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# Regional variation in modern radiocarbon ages and the hard-water effects in Lakes Michigan and Huron

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## Abstract

Eight new radiocarbon ages, all determined by accelerator mass spectrometry, on modern (pre-bomb) mollusks have been added to similar data provided from three samples in the Lake Michigan and Huron basins. These data confirm the existence of a substantial hard water effect correction ranging from about 250 years to 500 years in these lakes. They also show that the magnitude of these corrections form a spatially coherent pattern that can be related to the pattern of outcrop of Paleozoic (radioactively inert) carbonates that surround the basins and the pattern of circulation within the basins.

## Introduction

The advent of accelerator-mass-spectrometer (AMS) radiocarbon dating of carbonate material has opened the door to the use of comparatively small samples of shells (e.g. ostracodes) or inorganic precipitates in establishing a precise chronology for paleolimnologic studies. However, in studies of lake sediments investigators have been wary of such carbonate-based radiocarbon dates. This is because the bicarbonate reservoir in any lake is formed from a combination of dissolved atmospheric carbon dioxide and old carbon derived from limestone and dolomite in the rocks of the catchment basin and in the sediments of the lake basin. The radiocarbon ages of calcite formed in such natural waters may be too old by some unknown amount representing the disequilibrium between the atmosphere and the bicarbonate reservoir and depending on the relative portion of radioactively inert carbon contributing to the dissolved bicarbonate reservoir (Broecker & Walton, 1959; Benson. 1993, Mayle et al., 1993). Resulting errors in $^{14}$C dates caused by this 'hard-water effect' (HWE) can amount to many hundred years. In the Great Lakes region major changes in lake levels and other climatic events of the early Holocene may be separated by a few hundred years or less; thus, for the radiocarbon dates that help define this history and are dependent on calcite as the dated material, an accurate estimate of the HWE and its associated correction is critical.

Rea and Colman (1995) presented results that indicated the hard-water correction on three pre-bomb bivalves was substantial, ranging from –438 yrs in Lake Huron at Saginaw Bay to about –250 years in Lake Michigan. They also noted that the difference between the HWE corrections for the two lake basins is significant. This large difference in the corrections has prompted us to acquire additional samples of calcite shells from around the margins of Lakes Michigan and Huron to document the spatial variation in this correction and to elucidate the cause of the large difference in the HWE between the two basins.

## Determination of the hard water effect

In our study we have used eight mollusk shells obtained from the University of Michigan Museum of Zoology that were collected alive on known dates (Table 1) and at known locations (Figure 1). All shells were collected prior to 1944, before the addition of $^{14}$C to the atmosphere by nuclear explosions. These samples are combined with those reported by Rea and Colman (1995) to give as wide a spatial coverage as possible. To quantify the HWE in the radiocarbon ages of our samples, we obtained accelerator-mass-spectrometer

*Table 1.* Normalized radiocarbon dates from modern mollusk shells from Lake Michigan (M), Lake Huron (H), and Georgian Bay (GB)

| Sample | Location (lake) | Collection Date | $^{14}$C-AMS age | Sample ID |
|---|---|---|---|---|
| *W1-3 | Winnetka (M) | 1937 | 426 ± 52 | ‡ |
| *BI | Beaver Is. (M) | 1940 | 398 ± 60 | WHOI, OS 934 |
| G1 | Escanaba (M) | 1921 | 505 ± 40 | AA 45872 |
| NH1 | Chenaux Is. (H) | 1920 | 455 ± 40 | AA 89311 |
| NH2 | Whitney Bay (H) | 1937 | 540 ± 40 | AA 241698 |
| NH3 | Rogers City (H) | 1926 | 475 ± 40 | AA 36757 |
| *SB | Saginaw Bay (H) | 1908 | 513 ± 45 | AA 11504 |
| SH1 | Goderich (H) | 1931 | 650 ± 40 | AA 18926 |
| GB1 | Cape Croker (GB) | 1934 | 585 ± 40 | AA 18910 |
| GB2 | Sand Run Is. (GB) | 1910 | 420 ± 40 | AA 229746 |
| GB3 | East shore (GB) | 1911 | 355 ± 40 | AA 183931 |

* samples previously reported by Rea & Colman (1995).
‡ average of three measurements on the same sample (Rea & Colman, 1995).

*Table 2.* Determination of the hard water effect (HWE). HWE is the apparent age imparted to calcite of zero age because of the amount of inert carbon in the $HCO_3^-$ reservoir in the lake

| Sample | pre-1950 'true' age | normalized $^{14}$C date (BP) | inert CO2 corr'n | HWE |
|---|---|---|---|---|
| W1-3 | 14 y | 426 ± 52 y | –134 y | 278 ± 52 y |
| BI | 11 y | 398 ± 60 y | –150 y | 237 ± 60 y |
| G1 | 30 y | 505 ± 40 y | –93 y | 382 ± 40 y |
| NH1 | 31 y | 455 ± 40 y | –94 y | 330 ± 40 y |
| NH2 | 14 y | 540 ± 40 y | –134 y | 392 ± 40 y |
| NH3 | 25 y | 475 ± 40 y | –100 y | 350 ± 40 y |
| SB | 44 y | 513 ± 45 y | –31 y | 438 ± 45 y |
| SH1 | 20 y | 650 ± 40 y | –130 y | 500 ± 40 y |
| GB1 | 17 y | 585 ± 40 y | –147 y | 421 ± 40 y |
| GB2 | 41 y | 420 ± 40 y | –57 y | 322 ± 40 y |
| GB3 | 40 y | 355 ± 40 y | –57 y | 258 ± 40 y |

(AMS) ages on each of the shells from the NSF Arizona AMS Facility at the University of Arizona. All ages reported in Table 1 have been corrected ('normalized') for the fractionation of $^{14}$C during the precipitation of calcite by measuring the $\delta^{13}$C of the shell and using the relationship between the fractionation of $^{13}$C and $^{14}$C (Taylor, 1987). There remains two other errors in the radiocarbon dates on calcite that need to be applied before they can be used as an accurate estimate of calendar years before present (as measured prior to 1950). First, there is the correction needed to account for the radioactively inert carbon dioxide added to the Earth's atmosphere during the industrial revolution. This effect is responsible for a substantial offset in the measured age of relatively young material; however, extensive work on the radiocarbon content of tree rings has provided us with an ability to correct this offset (e.g., Stuiver & Quay, 1981; Stuiver & Pearson, 1993). We have used the year of sample collection and the tree-ring-derived measurements of atmospheric $\Delta^{14}$C values (averaged over three to four years of assumed shell growth; Table 1 of Stuvier & Quay, 1981) in equation 1 (below) to calculate the estimated age offset for each sample. This correction is listed in Table 2, column 4 (inert $CO_2$ correction).

$$(1)\quad \text{Age Offset} = -8033 \ln(1 + \Delta^{14}C/1000)$$

The second error we must calculate is the HWE itself. This is determined as the reported $^{14}$C date

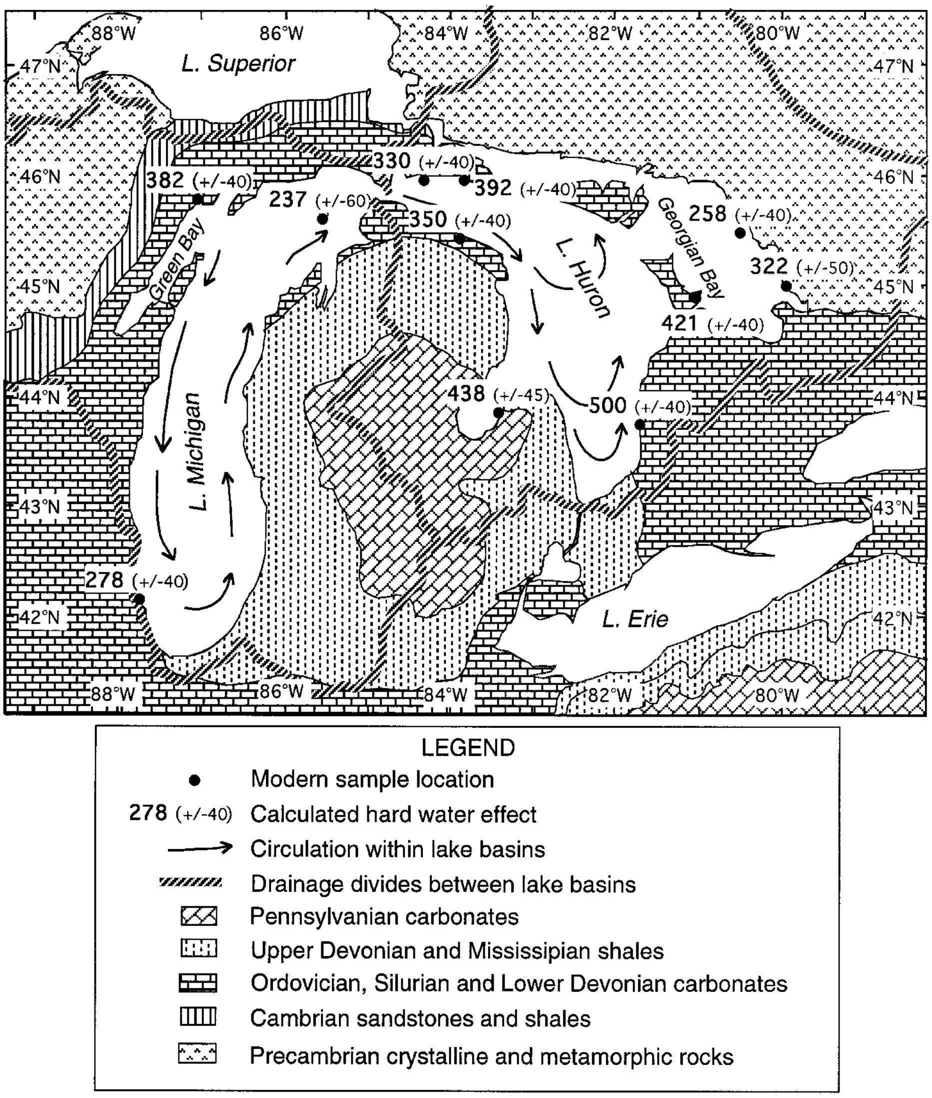

*Figure 1.* Locations of modern mollusk samples with AMS radiocarbon dates used in this study. Analytical errors are shown in parentheses (see Tables 1, 2). Outcrop and subcrop areas of Precambrian and Paleozoic rocks are indicated by patterns keyed to the legend. Map data are from Hough (1958) and from The Great Lakes, an Environmental Atlas and Resource Book (Anonymous, 1988).

(corrected for isotope fractionation effects, column 3, Table 2) less the 'true age' (column 2, Table 2) and less the inert CO$_2$correction (column 4, Table 2). The HWE correction for the data presented range from about –237 years in Lake Michigan to as much as –500 years in southern Lake Huron.

Rea and Colman (1995) suggested that much of the large difference between their two Lake Michigan and one Lake Huron estimates of the HWE was a result of Lake Huron being dominated by surrounding outcrops of Paleozoic limestone and dolomite or till with a large component of Paleozoic carbonate material. When plotted on a map of the Great Lakes, our new data compilation shows a spatial pattern that does appear to be linked to the distribution and character of outcropping rocks that surround the lakes , as suggested by Rea and Colman (1995), and to the drainage patterns into the lakes (Figure 1). The circulation pattern of waters within the lakes also appears to have some effect on the spatial patterns of HWE corrections.

The total runoff into Lake Michigan is about 67% of the water received through direct precipitation (Anonymous, 1988). Thus the amount of water coming into the lake that is fully equilibrated with the atmosphere is one third greater than the amount of water received from streams and may contain a substantial portion of radioactively inert bicarbonate. The two Lake Michigan samples reported by Rea and Colman (1995) are within the main body of Lake Michigan. The errors of the radiocarbon ages and in the resulting estimate of the HWE correction overlap (Tables 1, 2). Averaging the HWE for these two samples results in an estimate for the HWE correction of –257 ± 56 years (Rea & Colman, 1995). However, a sample taken from the northern reaches of Green Bay (which feeds into Lake Michigan) has a significantly older HWE correction of –382 ± 40 yrs. Streams near this sample location drain regions of Michigan's upper peninsula that are dominated by Silurian and Ordovician limestones and dolomites, and thus might be expected to supply waters relatively rich in dissolved, radioactively inert bicarbonate (Figure 1). These carbonate rocks extend down most of the western coast of Green Bay and Lake Michigan; however the width of the outcrop area is comparatively narrow and the western drainage area feeding into Lake Michigan narrows markedly south of about 44° N latitude (Figure 1). Along the eastern shores of Lake Michigan, the area of drainage from the lower peninsula of Michigan is dominated by Upper Devonian and Mississipian shales and sandstones.

Waters within Lake Michigan circulate in a counter-clockwise direction, feed into Lake Huron through the Straits of Mackinac, and then move along its western shore. The narrow straits prevent a great deal of mixing between the two lake basins and net flow is from Lake Michigan into Lake Huron at an average rate approximately equal to the rate of precipitation over the lakes ($1.5 \times 10^3$ $m^3$/sec; Anonymous, 1988). Lower Devonian carbonates ring the southern shore at the northern-most end of Lake Michigan and extend around into Lake Huron. The Silurian and Ordovician limestones and dolomites of the northern shore, the upper peninsula of Michigan, continue around the northern and northeastern shores of Lake Huron and separate the Huron basins from North Channel and Georgian Bay. Samples from this northern region of Lake Huron have HWE corrections ranging from about –330 years to –392 years, with the samples closer to the Straits of Mackinac and on the southwestern shore having slightly lower values (Figure 1).

Runoff rate into Lake Huron is about equal to the rate water is received by direct precipitation and 30–40% larger than the amount of runoff received by Lake Michigan (Anonymous, 1988); thus the impact of runoff on the composition of Lake Huron waters is larger than that of Lake Michigan. Waters within Lake Huron also circulate in a generally counter-clockwise direction. Waters passing through the Straits of Mackinac mix with the waters of the Huron basin and reach southward toward Saginaw Bay and the drainage from a region of Pennsylvanian carbonates. Circulation then returns along the eastern shore of Lake Huron with its Silurian, Ordovician, and lower Devonian carbonates. HWE corrections in the southern part of Lake Huron reach –400 to –500 years (Figure 1). These are the largest HWE corrections found in the Huron and Michigan basins.

On the return limb of its counter-clockwise gyres, Lake Huron waters feed into Georgian Bay. Here there is a very clear dependence of the HWE correction on the source area of waters coming into the bay. Along the western shore of Georgian Bay the Silurian carbonates of the Niagaran Series outcrop and the HWE correction is greater than –400 years. A scant 100 km away in the southeastern corner of the bay, near the boundary between the outcropping Paleozoic carbonates and the Precambrian crystalline basement, the HWE has fallen to –322 years. Farther up the eastern shore of Georgian Bay, in the heart of the drainage from the Precambrian outcrop region, the HWE correction falls to levels comparable to those found in Lake Michigan.

## Discussion

These data support the suggestion made by Rea and Colman (1995) that the large differences in the HWE corrections between Lakes Michigan and Huron derive mainly from the differences in the amount of radioactively inert bicarbonate ions supplied to the waters of the lake basins from Paleozoic carbonate terranes. The additional dates provided by this study reveal that there is a strong local control on differences in the HWE related to the lithology of the region being drained. They also indicate that in large lake basins there may be another, secondary control exerted on the spatial pattern of the measured HWE by water circulation patterns within the basins.

It is not certain how the very substantial HWE corrections measured in southern Lake Huron might impact HWE corrections in basins downstream. Does transport and mixing through the relatively narrow channels and basins promote the equilibration of the bicarbonate ions with the atmosphere, or does the addition of more radioactively-inert bicarbonate from catchments draining into Lakes Erie and Ontario further increase the magnitude of the HWE? Based on the comparison of HWE values in Lakes Michigan and Huron, it seems likely that the HWE corrections for Lakes Erie and Ontario may be even higher than those found in southern Lake Huron.

We cannot assume that the HWE corrections for the Great Lakes basins have remained constant with time and blindly apply the HWE corrections provided here to mid and early Holocene samples. This is especially true for those times when the Laurentian ice sheet was providing huge amounts of melt waters draining from the Paleozoic carbonate terranes of Canada into glacial Lake Agassiz and the Superior and Huron basins. In fact, carbonate dates from the Lake Huron basin reported in Rea et al. (1994a, Figure 13) suggest that the HWE correction for carbonate shells deposited during the later part of the middle Stanley lowstand (8500 to 9000 radiocarbon years BP) may amount to as much as –2000 years. For intervals younger than about 10,000 radiocarbon years BP, Lake Michigan does not appear to have received any substantial direct inflow of melt waters (Lewis & Anderson, 1989; Colman et al., 1994; Rea et al., 1994b); and thus, the HWE correction established here may provide a good estimate of the correct value for the mid to late Holocene of the Lake Michigan basin. However, it is always helpful to compare carbonate dates that have been ‘corrected’ for the HWE with dates based on organic carbon derived from identifiable plant material. We suggest that all paleolimnologists relying on radiocarbon dates on calcite from the lower to mid Holocene in other Great Lakes basins expand the data set presented here and to include, where possible, comparisons with dates based on identifiable organic material. For studies in other lake basins, paleolimnologists should repeat this experiment with at least two modern (pre-bomb) samples.

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## References

Anonymous, 1988. The Great Lakes, An Environmental Atlas and Resource Book. U.S. Environmental Protection Agency and Environment Canada, Chicago, 44 pp.

Benson, L., 1993. Factors affecting $^{14}$C ages of lacustrine carbonates: Timing of the last highstand in the Lahontan Basin. Quat. Res. 39: 163–174.

Colman, S. M., L. D. Keigwin & R. M. Forester, 1994. Two episodes of meltwater influx from gkacial Lake Agassiz intoi Lake Michigan and their climatic contrasts. Geology, 22: 547–550.

Hough, J. L., 1958. Geology of the Great Lakes. Univ. of Illinois Press, Urbana, 313 pp.

Broeker, W. S. & A. F. Walton, 1959. The geochemistry of $^{14}$C in freshwater systems. Geochem. Cosmochem Acta 16: 15–38.

Lewis, C. F. M. & T. W. Anderson, 1989. Oscillations if levels and cool phases of the Laurentian Great Lakes caused by inflows from glacial Lakes Agassiz and Barlow-Objibway. J. Paleolim. 2: 99–146.

Mayle, F. E., A. J. Lavesque & L. C. Cwynar, 1993. Accelerator-mass-spectrometer ages for the Younger Dryas event in Atlantic Canada. Quat. Res. 39: 355–360.

Rea, D. K. & S. M. Colman, 1995. Radiocarbon ages of pre-bomb clams and the hard-water effect in Lakes Michigan and Huron. J. Paleolimnol. 14: 89–91.

Rea, D. K., T. C. Moore, Jr., C. F. M. Lewis, L. A. Mayer, D. L. Dettman, A. J. Smith & D. M. Dobson, 1994a. Stratigraphy and paleolimnologic record of lower Holocene sediments in northern Lake Huron and Georgian Bay, Canadian Journal of Earth Sciences, 31: 1586–1605.

Rea, D. K., T. C. Moore, Jr., T. W. Anderson, C. F. M. Lewis, D. M. Dobson, D. L. Dettman, A. J. Smith & L. A. Mayer, 1994b. Great Lakes paleohydrology: Complex interplay of glacial meltwater, lake levels, and sill depths, Geology, 22: 1059–1062.

Stuiver, M. & C. W. Pearson, 1993. High precision bidecadal calibration of the radiocarbon time scale, AD 1950 –500 BC, and 2500–6000 BC. Radiocarbon, 35: 1–23.

Stuiver, M. & P. D. Quay, 1981. Atmospheric $^{14}$C changes resulting from fossil fuel $CO_2$ release and cosmic ray flux variability. Earth Plan. Sci. Letters, 53: 349–362.

Taylor, R. E., 1987. Radiocarbon dating: An Archeological Perspective. Academic Press. Orlando.