

SUPPLEMENTARY MATERIAL

Site Description

Lake McCarrons (Fig. DR1) is a small (33ha) meromictic lake with euxinic bottom waters located in a suburb of Minneapolis/St Paul called Roseville, MN (44°59'52"N 093°0'38"W). It has a maximum water depth of 17.3m. The depth of the chemocline varies seasonally between 6-12m (Myrbo, 2008). Total dissolved solid concentration is 200-300ppm in the surface water and 400-500ppm in the monimolimnion (Myrbo and Shapley, 2006).

The saturation state with respect to calcite is positive throughout the year in the surface water (Myrbo and Shapley, 2006). The saturation state in the monimolimnion is only above zero in mid to late summer and is undersaturated with respect to calcite for the rest of the year (Myrbo and Shapley, 2006). Thus, calcite precipitation occurs year round in the surface water, but preservation of calcite at depth occurs during mid to late summer.

The seasonality of calcite preservation at Lake McCarrons does not affect the $\delta^{34}\text{S}_{\text{CAS}}$ value because the lake is permanently stratified and therefore $\delta^{34}\text{S}$ of the surface water sulfate stays the same throughout the year. Average calcium carbonate concentration is 28.3 wt % at the euxinic site (ML2) and 54.0 wt % at the oxic site (ML3). CAS concentrations are low (<4ppm) at Lake McCarrons, thus it was difficult to obtain a $\delta^{34}\text{S}_{\text{CAS}}$ value for either site. The one $\delta^{34}\text{S}_{\text{CAS}}$ value that we were able to measure from the uppermost sediment of site ML2 was 3.9‰, which falls within the 95% confidence interval for the average surface water $\delta^{34}\text{S}_{\text{SO}_4}$ measured in July 2009. The measured $\delta^{34}\text{S}_{\text{CAS}}$ value as well as previous work indicating that the $\delta^{34}\text{S}_{\text{CAS}}$ of pelagic carbonates reflects surface water $\delta^{34}\text{S}_{\text{SO}_4}$ (Lyons *et al.*, 2004) is consistent with the definition of $\Delta^{34}\text{S}$ given in eq.1 that this value is the difference between the S isotope composition of surface water sulfate and sedimentary pyrite. Given that locations of S isotope preservation at Lake McCarrons are similar to the modern ocean, we argue that the S isotope geochemistry at Lake McCarrons serves as a suitable analog to low-sulfate oceans of the past.

Methods

Water column profiles of dissolved oxygen were taken with a hydrolab at each site and samples were retrieved at ML1 and ML2 with an Alpha Wildco sampler, filtered at $0.45\mu\text{m}$, and treated with 3% zinc acetate to fix sulfides. Sediment was collected with a freeze core at ML1, quickly sampled while still frozen, and then placed on ice until final storage in a freezer at the sedimentary geochemistry lab at Northwestern University. By contrast, sediment at ML2 and ML3 were retrieved with piston cores, which were quickly sealed with rubber stoppers, removed from sunlight, and kept in cold storage until the cores could be processed. Sediment contained in the piston cores was extruded in an N_2 -purged glovebag, sampled at 2cm intervals, and frozen.

Water column sulfate concentrations were measured with a Dionex DX120 ion chromatograph. Sulfide concentrations were determined spectrophotometrically on a Shimadzu UV-vis spectrophotometer via the Cline method (Cline, 1969). CAS was extracted from one sediment sample using a modified version of the procedure in Gill *et al.*, (2011), where a 30% H_2O_2 rinsing step and three additional deionized water rinses were done prior to acidification to oxidize and remove any acid-volatile sulfides (AVS). BaCl_2 (200g/L) was added to water column samples and extracted CAS samples to precipitate sulfate as barite (BaSO_4) for S isotope analysis.

A sequential extraction procedure was utilized to assess sediment concentrations of AVS-S and pyrite-S. AVS was extracted using 6 N HCl containing 15% SnCl_2 (room temperature, stirred, 1.5 hr; Chanton and Martens, 1985). The residual sediment was then analyzed for pyrite-S using the chromium reduction method (Canfield *et al.*, 1986). During each procedure, the extracted H_2S was driven via an N_2 carrier gas and trapped as ZnS for quantification by iodometric titration or as Ag_2S for S isotope analysis. S isotopes were measured at Northwestern University on a ThermoElectron Delta V continuous-flow isotope ratio mass spectrometer via combustion of BaSO_4 or Ag_2S to SO_2 gas. S isotopes are reported in permil (‰) notation standardized to Vienna Canyon Diablo Troilite (VCDT). S isotope results were reproducible within 0.2‰, based on repeat analysis of samples and standards.

An additional sequential extraction procedure was done to quantify concentrations of solid-phase Fe species: carbonate-associated Fe (Fe_{carb}), Fe (III) oxides and oxyhydroxides (Fe_{oxide}), magnetite (Fe_{mag}) and total Fe (Fe_T ; Poulton and Canfield, 2005). Fe concentrations in the liquid extracts from the sequential Fe extraction were analyzed on an Ionically Coupled Plasma-Optical Emission Spectrometer at the Integrated Molecular Structure Education and Research Center at Northwestern University. Relative standard deviations for Fe concentrations were <5% based on

replicate analyses. Fe as pyrite and AVS were quantified based on an assumed stoichiometry of Fe:S of 0.5 for pyrite and Fe:S of 1 for AVS for the two sequentially extracted sulfur fractions described previously.

Calcium carbonate concentrations were determined on a UIC carbon coulometer at Northwestern University.

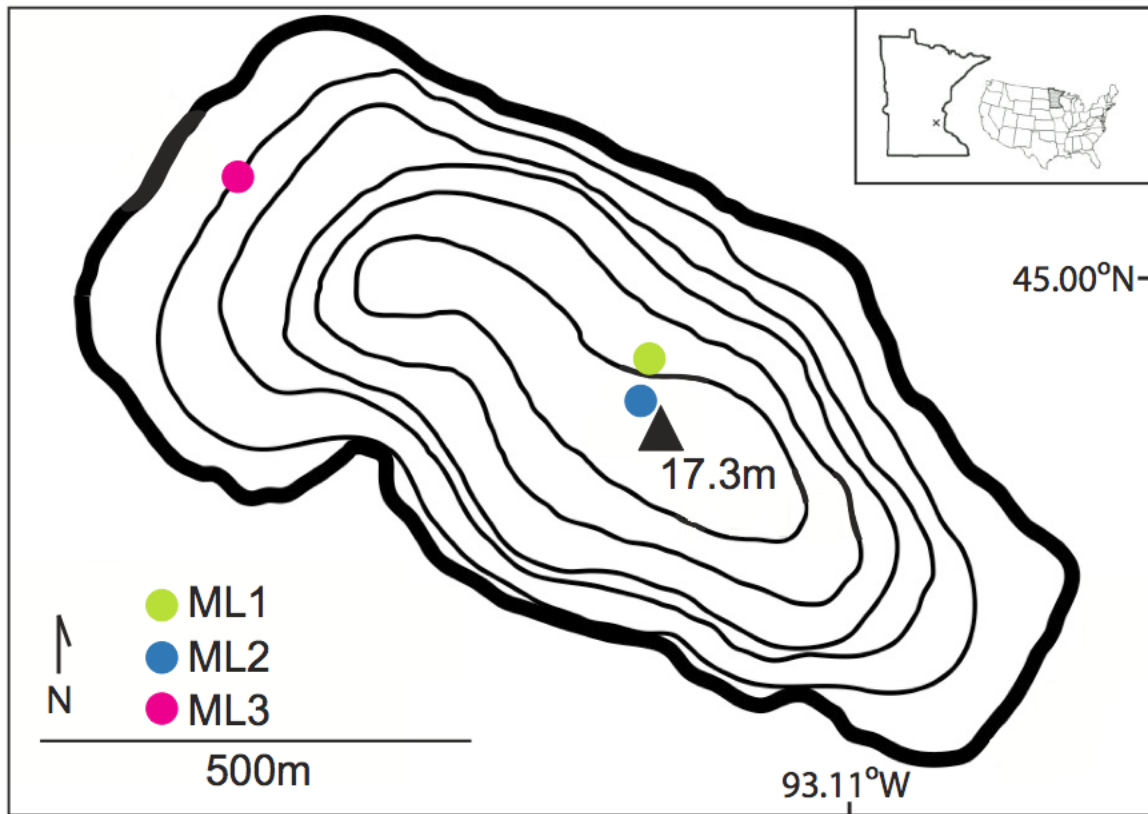


Figure DR1. Bathymetric map of Lake McCarrons (modified from Myrbo and Shapley, 2006). Bathymetric contours have a spacing of 3m. Location of Lake McCarrons in the United States and Minnesota are shown in the top right. Locations of sites ML1(light green circle), ML2 (blue circle) and ML3 (pink circle) are indicated on the map.

TABLE DR1. WATER COLUMN RESULTS

Depth (m)	SO ₄ ²⁻ concentration (μM)	H ₂ S concentration (μM)	δ ³⁴ S _{SO4} (‰)
<u>ML1 (Fall 2007)</u>			
0.0	N.D.*	0.0	5.3
1.0	346.7	0.0	5.1
3.0	344.8	0.0	5.2
5.0	331.3	0.0	5.2
7.0	N.D.*	0.0	5.2
8.0	358.6	0.0	5.1
9.0	319.8	0.0	5.1
9.5	329.3	2.0	5.1
10.0	315.5	0.0	5.1
10.5	323.4	0.0	5.2
11.0	319.7	0.0	5.0
11.5	320.5	0.0	5.3
12.0	313.9	0.4	5.8
12.5	221.9	108.0	18.7
13.0	N.D.*	218.6	N.D.*
13.5	151.4	N.D.*	26.2
14.0	101.2	484.8	35.7
<u>ML2 (July 2009)</u>			
1.0	273.4	0.0	5.9
2.0	268.1	0.0	4.1
3.0	273.2	0.0	4.5
4.0	260.8	0.0	N.D.*
5.0	257.5	0.0	4.0
5.5	275.3	0.0	4.4
6.0	258.1	0.0	4.9
6.5	279.8	0.0	4.7
7.0	271.8	0.0	4.7
7.5	263.3	0.0	5.0
8.0	284.7	0.0	N.D.*
8.5	278.5	0.0	4.7
9.0	289.9	0.0	4.7
9.5	284.5	0.0	4.9
10.0	277.8	0.0	4.5
10.5	274.0	0.0	4.6
11.0	262.8	0.0	4.6
11.5	233.5	20.1	7.2
12.0	228.1	25.0	N.D.*
12.5	238.9	29.1	11.1
13.0	232.2	40.8	13.4
13.5	198.7	49.9	14.3
14.0	180.7	70.7	18.7

TABLE DR1. WATER COLUMN RESULTS (CONTINUED)

Depth (m)	SO ₄ ²⁻ concentration (μM)	H ₂ S concentration (μM)	δ ³⁴ S _{SO4} (‰)
14.5	155.9	88.1	N.D. *
15.0	145.2	112.1	21.2
15.5	128.6	124.1	23.2

*N.D. = No data.

TABLE DR2. SEDIMENT SOLID PHASE S ISOTOPE GEOCHEMISTRY RESULTS

Depth (cm)	S _{AVS} (wt %)	S _{pyrite} (wt %)	$\delta^{34}\text{S}_{\text{AVS}}$ (‰)	$\delta^{34}\text{S}_{\text{pyrite}}$ (‰)
<u>ML1 (Fall 2007)</u>				
1	0.32	0.44	N.D.*	-1.96
<u>ML2 (July 2009)</u>				
1	0.36	0.71	2.70	-0.05
11	0.36	0.49	-0.11	-0.07
21	0.25	1.27	0.35	-1.16
31	0.13	0.70	-1.14	-1.96
<u>ML3 (July 2009)</u>				
1	0.09	0.14	-3.14	-5.01
11	0.07	0.37	-9.43	-4.32
21	0.06	0.34	-5.01	-3.81
31	0.03	0.43	-3.00	-7.51
*N.D. = No data.				

TABLE DR3. RESULTS OF WATER COLUMN
SULFIDE S ISOTOPE COMPOSITION CALCULATIONS

Depth (m)	$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ (‰)
<u>ML1 (Fall 2007)</u>	
11.5	-18.2
12.0	-17.7
12.5	-4.8
13.5	2.7
14.0	12.2
<u>ML2 (July 2009)</u>	
11.5	-16.3
12.5	-12.4
13.0	-10.1
13.5	-9.2
14.0	-4.8
15.0	-2.3
15.5	-0.3

Depth (cm)	Fe _{carb} (wt%)	Fe _{oxide} (wt%)	Fe _{mag} (wt%)	Fe _{AVS} (wt%)	Fe _{py} (wt%)	Fe _T (wt%)	Fe _{py} /Fe _{HR}	Fe _{HR} /Fe _T
<u>ML2 (July 2009)</u>								
1	0.09	0.21	0.02	0.63	0.62	3.33	0.79	0.47
5	0.17	0.21	0.03	0.70	0.55	2.95	0.76	0.56
11	0.17	0.19	0.03	0.62	0.42	3.82	0.72	0.38
15	0.15	0.22	0.05	0.37	1.28	4.26	0.79	0.49
21	0.13	0.21	0.06	0.44	1.11	4.40	0.80	0.44
25	0.09	0.25	0.07	0.39	1.01	4.83	0.77	0.38
31	0.10	0.16	0.06	0.22	0.61	4.83	0.72	0.24
<u>ML3 (July 2009)</u>								
1	0.07	0.15	0.03	0.15	0.12	2.18	0.53	0.24
5	0.06	0.10	0.01	0.15	0.35	0.76	0.74	0.88
11	0.06	0.16	0.02	0.12	0.32	2.02	0.65	0.34
15	0.06	0.08	0.01	0.12	0.47	0.81	0.79	0.91
21	0.05	0.10	0.02	0.11	0.30	0.66	0.70	0.88
25	0.05	0.10	0.01	0.06	0.18	0.58	0.61	0.67
31	0.05	0.05	B.D.*	0.05	0.38	0.75	0.81	0.70

*B.D. = Below detection limit

References

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