + {}^{33}R_A + {}^{34}R_A + {}^{36}R_A} + (1 - f)\frac{1}{1 + {}^{33}R_B + {}^{34}R_B + {}^{36}R_B} \tag{19}$$

$$^{33}S_{mixing} = f \cdot {}^{33}S_A + (1-f)\,{}^{33}S_B$$
$$= f \cdot \frac{^{33}R_A}{1 + {}^{33}R_A + {}^{34}R_A + {}^{36}R_A} + (1-f)\frac{^{33}R_B}{1 + {}^{33}R_B + {}^{34}R_B + {}^{36}R_B} \quad (20)$$

$$^{34}S_{mixing} = f \cdot {}^{34}S_A + (1-f)\,{}^{34}S_B$$
$$= f \cdot \frac{^{34}R_A}{1 + {}^{33}R_A + {}^{34}R_A + {}^{36}R_A} + (1-f)\frac{^{34}R_B}{1 + {}^{33}R_B + {}^{34}R_B + {}^{36}R_B} \quad (21)$$

$$^{36}S_{mixing} = f \cdot {}^{36}S_A + (1-f)\,{}^{36}S_B$$
$$= f \cdot \frac{^{36}R_A}{1 + {}^{33}R_A + {}^{34}R_A + {}^{36}R_A} + (1-f) \cdot \frac{^{36}R_B}{1 + {}^{33}R_B + {}^{34}R_B + {}^{36}R_B} \quad (22)$$

Therefore, the sulfur isotope of the mixing product can be obtained:

$$\delta^{34}S_{mixing} = 1000 \cdot \left[\frac{\left({}^{34}S/{}^{32}S\right)_{mixing}}{\left({}^{34}S/{}^{32}S\right)_{reference}} - 1 \right]$$
$$= 1000 \cdot \left[\frac{\left(\left(f \cdot \frac{^{34}R_A}{1+{}^{33}R_A+{}^{34}R_A+{}^{36}R_A} + (1-f)\frac{^{34}R_B}{1+{}^{33}R_B+{}^{34}R_B+{}^{36}R_B}\right) \Big/ \left(f \cdot \frac{1}{1+{}^{33}R_A+{}^{34}R_A+{}^{36}R_A} + (1-f)\frac{1}{1+{}^{33}R_B+{}^{34}R_B+{}^{36}R_B}\right) \right)_{mixing}}{\left({}^{34}S/{}^{32}S\right)_{reference}} - 1 \right]$$

(23)

$$\Delta^{33}S_{mixing}=1000\cdot\left[\frac{\left({}^{33}S/{}^{32}S\right)_{mixing}}{\left({}^{33}S/{}^{32}S\right)_{reference}}-\left(\frac{\delta^{34}S_{mixing}}{1000}+1\right)^{0.515}\right]$$

$$=1000\cdot\left[\frac{\left((f\cdot\frac{{}^{33}R_A}{1+{}^{33}R_A+{}^{34}R_A+{}^{36}R_A}+(1-f)\frac{{}^{33}R_B}{1+{}^{33}R_B+{}^{34}R_B+{}^{36}R_B})/(f\cdot\frac{1}{1+{}^{33}R_A+{}^{34}R_A+{}^{36}R_A}+(1-f)\frac{1}{1+{}^{33}R_B+{}^{34}R_B+{}^{36}R_B})\right)_{mixing}}{\left({}^{33}S/{}^{32}S\right)_{reference}}\right.$$

$$\left.-\left(\frac{\delta^{34}S_{mixing}}{1000}+1\right)^{0.515}\right] \tag{24}$$