PROCEEDINGS OF THE TWENTY-SIXTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

April 2013
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Dr. Robert J. Varga, Editor
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Pomona College

Dr. Jade Star Lackey
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Pomona College

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Keck Geology Consortium Administrative Assistant

Christina Kelly
Symposium Proceedings Layout & Design
Office of Communication & Marketing
Scripps College

Keck Geology Consortium
Geology Department, Pomona College
185 E. 6th St., Claremont, CA 91711
(909) 607-0651, keckgeology@pomona.edu, keckgeology.org

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Robert J. Varga
Editor and Keck Director
Pomona College

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Pomona College
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91711

Christina Kelly
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LAURA HAYNES, Pomona College
Research Advisor: Dr. Robert Gaines

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ALYSSA DONOVAN, Amherst College
Research Advisor: Anna Martini

Keck Geology Consortium
Pomona College
185 E. 6th St., Claremont, CA 91711
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LATE HOLOCENE CLIMATE VARIABILITY FROM LOUGH CARRA, COUNTY MAYO, WESTERN IRELAND

LAURA HAYNES, Pomona College
Research Advisor: Dr. Robert Gaines

29INTRODUCTION

Linkages between high and lower-latitude terrestrial systems drive climatic variability throughout the Holocene. Rapid high-latitude shifts are evident in Ireland and the British Isles (Watson et al. 2010; van Asch et al. 2012). The records from these systems are often sparse, but sediment records from carbonate lakes within these regions allow high-resolution investigation of paleoclimate throughout the Holocene (e.g. Diefendorf et al. 2006; Watson et al. 2010).

The geochemistry of carbonate marl sediments is often touted as containing many excellent and high-resolution proxies for climate and environmental change throughout terrestrial ecosystems (Oviatt 1997). In particular, stable oxygen and carbon isotopes have been widely interpreted to represent changes in temperature and lake water isotopic composition in many lacustrine records (e.g. Diefendorf et al. 2006). The carbonate producing lake of Lough Carra, Western Ireland is an excellent source of these records due to its proximity to oceanic precipitation sources and apparently continuous accumulation of carbonate and organic-rich sediments throughout the Holocene. Sedimentation of carbonates in the lake system is primarily driven by the supersaturation of carbonate in lake waters due to input from dissolution of surrounding bedrock and photosynthesis-driven alkalinity (Dean 1983). Following the retreat of continental glaciers at 10500 cal BP, sediments began to accumulate in the Lough Carra basin (Mitchell 1981), recording annual changes in primary productivity, temperatures, and nutrient input to the lake system (Hobbs et al. 2005).

Previous studies of Lough Carra have yielded paleoclimate and paleoenvironmental records from shallow gravity cores, but a comprehensive long-term climate record has not been constructed to date. To this end, the Keck Ireland team collected a continuous 8-meter core from a deep section of the Twin Islands (southern) lake basin during the summer of 2012. This study seeks to quantify the nature of sedimentation and the Holocene paleoclimate record from one of the deepest sections of Lough Carra. Stable oxygen and carbon isotope ratios, sedimentary geochemical analyses, and radiocarbon dating methods were utilized in order to evaluate long-term variability in paleotemperature, paleoproductivity, and sedimentation rates from the Lough Carra basin.

METHODS

Core Collection and Processing

During the summer of 2012, the Keck Ireland group collected eight continuous 1-meter core sections from a deep region of the Twin Island southern basin using a modified Livingston core device. At 8m depth, a boundary layer was hit-likely a clay layer-and coring could not continue. Cores were extruded, split, and photographed at the National University of Ireland-Galway core processing facility. Following description and digital documentation, small samples were extracted at 14 cm resolution for stable oxygen and carbon isotopes and trace and heavy metal concentrations. Cores were then sub-sampled at 1cm resolution and packaged into heat-sealed bags and shipped back to the laboratory. Bulk densities of core samples were measured at every 30cm interval by dividing dry sediment weights over wet sediment volumes.

Oxygen and Carbon Isotope Analyses

Bulk sediment samples were sent to the University of Massachusetts-Amherst for stable oxygen and carbon isotope analyses. Analyses were made on a Thermo-Finnigan MAT mass spectrometer with a front end Kiel device. Oxygen isotope values were recorded with respect to VPDB and were converted into temperature values using the carbonate-water fractionation equation of Kim & O'Neil (1997):

$$1000\ln\alpha=18.03*(1000T^{-1}) -32.42$$
(Equation 1)

Sediment Geochemistry and Structures

Core samples were dried, homogenized and analyzed for carbon, hydrogen, nitrogen, and sulfur elemental analysis and loss on ignition (Heiri et al. 2001) to determine total wt % carbon and wt % organic carbon. Samples were also analyzed using X-ray diffraction in order to gain a first-order understanding of representative mineralogy. Digital images were stitched and compiled to create a long-core digital record, and from these images laminations and structural sedimentary patterns were analyzed and counted to a first order.

Radiocarbon Dating and Sedimentation Rates

Two macro-organics and six *Bithynia tentaculata* (gastropod) specimens were analyzed using AMS dating for radiocarbon age measurements. Samples were washed with de-ionized water and then sent to Accium Biosciences, Seattle, USA for etching and analysis. Dated samples were then calibrated for age using the CALIB 6.0 freeware program and compared to linear sedimentation rates (LSR) and mass accumulation rates (MAR):

LSR: cm accumulated/calendar years
(Equation 2)

MAR: LSR * Bulk Density
(Equation 3)

RESULTS

Sedimentary Structures and Stratigraphy

The LC20 core exhibits fine lamination structures throughout beginning at ~1.3 m (Fig. 1; Fig. 3). These laminations decrease in thickness down-core, and show varying thicknesses periodicities, color distinctions, and effects of bioturbation throughout the core (Fig. 1; Fig. 3). However, the two main sedimentary facies are lightly colored tan-white layers (carbonate-rich) and darker brown-black layers (organic-rich). In general, lighter laminations appear to be thicker than darker ones, with a graying gradient often between the two. Four general facies association types were identified that are present at different intervals throughout the core: 1) 5-7 cm of regularly alternating, equal-width ~0.25 cm dark and light laminations, 2) Non-patterned light and dark laminations with variation in lamination width, 3) Weakly defined lamination structures with a subtle light-dark alteration, and 4) bioturbated sequences (Fig. 1). Laminations become generally fainter, lamination thickness decreases and bulk density increases down-core, likely indicating compaction. Soft sediment deformation is also common in down-core sections.

Layer Counting, Radiocarbon Dates and Sedimentation Rates

Radiocarbon dates were measured from 2 macro-organics and 6 *Bithynia tentaculata* gastropods. Only one terrestrial organic sample was recovered (Leaf, 154cm) and could thus be used to estimate the local reservoir effect of Lough Carra.

Depth	Type	14C Age	1 σ Error	Age range 1	Corrected Age	Probability
70	b. tentaculata	modern	n/a	1950 or older	1950 or older	n/a
113	b. tentaculata	modern	n/a	modern	modern	n/a
154	Leaf	103	21	1840	1840*	0.716
154	b. tentaculata	1057	25	990	1840	0.882
277	Reed	196	23	1773	1773*	0.575
277	b. tentaculata	3057	27	-1340	-490	0.386
392	b. tentaculata	1113	28	936	1786	0.998
505	b. tentaculata	1395	28	643	1493*	1

Table 1. Radiocarbon Age Estimates and Corrections for LC20.

**Ages used for sedimentation rate determination*
+See equation 2
×See equation 3

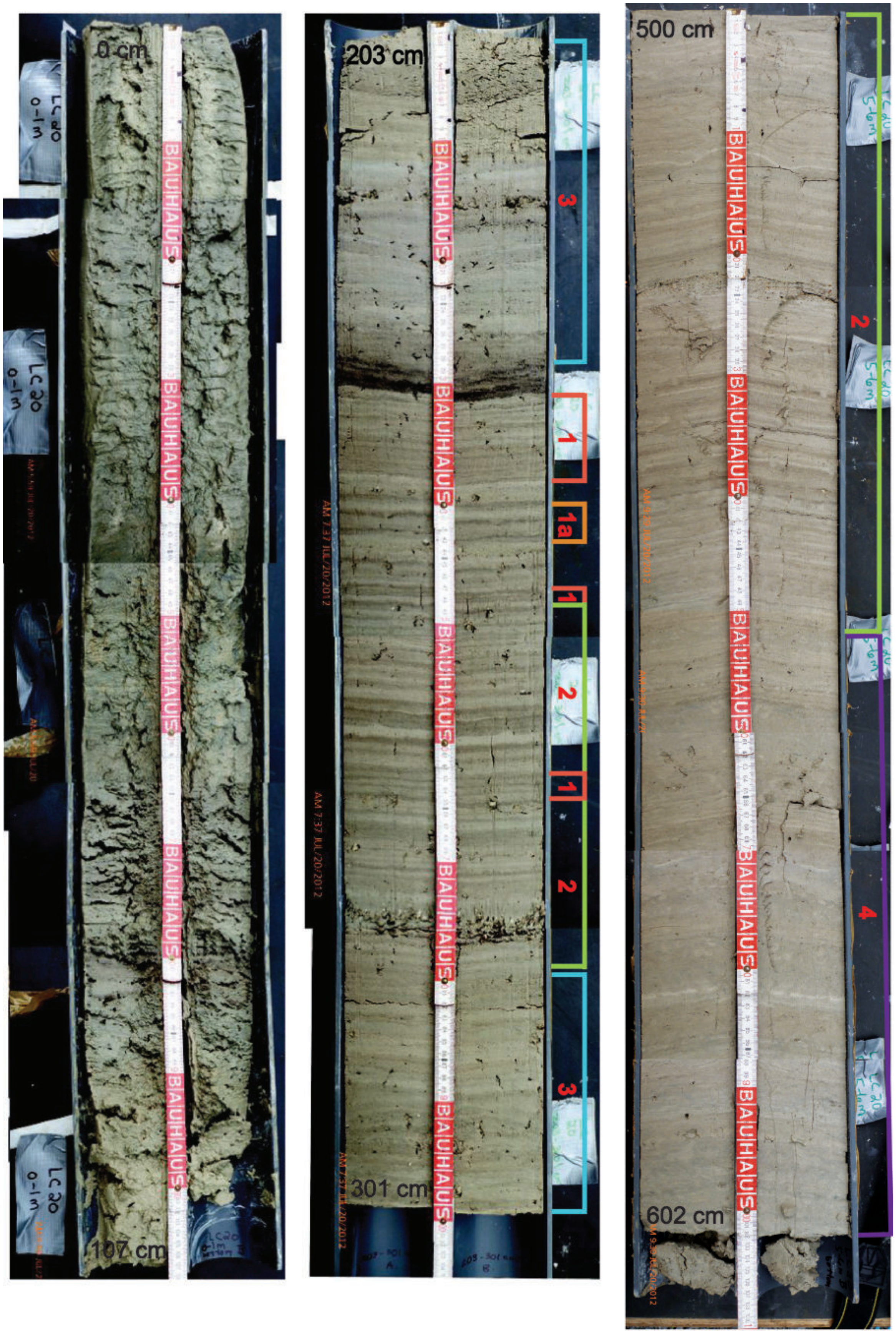

Figure 1. LC20 annotated and enhanced contrast images of core sections. Meters 1, 2 and 5 are shown with labeled representative lithologies. Meter 1 shows no lamination structures, which occur at 130 cm in Meter 2. In Meter 2, sections labeled 1, 2, 3, and 4 represent the noted lithologies above. Section 1a shows equally-sized alternating light and dark laminations at a larger thickness.

The difference between the ages of the terrestrial leaf and gastropod samples at 154 cm (850 calendar years) was calculated and subtracted from subsequent gastropod ages. This is lower than the estimated hard water effect measured by Diefendorf et al. (2006) of 1575 yrs, but is reasonable given the continuous input of carboniferous-aged bicarbonate ions into Lough Carra (Dole 2004). Though the hard water effect may change over time, only one comparison was available for hard water correction. It is also likely that the age of the measured reed at 277 cm is affected by the hard water effect given the appearance of a younger corrected age 115 years later. Thus, the corrected radiocarbon age at 159 (392 cm) may in fact be more robust. However, the accumulation of 238 cm of sediment in 115 calendar years would imply a sedimentation rate of 2.069 cm/year. Given the thinning of presumably annual laminations during this core segment, this rapid sedimentation rate is thus unlikely.

Layer counting was determined from five sections in which laminations were more easily distinguishable. Down-core counts are likely a lower estimate given increasing compaction and lower visibility of laminations. Counts from 200-300 cm (95 lams.), 305-393 cm (71 lams.), 516-567 cm (45 lams.), and 749-778 cm (39 lams.) yield MARs of respectively 0.646 $g/cm^2/yr$, 0.836 $g/cm^2/yr$, 0.667 $g/cm^2/yr$, and 0.540 $g/cm^2/yr$.

Total CHNS Measurements and Loss on Ignition Analyses

Carbon, Hydrogen, Nitrogen, and Sulfur wt% measurements were made using the varioCUBE Elemental Analyzer at Pomona College (Fig. 2). Carbon values stayed relatively constant and between 12.74 and 14.83 %. Values over 12% C indicate the abundance of organic matter within the sediment, as the mass ratio of Carbon in $CaCO_3$ is 12/100. A large spike in C, H, N and S at 233 reflects the dark, organic rich layer visible in figure 1. Total wt. % Carbon also generally increases in the upper 2 m of the core, which is synchronous with increasing $\delta^{13}C$ values. LOI analyses were only performed on 8 core samples at this time. Samples ranging from 14-770 cm were analyzed, and organic carbon values ranged from 43.1-45.9 %. Wt. % organic carbon values increase down-core and reach a maximum value at 770 cm.

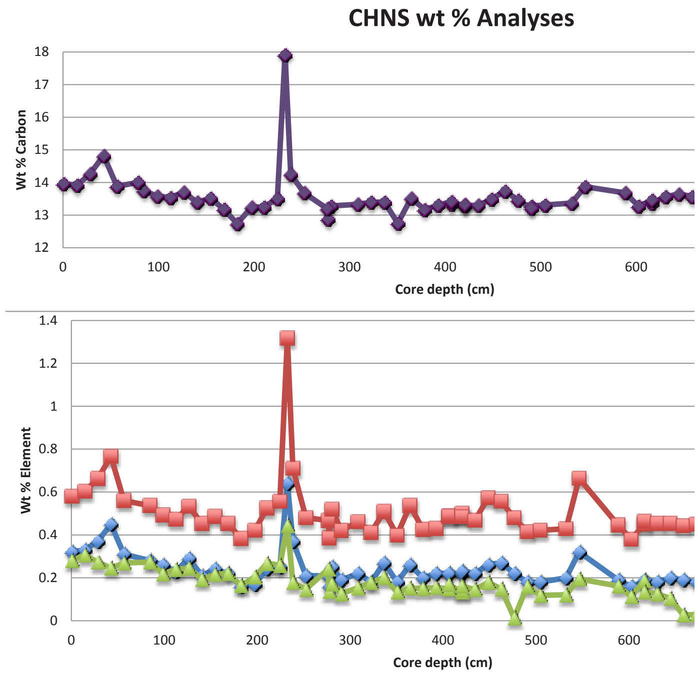

Figure 2. Carbon, Hydrogen, Nitrogen and Sulfur elemental analyses of marl samples.

Oxygen and Carbon Isotopes

~45 oxygen and carbon isotope measurements were determined at 14cm resolution along the core. $\delta^{18}O$ values varied between -4.2 and -5.2 ‰ VPDB and had a standard deviation of 0.1967 ‰. Oxygen isotope values generally increase down-core. Carbon isotope values plot between -1.96 and -5.04 ‰ and decrease steadily from 200 to 0 cm depth. The standard deviation of $\delta^{13}C$ measurements is 1.015, a reflection of the steady increase in values from 0 to 200 cm depth.

DISCUSSION

LC20 Age Model and Sedimentation Rates

Based on radiocarbon dating of macro-organics and layer counting of laminations, sedimentation at in the Twin Islands basin is likely much more rapid than anticipated. Previous studies of sedimentation from short cores in Lough Carra have yielded sedimentation rates of 0.247 cm/year, 0.842 cm/year, and 0.269 cm/year (Dole 2004). O'Reilly et al. (2011) estimate MARs in Lough Carra using ^{210}Pb data as 0.137-0.148 $g/cm^2/yr$. Given these estimates, it is clear that the 8-meter core from LC20 represents a much shorter but higher-resolution late Holocene record. Some parameter of the lake system, such as enhanced primary productivity in this region, may stimulate rapid and seasonally cyclical sedimentation. LOI analyses from eight samples show organic carbon values between 43.1-45.9%, indicating a higher input of organic matter than previously anticipated. Increased levels of primary productivity could be due to an increased nutrient flux from nearby springs or riverine inputs. Thus, detailed investigations of the nature of nutrient levels within the lake must proceed in order to understand the heightened sedimentation rates at the LC20 site.

Based on layer counting of sediments during dated intervals, we propose an annual lamination model for this high-resolution record. During summer periods of warm water conditions and high levels of primary productivity, carbonate-rich sediments accumulate, and during cold, winter months, organic-rich layers are deposited. The appearance of thin, organic-rich layers followed by thick carbonate layers indicates high levels of sediment productivity during warm summer months at Lough Carra. MARs from radiocarbon dating from 154-277 and layer counting from 200-300 cm also roughly agree (.638 and .646, respectively), supporting an annual depositional model. MSRs from layer counting decrease down-core, which may be an artifact of decreased lamination visibility and an under-estimation of total years represented in these sequences.

In the top 130 meters of the core, laminations are not widely present and broad zones of light and dark color of 3-10 cm are common (Fig. 1). However, beginning at 135 cm, laminations are present and are .5-1 cm thick. Given this relatively abrupt transition to lamination sizes representative throughout the next 2-3 meters of the core, and given that reed segments are only slightly compacted, depositional patterns may have changed in nature throughout the topmost 1.3 meters of core. Increased primary productivity due to eutrophication may have also increased carbonate genesis during recent periods.

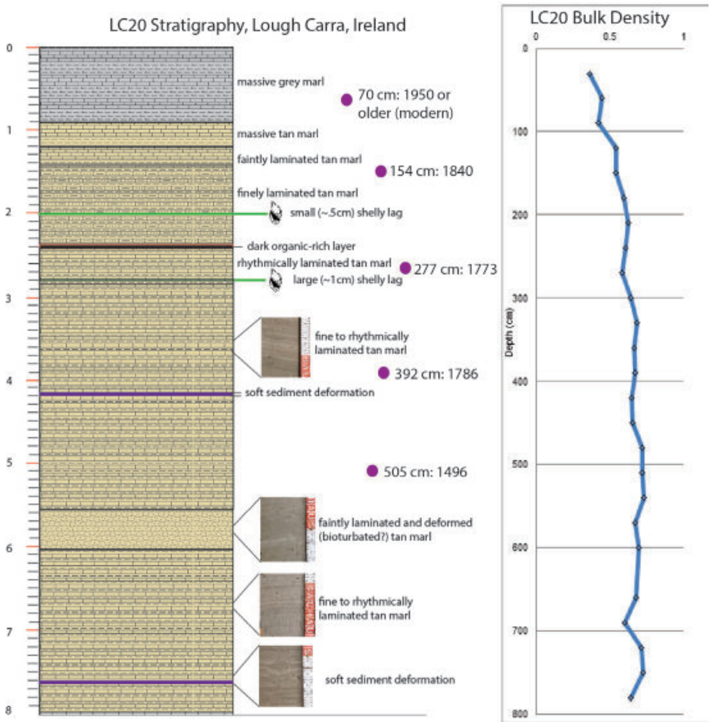

Figure 3. LC20 stratigraphy and bulk density.

Stable Isotopes and Paleotemperature Record

Based on the Kim & O'Neil (1997) calcite-water fractionation equation, paleotemperatures varied between 11.06 and 15.87 °C with a standard deviation of .92 degrees. Given that our record likely does not span beyond the past 1,000 years, and given that the 1-cm homogenized samples likely represent one or more averaged years of temperature variability, a >4 °C change in temperature is unlikely. Thus, other hydrological effects likely play a role in determining oxygen isotope values in Lough Carra, such as changes in the Circumpolar Vortex or the North Atlantic oscillation, most prominently at decadal scales (Diefendorf et al. 2006). Oxygen isotope data show less variability than those found by Diefendorf et al. (2006) from a longer record of Lough Inchiquin.

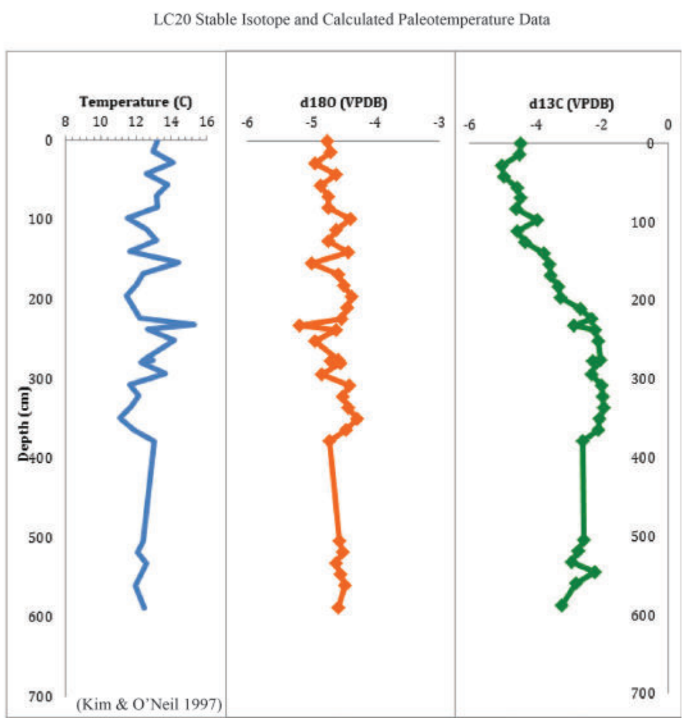

Figure 4: LC20 Stable Isotope and Paleotemperature analyses. Paleotemperature data were determined using the calcite-water fractionation equation by Kim & O'Neil (1997). Note the depletion of $\delta^{13}C$ values up-core.

The general decrease in $\delta^{13}C$ measurements starting at 200 cm depth may reflect the general depletion of heavy carbon isotopes from the anthropogenic burning of fossil fuels known as the Seuss effect. This lightening trend is observed in other LC short cores at a depth of 30 cm, further indicating heightened sedimentation rates within this deep section of the basin. Though methanogenesis in pore spaces may alter $\delta^{13}C$ values as well, our observations are more consistent with increased atmospheric pCO_2 and thus increased DIC levels in Lough Carra lake waters.

CONCLUSION

The 8-meter core from the deep section of the Twin Islands basin of Lough Carra records a much shorter and high-resolution record than anticipated. Laminations appear at ~130 cm depth and continue throughout the core. Layer counting and radiocarbon age measurements indicate a variable sedimentation rate throughout the core, but mass accumulation rates vary between 0.54-0.86 g/cm^2/year, which is much higher than previously documented in short cores from Lough Carra (O'Reilly 2011). This enhanced sedimentation rate may be due to increased nutrient flux in the deep basin from river inputs or deep springs. Oxygen isotope data show an estimated paleotemperature variability of > 4 °C, likely indicating the influence of hydrological variability on lakewater oxygen isotope values. Increasing $\delta^{13}C$ values down-core likely reflect the input of anthropogenic CO_2 into the atmosphere during the last 150 years. Future work should focus on fine-scale lamination and stable isotope analyses of the 8-m core, which may illuminate annual and even seasonal climate variability.

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