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GEOCHEMICAL METHODS

The samples were first carefully trimmed to remove visible veins and weathering rinds then are clean by ultrasonic in distilled de-ionized (DDI) water. Subsequently, approximately 100-200 g of whole rock was crushed and then pulverized into powder of <200 mesh size using a splitdiscus mill. Sulfate extraction followed a recommended protocol of Wotte et al. (2012). Ultrapure Milli-Q water (18.2 M Ω), purified NaCl, and distilled HCl were used to create solutions for leaching and acid digestion of the samples. The powder was immersed in 10 % NaCl solution under constant magnetic stirring at room temperature for time durations of 24 hour, 24 hour, 48 hour, 72 hours, and 72hours, respectively. No sulfate was present in filtered solutions after the 5th leaching for all samples. After the five water-leaching steps, the carbonate sample was dissolved in 3.5% HCl solution. The slurry was decanted and vacuum filtered through a 0.45 um cellulose membrane filter. The acid-leached sulfate was collected as BaSO₄ by adding saturated BaCl₂ solution. All collected BaSO₄ samples were further purified with a DDARP method in order to remove nitrate (Bao, 2006). The sulfide in residues after acid leaching was extracted as Ag₂S using the chromium reduction method (Canfield et al., 1986). Concentrations of sulfur from sulfate and sulfide were determined by gravimetrical method. The Milli-Q water and concentrated HCl used to make stock leaching and digestion solutions were tested and shown to contain less than 500 ppb sulfate, suggesting that these were not the source of the atmospheric sulfate contaminant.

Oxygen isotope measurement of sulfate was conducted at Oxy-Anion Stable Isotope Consortium (OASIC) in Louisianan State University. The Δ^{17} O of BaSO₄ was determined using O₂ generated in a CO₂ laser-fluorination system (Bao and Thiemens, 2000) and run on a MAT 253 in a duel inlet model. The standard deviation (1 σ) associated with the Δ^{17} O was \pm 0.03 ‰ based on multiple runs of the same O₂ gas on the MAT 253, and was < \pm 0.05 ‰ for replicates of the same BaSO₄ via laser-fluorination. The δ^{18} O of barite was measured using CO gas converted from BaSO₄ using a Thermal Conversion Elemental Analyzer (TCEA) at 1450 °C coupled with the MAT253 in a continuous-flow mode. The standard deviation (σ) associated with δ^{18} O_{SO4} was \pm 0.5 ‰. Here the $\delta^* = (R_{sample}/R_{VSMOW} - 1)$, in which R is the ratio of 18 O/ 16 O, 17 O/ 16 O, and Δ^{17} O $\equiv \delta'{}^{17}$ O – 0.52 × $\delta'{}^{18}$ O in which the $\delta' \equiv \ln (R_{sample}/R_{VSMOW})$. Sample pretreatment and the δ^{34} S measurement of sulfate and pyrite were conducted at Indiana University where BaSO₄ and Ag₂S was converted to SO₂ using an Elemental Analyzer (EA) at 980 °C and run on a Thermo-Electron Delta V Plus Advantage mass spectrometer in a continuous-flow mode. The standard deviation associated with δ^{34} S measurement was \pm 0.3 ‰.

To evaluate the effect of SAS on isotope composition of extracted CAS, we employed a twoend-member mixing model. We assumed that extracted CAS was a mixture of two end members: SAS and original CAS. We assume that the values of Δ^{17} O of SAS vary from 0.4 ‰, 0.6 ‰, 0.7 %, 0.8 %, 1.0 %, 1.2 %, 1.4 % to 1.6 % and the Δ^{17} O of original CAS is -0.2 %; the values of δ^{34} S of original CAS vary from 20 ‰, 30 ‰, 40 ‰, 50 ‰, 60 ‰, 70 ‰ to 80 ‰ and δ^{34} S of SAS is 1.1 ‰. The model shows that 20 % of SAS in extracted CAS can result in δ^{34} S of extracted CAS changing up to 16 % and Δ^{17} O to 0.36 %, which depends on the amount fraction of SAS and isotope difference between SAS and original CAS. Recent sampling campaigns (Jenkins and Bao, 2006; Li et al., 2013) and modeling (Sofen et al., 2011) show that the average Δ^{17} O value for SAS in mid-latitudes of the northern hemisphere is ~ +0.7 ‰ (a range of +0.2 ‰ to +3.0 %), suggesting that acid-leachable sulfate still contains a fraction of SAS, with some more than 50 % (e.g. samples YB12 and AH-11-28-17) (Fig. DR1). Note that the parameters in this model didn't include all ranges of Δ^{17} O and δ^{34} S of SAS and original CAS. This simple two-end-member mixing model serves as an example to estimate the magnitude of SAS contamination. To accurately quantify the magnitude of SAS contamination. the Δ^{17} O values of local SAS and original CAS or ancient seawater sulfate must be known but it changes from site to site and through geological time.

A TWO-END-MEMBER MIXING MODEL

The extracted CAS amount can be expressed by equation:

$$M_{CASext} = M_{CAS} + M_{SAS}$$
(1)

For isotopic composition,

$$\Delta_{\rm CASext}^{17} O_{\rm CASext} \times M_{\rm CASext} = \Delta_{\rm CAS}^{17} O_{\rm CAS} \times M_{\rm CAS} + \Delta_{\rm CAS}^{17} O_{\rm SAS} \times M_{\rm SAS}$$
(2)

$$\delta^{34}S_{CASext} \times M_{CASext} = \delta^{34}S_{CAS} \times M_{CAS} + \delta^{34}S_{SAS} \times M_{SAS}$$
(3)
We now substitute Eq. (1) into Eq. (2) and (3) and obtain

$$\Delta_{A}^{17}O_{CASext} = (\Delta_{A}^{17}O_{SAS} - \Delta_{A}^{17}O_{CAS}) \times M_{SAS} / M_{CASext} + \Delta_{A}^{17}O_{CAS}$$
(4)

$$\delta^{34}S_{CASext} = (\delta^{34}S_{SAS} - \delta^{34}S_{CAS}) \times M_{SAS} / M_{CASext} + \delta^{34}S_{CAS}$$
(5)

M _{CASext}	amount of sulfate extracted by acid-leaching,
M _{CAS}	amount of original CAS,
M _{SAS}	amount of SAS,
$\Delta^{17}O_{CASext}$	Δ^{17} O of sulfate extracted by acid-leaching,
$\Delta^{17}O_{CAS}$	Δ^{17} O of original CAS,
$\Delta^{17}O_{SAS}$	Δ^{17} O of SAS,
$\delta^{34}S_{CASext}$	δ^{34} S of sulfate extracted by acid-leaching,
$\delta^{34}S_{CAS}$	δ^{34} S of original CAS,
$\delta^{34}S_{SAS}$	δ^{34} S of SAS.



Figure DR1. Plot of modeled $\delta^{34}S_{CASext}$ and $\Delta^{17}O_{CASext}$ values versus M_{SAS}/M_{CASext} values. Solid triangle presents the model result of $\delta^{34}S_{CASext}$ and solid circle presents the model result of $\Delta^{17}O_{CASext}$.

	Sequential	δ ³⁴ S	δ ³⁴ S		[SO ₄] or	Site of collecting				
Sample Name	extraction	(VCDT)	δ ¹⁸ Ο	$\Delta^{17}O$	[Ag₂S]	sample	Age	Formation		
	number				(ppm)					
AFT-X-313-W-1	1	11.5	7.6	0.09	114	Kuluketage,	Lower	Jinlonggou		
AFT-X-313-W-2	2	15.2	9.1	0.10	57	Xinjiang, NW	Ordovician			
AFT-X-313-W-3	3	28.5	9.8	0.39	24	China				
AFT-X-313-W-4	4	33.8	11.2		6					
AFT-X-313-CAS	5	35.6	13.5	-0.04	166					
AFT-X-313-CRS	6	27.1			22					
AET V 200 W 1	1	77	7.4	0.25	167	Vulukataga	Linnar	Hadabulakataga		
AFT-X-390-W-1	1	/./	7.4	0.23	107	Viniiona NW	Ordevicion	пацаритакетаде		
AF1-X-390-W-2	2	8.7	/.1	0.04	109	China	Oldoviciali			
AF1-X-390-W-3	3	9.5	8.1	0.06	33	Cinina				
AF1-A-390-W-4	4	10.2	/.5	0.00	10					
AFT-X-390-CAS	5	13.0	10.2	0.00	22					
AF1-A-390-CK5	0	18.0			52					
AFT-X-395-W-1	1	9.8	5.7	0.10	837	Kuluketage,	Upper	Hadabulaketage		
AFT-X-395-W-2	2	11.9	6.6	-0.11	453	Xinjiang, NW	Ordovician			
AFT-X-395-W-3	3	10.4	6.5	-0.02	174	China				
AFT-X-395-W-4	4	14.7	6.0	0.19	37					
AFT-X-395-CAS	5	15.1	8.4	-0.08	40					
AFT-X-395-CRS	6	21.8			16					
WS-28-W-1	1	10.7	8.9	0.06	82	Wushi, Xinjiang,	Cambrian	Xiao'erbulake		
WS-28-W-2	2	14.3	7.3	-0.03	33	NW China	Terreneuvian			
WS-28-W-3	3	13.0	4.8		3					
WS-28-W-4	4				0					
WS-28-CAS	5				0					
WS-28-CRS	6	-0.9			14					
WS-41-W-1	1	11.2	7.2	0.02	45	Wushi, Xinjiang,	Cambrian	Xiao'erbulake		
WS-41-W-2	2	15.2	7.0		19	NW China	Terreneuvian			
WS-41-W-3	3	10.9			3					
WS-41-W-4	4				0					
WS-41-CAS	5				0					
WS-41-CRS	6	5.0			28					
WS-64-W-1	1	8	11.5	0.18	423	Wushi, Xinijang	Cambrian	Shavilike		
WS-64-W-2	2	8.6	6	0.08	457	NW China	Series 2			
WS-64-W-3	3	9.3	7.5	0.12	46					
WS-64-W-4	4	10.8	6.7	0.15	14					
WS-64-CAS	5	32.2	14.2	0.05	176					
WS-64-CRS	6	8.0			26					
Delta-120-W-1	1	10.1	7.2	0.01	68	Yukkengo,	Neoproterozoic	Zhamoketi		

Table DR1. Geochemical data of this study (blanks = no data obtained).

Delta -120-W-2	2	11.6	7.9	0.05	68	Xinjiang, NW		(Tereeken cap	
Delta -120-W-3	3	13.7	6.2		4	China		carbonate)	
Delta -120-W-4	4				0				
Delta -120-CAS	5	15.7	11.6	-0.15	64				
Delta -120-CRS	6	19.5			34				
Delta -123-W-1	1	5.0	8.1	0.06	155	Yukkengo,	Neoproterozoic	Zhamoketi	
Delta -123-W-2	2	10.8	9.3	0.07	71	Xinjiang, NW		(Tereeken cap	
Delta -123-W-3	3	12.7	7.7		13	China		carbonate)	
Delta -123-W-4	4				0				
Delta -123-CAS	5	17.3	13.0	-0.11	92				
Delta -123-CRS	6	23.3			24				
Delta -89-W-1	1	95	10.1	0.03	176	Yukkengo Xinijang	Neoproterozoic	Zhamoketi	
Delta -89-W-2	2	10.7	8.0	-0.02	58	NW China		(Tereeken cap	
Delta -89-W-3	3	10.7	0.0	0.02	0			carbonate)	
Delta -89-W-4	4				0				
Delta -89-CAS	5	17.0	12.4	-0.15	290				
Delta -89-CRS	6	15.1			26				
AH-11-28-10-W-1	1	10.2	4.4	0.89	67	Death Valley, US	Neoproterozoic	Noonday	
AH-11-28-10-W-2	2	12.7	4.5	0.69	41				
AH-11-28-10-W-3	3	17.2	6.2		21				
AH-11-28-10-W-4	4	17.9	6.1		0				
AH-11-28-10-CAS	5	18.4	11.1	0.55	58				
AH-11-28-10-CRS	6	7.9			25				
AH-11-28-11-W-1	1	10.2	4.3	1.41	151	Death Valley, US	Neoproterozoic	Noonday	
AH-11-28-11-W-2	2	12.6	6.3	0.71	94				
AH-11-28-11-W-3	3	15.4	6.6	0.39	25				
AH-11-28-11-W-4	4				0				
AH-11-28-11-CAS	5	22.9	13.3		31				
AH-11-28-11-CRS	6	16.0			31				
AH-11-28-15-W-1	1	11.8	4.6	0.64	35	Death Valley, US	Neoproterozoic	Noonday	
AH-11-28-15-W-2	2	14.2	6.7		22				
AH-11-28-15-W-3	3	16.8	6.2		1				
AH-11-28-15-W-4	4				0				
AH-11-28-15-CAS	5	19.8	14.3		25				
AH-11-28-15-CRS	6	12.4			14				
AH-11-28-17-W-1	1	8.3	4.7	1.32	298	Death Valley, US	Neoproterozoic	Noonday	
AH-11-28-17-W-2	2	9.5	4.4	1.11	238		1	5	
AH-11-28-17-W-3	3	10.8	5.8	0.90	61				
AH-11-28-17-W-4	4	12.9	6.2	0.78	3	1			
AH-11-28-17-CAS	5	12.0	7.9	0.68	325				
AH-11-28-17-CRS	6	15.0			28				
AH-11-28-2-W-1	1	10.5	8.8	0.04	12	Death Valley, US	Neoproterozoic	Beck Spring	
AH-11-28-2-W-2	2	12.9	7.3	0.12	10				

AH-11-28-2-W-3	3	13	4.8		5			
AH-11-28-2-W-4	4				0			
AH-11-28-2-CAS	5				0			
AH-11-28-2-CRS	6	16.7			29			
AH-11-28-4-W-1	1	9.5	4.1	0.68	28	Death Valley, US	Neoproterozoic	Beck Spring
AH-11-28-4-W-2	2	13.4	4.4		26			
AH-11-28-4-W-3	3	17.9	7.0		7			
AH-11-28-4-W-4	4				0			
AH-11-28-4-CAS	5				0			
AH-11-28-4-CRS	6	18.1			0			
AH-11-28-7-W-1	1	12.5	5.5	0.34	68	Death Valley, US	Neoproterozoic	Crystal Spring
AH-11-28-7-W-2	2	16.3	6.8	0.07	38			
AH-11-28-7-W-3	3	16.5	8.0	0.04	46			
AH-11-28-7-W-4	4	17.6	6.8		30			
AH-11-28-7-CAS	5				0			
AH-11-28-7-CRS	6	10.9			22			
AH-11-28-9-1-W-1	1	14.5	5.8	0.14	72	Death Valley, US	Neoproterozoic	Crystal Spring
AH-11-28-9-1-W-2	2	16.4	6.9	0.10	40			
AH-11-28-9-1-W-3	3	17.5	9.0		33			
AH-11-28-9-1-W-4	4				0			
AH-11-28-9-1-CAS	5				0			
AH-11-28-9-1-CRS	6	11.0			24			
AH-11-28-9-2-W-1	1	11.9	5.0	0.09	73	Death Valley, US	Neoproterozoic	Crystal Spring
AH-11-28-9-2-W-2	2	16.3	7.1	0.05	45			
AH-11-28-9-2-W-3	3	17.0	8.0		47			
AH-11-28-9-2-W-4	4	17.8	6.7		29			
AH-11-28-9-2-CAS	5				0			
AH-11-28-9-2-CRS	6	8.8			25			
CRCP-T-W-1	1	9.9	1.4	0.29	238	Caborca, Mexico	Cambrian Series	Cerro Rajon
CRCP-T-W-2	2	11.9	2.9	0.10	9		2	
CRCP-T-W-3	3				0			
CRCP-T-W-4	4				0			
CRCP-T-CAS	5	10.0	8.7	0.00	300			
CRCP-T-CRS	6	14.8			56			
WC5-W-1	1	14.9	6.4	0.11	181	Emigrant Pass	Cambrian Series	Wood Canyon
WC5-W-2	2	15.1	6.0	0.10	97	Eastern California,	1	
WC5-W-3	3	18.9	5.6	0.05	2	US		
WC5-W-4	4	20.0	9.2		92			
WC5-CAS	5	24.3	10.0	-0.02	334			

WC5-CRS	6	22.5			46								
AFQ649-CAS	5	10.5	12.7	0.07		Heishan, Xinjiang,	Neoproterozoic	Zhamoketi					
AFQ650-CAS	5	9.7	10.9	0.09		NW China		(Tereeken cap					
AFQ650-CRS	6	39.1						carbonate					
AFQ651-CAS	5	10.6	12.7	0.10									
AFQ652-CAS	5	10.1	13.4	0.04									
AFQ653-CAS	5	10.3	12.6	0.04									
AFQ654-CAS	5	9.3	12.1	-0.04									
AFQ655-CAS	5	13.4	13.7	-0.03									
AFQ657-CAS	5	10.9	13.8	0.03									
AFQ658-CAS	5	9.5	12.3	0.04									
AFQ659-CAS	5	11.2	13.0	-0.03									
AFQ660-CAS	5	9.5	11.8	-0.02									
AFQ661-CAS	5	8.2	12.2	0.15									
AFQ661-CRS	6	17.0											
AFQ662-CAS	5	9.9	12.5	0.10									
AFQ663-CAS	5	12.0	15.0	0.06									
AFQ664-CAS	5	13.1	15.3	-0.04									
AFQ665-CAS	5	10.0	11.9	0.06									
AFQ666-CAS	5	9.1	12.0	0.01									
AFQ666-CRS	6	23.7											
AFQ667-CAS	5	10.0	12.1	-0.02									
AFQ668-CAS	5	10.5	12.6	-0.04									
AFQ669-CAS	5	9.2	12.3	0.00									
AFQ670-CAS	5	8.4	11.7	0.02									
AFQ672-CAS	5	14.0	12.1	-0.17									
AFQ672-CRS	6	30.4											
AFQ673-CAS	5	17.5	12.7	-0.36									
AFQ674-CAS	5	15.7	12.3	-0.33									
AFQ675-CAS	5	8.1	11.2	0.09									
AFQ677-CAS	5	18.8	15.1	-0.28									
AFQ678-CAS	5	23.2	14.1	-0.24									
AFQ634-CAS	5	11.2	13.1	0.02									
AFQ634-CRS	6	28.5											
AFQ635-CAS	5	11.3	11.2	-0.04									
AFQ636-CAS	5	12.1	12.4	0.03									
AFQ637-CAS	5	12.4	13.8	0.05									
AFQ637-CRS	6	38.9											
AFQ638-CAS	5	11.0	13.5	-0.02									
AFQ638-CRS	6	39.4											
AFQ639-CAS	5	10.3	12.8	0.12									
AFQ639-CRS	6	31.8											
AFQ642-CAS	5	10.0	13.2	-0.04									
AFQ642-CRS	6	39.2]							
AFQ647-CAS	5	11.4	13.7	-0.05									

AFQ647-CRS	6	29.9					
YB12-5-CAS	5	10.5	19.5	0.20			
YB12-6-CAS	5	13.1	9.9	0.36	Yongji, Shanxi,	Mesoproterozoic	
YB12-15-CAS	5	11.1		0.27			
YB12-18-CAS	5	10.8	3.9	0.34	north-central China		Beidajian

"Sample name-W-1, 2, 3, 4" refers to water-leachable sulfate after leaching of 24 hours, 24 hours, 48 hours, and 72 hours, respectively. "Sample name-CAS" refers to acid-leachable sulfate, which is extracted from the residue after multiple water leaching steps. "Sample name-CRS" refers to sulfide in the residue of acid-leaching and was extracted as Ag₂S by chromium reduction method. Water-leachable sulfate of samples series AFQ and YB12 from Xinjiang and Shanxi were not collected and not all CRS of these samples were extracted.

Table DR2. Summary of geochemical data of this study. WLS is water-leachable sulfate; ALS is acid-leachable sulfate extracted; CRS is chromium reduction sulfur; [S] is sulfur (SO₄ or Ag₂S) concentration.

			Δ^1	'o	δ ³⁴ S		δ ¹⁸ O		[8]			
		Positive (+)		Negative (-)			Sample	Range	Sample	Range	Sample	Range
	Sample number Range			Sample number Rang			number	(‰)	number	(‰)	number	(ppm)
	δ ³⁴ S ₅₀₄ >δ ³⁴ Scrs	δ ³⁴ S ₅₀₄ <δ ³⁴ Scπs	(‰)	8 ³⁴ S504>8 ³⁴ Scrs 8 ³⁴ S504<8 ³⁴ Scrs		(‰)						
WLS	20	28	+0.01to	1	3	-0.11 to	67	+5.0 to	66	+1.4 to	67	0 to
			+1.41			-0.02		+33.8		+11.5		837
ALS	2	9	0.00 to	3	7	-0.36 to	52	+8.1 to	51	+3.9 to	20	0 to
			+0.68			-0.02		+35.6		+19.5		334
CRS	-	_	-		-	30	-0.9 to	-	-	20	0 to 56	
								+39.4				



Figure DR2. Plots of Δ^{17} O, δ^{34} S, and δ^{18} O values of sequentially extracted sulfates by NaCl and HCl solutions for all 60 carbonate outcrop samples. Solid filled symbols (except AFQ and YB12 serials) present acid-leachable sulfates.

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