

1 **Increased Accumulation of Sulfur in Lake Sediments of the High Arctic**

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3 Paul E. Drevnick^{1,2,*}, Derek C.G. Muir³, Carl H. Lamborg², Martin J. Horgan⁴, Donald E.
4 Canfield⁵, John F. Boyle⁶, and Neil L. Rose⁷

5

6 1. INRS-ETE, Université du Québec, 490 de la Couronne, Québec, QC G1K 9A9, Canada

7

8 2. Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution,
9 Woods Hole, MA 02543, USA

10

11 3. Aquatic Ecosystem Protection Research Division, Environment Canada, 867 Lakeshore Road,
12 Burlington, Ontario L7R 4A6, Canada

13

14 4. 230 Northridge Drive, Oxford, OH 45056, USA

15

16 5. Nordic Center for Earth Evolution, Institute of Biology, University of Southern Denmark,
17 Campusvej 55, 5230 Odense M, Denmark

18

19 6. Department of Geography, University of Liverpool, Liverpool L69 7ZT, UK

20

21 7. Environmental Change Research Centre, University College London, Gower Street,
22 London WC1E 6BT, UK

23

24 *Corresponding author: paul.drevnick@ete.inrs.ca; Tel. +1 418 654 2519; Fax +1 418 654 2600

25

26 **Abstract**

27 We report a synchronous increase in accumulation of reduced inorganic sulfur since c. 1980 in
28 sediment cores from eight of nine lakes studied in the Canadian Arctic and Svalbard (Norway).
29 Sediment incubations and detailed analyses of sediment profiles from two of the lakes indicate
30 that increases in sulfur accumulation may be due ultimately to a changing climate. Warming-
31 induced lengthening of the ice-free season is resulting in well-documented increases in algal
32 production and sedimentation of the resulting detrital matter. Algal detritus is a rich source of
33 labile carbon, which in these sediments stimulates dissimilatory sulfate reduction. The sulfide
34 produced is stored in sediment (as acid volatile sulfide), converted to other forms of sulfur, or
35 reoxidized to sulfate and lost to the water column. An acceleration of the sulfur cycle in Arctic
36 lakes could have profound effects on important biogeochemical processes, such as carbon burial
37 and mercury methylation.

38 **Introduction**

39 Unprecedented warming of the Arctic is resulting in a cascade of events to push lake
40 biogeochemistry beyond its Holocene limits (1). Surface air temperatures across the Arctic
41 increased, on average, by 1.5°C during c. 1840-1950, decreased slightly during c. 1950-1970,
42 and since then are increasing again, but at an accelerated rate (2, 3). From c. 1980 to the present,
43 weather stations in the Canadian Arctic archipelago and Svalbard (Norway), for example, have
44 commonly recorded upwards of 2°C increases in annual mean temperature (4, 5). The effect on
45 lake physics thus far has been to delay the formation of ice cover and to accelerate its breakup
46 (6). Quantitative records are rare, but a recent analysis of satellite images of “perennially ice-
47 capped lakes” on northern Ellesmere Island, for example, revealed that the lakes now lose a
48 substantial portion (sometimes 100%) of ice cover during summer (7). Ice cover limits the
49 sunlight available to photosynthetic autotrophs underneath in the unfrozen water, and
50 lengthening of the ice-free season has, in effect, resulted in a longer growing season (8). Algae
51 have responded with dramatic increases in abundance and diversity (9), which, in turn, is
52 resulting in a greater flux of algal detritus to sediments. The latter is evidenced by pigment
53 records (10, 11), Rock Eval pyrolysis of bulk organic matter (12), and up-core increases in both
54 the accumulation of organic carbon (beyond what is expected from progressive diagenetic
55 consumption of a constant supply of organic carbon) and the ratio of ^{13}C to ^{12}C (13).

56 Our objective was to determine if this cascade extends to sedimentary sulfur cycling.
57 Sulfur is a major nutrient for all organisms and also plays an important role in the cycling of
58 other nutrients, trace metals, and radioisotopes, largely via dissimilatory sulfate reduction and the
59 sulfide that is produced (14). Sediments of ultraoligotrophic Arctic lakes have been compared
60 (15) to deep-sea sediments, where low rates of organic carbon flux limit sulfate reduction (16).

61 It is an imperfect comparison, however, because sulfate reduction in freshwater systems is also
62 generally limited by low sulfate concentrations. Still, in sediments of Toolik Lake (68° N; 15)
63 and Lake DV-09 (75° N; 17) sulfide formation was thought to be at least co-limited by low
64 organic carbon content. As aptly pointed out by Chételat and Amyot (18), though, drastic effects
65 can occur with even slight increases in algal production in these resource-poor lakes. Increases
66 in the sedimentation of algal detritus rich in organic carbon may act, as is the case for sediments
67 in deep basins of the Arctic Ocean (19), to stimulate sulfate reduction. We tested this hypothesis
68 with sediment archives, incubation experiments, and newly-collected sediment cores processed
69 to preserve sulfur redox chemistry.

70

71 **Experimental Section**

72 Archived sediment cores from five lakes in the Canadian Arctic archipelago (20) and four lakes
73 in Svalbard (21) were analyzed for total reduced inorganic sulfur. Information about the lakes is
74 given in Table 1. Details of the collection, processing, and dating of cores can be found in the
75 supporting information. Sulfur analysis followed the chromium reduction method of Canfield et
76 al. (22). We selected this method because although the handling of the archived cores very likely
77 resulted in oxidation of some forms of reduced inorganic sulfur (e.g., FeS), the oxidation
78 products are still obtainable by chromium reduction. One out of every ten samples was analyzed
79 in duplicate, and the mean percent relative standard deviation (%RSD) of duplicates was 8.6%.
80 Concentrations were multiplied by sedimentation rates to calculate accumulation (or flux) rates
81 of total reduced inorganic sulfur.

82 Inferential statistics were used to relate accumulation rates of total reduced inorganic
83 sulfur to variables that may explain trends both within and among cores. Variables included

84 other elements analyzed in the cores (Canada: Al, Zn, reactive Fe, reactive Mn, Pb, Hg, organic
85 C, organic N; Svalbard: Si, Ti, Ca, K, Fe, Mn, Cu, Pb, Zn, loss-on-ignition (LOI) as a proxy for
86 organic matter) and records of sulfate deposition and temperature. Elemental data are from Muir
87 et al. (20) and Boyle et al. (23). Sulfate deposition records are from ice cores (24, 25).
88 Temperature records (mean surface air temperature during June, July, and August) are from
89 Overpeck et al. (2) and were extended to the year 2000 with data from Environment Canada (4)
90 and the Norwegian Meteorological Institute (5). Within lakes, accumulation of total reduced
91 inorganic sulfur was related to each variable with simple linear regression. Among lakes,
92 relationships of possible predictors and accumulation of total reduced inorganic sulfur were
93 evaluated with a random-effects analysis-of-variance (ANOVA) approach.

94 Two lakes in the Canadian Arctic archipelago, Amituk Lake and Char Lake, were cored
95 again to better elucidate the factors controlling the sedimentary accumulation of inorganic sulfur.
96 These lakes were chosen because they are relatively easy to access from the Polar Continental
97 Shelf Program base and, for High Arctic lakes, they are well studied. Importantly, both lakes
98 have recently documented climate-induced increases in algal production (17, 26, 27). Details of
99 core collection and processing, which was performed to minimize exposure to air and thus
100 preserve sulfur redox chemistry, can be found in the supporting information. For each lake, one
101 core was used for incubation experiments and two cores were used for analysis of sulfur forms
102 and their isotopic compositions.

103 Incubation experiments with the sediment slurries from Amituk Lake and Char Lake
104 were conducted to determine the effects of sulfate and labile carbon supplies on sulfide
105 formation. The experiment consisted of nine treatments (each consisting of three replicates): (1)
106 time-zero control (frozen at beginning of incubation), (2) control, (3) 200 μM molybdate

107 (metabolic inhibitor of sulfate-reducing bacteria), (4) 200 μM sulfate, (5) 200 μM acetate (labile
108 carbon), (6) 200 μM molybdate and 200 μM sulfate, (7) 200 μM molybdate and 200 μM acetate,
109 (8) 200 μM sulfate and 200 μM acetate, and (9) 200 μM molybdate, 200 μM sulfate, and 200
110 μM acetate. Details of incubation set up, which was (again) performed to minimize exposure to
111 air, can be found in the supporting information. Incubations were run for 16 d and 18 d for
112 sediments from Amituk Lake and Char Lake, respectively, and then terminated by freezing at -
113 20°C. The incubated sediment slurries were then freeze-dried, and the dried sediment was
114 analyzed for acid volatile sulfide (AVS) according to Canfield et al. (28). We were specifically
115 interested in AVS because it represents the short-term end products of sulfate reduction. By
116 excluding other forms of reduced inorganic sulfur, which can constitute a majority of the total,
117 the likelihood of observing significant effects in these brief experiments was increased. To test
118 for differences in AVS among treatments, a one-way ANOVA and Tukey-Kramer posthoc tests
119 were performed for each lake. It should be noted that the incubations were likely not anoxic, at
120 least at the beginning, but the results indicate that sulfate reduction occurred.

121 To analyze sulfur forms and their isotopic compositions in the sediment cores from
122 Amituk Lake and Char Lake, we used a sequential extraction method similar to that of Canfield
123 et al. (28). The reduced inorganic forms extracted include AVS (primarily HS^- and FeS),
124 elemental sulfur (S^0), and pyrite (as Cr-reducible S; CRS). The organic forms extracted include
125 hydrolyzable S (HyS) and non-CRS, both of which likely are derived from biosynthesis, but the
126 latter being more refractory than the former. One out of every ten samples was analyzed in
127 duplicate, and the mean %RSD of duplicates was 8.8%. Further details of the extractions can be
128 found in the supporting information. Stable sulfur isotopic compositions ($\delta^{34}\text{S}$) were analyzed in
129 AVS, S^0 , and pyrite by isotope-ratio mass spectrometry (29), with a precision of at least $\pm 0.5\%$.

130 Concentrations of total sulfur were directly measured on a separate subsample of sediment and
131 also calculated as the sum of inorganic and organic forms. There is close agreement between the
132 measured and calculated values (see supporting information), indicating consistent recovery of
133 the different forms of sulfur. In addition to sulfur analyses, sediments were also analyzed for
134 concentrations and isotopic compositions ($\delta^{13}\text{C}$) of total organic carbon (30).

135

136 **Results and Discussion**

137 Sediment archives from the Canadian Arctic archipelago and Svalbard show variable trends in
138 accumulation rates of total reduced inorganic sulfur, except at the top of the cores, corresponding
139 to the period 1980-present, where there is a synchronous increase among lakes (Figure 1). The
140 only exception to this recent increase is in Romulus Lake, which shows a decreasing trend of
141 total reduced inorganic sulfur towards the sediment surface (see supporting information, Figure
142 S1). Unlike all the other lakes in the study, Romulus Lake is meromictic and is anoxic below the
143 chemocline because of hypersaline groundwater inflow (31). Meromictic lakes are not
144 uncommon in coastal areas of the High Arctic and exhibit a dynamic sulfur cycle. At the
145 chemocline, sulfate-reducing bacteria create a sulfidic environment in which photosynthetic
146 sulfur bacteria thrive by using sulfide and other forms of reduced sulfur to fix carbon dioxide.
147 We do not know specifically the reason the surface sediment of Romulus Lake is low in total
148 reduced inorganic sulfur, but it likely relates to the biologically-active nature of sulfur in these
149 systems. In our within-lake regression modeling (see supporting information, Table S1) we
150 found no suitable predictors for total reduced inorganic sulfur in Romulus Lake. In contrast, the
151 other eight lakes in this study exhibit limnological characteristics considered more typical of the
152 Arctic – holomictic and fully oxygenated. In these lakes, sulfate reduction is limited to anoxic

153 sediments, and the sulfide produced is either reoxidized to sulfate and lost to the water column or
154 is bound to Fe or organic matter and retained in the sediment. Accordingly, Fe and organic
155 matter (organic C, organic N, or LOI) were generally good predictors, in the within-lake
156 regression models, of total reduced inorganic sulfur. Manganese was also a good predictor in the
157 models, likely because, as for sulfur (and N and Fe), it is involved in the mineralization of
158 organic carbon.

159 Sulfate deposition, from ice core records, was a suitable predictor of total reduced
160 inorganic sulfur in only Char Lake, and this correlation may be a function of local disturbance
161 that coincided with peaks in the ice core record. In 1949, an air base was built near Char Lake
162 that may have caused local atmospheric pollution (32). Also, during 1969-1972 gravel was taken
163 from the lake's watershed to construct a new airstrip and this action caused a "great increase" in
164 sulfate concentration in one inflow stream (33), although the effect was temporary (26).
165 Tendammen in Svalbard may also be affected by local pollution, as this lake is located near a
166 coal-fired power plant and coal mining operations. Modern accumulation of reduced inorganic
167 sulfur in the sediments of Tendammen is an order of magnitude greater than the other Svalbard
168 lakes. In the other study lakes, however, local disturbance is slight or nonexistent, and geology
169 (sedimentary rock) and proximity to the ocean (i.e., exposure to marine aerosols) indicate that
170 natural sources of sulfate should dominate input (34), even with the human-caused circum-arctic
171 increase in sulfate deposition during the past century (24). It thus seems unlikely that the surface
172 enrichment of sulfur as observed in these sediments results from increased anthropogenic sulfur
173 sources, as is true of lakes nearer industrial centers and underlain by crystalline bedrock (35, 36).

174 From our statistical analyses, temperature is the most important predictor of sedimentary
175 accumulation of total reduced inorganic sulfur, and we hypothesize this relationship is not direct

176 but rather mediated through a warming-induced biogeochemical cascade. In the within-lake
177 regression modeling, temperature was the variable most consistently associated with total
178 reduced inorganic sulfur. Further, temperature was the only significant covariate in the among-
179 lakes random-effects ANOVA modeling (Canada: $r^2 = 0.74$, $p = 0.011$; Svalbard: $r^2 = 0.68$, $p =$
180 0.032). Rates of sulfate reduction do increase with temperature as an Arrhenius function (e.g.,
181 37), but there is no data to suggest that temperatures in profundal sediments of these lakes have
182 followed trends in air temperature. Instead, there is overwhelming evidence from the study lakes
183 that warming-induced lengthening of the ice-free season is resulting in increases in algal
184 production (17, 26, 27, 38). In the Svalbard lakes, there is additional evidence that the increases
185 in algal production are causing greater fluxes of organic matter to sediments (23). A link to
186 organic matter flux is also being made for the study lakes in the Canadian Arctic. For Amituk,
187 Char, and Romulus lakes, Muir et al (20) found that concentrations of organic carbon were >10%
188 higher in surface sediments compared to pre-1900 horizons. This trend is likely, in part, due to
189 the progressive diagenetic consumption of carbon following sedimentation. Outridge et al. (12),
190 however, used Rock Eval pyrolysis to show an increase in the sedimentary flux of “S2” carbon
191 in Amituk Lake. S2 is an operationally-defined term (it is measured during step 2 of the Rock
192 Eval method) and is thought to be of algal origin and resistant to diagenesis. More recently, Kirk
193 et al. (27) determined sedimentary fluxes of S2 in Amituk Lake, Char Lake, and Lake Hazen and
194 found increasing S2 in all three lakes, along with shifts in the algal community. Also, we found
195 modest up-core increases in $\delta^{13}\text{C}$ in sediments from Amituk Lake (-27.2‰ to -26.5‰) and Char
196 Lake (-25.8‰ to -24.7‰) (see supporting information, Figure S2) that could suggest that the
197 sedimentation of autochthonous carbon has increased recently (39).

198 Urban (14) predicted that increases in autochthonous carbon flux will stimulate sulfate
199 reduction in surface sediments of ultraoligotrophic lakes with low rates of carbon sedimentation
200 and oxic hypolimnia, a fitting description of our study lakes. Sulfate-reducing bacteria derive
201 energy by transferring electrons from organic carbon compounds or H₂ to sulfate (40).
202 Laboratory experiments have shown that the amendment of lake sediments with labile carbon
203 stimulates sulfate reduction (e.g., 41), which may lead to increases in storage of reduced sulfur in
204 sediments. There is a well-established relationship among algal productivity, organic carbon
205 sedimentation, and sulfur content of sediment in temperate lakes that exhibit seasonal water-
206 column anoxia (e.g., 42), but not for Arctic lakes with oxic hypolimnia. Recently, however,
207 Korhola et al. (10) and Klug et al. (43) reported concomitant increases in concentrations of
208 organic carbon and total sulfur in sediment cores from lakes in Finnish Lapland (Lake
209 Saanajärvi, 69° N) and northeast Greenland (Melles Lake, 76° N), respectively. In both cases,
210 the increases in sedimentary sulfur were thought to ultimately relate to climate.

211 Variation among lakes in pre-1980 accumulation rates of total reduced inorganic sulfur
212 may reflect the non-conservative nature of this element. The records from Amituk and Daltjørna
213 seem to follow trends in air temperature since the 19th century. Char and Tendammen have large
214 peaks that could be due to local pollution. BI-02 and Yterjørna have no discernable trends. For
215 all of these lakes, however, subsurface peaks could be associated with redox gradients. Sulfur,
216 depending upon speciation, is subject to steep diffusion gradients and biological and chemical
217 redox reactions. Consequently, sulfur profiles in sediments can reflect both historical records
218 and contemporary processes. The latter can prevent interpretation of the former (36), which may
219 be the case for the pre-1980 sediments in our study lakes. The recent (post-1980) record of
220 increased accumulation rates may be evident because, as we hypothesize, it is process driven.

221 Results from our incubation experiments provide clear evidence that increased supply of
222 labile carbon to Arctic lake sediments can result in increased storage of reduced sulfur (Figure
223 2). There were statistically significant differences in AVS among treatments in the incubations
224 from both Amituk Lake ($F_{7,14} = 26.4, p < 0.001$) and Char Lake ($F_{7,16} = 75.2, p < 0.001$). The
225 control treatments had AVS concentrations greater than initial test conditions (time-zero).
226 Conversely, all treatments involving molybdate, a metabolic inhibitor of sulfate-reducing
227 bacteria, had AVS concentrations equivalent to that of time-zero. Collectively, the results from
228 the control and molybdate treatments indicate that AVS formation is a normal process in these
229 sediments and is due to the activities of sulfate-reducing bacteria. The sulfate treatments and the
230 acetate (labile carbon) treatments had AVS concentrations greater than controls, although this
231 was only significant in the sediment from Char Lake. (A missing replicate in the control for
232 Amituk Lake caused the control to not be statistically different from several of the other
233 treatments.) Sulfate and acetate in combination resulted in even greater AVS concentrations in
234 Amituk Lake. We do not completely understand the responses to sulfate, acetate, and the two in
235 combination (i.e., how is it that sulfate alone and acetate alone caused the same relative increase
236 in AVS?). However, it is clear that both sulfate (electron acceptor) and acetate (electron donor)
237 limit sulfate reduction in the sediments of these lakes. Logic dictates, though, that if sulfate
238 concentrations in the lakes are not changing (26) but organic carbon flux to sediments is
239 increasing, it is more likely that organic carbon is driving the increases in accumulation rates of
240 total reduced inorganic sulfur observed in the sediment archives.

241 In the cores from Amituk Lake and Char Lake that were processed to preserve redox
242 chemistry, examination of the sulfur forms that comprise total reduced inorganic sulfur (AVS,
243 S^0 , pyrite) indicates that AVS is likely oxidized to S^0 , which is then stored in sediment (Figure

244 3). Concentrations of AVS are low at the sediment surface (0-2 cm), but increase with depth.
245 These AVS profiles are typical for lakes in which, at least seasonally, oxygen penetrates into
246 surficial sediments (44). Oxygen both inhibits sulfate reduction and oxidizes reduced sulfur.
247 These cores were collected in the winter season through thick ice cover – a time when, because
248 of limited algal production and sedimentation of organic matter, there is little oxygen demand in
249 the sediments and thus oxygen penetrates relatively deeply. Gobeil et al. (19) described that
250 during the open water season, however, greater algal production results in a pulse of organic
251 matter that consumes oxygen in the sediments. The oxic-anoxic boundary moves near the
252 sediment surface, below which sulfate reduction produces AVS. It is this seasonal pattern that
253 can explain the spike in concentration at the top of the S^0 profiles. There is likely an increase in
254 AVS formation during the open water season, but it is oxidized to S^0 during winter. This
255 explanation is supported by a simple mass balance, as the decrease in AVS concentration is
256 roughly equal to the increase in S^0 concentration. It is also supported by the nearly identical $\delta^{34}S$
257 values of AVS and S^0 , thus indicating a common source (i.e., sulfate reduction) (45). In contrast,
258 pyrite is considerably enriched in ^{34}S compared to AVS and S^0 . Sedimentary pyrite formation is
259 traditionally thought to occur from the reaction of iron monosulfide (a major component of AVS)
260 and S^0 (46), and results in negligible sulfur isotope fractionation (47). The pyrite in these
261 sediments, therefore, may not be formed *in situ* (48) but instead derive from a different source,
262 such as from weathering of sedimentary rocks in the lakes' watersheds. Values of $\delta^{34}S$ in
263 sulfides, including pyrite, from rocks on Cornwallis Island and nearby islands (typically +10‰
264 (49), but reported as low as -9‰ (50)) overlap with the values we find for pyrite in sediment.
265 The delivery of substances from watershed to lake has generally not yet been significantly
266 altered by climate change in the High Arctic (1, 20, 26), and fittingly, the concentration profiles

267 for pyrite are relatively stable, except at the bottom of the profiles from Char Lake. The
268 concentrations profiles for AVS and S^0 , as well as the $\delta^{34}S$ values of all three sulfur forms are
269 similarly affected at this depth, and we think the change is due to a marine origin of the sediment
270 below 8-cm depth (Char Lake was created with post-glacial rebound approximately 6000 years
271 ago (33) and did not clear of seawater for some time (51, see figure 3 therein)).

272 An alternate hypothesis to explain the presence of S^0 in the sediment cores is that it is an
273 artifact of sample processing. Acid volatile sulfide is oxygen sensitive and, even with our
274 attempts to preserve redox chemistry (sampling ports, zinc acetate), it could have been oxidized
275 to S^0 upon freeze-drying or treatment with HCl. We cannot reject this hypothesis, but regardless,
276 it does not change our finding that the accumulation of reduced inorganic sulfur is increasing in
277 sediments of High Arctic lakes, possibly due to an increasing sedimentary flux of organic carbon
278 that is stimulating sulfate reduction. The sulfide produced is being stored as AVS and/or S^0 .

279 Similar to the trends in total reduced inorganic sulfur, the profiles of organic sulfur show
280 an increase at the top of the cores (see supporting information, Figure S3). In both Amituk Lake
281 and Char Lake, HyS and nonCRS (forms of organic sulfur; defined in experimental section)
282 similarly show subtle increases up core and then a big jump in concentration at the sediment
283 surface (0-2 cm). With HyS and nonCRS added together to calculate total organic sulfur, the
284 atomic C_{org}/S_{org} ratios are relatively constant throughout the profiles for each lake and average
285 193 for Amituk Lake and 103 for Char Lake. These high C_{org}/S_{org} ratios strongly suggest that the
286 source of organic sulfur is sedimenting algae, which have C_{org}/S_{org} ratios > 84 (52), and not from
287 the diagenetic addition of reduced sulfur to organic matter. The profiles of HyS and nonCRS
288 thus reflect the loss of sulfur from the decomposition of algae.

289 There is little other data on sedimentary sulfur in Arctic lakes to which we can compare
290 our results. Studies have documented sulfur profiles that increase towards the surface (10), have
291 a distinct subsurface peak associated with a redox gradient (17, 53), or decrease towards the
292 surface (15). Bindler et al. (54) suggested that a decrease in sulfur concentration towards the
293 surface, due to sulfide oxidation, is the steady state for lakes in the Swedish Arctic. Our results
294 indicate, however, that there is either a different steady state in lakes of the High Arctic or
295 climate warming is pushing these systems out of steady state. Perhaps, as suggested by Mueller
296 et al. (7), warming crossed a critical threshold in the 1980s and we are now witnessing a
297 “cascading regime shift”. A 250,000-year sediment record from Lake El’gygytgyn (67° N) in
298 Siberia provides several examples of shifts in sulfur cycling in response to changes in climate
299 (55). The key to increased sulfur accumulation in the sediments of Lake El’gygytgyn is the
300 development of a stratified water column and, subsequently, the depletion of oxygen in the
301 bottom water. Our study lakes remain holomictic and fully oxygenated, but results from lakes
302 further south that receive intensive monitoring efforts (Lake Saanajärvi, Toolik Lake) indicate
303 that warmer air temperatures and extended ice-free periods will cause thermal stratification and
304 in some years oxygen-depleted bottom waters (56). Studies of Meretta Lake, located near Char
305 Lake on Cornwallis Island, but which has experienced eutrophication due to sewage inputs,
306 indicate that High Arctic lakes are indeed prone to oxygen depletion. In the early 1970s,
307 Schindler et al. (57) documented increased primary production in Meretta Lake, which led to
308 near anoxic conditions in bottom waters and a perturbation of sulfur cycling. Thirty percent of
309 sulfate in lake water was lost over winter. Sulfide was not measured in water or sediments, but
310 the missing sulfate was likely reduced and stored in sediment.

311 In summary, the accumulation of sulfur appears to be increasing in sediments of Arctic
312 lakes, and we argue that the cause is a climate-induced biogeochemical cascade. It is unknown if
313 the cascade extends beyond sulfur, but sulfur does play an important role in the cycling of other
314 elements. For example, sulfate reduction mineralizes organic carbon (to CO₂ that then may be
315 lost to the atmosphere) and thus works against the burial of carbon in sediments, which is an
316 important sink in the global carbon budget (58). As a side, increased carbon flux may stimulate
317 other anaerobic metabolisms, such as methanogenesis, which produces CO₂ and methane, both
318 greenhouse gases, and thus would constitute a positive feedback to climate warming. Sulfate
319 reduction is also the process believed to be primarily responsible for the transformation of
320 inorganic mercury to methylmercury (59; but see 60), which biomagnifies in food webs and
321 results in high concentrations of this toxic metal in fish (61-63). A ramping up of the sulfur cycle
322 in Arctic lakes could have local to global effects on the biogeochemistry of these elements and
323 others. Further study of the flux of carbon (quality, quantity) to Arctic lake sediments and
324 effects on sulfur cycling and beyond is warranted.

325

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332

333 **Supporting Information Available**

334 Methods, acknowledgements, one table, three figures, and all original data.

335

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512 *Toxicol. Chem.* **2010**, *29*, 633-643.

513 Table 1. Information about the study lakes, including the years archived sediment cores were collected.

Lake	Country, locality	Lat. N	Long. E/W	Area (km ²)	Max. depth (m)	Epilimnetic SO ₄ (μM)	Sed. rate ¹ (g/m ² ·yr)	Sed. org. C ^{1,2} (%)	Yr. collected
Amituk	Canada, Cornwallis Is.	75°02'40"	93°48'40" W	0.38	43	16.6	260	0.89	2003
Char	Canada, Cornwallis Is.	74°42'20"	94°53'50" W	0.53	28	132	240	1.73	2003
BI-02	Canada, Bylot Is.	73°02'30"	80°05'45" W	0.033	3	4.37	200	6.04	2005
Hazen	Canada, Ellesmere Is.	81°49'20"	70°37'50" W	538	267	108	280	1.67	2005
Romulus	Canada, Ellesmere Is.	79°52'15"	85°05'10" W	4.4	60	.	820	2.16	2000
Daltjørna	Norway, Svalbard	77°33'50"	14°13'55" E	0.054	11	16.2	460	.	1995
Tenndammen	Norway, Svalbard	78°06'00"	15°02'00" E	0.15	2.5	164	540	.	1995
Yterjørna	Norway, Svalbard	78°13'52"	12°56'30" E	0.14	2.6	36.9	140	.	1995
Ossian Sarsfjellet	Norway, Svalbard	78°57'04"	12°28'38" E	0.13	26	25.4	88	.	1995

¹Data for recent horizons (post-1990)

²Organic C not measured in sediments from Svalbard lakes; LOI data can be found in Boyle et al. (23).

514 Figure captions

515

516 Figure 1. Accumulation rates of reduced inorganic sulfur in lake sediments from the Canadian
517 Arctic archipelago (A) and Svalbard (B). Note that the scale is different for each lake. Also
518 presented for each region are records of air temperature in summer (JJA = June, July, August)
519 and sulfate concentration in ice cores. The temperature anomaly records have sigma units, which
520 are defined in Overpeck et al. (2). Details about the sources for the temperature and sulfate
521 records can be found in the text.

522

523 Figure 2. Concentrations of acid volatile sulfide (AVS) in sediment slurries from Amituk Lake
524 (A) and Char Lake (B) after incubation with treatments of molybdate (MoO_4 ; metabolic inhibitor
525 of sulfate-reducing bacteria), sulfate (SO_4 ; electron acceptor for sulfate-reducing bacteria),
526 and/or acetate (CH_3COO ; electron donor for sulfate-reducing bacteria). Further details about the
527 treatments can be found in the text. Values represent the mean (± 1 SE) of three replicates; units
528 are in dry weight. Lowercase letters (a, b, c, d) denote statistically significant groupings as
529 determined, for each lake, by a one-way ANOVA and Tukey-Kramer posthoc tests. The x -axis
530 meets the y -axis at the initial (time zero) concentration in sediment slurries for each lake.

531

532 Figure 3. Sediment profiles from Amituk Lake (A) and Char Lake (B) of acid volatile sulfide
533 (AVS; circles), elemental sulfur (S^0 ; triangles), pyrite (squares), and the stable sulfur isotopic
534 compositions ($\delta^{34}\text{S}$) of each of these forms of reduced inorganic sulfur. For profiles of AVS, S^0 ,
535 and pyrite, values represent the mean (± 1 SD) of two cores; units are in dry weight. For profiles
536 of $\delta^{34}\text{S}$, materials from the two cores from each lake were pooled for analysis.

537

538 **Brief**

539 A recent increase in sedimentary accumulation of reduced sulfur in High Arctic lakes may be
540 due ultimately to a changing climate.