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Repeating the calculation reported by Murray *et al.* by using the value of D_0 determined in our experiments suggests that the fraction of OH bound to O_2 is less than 0.1% at all altitudes in the Earth's atmosphere.

Consequently, the formation of HO_3 through the association of OH radicals with O_2 plays no meaningful role in the chemistry of Earth's atmosphere.

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- The acronym CRESU stands for Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow. The technique was originally developed by Rowe and his co-workers for the study of ion-molecule reactions (23).
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Supporting Online Material

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Materials and Methods

SOM Text

Figs. S1 and S2

Tables S1 and S2

References

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Freshwater Outburst from Lake Superior as a Trigger for the Cold Event 9300 Years Ago

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Paleoclimate proxy records reveal a pervasive cooling event with a Northern Hemispheric extent ~9300 years ago. Coeval changes in the oceanic circulation of the North Atlantic imply freshwater forcing. However, the source, magnitude, and routing of meltwater have remained unknown. Located in central North America, Lake Superior is a key site for regulating the outflow of glacial meltwater to the oceans. Here, we show evidence for an ~45-meter rapid lake-level fall in this basin, centered on 9300 calibrated years before the present, due to the failure of a glacial drift dam on the southeast corner of the lake. We ascribe the widespread climate anomaly ~9300 years ago to this freshwater outburst delivered to the North Atlantic Ocean through the Lake Huron–North Bay–Ottawa River–St. Lawrence River valleys.

Greenland ice-core records reveal that Earth's climate system was very unstable during the last deglaciation and early Holocene and that it experienced repeated abrupt cooling at millennial time scales (1). One of these large climate anomalies is a nearly 2°C cooling (2) in the North Atlantic sector at about 9300 calibrated years before the present (cal yr B.P.).

High-resolution and well-dated proxy records (3–7) indicate that this climate anomaly, albeit not the most prominent in the North Atlantic region (8, 9), had a Northern Hemispheric expression, with a spatial pattern nearly identical to that of the so-called 8.2-thousand-year event (10), a widespread cooling associated with the sudden drainage of the glacial Lake Agassiz–Ojibway complex through the Hudson Strait (11). This resemblance implies a common cause for the two events (12) and suggests that freshwater forcing played a prominent role in millennial-scale climate change during the last deglaciation and early Holocene (13, 14).

Numerous lines of evidence from the North Atlantic reveal substantial changes in both surface (2) and deep (15) oceanic conditions corresponding to the event at 9300 cal yr B.P. Studying the cause of this event may provide a valuable perspective on the sensitivity of the North Atlantic meridional overturning circulation (MOC) to freshwater forcing, which in turn would improve

the predictability of future climate changes due to freshwater influx associated with accelerated melting of the Arctic ice pack or the Greenland Ice Sheet. Here we present some observational constraints on the magnitude and routing of a surge of fresh water from Lake Superior at 9300 cal yr B.P.

Located in the middle of the North American continent (Fig. 1A), Lake Superior has experienced a complex evolution after the retreat of the Laurentide Ice Sheet, at about 11,500 cal yr B.P., from the southern edge of the basin, in response to glacioisostatic adjustment and outlet switching (16–18). Middle to late Holocene relative lake-level (RLL) changes in this basin are known from the dating of raised strandplain sequences (19, 20), but older RLL changes are not as well constrained (21). In contrast to this method, we reconstruct RLL changes in the Lake Superior basin by dating isolation and reconnection events recorded in sediments of small marginal lakes that were once embayments of a larger Lake Superior. Details of this method are described in the supporting online material (SOM). The isolation of a small marginal basin from the main water body could be due to changes in localized geomorphic or hydrologic conditions. For example, changes in predepositional slope can mobilize enough sediment in the coastal zone to partially limit the connectivity of a marginal basin with the major water body, thereby supporting quiet water conditions. However, the lakes used in our study are situated at substantially different elevations. The isolation of all of these elevated lakes from Lake Superior requires a RLL fall.

Continuous and undisturbed sediment sequences were recovered from frozen lake surfaces from two marginal lakes on the eastern Upper Peninsula of Michigan (Fig. 1B) and from four marginal lakes on the Sibley Peninsula of Ontario (Fig. 1C). All these basins are today hydrologically closed by a bedrock sill, except for Little Harbor, which is currently a lagoon of

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Lake Superior with a surface elevation of 183 m above sea level (a.s.l.). In addition, a naturally exposed fluvial-lacustrine channel infill sequence in the Thunder Bay area of Ontario was studied (numbered square 7, fig. S1). More detailed information about the geographical coordinates, elevation, and radiocarbon ages of these sites is given in table S1.

Lithology, magnetic susceptibility, and loss-on-ignition data are presented in Fig. 2 along with radiocarbon ages. The latter are plotted on the right-hand side of each core. We interpret the sharp decrease in magnetic susceptibility and the corresponding increase in loss on ignition within the cores as marking the isolation of marginal basins from Lake Superior, and the reverse changes in terms of reconnection to Lake Superior. Specifically, once a marginal basin was isolated by RLL fall in Lake Superior, autochthonous and allochthonous organic matter increased in this small lake, thereby diluting the concentration of magnetic grains in the sediment delivered from the surrounding catchment, and vice versa for when the basin reconnected to Lake Superior. Thus, by knowing the elevation of these small marginal basins, along with when isolation from and/or reconnection to Lake Superior occurred,

the RLL changes in the Lake Superior basin may be constrained.

Data from Little Harbor and Lake Culhane near Whitefish Point on the eastern Upper Peninsula of Michigan (Fig. 1B) can be used to illustrate this approach. For Little Harbor, the organic-rich fibrous peat layer with extremely low magnetic susceptibilities (Fig. 2) records isolation from Lake Superior between 8365 ± 100 and 5340 ± 50 ^{14}C yr B.P. After this initial isolation, a temporary influx of clastic sediments occurred, which may be associated with a RLL rise to the middle Holocene Nipissing highstand (22). The sharp lithostratigraphic transition from silty clay to gyttja, along with a substantial rise in loss on ignition and the corresponding decrease in magnetic susceptibility at 3860 ± 35 ^{14}C yr B.P., indicates a RLL fall after the transgression, turning the embayment environment into a lagoon that otherwise would be isolated from Lake Superior because of its low elevation. Lake Culhane is 17 m higher on the landscape, and its isolation at 8425 ± 65 ^{14}C yr B.P. is recorded at 21 m depth below the lake surface.

Of the studied lakes on the Sibley Peninsula of Ontario (Fig. 1C), from highest to lowest, Ravine Lake was isolated at 8180 ± 45 ^{14}C yr

B.P. and Grassy Lake at 8210 ± 50 ^{14}C yr B.P. For Roadside Lake, we are unable to determine when the initial isolation occurred during the early Holocene, because the older sediments were scoured away in this channel-like basin while RLL was falling. However, the results show the lake reconnecting to Lake Superior during the RLL rise to the Nipissing highstand and being isolated again at 3600 ± 40 ^{14}C yr B.P. A thin gyttja layer sandwiched in the thick silty clay may indicate a short-lived inwashing event. Surprise Lake was initially isolated at 8170 ± 40 ^{14}C yr B.P., reconnected to Lake Superior at 8010 ± 40 ^{14}C yr B.P., and was finally isolated at 1900 ± 65 ^{14}C yr B.P. The RLL fall from the Nipissing highstand may explain the final isolation. At Old Fort William, in an embayment of Lake Superior near Thunder Bay, a substantial drawdown of the lake is recorded by channel incision into fluvial sediments of the Kaministiquia delta. Radiocarbon ages of terrestrial macrofossils preserved in the bottom of this paleochannel (at 187 m a.s.l.) indicate that a low water level was established there before 8000 ^{14}C yr B.P. (Fig. 2).

Taken together, our results indicate a general trend of RLL fall on both the eastern Upper

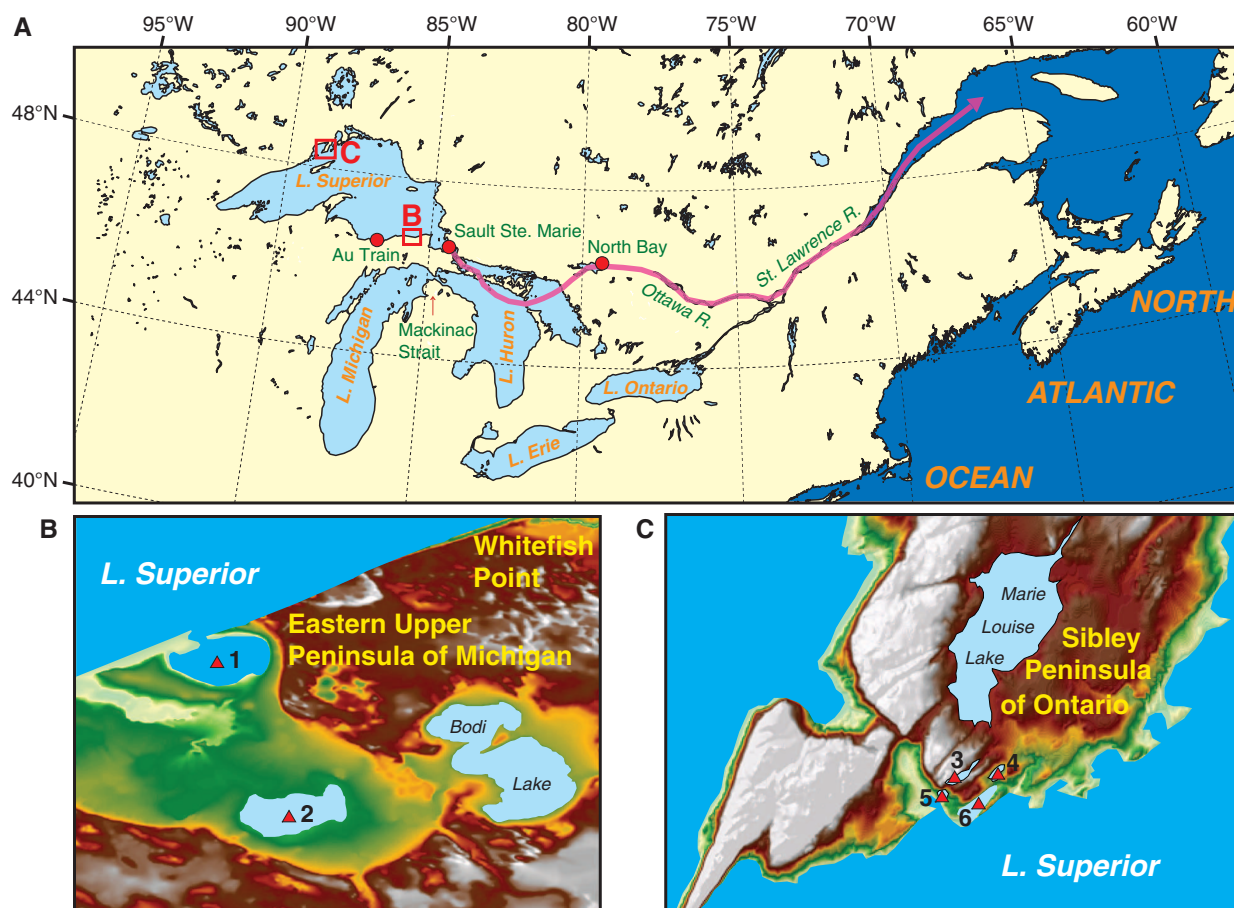


Fig. 1. (A) Location of the Laurentide Great Lakes system and its connecting river channels. Red solid dots indicate outlets mentioned in the text. The arrow denotes the proposed route of the Lake Superior flood through the Lake Huron–North Bay–Ottawa River–St. Lawrence River valleys that was coeval

with the event at 9300 cal yr B.P. (B) Shaded relief map showing the present-day topography of the eastern Upper Peninsula of Michigan. 1, Little Harbor; 2, Lake Culhane. (C) Modern shaded relief map of the Sibley Peninsula of Ontario. 3, Lake Ravine; 4, Lake Grassy; 5, Lake Roadside; 6, Lake Surprise.

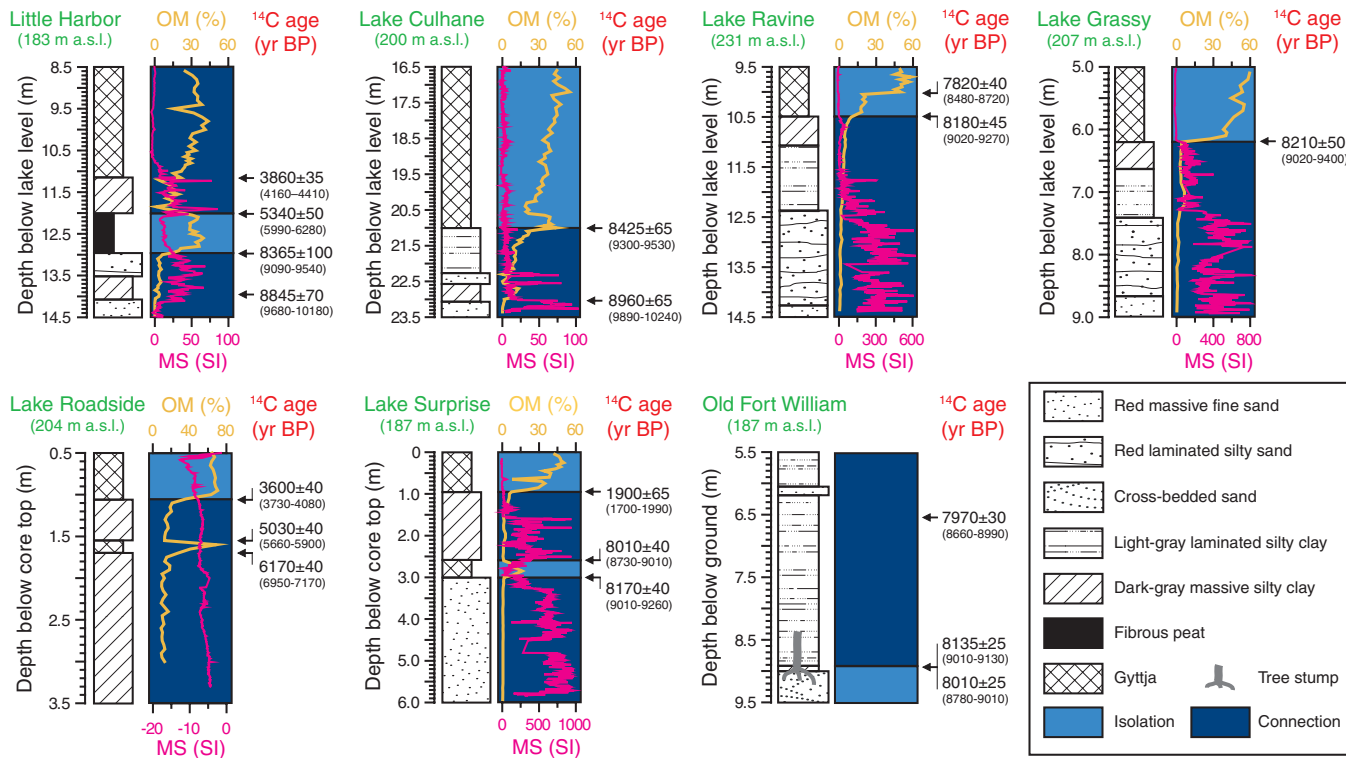


Fig. 2. Lithostratigraphic logs of lacustrine sediment cores from the eastern Upper Peninsula of Michigan and Sibley Peninsula of Ontario, as well as a fluvial-lacustrine channel infill sequence from the Old Fort William cutbank site, Ontario. Arrows indicate accelerator mass spectrometry ^{14}C -dated levels. Detailed in-

formation about the cores and radiocarbon ages is in table S1. The identification of lake status in terms of isolation and connection with Lake Superior is based on magnetic susceptibility (MS) and organic matter (OM) measurements. Numbers in brackets are calibrated radiocarbon ages with 2σ error.

Peninsula of Michigan and Sibley Peninsula of Ontario until about 9000 cal yr B.P., followed by a RLL rise thereafter. To get a broader perspective on long-term RLL changes, we compiled published data from around Lake Superior for ^{14}C -dated lake isolation and reconnection events as well as for fluvial/lacustrine sediment contacts in estuaries (fig. S1 and table S2). With detailed information on these RLL indicators, we reconstruct RLL changes in the Lake Superior basin by synthesizing these data with our results.

To estimate the magnitude of RLL changes from these data sites and place them into a time-varying rate-of-change context, each site must be corrected for differential uplift with respect to a reference site (SOM). We predicted land uplift at each site during the past 11,500 years due to glacioisostatic adjustment, using the ICE-3G ice loading model (23) and a multilayered, radially symmetric, and self-gravitating Maxwell Earth model (24). We also used the ICE-5G ice model (25), but predictions based on it were less compatible with the instrumental data (26) than were those generated using ICE-3G (fig. S2). The elastic and density structure of the Earth model is based on seismic constraints (27), and the viscous structure was varied to explore the sensitivity of the predictions to this aspect of the model. The algorithm used to compute vertical land motion is based on that described in Mitrovica *et al.*

Fig. 3. Holocene RLL change at Sault Ste. Marie, southeastern Lake Superior, calculated by correcting observed paleo-RLL heights using an isostatic Earth model. Horizontal error bars are defined by tree-ring calibration of ^{14}C ages with 2σ error. Vertical bars denote maximum error as a sum of uncertainties arising from both elevation estimates and the indicative range of RLL indicators. Elevation of the Nadoway barrier is estimated from the lowest point of the present-day surface (271 m a.s.l.). The difference in elevation between this barrier and the bedrock sill at Sault Ste. Marie (181 m a.s.l.) provides a maximum-limiting constraint on the rapid RLL fall about 9300 years ago.

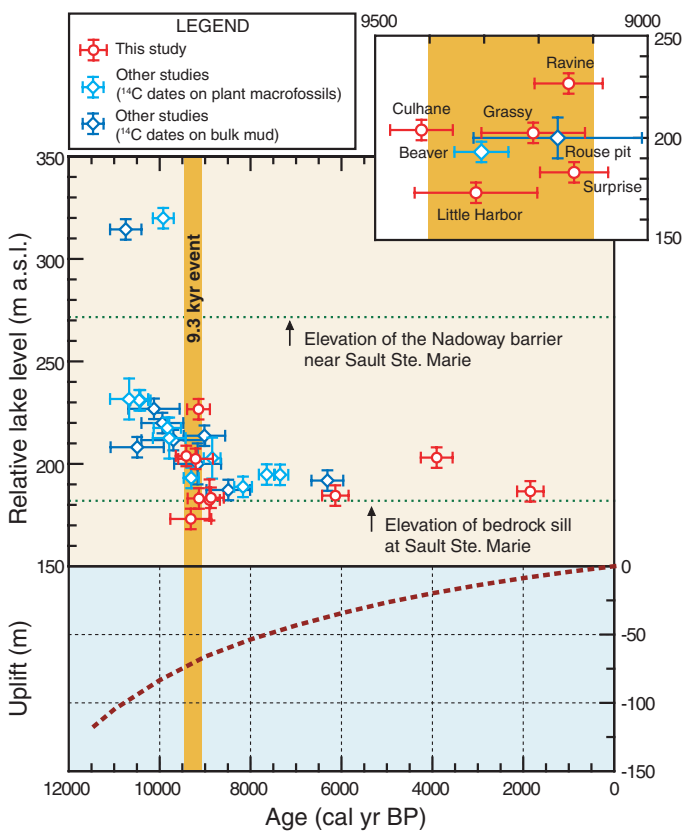
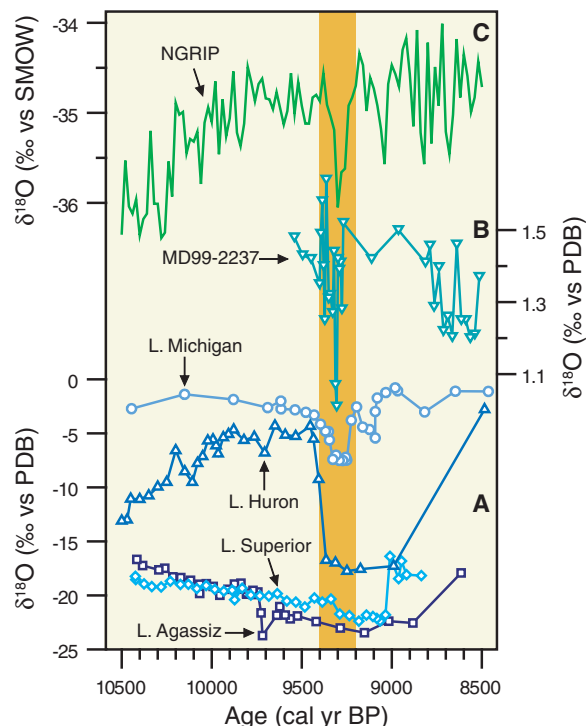


Fig. 4. Comparison of $\delta^{18}\text{O}$ records from Lake Agassiz (32), the upper Great Lakes (18, 31, 33), core MD99-2237 from the southwestern Labrador Sea (36, 37), and an ice core from the North Greenland Ice Core Project (NGRIP) (1). The vertical bar denotes a substantial depletion of $\delta^{18}\text{O}$ corresponding to the event at 9300 cal yr B.P. PDB, Pee Dee belemnite standard; SMOW, standard mean ocean water.



(28, 29), but extended to include the influence of Earth rotation (30). Varying the viscosity structure substantially affects the amplitude and rate of land uplift at specific sites (fig. S3); however, predictions of uplift between sites are remarkably insensitive to a wide range of plausible viscosity structures (fig. S4). This is a key point because it means that our corrections for differential uplift are largely independent of this poorly defined model parameter.

Sault Ste. Marie (Fig. 1A) was arbitrarily chosen as a reference site for our basin-scale RLL reconstruction. Today, it functions as the outlet draining Lake Superior to the North Atlantic Ocean through the lower Great Lakes and the St. Lawrence River valley. The modeled RLL projected to Sault Ste. Marie fell progressively from about 11,000 to 9300 cal yr B.P. (Fig. 3), primarily controlled by the isostatic rebound of the deformed basins. Overflow from the Lake Superior basin may have flowed into Lake Michigan through the Au Train–Whitefish channel before 10,600 cal yr B.P. (31). Subsequent isostatic rebound may have closed this outlet, and Lake Superior was dammed up by a drift moraine across the Nadoway barrier near Sault Ste. Marie (21), keeping the RLL higher at this time than the low-water Chippewa and Stanley phases in the Lake Michigan and Huron basins, respectively (17). Although earlier studies have suggested that the outlet across the Nadoway dam was progressively lowered by erosion (22), we suggest that the drift moraine dam was eroded and breached abruptly, as suggested by our lake-isolation data, which indicate an ~45-m rapid RLL fall from 226 to 181 m a.s.l. relative to Sault Ste. Marie between 9400 and 9100 cal yr

B.P. (inset, Fig. 3). The rapidity and magnitude of this RLL fall are independent of the choice of reference site used for the corrections of differential uplift (fig. S5).

The $\delta^{18}\text{O}$ records from Lake Agassiz (32) and the upper Great Lakes (18, 31, 33) support our interpretation of a sudden RLL drop about 9300 years ago. We ascribe the large and abrupt negative shift of the Lake Huron $\delta^{18}\text{O}$ record at ~9300 cal yr B.P. (Fig. 4A) to this ~45-m rapid RLL fall, due most likely to a sudden failure of the Nadoway drift moraine dam, which would have released about $4 \times 10^{12} \text{ m}^3$ of isotopically light glacial meltwater into Lake Huron through the St. Marys River. Increased mass exchange between Lakes Huron and Michigan may have occurred through the Mackinac Strait, as indicated by a substantial decrease of $\delta^{18}\text{O}$ values in the Lake Michigan record (31) (Fig. 4A). Although our chronology of marginal lakes in the Lake Superior basin and the isotope chronology in several of the Great Lakes' basins constrain the duration of this event only within a century or two, the breach of a sandy moraine dam may have occurred rapidly, and if within 1 year, a RLL fall of 45 m is equivalent to a flux of ~0.15 sverdrup (1 sverdrup = $10^6 \text{ m}^3/\text{s}$). Because there are no substantial changes in the $\delta^{18}\text{O}$ records from Lakes Erie (34) and Ontario (35) during this period, we infer that this cataclysmic outflow was delivered through the Ottawa River–St. Lawrence River route to the North Atlantic Ocean (Fig. 1A). Although previous to this outburst flood, water from Lake Superior was also being routed to the North Bay–Ottawa–St. Lawrence River; the sudden decrease of $\delta^{18}\text{O}$ in the surface waters of the southwestern Labrador Sea at about

9300 cal yr B.P. (36, 37) can be explained by a short-lived flood (Fig. 4B). Within dating uncertainties, we propose that it was the rapid drawdown of water in the Lake Superior basin that caused the widespread abrupt cooling in the North Atlantic (Fig. 4C) and elsewhere in the Northern Hemisphere (3–7).

We provide evidence for a rapid and large drawdown of Lake Superior, due most likely to the sudden failure of an end-moraine dam at its southeastern corner at about 9300 cal yr B.P. The catastrophic breaching of this glacial drift dam lowered the RLL by about 45 m, releasing a surge of fresh water to the North Atlantic Ocean, thereby leading to a widespread cooling. Our findings not only support the hypothesis of freshwater forcing of rapid climate changes during the last deglaciation and early Holocene, but also provide quantitative control on the sensitivity of the North Atlantic MOC to freshwater perturbation within the context of a relatively warm early Holocene climate.

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Figs. S1 to S5

Tables S1 and S2

References

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Fractal Organic Hazes Provided an Ultraviolet Shield for Early Earth

E. T. Wolf and O. B. Toon

The Archean Earth (3.8 to 2.5 billion years ago) was probably enshrouded by a photochemical haze composed of fractal aggregate hydrocarbon aerosols. The fractal structure of the aerosols would have had a strong effect on the radiative properties of the haze. In this study, a fractal aggregate haze was found to be optically thick in the ultraviolet wavelengths while remaining relatively transparent in the mid-visible wavelengths. At an annual production rate of 10^{14} grams per year and an average monomer radius of 50 nanometers, the haze would have provided a strong shield against ultraviolet light while causing only minimal antgreenhouse cooling.

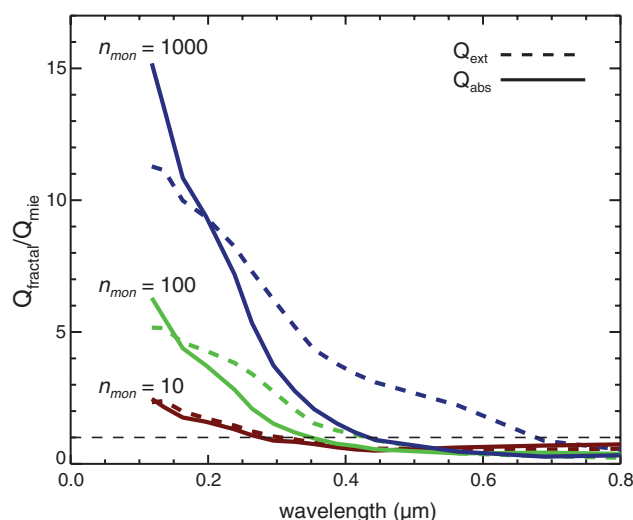
The atmosphere of the Archean Earth (3.8 to 2.5 billion years ago) was much different from the present one. The prevailing view of the Archean atmosphere is that it consisted primarily of N_2 with lesser amounts of CO_2 , CH_4 , H_2 , and H_2O . Solar evolutionary models predict that the young Sun was up to ~30% less luminous than now (1), but the lack of evidence of glaciation combined with positive evidence of primitive life indicates that Archean surface temperatures were generally as warm or warmer than today (2, 3). Resolving this paradox is important for understanding the environment of Earth at the time of the origin of life. Although a dense CO_2 atmosphere could theoretically have warmed the early Earth, the absence of siderite in fossil weathering profiles constrains the amount of CO_2 present in the young atmosphere (4). Combined greenhouse warming from CO_2 , CH_4 , NH_3 , and other less abundant gases is typically invoked to resolve this apparent paradox. Past studies indicate that N_2 - CH_4 photochemistry produces an organic haze at high altitudes that could cool the planet, offsetting any greenhouse warming (5, 6). In contrast, we show here that the haze would be optically thin at visible wavelengths and therefore have little cooling effect on climate, but would be optically thick at ultraviolet (UV) wavelengths and thus could shield reduced gases from photolysis. The key is to consider the fractal nature of the haze particles.

Atmospheric conditions similar to those that prevailed on the young Earth exist currently on Titan, a moon of Saturn. Titan's atmosphere is strongly reducing, consisting of 98.4% N_2 along with 1.6% CH_4 and other hydrocarbons. Photochemical production of organic aerosols on Titan produces an optically thick haze that has been much studied (7). Similar organic aerosols are observed to form readily even in weakly reducing early-Earth-like laboratory gas mixtures having CO_2 : CH_4 ratios as high as 10:1 (8). A Titan-like photochemical haze should have formed high in the Archean atmosphere as well. Sagan and

Chyba (9) argued that an organic haze may have provided a strong UV shield, protecting underlying constituents and primitive organisms from photochemical destruction. It is of particular interest that if NH_3 is protected by a strongly UV-absorbing haze and allowed to accumulate, a surface mixing ratio of 10^{-5} could alone provide sufficient greenhouse warming to keep Archean surface temperatures above freezing (1). However, recent modeling studies have suggested that the haze would be of a similar optical thickness in both the UV and visible wavelengths (5, 6). Thus, any increase in UV shielding is accompanied by a thickening at visible wavelengths, which would cause intense antgreenhouse cooling and freeze the planet.

Previous models of the Archean haze have inaccurately made the simplifying assumption of particle sphericity. Hydrocarbon aerosols have long been known to form fluffy aggregates that exhibit fractal structure (10). This fractal structure affects both the microphysical and radiative properties of the haze. Given the expected chemical and microphysical similarities between Titan and early Earth, we simulated haze particles as fractal aggregates (11), using a scheme introduced by Cabane *et al.* (12) and later used by Rannou *et al.* (13–15), to model fractal aggregate hazes in Titan's atmosphere. The fractal model is successful in reproducing the scattering properties of Titan's haze (7).

Fig. 1. The ratio of absorption (Q_{abs} , solid line) and extinction (Q_{ext} , dashed line) efficiencies calculated for fractal aggregate particles ($Q_{fractal}$) to those calculated for Mie particles of equal mass (Q_{mie}). A value of unity indicates that the aggregate particle is radiatively indistinguishable from the Mie particle. The particles illustrated have $D_f = 2$, $r_{mon} = 50$ nm, and $n_{mon} = 10$, 100, and 1000, corresponding to fractal radii of 0.16, 0.5 and 1.6 μm , respectively (Eq. 1). We assume refractive indices for Titan analogs (19). Fractal aggregate particles are an order of magnitude more absorbing in the UV while being slightly less absorbing in the visible than are Mie particles of equal mass. The gradient increases for larger aggregates containing more monomers.



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Supporting Online Material for
**Freshwater Outburst from Lake Superior as a Trigger for the Cold
Event 9300 Years Ago**

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This PDF file includes:

Materials and Methods
Figs. S1 to S5
Tables S1 and S2
References

Other Supporting Online Material for this manuscript includes the following:
(available at www.sciencemag.org/cgi/content/full/science.1187860/DC1)

Table S3

Supporting Online Material

Materials and Methods

1. Lake-level indicators

We reconstruct relative lake-level (RLL) changes in the Lake Superior basin by dating isolation and (re-)connection events of small marginal lakes situated at different elevations above present-day lake level (183 m a.s.l.) using radiocarbon-controlled stratigraphy. In contrast to dating strand lines (beaches and wave-cut cliffs) around the Lake Superior basin, this method is advantageous in several aspects. First, the surface elevation of hydrologically closed small lake basins enables a precise estimate of Lake Superior's past RLL elevation when these marginal basins were isolated from and/or (re-)connected to Lake Superior. Second, RLL changes as marked by these basins' isolation from and (re-)connection to Lake Superior are clearly recorded in the stratigraphic context of these small lakes. Third, abundant and well-preserved plant remains in lacustrine sediment ensure precise radiocarbon dating of the isolation and (re-)connection events in these marginal basins.

Two lakes were studied near Whitefish Point on the eastern Upper Peninsula of Michigan (numbered squares 1–2, Fig. S1), and four on the Sibley Peninsula of Ontario (numbered squares 3–6, Fig. S1). These lakes were cored during winters of 2005 and 2006 using a Livingstone piston corer except for Surprise and Roadside Lakes, which were cored using a piston-equipped vibracorer (*S1*). In addition, a glaciofluvial-lacustrine complex exposed in outcrops along the Kaministiquia River in an embayment near Thunder Bay, Ontario was described and dated (numbered square 7, Fig. S1).

All lacustrine cores were imaged, described, and archived in the National Lacustrine Core Laboratory, University of Minnesota Minneapolis. Core analyses included continuous magnetic-susceptibility scanning and high-resolution (2 cm sample interval) loss-on-ignition measurements to quantify consistent and distinct changes in concentration of fine magnetic grains and organic matter in the cores. Ages of the isolation and (re-)connection events were determined by AMS radiocarbon dating of terrestrial plant macrofossils identified under a dissecting microscope after wet sieving through a 250- μ m screen. Radiocarbon ages were calibrated using the computer software CALIB 5.1 in conjunction with the INTCAL04 tree-ring dataset (*S2*). The $\delta^{13}\text{C}$ values (ca. -25‰) confirm that all of our dated samples are derived from terrestrial plants (Table S1); therefore they are not subject to radiocarbon “hardwater” effects.

For our basin-scale reconstruction of RLL changes in the Lake Superior basin, we surveyed data from various published sources (numbered dots 1–19, Fig. S1 and Table S2). These data include ^{14}C -dated isolation and (re-)connection events of small marginal lakes and glaciofluvial/lacustrine sediment contacts in estuarine settings, which have different indicative meanings related to RLL. For example, marginal lakes are precise RLL index points, while the glaciofluvial-lacustrine complex gives only a minimum-limiting estimate of RLL. Therefore, for deep marginal lakes, RLL is simply defined by the surface elevation of the lakes when isolation from or (re-)connection to Lake Superior occurred. For shallow marginal lakes (e.g. Little Harbor and Beaver Lake), peat usually developed once the basins were isolated, and the basins turned into an anaerobic waterlogged subaerial environment supported by groundwater with a water table partly controlled by the water level of Lake Superior (*S3*), and thus the basal elevation of peat provides a maximum-limiting estimate of RLL in the Lake Superior basin; for estuarine sediments, RLL is approximately defined by the elevation of the fluvial/lacustrine sediment contact.

Different vertical errors are assigned to these RLL indicators based on their indicative meaning and uncertainties in elevation estimates. For small marginal lakes, a ± 2 m error is given according to the

uncertainty in lake surface elevation estimates from topographical maps with a 5 m resolution; for estuarine sediment complexes, a larger error of ± 10 m is assigned because lacustrine sediments cannot be deposited until the channel was inundated with relatively quiet water.

2. Correction for differential uplift

In this active rebound setting, the magnitude of strandline uplift and tilting is dependent upon the regional ice loading history and sub-surface Earth structure. Long-term instrumental data indicate that this process continues today (S4), and in the Lake Superior basin, land emerges to the northeast and submerges to the southwest of the zero isobase passing through the Sault Ste. Marie outlet, and approximately following the US-Canada border (Fig. S1). As the data sites used in our RLL reconstruction are spread over a large area around Lake Superior (Fig. S1), differential uplift (i.e. uplift of one site relative to another) must be removed in order to accurately determine the magnitude of RLL fall (and therefore water volume loss) in this basin.

To remove the differential uplift, we predicted land uplift at the data sites using an ice-sheet loading model (e.g. ICE-3G and ICE-5G) and an isostatic Earth model in which three key parameters are changed: thickness of lithosphere (71 to 120 km), viscosity in the upper mantle (beneath the lithosphere to 660 km depth; 0.1 to 1.0×10^{21} Pa·s), and viscosity in the lower mantle (660 km to core-mantle boundary; 1 to 50×10^{21} Pa·s). Compared to the ICE-5G model, using ICE-3G results in rates of vertical land motion with an orientation that better fits the pattern of the present-day uplift as defined by instrumental data (Fig. S2). The predicted uplift, as illustrated in Fig. S3, appears to be less sensitive to the lithospheric thickness and more sensitive to the viscosity of the mantle, which governs both the amplitude and rate of the uplift. However, the predicted differential uplift tends to be remarkably insensitive to a large range in Earth model parameters (Fig. S4). This means that our RLL reconstruction is not significantly influenced by uncertainty in these parameter values.

To correct the observational data for differential uplift, first we used an Earth model with parameters that lie in the middle of the ranges given above (i.e. a lithospheric thickness of 96 km, an upper mantle viscosity of 0.5×10^{21} Pa·s, and a lower mantle viscosity of 1×10^{22} Pa·s) to predict land uplift at each site since 11,500 cal yr BP when the Laurentide Ice Sheet began to retreat from the southern edge of the Lake Superior basin. Then we chose the modern lake outlet at Sault Ste. Marie as the reference site, and calculated the difference in land uplift through time at each site with respect to it. Finally we reconstructed RLL changes at the reference site by removing this offset from observational data:

$$RLL_{\text{sault}} = RLL_{\text{site}} - \Delta U$$

where RLL_{sault} is the reconstructed RLL at Sault Ste. Marie, RLL_{site} is the observed RLL at each site, and ΔU is the predicted differential uplift.

Choosing this reference site is arbitrary. We projected the RLL data to other reference sites, e.g. the Pic River channel and the Au Train-Whitefish Bay channel (Fig. S5), which have been proposed as major outflow spillways during the early Holocene (S5, S6). All of our reconstructed RLL changes exhibit the same general trend, particularly prior to ca. 9000 cal yr BP, though the amplitudes vary as a function of distances from the ice-loading center. The differential uplift also leads to a disparate pattern of RLL changes across the Lake Superior basin in response to the Nipissing transgression (S7) resulting from isostatic rebound at the North Bay outlet after ca. 9000 cal yr BP. Specifically, Pic River represents an area of strong uplift, where RLL changes were characterized by a gradual fall (Fig. S5 A), whereas at Au Train-Whitefish Bay, the Nipissing transgression outpaced the uplift, resulting in a substantial RLL rise (Fig. S5 B).

Supporting Figures

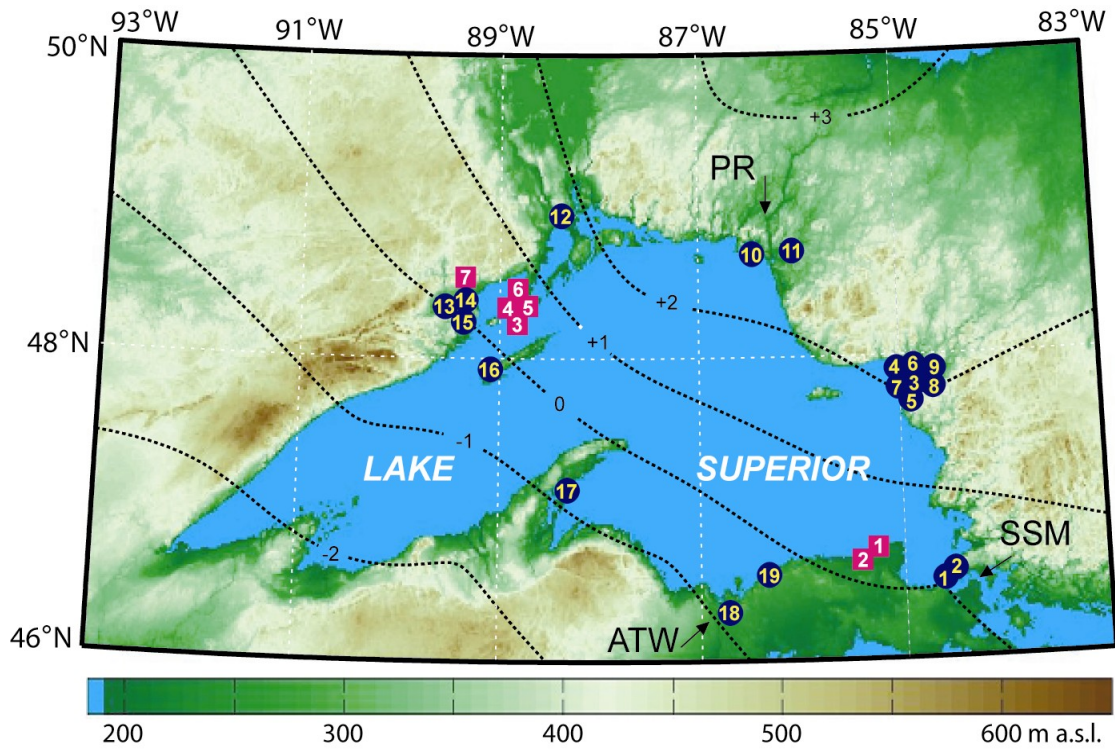


Figure S1. Shaded relief map showing topographical features of the Lake Superior basin. Numbered squares denote sites studied in this project (Table S1), and circles indicate sites investigated by others (Table S2). Contours are rates of modern vertical land motion in mm/yr determined by water-level gauges in relation to modern overflow channel at Sault Ste. Marie (*S4*). PR = Pic River channel; ATW = Au Train-Whitefish Bay channel; SSM = Sault Ste. Marie channel.

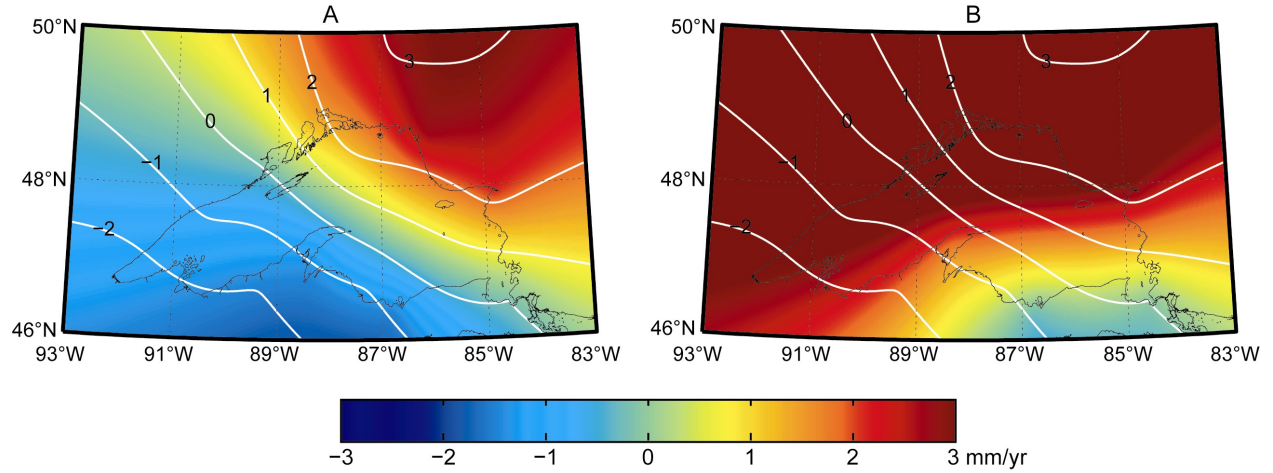


Figure S2. Comparison of rates of modern vertical land motion in mm/yr between instrumental data (numbered contours) and predictions (filled contours) using the same Earth model parameters (a lithospheric thickness of 96 km, an upper mantle viscosity of 0.5×10^{21} Pa·s, and a lower mantle viscosity of 1×10^{22} Pa·s) but different ice loading models: ICE-3G (A), and ICE-5G (B).

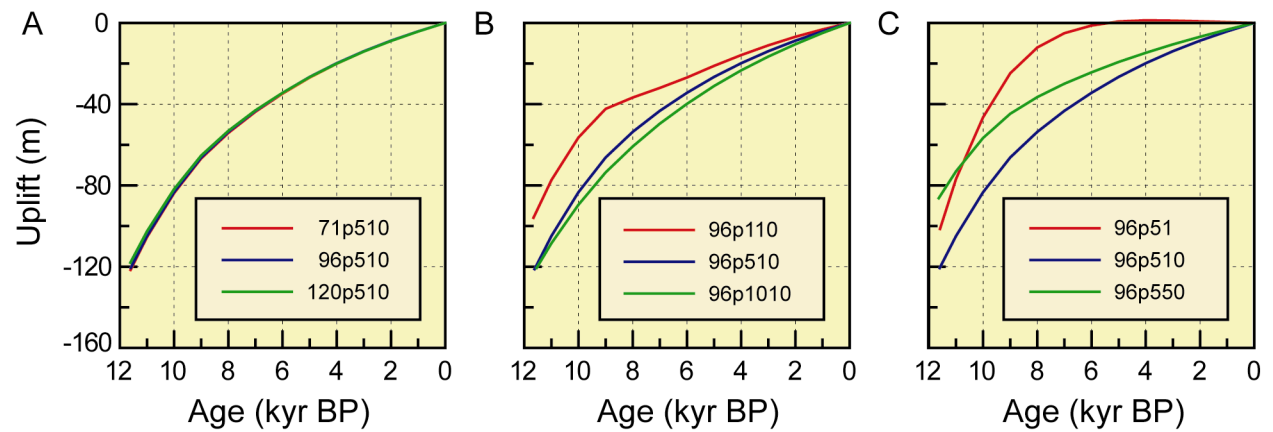


Figure S3. Predicted land uplift at Sault Ste. Marie using the ICE-3G ice loading model and a variety of Earth models (see main text). These results demonstrate the sensitivity of the model predictions to variations in key Earth model parameters: lithospheric thickness (A), upper mantle viscosity (B), and lower mantle viscosity (C).

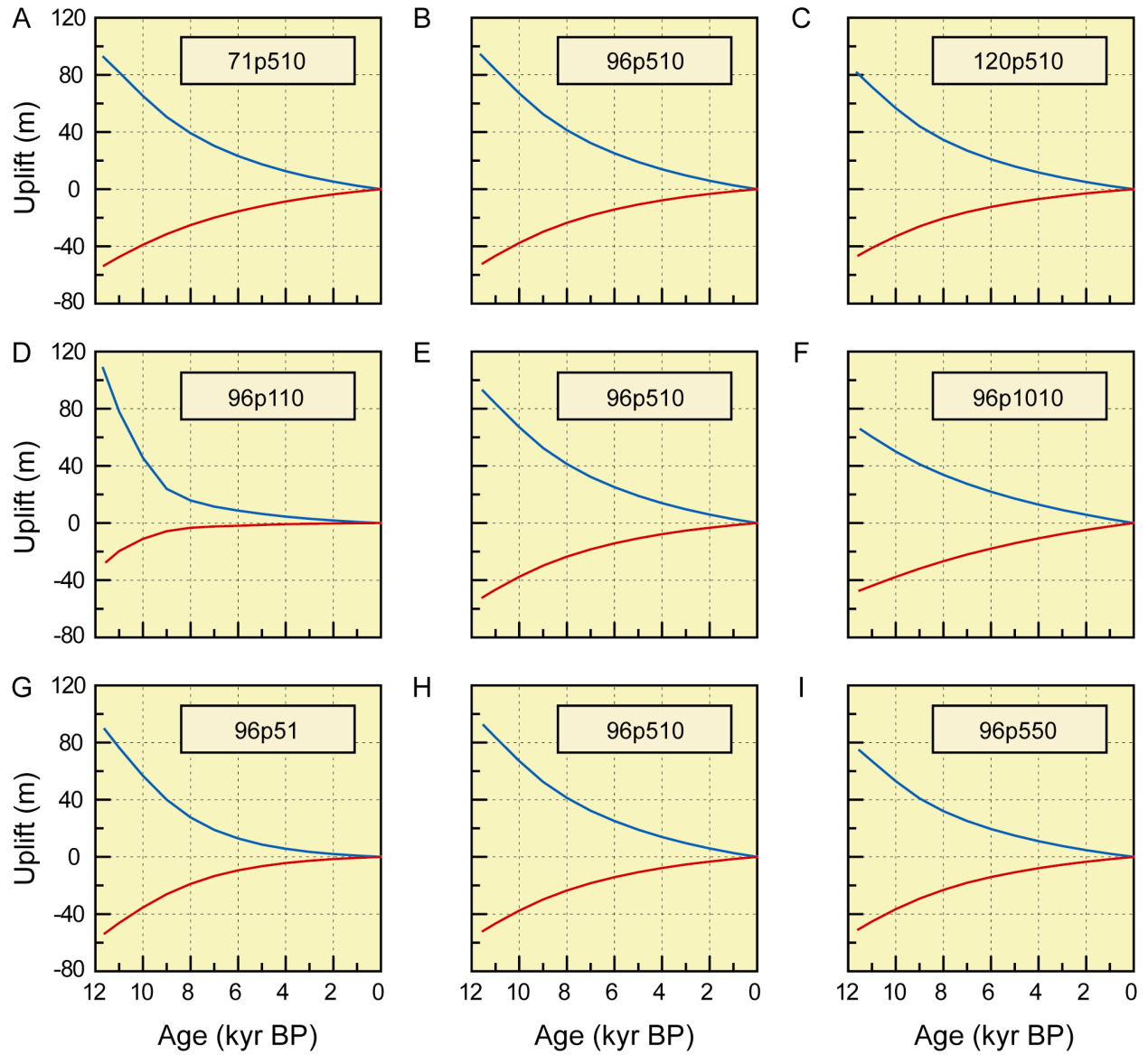


Figure S4. Predicted differential land uplift at outlets in the northeastern (Pic River channel, blue solid line) and southern (Au Train-Whitefish Bay channel, red solid line) parts of the Lake Superior basin with respect to Sault Ste. Marie using the ICE-3G ice loading model and a variety of Earth models (see main text). This is done to illustrate the low sensitivity of our RLL reconstructions to variations in key Earth model parameters: lithospheric thickness (A–C), upper mantle viscosity (D–F), and lower mantle viscosity (G–I).

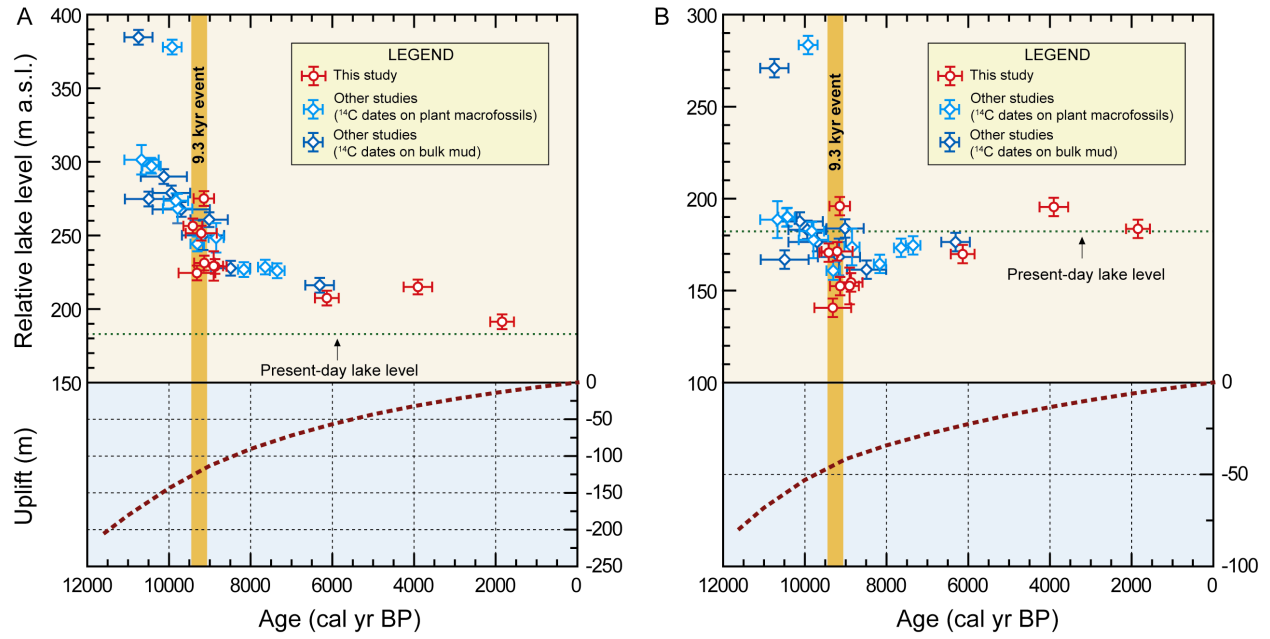


Figure S5. Holocene RLL change calculated by correcting observed RLL altitudes using the ICE-3G ice loading model and an intermediate Earth model (see text for details). A. Pic River channel, northeastern Lake Superior; B. Au Train-Whitefish Bay channel, southern Lake Superior. Horizontal error bars are defined by tree-ring calibration of radiocarbon ages with a 2σ error. Vertical bars denote maximum error as a sum of uncertainties arising from both elevation estimates and the indicative range of the RLL indicators.

Supporting Tables

Table S1. Radiocarbon ages of sites investigated in this study.

Depth (m)	Lab. ID	Materials dated	$\delta^{13}\text{C}$ (‰ PDB)	^{14}C age (yr BP)	2 σ calibrated age (yr BP)
1. Little Harbor (46°42.9'N, 85°21.7'W; 183 m a.s.l.)					
10.800	OS-63146	Wood fragments	-26.86	3860±35	4160-4410
11.935	OS-63240	Twigs	-29.01	5340±50	5990-6280
12.970	ETH-32328	Birch leaves and twigs	-23.50	8365±100	9090-9540
13.850	ETH-32329	Birch seeds and bud scales	-27.80	8845±70	9680-10180
2. Lake Culhane (46°41.7'N, 85°21.3'W; 200 m a.s.l.)					
21.000	ETH-32330	Twigs	-32.10	8425±65	9300-9530
22.990	OS-63239	Wood fragments	-27.39	8960±65	9890-10240
3. Ravine Lake (48°20.8'N, 88°49.1'W; 231 m a.s.l.)					
10.025	Beta-230951	Birch seeds and bud scales	-30.30	7820±40	8480-8720
10.505	OS-63258	Pine twigs and needles	-25.77	8180±45	9020-9270
4. Grassy Lake (48°20.7'N, 88°48.4'W; 207 m a.s.l.)					
6.18	OS-63243	Plant remains	-27.02	8210±50	9020-9400
5. Roadside Lake (48°20.3'N, 88°49.5'W; 204 m a.s.l.)					
1.03	Beta-230954	Birch seeds and pine needles	-26.10	3600±40	3730-4080
1.57	Beta-230955	Birch seeds and twigs	-23.60	5030±40	5660-5900
1.75	Beta-230956	Twigs	-28.10	6170±40	6950-7170
6. Surprise Lake (48°20.1' N, 88°49.3'W; 187 m a.s.l.)					
0.945	OS-64235	Birch twigs and seeds	-32.74	1900±65	1700-1990
2.730	Beta-230959	Birch leaves and twigs	-26.90	8010±40	8730-9010
2.950	Beta-230960	Birch leaves and catkin scales	-27.50	8170±40	9010-9260
7. Old Fort William cutbank site (48°20.6' N, 89°21.1'W; 187 m a.s.l.)					
	UCIAMS 26800	Vertical log rooted in sand buried by silty clay	–	8135±25	9010-9130
	UCIAMS 26801	Spruce cone near base of silt in organic detritus laminae	–	8010±25	8780-9010
	UCIAMS 26802	Horizontal (reworked) log in silty clay 2.5 m above base of unit	–	7970±30	8660-8990

Table S2. Radiocarbon ages of RLL indicators around the Lake Superior basin.

Number	Site name	Elevation (m a.s.l.)	Latitude (N)	Longitude (W)	Materials dated	¹⁴ C age (yr BP)	Comment	Data source
1	Upper Twin Lakes	302.0	46°32.5′	84°35.0′	Basal gyttja	10650±265	Lake isolation	(S8)
2	Prince Lake	290.0	46°33.5′	84°33.0′	Basal gyttja	10800±360	Lake isolation	(S8)
3	Alfies Lake	288.3	47°53.0′	84°51.5′	Basal gyttja	9210±100	Lake isolation	(S9)
4	Antoine Lake	271.0	47°54.0′	84°54.5′	Basal gyttja	8830±200	Lake isolation	(S9)
5	Last Lake	265.2	47°52.4′	84°52.4′	Basal gyttja	9220±180	Lake isolation	(S9)
6	Blackington Lake	260.9	47°53.8′	84°50.4′	Basal gyttja	8640±280	Lake isolation	(S9)
7	Fenton Lake	253.3	47°51.3′	84°52.8′	Basal gyttja	8100±180	Lake isolation	(S9)
8	Crozier Lake	223.1	47°54.2′	84°49.3′	Basal gyttja	7590±180	Lake isolation	(S9)
9	Roller Lake	213.4	47°54.5′	84°49.3′	Basal gyttja	5540±150	Lake isolation	(S9)
10	Jock Lake	290.0	48°41.0′	86°27.0′	Basal gyttja	9060±200	Lake isolation	(S9)
11	Rous Lake pit	256.0	48°42.0′	86°02.7′	Wood	8310±200	Fluvial sediments	(S10)
12	Nipigon	244.0	48°56.5′	88°23.0′	Plant detritus	8640±130	Flood fan sediments	(S11)
13	Rosslyn pit	227.0	48°21.8′	89°27.3′	Wood	9380±150	Nearshore sediments	(S12)
14	Cummins Pond	230.0	48°24.3′	89°20.9′	Wood	9260±70	Basal sand	(S13)
15	Boyd Cut	199.0	48°20.4′	89°21.5′	Charcoal	8030±48†	Fluvial sediments	(S14)
16	Lily Lake	300.0	47°55.7′	89°05.4′	Bulk gyttja	9420±90	Lake isolation	(S15)
17	Mud Lake	189.0	47°08.0′	88°19.0′	Plant macrofossil	8700±90	Lake isolation	(S16)
18	Ackerman Lake	283.5	46°19.9′	86°47.9′	Wood	8811±39¶	Lake isolation	(S17)
19	Beaver Lake, Core 2	174.07	46°34.0′	86°20.2′	Bulk basal peat	8320±60	Lake isolation	(S3)
	Beaver Lake, Core 2	174.39	46°34.0′	86°20.2′	Wood in basal peat	7340±50	Lake transgression	(S3)
	Beaver Lake, Core 4	182.00	46°34.0′	86°20.2′	Wood in basal peat	6800±50	Lake transgression	(S3)
	Beaver Lake, Core 1	182.73	46°34.0′	86°20.2′	Wood in basal peat	6420±50	Lake transgression	(S3)

Notes:

†Weighted mean of two radiocarbon ages.

¶Weighted mean of three radiocarbon ages.

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