

# Data report: $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ measurements of dissolved sulfate from interstitial water samples, IODP Expedition 311<sup>1</sup>

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## Chapter contents

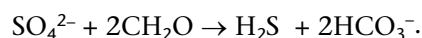
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## Abstract

$\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  measurements of dissolved sulfate were made from interstitial water samples collected during Integrated Ocean Drilling Program Expedition 311.  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  ratios of dissolved sulfate are modified by microbial processes involving sulfur redox processes; therefore, they can be used to better constrain microbial sulfur cycling. All Expedition 311 sites show clear evidence of organotrophic and methanotrophic sulfate reduction. A full interpretation of these results, however, requires careful reaction-transport modeling, which will be given elsewhere.

## Introduction

Microbial sulfate reduction is the major pathway of organic matter oxidation in coastal marine and continental shelf sediments (Jørgensen, 1982) and is a fundamental process linking the geochemical cycles of carbon, sulfur, and oxygen (e.g., Schidlowski et al., 1983; Berner, 1982; Garrels and Lerman, 1984; Wortmann and Chernyavsky, 2007). Sulfate-reducing microorganisms reduce  $\text{SO}_4^{2-}$  according to the following net reaction:



Microbially mediated sulfate reduction affects the isotopic composition of dissolved and solid sulfur species in marine sediments. Although several details of the fractionation process remain controversial, the overall process is well understood and can be described as the sum of several mass-dependent fractionations during the stepwise reduction of sulfate to sulfide and the ratio between the forward and backward reactions (Rees, 1973; Bruechert, 2004; Brunner and Bernasconi, 2005). Experiments and field data show that the  $\delta^{18}\text{O}_{\text{SO}_4}$  composition is also modified in the presence of sulfate-reducing microorganisms (Mizutani and Rafter, 1973; Böttcher et al., 1998; Brunner et al., 2005). This has been attributed either to a kinetic isotope effect during the reduction of sulfate to sulfite or cell-internal exchange reactions between enzymatically activated sulfate (adenosine phosphosulfate [APS]) and/or sulfite with cytoplasmic water (Mizutani and Rafter, 1973; Fritz et al., 1989; Wortmann et al., 2007) and/or between sulfite and adenosine monophosphate during APS formation. The isotopic fingerprint of these processes may be further modified by

<sup>1</sup>Wortmann, U.G., 2008. Data report:  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  measurements of dissolved sulfate from interstitial water samples, IODP Expedition 311. In Riedel, M., Collett, T.S., Malone, M.J., and the Expedition 311 Scientists, *Proc. IODP*, 311: Washington, DC (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.311.209.2008

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the cell-external reoxidation of sulfide to elemental sulfur and the subsequent disproportionation to sulfide and sulfate or by the oxidation of sulfite to sulfate.

This data report offers  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  data which may help to better constrain these processes. However, a detailed interpretation is only possible using rigorous reaction-transport modeling (Wortmann, 2006; Chernyavsky and Wortmann, 2007; Wortmann et al., 2007), which will be published elsewhere.

## Methods

Interstitial water samples were taken on board the *JOIDES Resolution* following procedures given in the “**Methods**” chapter. Samples were treated immediately after collection by adding 100  $\mu\text{L}$  of a saturated cadmium acetate solution per 5 mL of sample to precipitate all  $\text{H}_2\text{S}$  and inhibit further activity of sulfate-reducing microorganisms. The precipitated  $\text{CdS}$  was separated using a centrifuge, and the supernatant was filtered through a 0.45  $\mu\text{m}$  membrane filter and acidified with  $\text{HCl}$ . The sulfate was precipitated as  $\text{BaSO}_4$  by adding  $\text{BaCl}_2$  within 1 h of acidification. Samples were centrifuged, washed with hot water, and dried overnight at 60°C.

For  $\delta^{34}\text{S}$  measurements, the sulfate samples were weighed in Sn cups together with vanadium pentoxide as catalyst and measured on a Thermo Finnigan Mat 253 stable isotope mass spectrometer in continuous flow mode using the Conflo III open split interface and an Eurovector 3000 elemental analyzer.  $\text{SO}_2$  reference gas was injected through the dual inlet system. The system was calibrated by using International Atomic Energy Agency (IAEA)-SO-5 (0.49‰ Vienna Canyon Diablo Triolite [VCDT]) and National Bureau of Standards (NBS)-127 (21.1‰ VCDT) international standards. Analytical reproducibility as determined by a  $\text{BaSO}_4$  in-house standard (8.2‰ VCDT) is  $\pm 0.17\%$ . Analytical reproducibility as determined by IAEA-SO-5 is  $\pm 0.08\%$ . Data are reported in conventional delta notation with respect to VCDT.

For  $\delta^{18}\text{O}_{\text{SO}_4}$  measurements,  $\sim 135 \mu\text{g}$   $\text{BaSO}_4$  was added to Ag cups and pyrolyzed at 1350°C on a Hekatech HT-EA using He as a carrier gas. The produced CO gas was routed through an Ascarite trap, separated on a Molsieve 5A column, and subsequently measured on a Thermo Finnigan Mat 253 mass spectrometer in continuous flow mode using the Conflo III open split interface. The CO reference gas was injected via the Conflo III interface. The system was calibrated by using U.S. Geological Survey (USGS) 32 (25.7‰ Vienna standard mean ocean water [VSMOW]), NBS-127 (8.6‰ VSMOW), and IAEA-SO-6 (−11.34‰ VSMOW) international standards. Analytical repro-

ducibility of the measurements was determined by running several replicates of NBS-127. We report the 1  $\sigma$  value as  $\pm 0.12\%$ . The data are reported in conventional delta notation with respect to VSMOW.

## Results

Several  $\delta^{18}\text{O}$  measurements have no matching  $\delta^{34}\text{S}$  result. This is caused by the different linearity response of the elemental analyzer/mass spectrometer combination when measuring CO versus  $\text{SO}_2$  gas. We were generally able to obtain a linear response for CO with signal sizes to 1 V, whereas linear  $\text{SO}_2$  measurements were only obtained with signals  $>2$  V. We therefore excluded all  $\delta^{34}\text{S}$  values where the signal was  $<2$  V.

Hole U1325B yielded results to 5.15 meters below seafloor (mbsf), whereas shipboard data indicate that sulfate was consumed at 2.15 mbsf. I suspect that this was caused by mislabeling samples from Hole U1325D, where sulfate depletion does not occur above 4–5 mbsf. However, we list the results here as recorded in the Integrated Ocean Drilling Program (IODP) database. The data are reported in Tables **T1**, **T2**, **T3**, **T4**, and **T5** and shown in Figures **F1**, **F2**, **F3**, **F4**, **F5**, and **F6**.

## Acknowledgments

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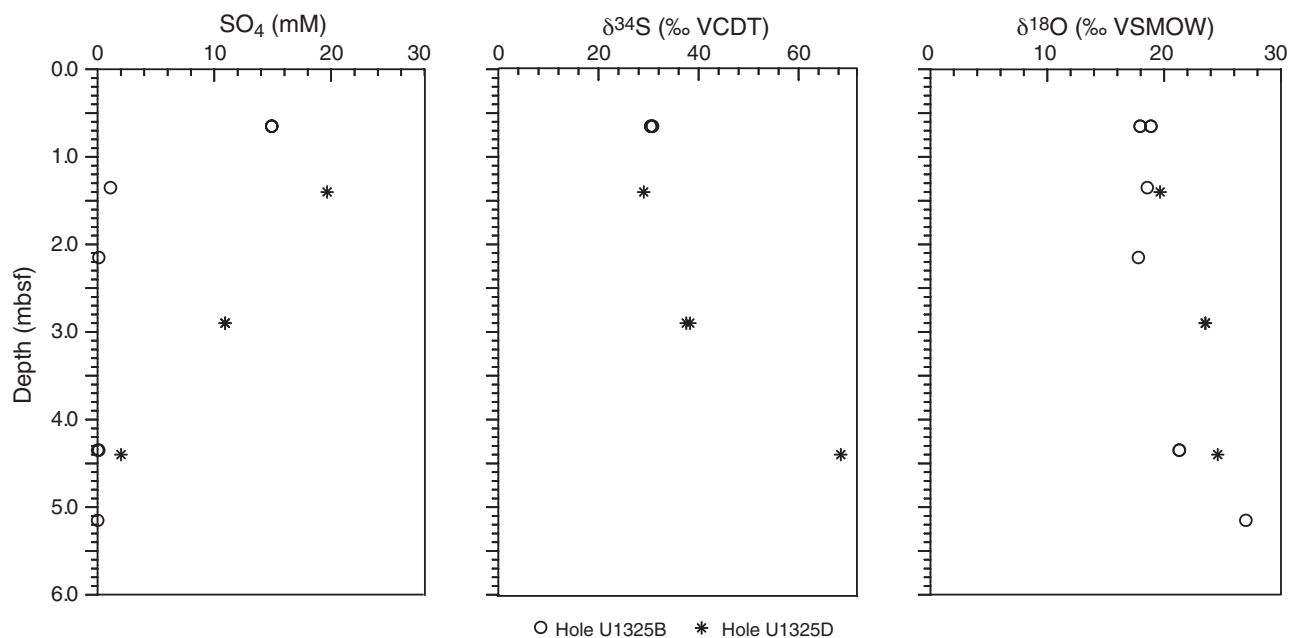
**Initial receipt:** 26 June 2008

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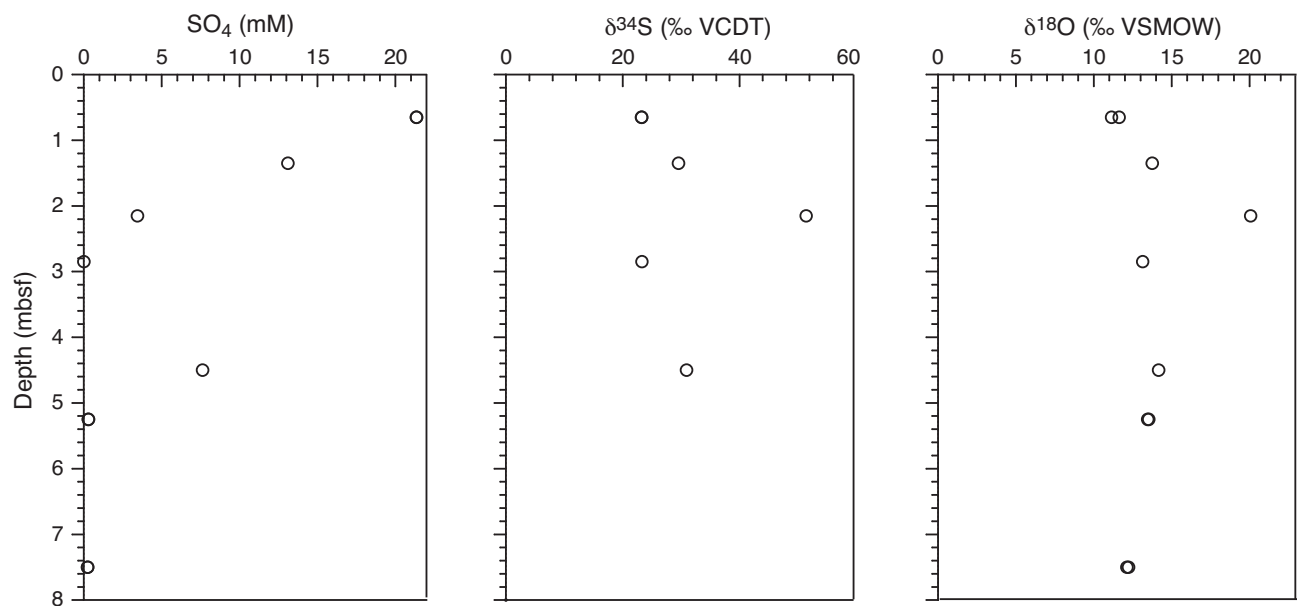
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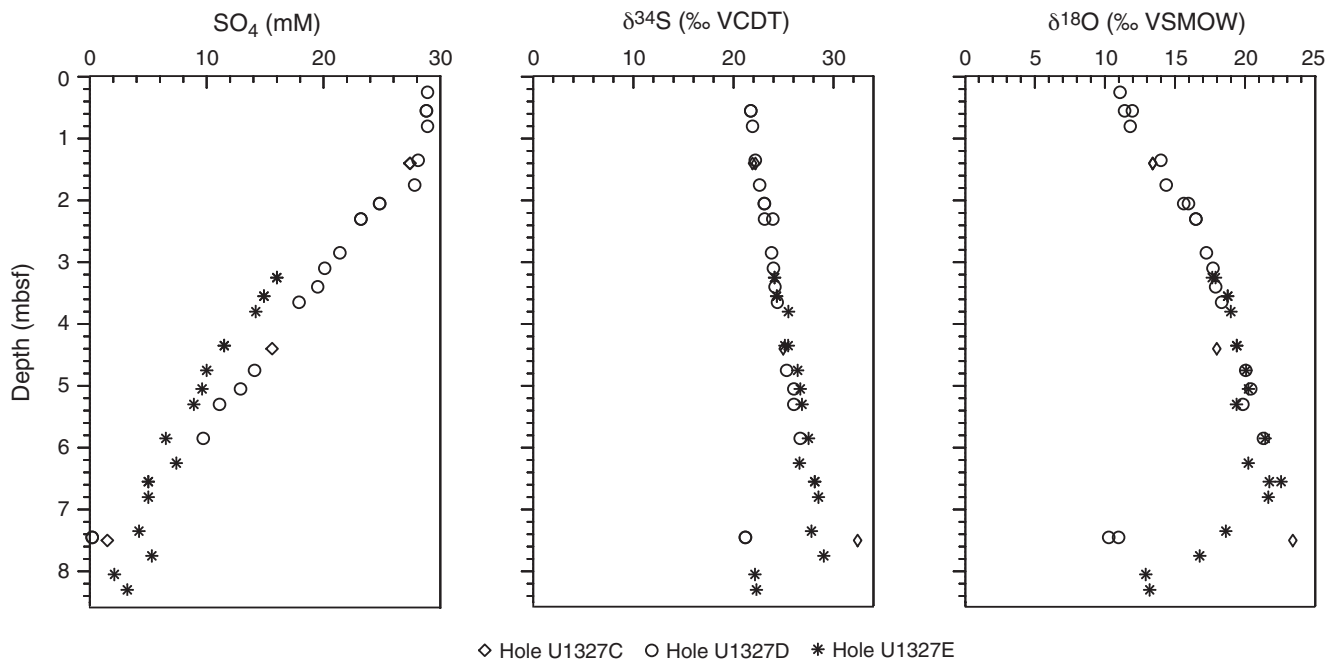
**Figure F1.** Dissolved sulfate and isotope values, Site U1325. VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water.



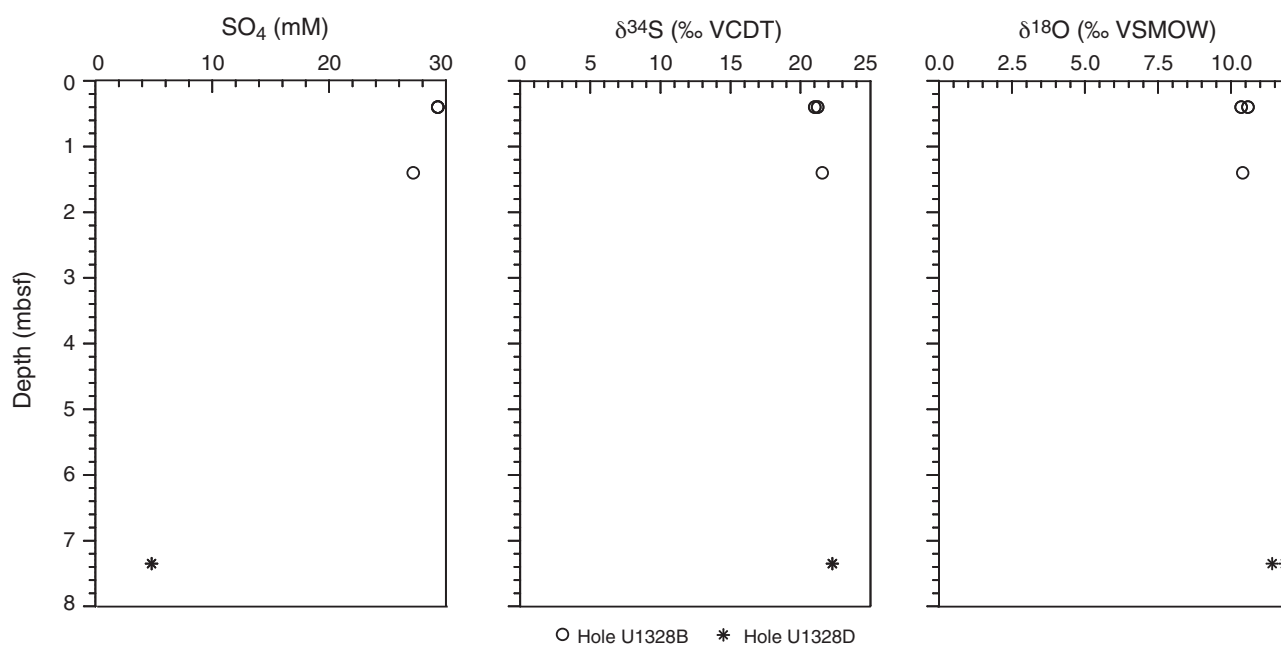
**Figure F2.** Dissolved sulfate and isotope values, Site U1326. VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water.



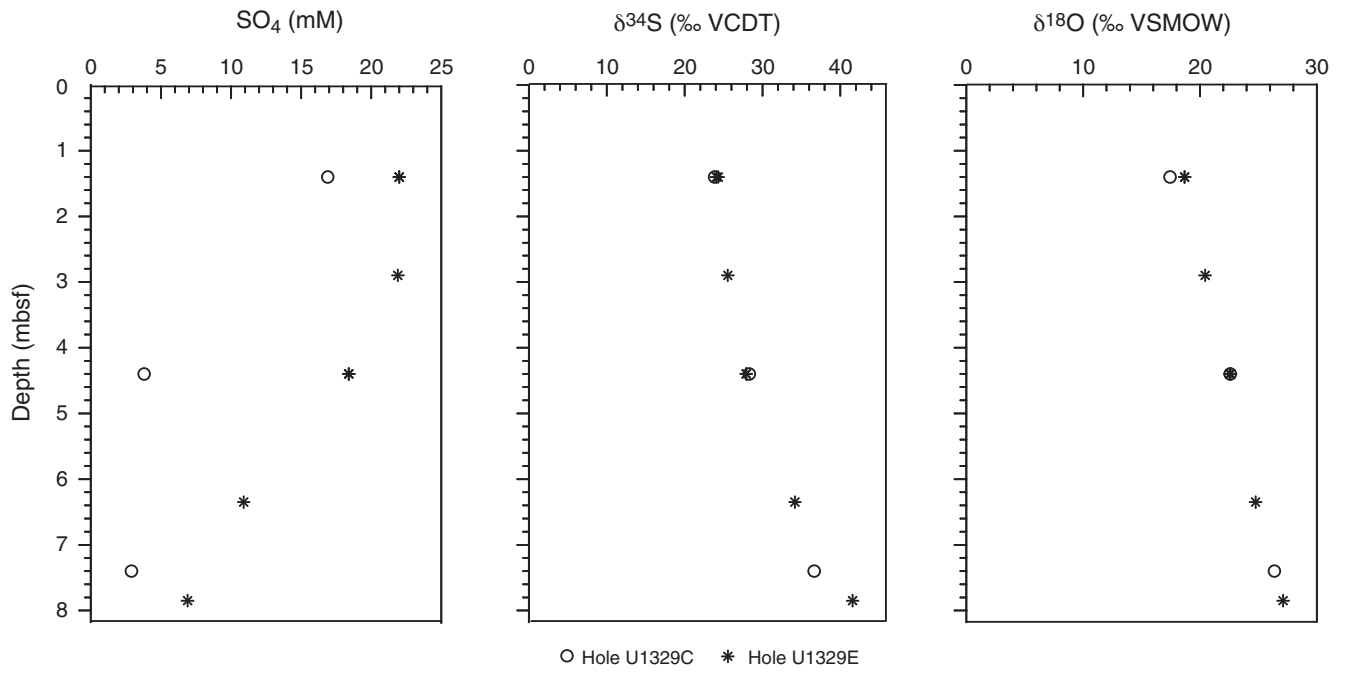
**Figure F3.** Dissolved sulfate and isotope values, Site U1327. VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water.



**Figure F4.** Dissolved sulfate and isotope values, Site U1328. VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water.

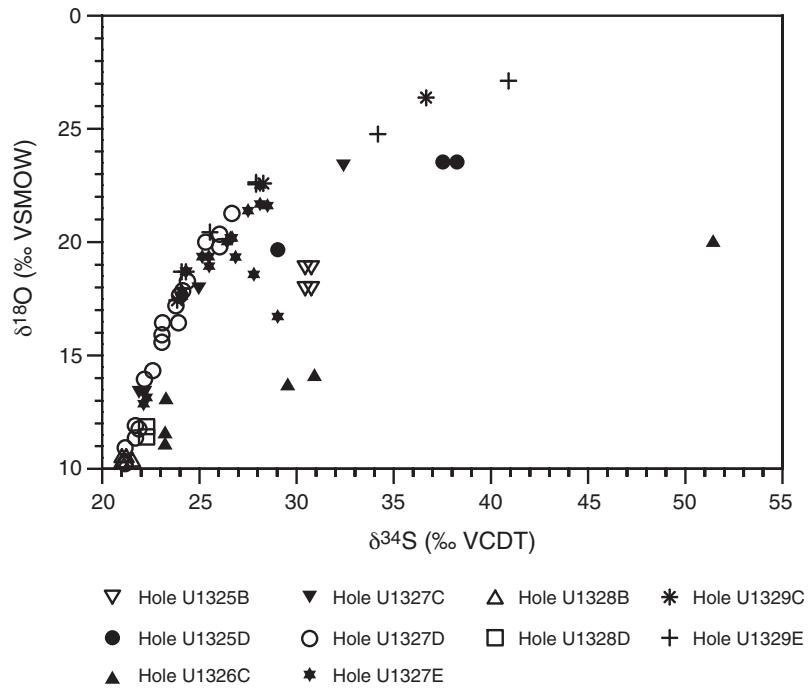


**Figure F5.** Dissolved sulfate and isotope values, Site U1329. VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water.





**Figure F6.** Cross-plot of oxygen and sulfur isotopes. VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water.



**Table T1.** Sulfate and isotope data, Site U1325. (See table notes.)

Core, section, interval (cm)	Depth (mbsf)	SO <sub>4</sub> <sup>2-</sup> (mM)	δ <sup>34</sup> S <sub>SO<sub>4</sub><sup>2-</sup> (‰ VCDT)</sub>	δ <sup>18</sup> O <sub>SO<sub>4</sub><sup>2-</sup> (‰ VSMOW)</sub>
311-U1325B-				
1H-1, 65–80	0.65	14.9	30.8	18.9
1H-1, 65–80	0.65	14.9	30.4	18.9
1H-1, 65–80	0.65	14.9	30.8	18.0
1H-1, 65–80	0.65	14.9	30.4	18.0
1H-1, 135–150	1.35	1.1	—	18.6
1H-2, 65–80	2.15	0.1	—	17.8
1H-3, 135–150	4.35	0.1	—	21.3
1H-3, 135–150	4.35	0.0	—	21.3
1H-4, 65–80	5.15	0.0	—	27.0
311-U1325D-				
1H-1, 140–150	1.4	19.6	29.0	19.7
1H-2, 140–150	2.9	10.9	37.5	23.5
1H-2, 140–150	2.9	10.9	38.3	23.5
1H-3, 140–150	4.4	2.0	68.4	24.6

Notes: VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water. — = not applicable.

**Table T2.** Sulfate and isotope data, Site U1326. (See table notes.)

Core, section, interval (cm)	Depth (mbsf)	SO <sub>4</sub> <sup>2-</sup> (mM)	δ <sup>34</sup> S <sub>SO<sub>4</sub><sup>2-</sup> (‰ VCDT)</sub>	δ <sup>18</sup> O <sub>SO<sub>4</sub><sup>2-</sup> (‰ VSMOW)</sub>
311-U1326B-				
1H-1, 65–80	0.65	21.4	23.2	11.1
1H-1, 65–80	0.65	21.4	23.2	11.6
1H-1, 135–150	1.35	13.1	29.5	13.8
1H-2, 65–80	2.15	3.4	51.4	20.1
1H-2, 135–150	2.85	0.0	23.3	13.1
2H-1, 60–75	4.5	7.6	30.9	14.2
2H-1, 135–150	5.25	0.3	—	13.5
2H-1, 135–150	5.25	0.3	—	13.5
2H-3, 60–75	7.5	0.2	—	12.2
2H-3, 60–75	7.5	0.2	—	12.1

Notes: VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water. — = not applicable.

Table T3. Sulfate and isotope data, Site U1327. (See table notes.)

Core, section, interval (cm)	Depth (mbsf)	SO <sub>4</sub> <sup>2-</sup> (mM)	δ <sup>34</sup> S <sub>SO<sub>4</sub><sup>2-</sup> (‰ VCDT)</sub>	δ <sup>18</sup> O <sub>SO<sub>4</sub><sup>2-</sup> (‰ VSMOW)</sub>
311-U1327C-				
1H-1, 140–150	1.4	27.4	21.9	13.4
1H-1, 140–150	1.4	27.4	22.2	13.4
1H-3, 140–150	4.4	15.6	25.0	17.9
13X-2, 115–150	105.15	0.2	20.3	12.2
13X-6, 110–150	110.56	0.3	21.0	10.0
2H-1, 140–150	7.5	1.5	32.4	23.4
311-U1327D-				
1H-1, 25–40	0.25	28.9	—	11.0
1H-1, 55–70	0.55	28.8	21.7	11.9
1H-1, 55–70	0.55	28.8	21.7	11.4
1H-1, 80–95	0.8	28.9	21.9	11.8
1H-1, 135–150	1.35	28.1	22.2	14.0
1H-2, 25–40	1.75	27.8	22.6	14.3
1H-2, 55–70	2.05	24.8	23.1	15.6
1H-2, 55–70	2.05	24.8	23.1	15.9
1H-2, 80–95	2.3	23.2	23.9	16.4
1H-2, 80–95	2.3	23.2	23.1	16.4
1H-2, 135–150	2.85	21.4	23.8	17.2
1H-3, 10–25	3.1	20.1	24.0	17.7
1H-3, 40–55	3.4	19.5	24.1	17.9
1H-3, 65–80	3.65	17.9	24.4	18.3
1H-4, 25–40	4.75	14.1	25.3	20.0
1H-4, 55–70	5.05	12.9	26.0	20.4
1H-4, 80–95	5.3	11.1	26.0	19.8
1H-4, 135–150	5.85	9.7	26.7	21.3
2H-1, 55–70	7.45	0.2	21.2	10.2
2H-1, 55–70	7.45	0.2	21.2	10.9
311-U1327E-				
1H-1, 25–40	3.25	16.0	24.1	17.8
1H-1, 25–40	3.25	16.0	24.1	17.6
1H-1, 55–70	3.55	14.9	24.3	18.7
1H-1, 55–70	3.55	14.9	24.3	18.7
1H-1, 80–95	3.8	14.2	25.5	18.9
1H-1, 135–150	4.35	11.5	25.1	19.4
1H-1, 135–150	4.35	11.5	25.5	19.4
1H-2, 25–40	4.75	10.0	26.4	20.0
1H-2, 55–70	5.05	9.6	26.7	20.2
1H-2, 80–95	5.3	8.9	26.9	19.3
1H-2, 135–150	5.85	6.5	27.5	21.4
1H-3, 25–40	6.25	7.4	26.6	20.2
1H-3, 55–70	6.55	5.0	28.1	21.7
1H-3, 55–70	6.55	5.0	28.1	22.5
1H-3, 80–95	6.8	5.0	28.5	21.6
1H-3, 135–150	7.35	4.2	27.8	18.6
1H-4, 25–40	7.75	5.3	29.0	16.7
1H-4, 55–70	8.05	2.1	22.1	12.9
1H-4, 80–95	8.3	3.2	22.3	13.2

Notes: VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water. — = not applicable.

**Table T4.** Sulfate and isotope data, Site U1328. (See table note.)

Core, section, interval (cm)	Depth (mbsf)	SO <sub>4</sub> <sup>2-</sup> (mM)	δ <sup>34</sup> S <sub>SO<sub>4</sub><sup>2-</sup> (‰ VCDT)</sub>	δ <sup>18</sup> O <sub>SO<sub>4</sub><sup>2-</sup> (‰ VSMOW)</sub>
311-U1328B-				
1H-1, 40–50	0.4	29.3	21.2	10.6
1H-1, 40–50	0.4	29.3	21.0	10.6
1H-1, 40–50	0.4	29.3	21.2	10.4
1H-1, 40–50	0.4	29.3	21.0	10.4
1H-1, 140–150	1.4	27.2	21.6	10.4
311-U1328C-				
26X-4, 0–30	288.2	0.8	21.4	24.7
311-U1328D-				
1X-5, 135–150	7.35	4.8	22.3	11.4
1X-5, 135–150	7.35	4.8	22.3	11.9

Note: VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water.

**Table T5.** Sulfate and isotope data, Site U1329. (See table note.)

Core, section, interval (cm)	Depth (mbsf)	SO <sub>4</sub> <sup>2-</sup> (mM)	δ <sup>34</sup> S <sub>SO<sub>4</sub><sup>2-</sup> (‰ VCDT)</sub>	δ <sup>18</sup> O <sub>SO<sub>4</sub><sup>2-</sup> (‰ VSMOW)</sub>
311-U1329C-				
1H-1, 140–150	1.4	16.9	23.9	17.4
1H-3, 140–150	4.4	3.8	28.3	22.6
1H-5, 140–150	7.4	2.9	36.7	26.4
311-U1329E-				
1H-1, 140–150	1.4	22.0	24.3	18.7
1H-1, 140–150	1.4	22.0	24.1	18.7
1H-2, 140–150	2.9	21.9	25.5	20.4
1H-3, 140–150	4.4	18.4	27.9	22.6
1H-3, 140–150	4.4	18.4	27.9	22.6
2H-1, 135–150	6.35	10.9	34.2	24.8
2H-2, 135–150	7.85	6.9	40.9	27.1

Note: VCDT = Vienna Canyon Diablo Triolite, VSMOW = Vienna standard mean ocean water.