from arid areas, is also unlimited. It is probable that living plants and animals that naturally completely lack ^{14}C are unreported only because the proper environments have yet to be tested.

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1. The hard water effect is a dilution of ^{14}C content by the dissolution of dead mineral phase carbonate that buffers the acidity caused by dissolution of modern soil zone CO_2 into the infiltrating ground water. For stoichiometric reasons, the amount of mineral carbon dissolved cannot exceed the amount of soil zone carbon present. Dilution of the soil zone carbon is therefore limited to 50 percent, or one half-life of ^{14}C (about 5700 years). For the original description see E. Deevey, Jr., *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **40**, 285 (1954).
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Enhanced Atmospheric Circulation over North America During the Early Holocene: Evidence from Lake Superior

Abstract. *Profiles of grain sizes in five cores recovered from Lake Superior show that grain size increased with burial depth to the postglacial-glacial contact. The results reflect a substantial reduction in bottom-current velocity and the corresponding wind velocity from 9500 to 6500 years ago.*

Some models of atmospheric circulation and of paleoclimate predict that the midlatitude westerlies over North America were stronger during early Holocene as compared with late Holocene because of enhanced anticyclonic circulation over the Laurentide ice sheet (*1–4*), but little direct evidence supports them. The morphology of the Nebraskan sand dunes suggests that the north-northwest winds during the late Pleistocene were stronger than the southwest winds during the mid-Holocene, but the stratigraphic record lacks a definite and continuous chronology (*5*). The fluvial deposits in the driftless area indicate that there were more episodes with high runoff in early than late Holocene time; these may reflect storm frequency (*6*).

We present evidence of major fluctuations in atmospheric circulation throughout the Holocene over Lake Superior. The prevailing signal is one of decreasing wind intensity or storm frequency beginning 9500 years ago. The results are based on analyses of sediments from a deep-water environment just north of the Keweenaw Peninsula in Lake Superior. Seismic profiles (3.5 kHz) and side-scan sonar records, collected along 500 km of shiptrack, plus 2 piston (P), 10 gravity (G), and 12 box (B) cores recovered from 220 to 260 m water depth revealed sedimentary features that indicate weak bottom currents 25 km offshore and progressively stronger bottom currents southeastward toward the base of the slope off the peninsula (*7, 8*). A scoured trough, 20 m deep, 2 km wide, and 20 km long, is at the base of the slope where bottom currents may be strongest. The bottom currents probably intensify during major storms, particularly in the spring and fall when the lake is isothermal and the wind-driven Keweenaw current may extend to depths exceeding 200 m (*9, 10*).

Sediment cores were recovered along two 15 km-long transects perpendicular to the shoreline and to the direction of bottom-current flow inferred from geophysical data (*7, 8*) (Fig. 1). An additional core, 37P, was recovered from the western arm of Lake Superior, outside the main study area (Fig. 1). Surface sediment samples from all cores in the study area and subsurface samples from cores 14G, 23P, and 24P, were analyzed for percentages of sand, silt, and clay by sieve and pipette techniques. The subsurface samples extended downcore to below the postglacial-glacial contact (*11*), or for the length of the core if the contact did not exist. The silt fraction (5.85 to 71.44 μm) of all subsamples plus additional subsurface samples from cores 4G, 8G, and 37P were analyzed for grain size with an Elzone electronic particle analyzer (*12, 13*), which determined the relative abundance of particles in 128 discrete increments of approximately 0.03 phi (*14*). All samples were analyzed at least in duplicate and in triplicate if the median grain size of the first two analyses was not within 0.09 phi. The average of the individual analyses was used to calculate the median grain sizes reported. The average deviation of the median grain size between duplicate analyses was 0.05 phi, which is 1.0 to 1.5 μm at this size range.

Cores 23P and 24P were dated paleomagnetically—the best technique available for dating Holocene sediments in the Great Lakes (*15–17*). The downcore profiles of the magnetic declination and inclination variations provide chronostratigraphic events for correlation between adjacent cores.

It has been shown that dominant grain size of surface samples changes from sand in the trough to clay farther offshore (*18*). The median grain size of the silt fraction for the same samples changes from 36 to 15 μm—a change attributed to regional variation in bottom-current intensity.

Downcore analyses show a noisy but significant coarsening in median grain size of the silt fraction with burial depth in five of six cores examined (Fig. 1). The exception is core 14G, which may be anomalous because of localized current eddies at this site (*18*). The increase in grain size downcore may be the result of (i) a change in lake level during postglacial times that altered bottom currents or the sediment source; (ii) a change in vegetation during the Holocene that affected sediment influx; or (iii) a decrease in bottom-current velocity through the Holocene. Fluctuations in the lake level during the Holocene apparently influenced the grain size of sediments in the lower Great Lakes (*19*). Lake level in our study area dropped about 25 m from the Lake Minong Stage about 9500 years ago to the Lake Houghton Stage about 8000 years ago (*20, 21*). Lake level has been controlled by isostatic rebound at the outlet at Sault Sainte Marie for the last 8000 years. The study area is near the isobase of isostatic rebound that passes through Sault Sainte Marie (*22*) and has not been subjected to any significant change in water depth since the Lake Houghton Stage. Strand lines of lake levels younger than Lake Houghton in the Keweenaw area are near the present lake level (*20, 23*); this supports the stable water depth for the last 8000 years. Thus a changing lake level could have caused median grain size to coarsen upward in the cores between 9500 and 8000 years ago, but would not have affected grain size in the overlying deposits, except perhaps in core 37P from outside the Keweenaw area.

Palynological studies in the Lake Superior region indicate that forestation after deglaciation occurred by 11,000 years ago and that the conifer forest remained stable in composition throughout postglacial times (*24, 25*). Vegetation density probably increased rapidly to that comparable at present; recently deglaciated areas in the Yukon Territory required only 40 years for forestation (*26*). These arguments do not rule out the possibility that sediment influx changed through the Holocene, but they lead us to the third possibility as the most plausible—that the observed change in grain size is due primarily to a gradual weakening of bottom currents. Since deep-water circulation in the Laurentian Great Lakes is ephemeral and the result of storms (*27*), the grain size distribution probably indicates that there were more frequent or intense wind events in the early Holocene than there are today. Alternatively, deep-water circulation may have been stronger because the prevailing wind direction in early Holocene times was different than that at present and more conducive to development of strong bottom currents near the Keweenaw Peninsula. Current mathematical models do not support this (*28*), but they may be incomplete.

Age assignment of the grain size profiles allows the fluctuations to be dated. Four cores from the Keweenaw area that showed postglacial-glacial contact, which is dated at 9500 years ago (*20*), are 4G, 23P, 24P, and 37P. If a constant sedimentation rate is assumed in each core from 9500 years ago to the present, then the median grain size decreases fairly rapidly upcore from the glacial-postglacial contact to the average grain size for the core at a depth corresponding to an age of 6400 to 7500 years in cores 4G, 24P, and 37P. This suggests that wind intensity over the Lake Superior region decreased more rapidly between 9500 and 6500 years ago than during the later Holocene. With the final disintegration of the Laurentide ice sheet 6500 years ago (*29*), intense atmospheric circulation associated with it would have terminated.

Paleomagnetic dating of cores 23P and 24P allows more detailed examination of their grain size profiles. Core 23P contains a sand layer at 200 cm that is interpreted as an erosional lag deposit. Visual matching of the paleomagnetic declination and inclination curves between 23P and 24P suggests that the sand layer is a missing sediment interval of about 20 cm (Fig. 2). The magnetic stratigraphies of the two cores match well when the missing interval is accounted for by shifting the profiles above 200 cm in core 23P upward by 20 cm.

The lower halves of the adjusted declination profiles correlate well with other paleomagnetic profiles for Lake Superior that have been dated by correlation to radiocarbon-dated profiles in sediments from small lakes nearby (*15, 16*). The profiles in cores 23P and 24P indicate fairly constant sedimentation rates between 5000 and 8000 years ago and show that the median grain size in core 24P dropped to the average value for the core

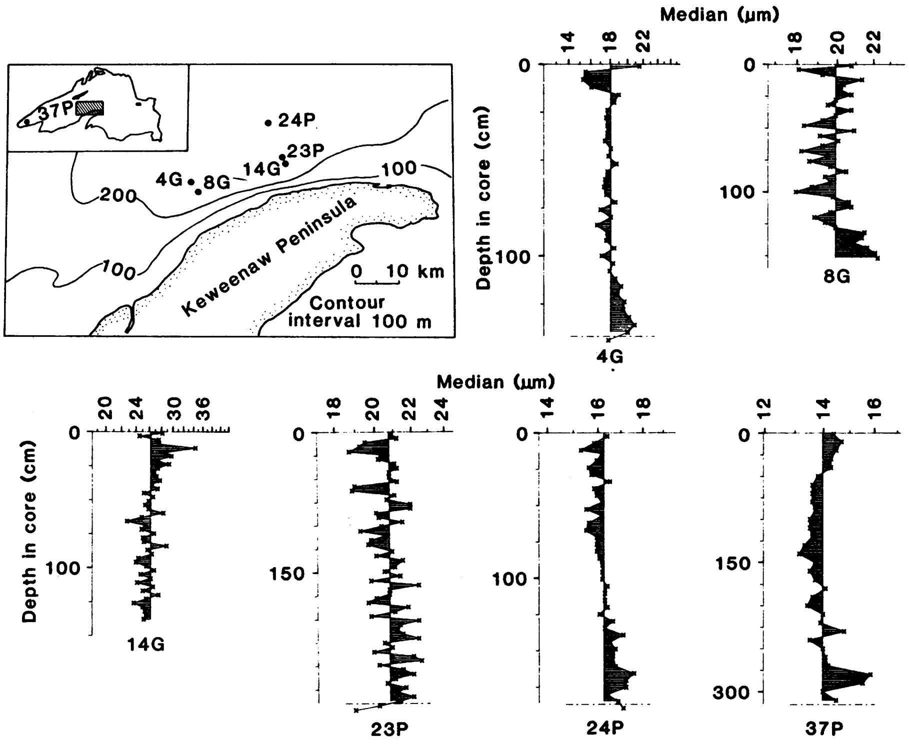

Fig. 1. Core locations and median grain size of the silt fraction plotted as a function of depth in each core. The vertical line represents the average median grain size for that core. The dashed horizontal line (4G, 23P, 24P, and 37P) represents the postglacial-glacial contact approximately 9500 years ago.

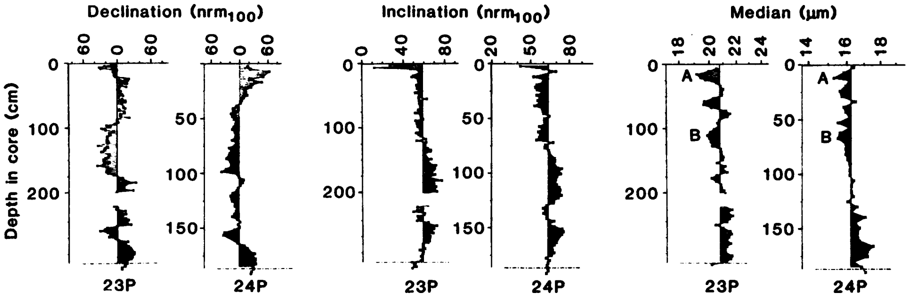

Fig. 2. The declination and inclination of the natural remanent magnetization after demagnetization at 100 Oe (nrm_{100}) and median grain size of the silt fraction for cores 23P and 24P. The vertical line represents the average value for that core. The dashed horizontal line represents the postglacial-glacial contact (*11*). The depth scale for 23P is modified to account for a hiatus at 200 cm, and the grain size profile for core 23P is a running three-point average.

about 6400 years ago. This is at least 1500 years after major changes in lake level or vegetation occurred in or near the study area.

The grain size profile of 23P is too noisy to compare with 24P (Fig. 1), perhaps because of local current eddies in the vicinity of site 23P. The profile was smoothed by plotting a running three-point average of median grain size—that is, the median grain size at each depth was changed to the average of the medians of the sample above, the one at the depth, and the one below. This profile compares roughly with the unaltered profile in core 24P (Fig. 2). No strong episodic signal emerges of grain size versus depth other than downcore coarsening. There appears to be a slight correlation of two relatively fine-grained intervals (A and B in Fig. 2). Assignment of absolute ages to the intervals on the basis of their magnetic profiles is not possible because the upper parts cannot be correlated with confidence to other dated profiles (*15*, *16*). Linear interpolation between core top and the postglacial-glacial contact date events A and B at about 500 and 3500 years ago, respectively.

In summary, the five cores from Lake Superior that show a downcore increase in the median grain size indicate that bottom-water circulation in Lake Superior was stronger between 9500 and 6500 years ago than afterward. Because the bottom currents are driven primarily by large storms, the data on grain size suggest more frequent or more intense storms in the early Holocene as the Laurentide ice sheet retreated than after its disappearance at about 6500 years ago. Grain size and paleomagnetic data for the late Holocene provide weak evidence for periods of decreased storm activity about 500 and 3500 years ago.

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Precipitation of Sulfide Ores and Organic Matter: Sulfate Reactions at Pine Point, Canada

Abstract. *Bitumen is a common associate of carbonate-hosted lead-zinc deposits. On the Pine Point lead-zinc property, Northwest Territories, Canada, there are two forms of bitumen. Unaltered bitumens have atomic hydrogen/carbon ratios of about 1.4, sulfur contents of about 7.8 percent, and sulfur isotope ratios* ($\delta^{34}S$) *of approximately +4.6 per mil. Altered bitumens occur in proximity to sulfide ore bodies and white sparry dolomite. Their hydrogen/carbon ratios are about 1.02, the sulfur contents average 22 percent, and the* $\delta^{34}S$ *values are about +12.4 per mil. These data indicate that some bitumen has participated in the thermochemical reduction of sulfate to produce hydrogen sulfide required to precipitate the ores. Mass balance considerations show that the amount and degree of alteration of bitumen is more than adequate to account for the reduced sulfur species (lead, zinc, and iron sulfides) deposited at Pine Point. These reactions may provide an important means of generating the large volumes of sulfide necessary to precipitate ore bodies in carbonate rocks.*

Lead-zinc deposits hosted by unmetamorphosed sedimentary carbonate rocks are thought to originate by normal sedimentary and diagenetic processes (*1*). Nevertheless, these deposits present many perplexing problems, including the sources of metals and sulfides, the precipitation mechanisms, and the environment and timing of precipitation (*2*). Bitumen and heavy oil are often intimately associated with the ore bodies, and it has been a continuing question whether such organic matter is involved in the formation of the sulfide (*1*, *3*).

The Pine Point lead-zinc field, Northwest Territories, Canada, is located in a Middle Devonian carbonate barrier complex (*4*). It has served as a model for the popular Jackson-Beales hypothesis of a sedimentary-diagenetic origin for carbonate-hosted lead-zinc deposits (*5*). As is common with this type of deposit, bitumen is intimately associated with the ore. Organic geochemical studies (*6*) have shown that the host rocks at Pine Point occur at the threshold of petroleum generation (60°C or less), and that the heavy oil–bitumen has originated, more or less in situ, from relatively immature organic-rich rocks in the barrier complex. Fluid inclusion data indicate that the dolomitized and mineralized zones represent thermal anomalies [up to 100°C (*7*)] with respect to the host rocks. Within these zones, heavy oils and bitumens have been altered by heat and reaction with sulfur to form an insoluble pyrobitumen (*6*). Sulfur isotopic measurements on a few bitumens have suggested that thermochemical reduction of sulfate (*8*) by bitumen was the mechanism for formation of hydrogen sulfide and the precipitation of the metals (*6*).

To further evaluate this process, we collected 50 additional samples ranging from liquid heavy oil to pyrobitumen from the Pine Point property. The bitumens were analyzed for carbon, hydrogen, nitrogen, and sulfur (*9*), and oxygen was determined by difference after cor-