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

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Research Advisor: Anna Martini

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ANNA M. MARTINI, Amherst College
TIMOTHY C.W. KU, Wesleyan University

INTRODUCTION

Carbonate sediments from lacustrine environments have provided long term records of climate and land-use changes through the use of geochemical and biological proxies such as stable isotopic data, trace metal concentrations, faunal assemblages and pollen analyses. More specifically, the oxygen isotope composition of carbonate minerals precipitated via biological mediation is assumed to be in near isotopic equilibrium with δ^{18}O of lake water and the δ^{13}C of the DIC pool (Drummond et al., 1995). In lakes with good drainage (~relatively short residence times) the δ^{18}O marl values reflect the isotopic composition of the meteoric precipitation, which is directly related to mean annual temperature (Dansgaard, 1964). The marl δ^{13}C values reflect lake water $\delta^{13}C_{DIC}$ values, which, in turn, are controlled by lake productivity, inflowing water $\delta^{13}C_{DIC}$ values, and exchange with the atmosphere $\delta^{13}C_{CO2}$ (Leng et al. 2004). Sediment concentrations of Hg, Pb, Cu, Cr, and Zn record anthropogenic activities and preserved invertebrate and pollen assemblages reveal vegetation and water quality changes (King and Champ, 2000; Donohue et al., 2010). Phosphate concentration also record anthropogenic activity in the watershed, and increasing concentrations are a good signal of eutrophication. Overall, carbonate lake deposits can provide excellent long-term paleoenvironmental records, but careful interpretations of these proxies is necessary since post-depositional processes may significantly alter the signal (e.g. Andrews et al, 2004).

Lough Carra provides an excellent opportunity to examine long-term climatic (Holmes et al., 2010) and land use changes (Donohue et al., 2010) in an area with an extensive history of human inhabitation. Sediment ages from surrounding peat and lakes have been determined by pollen assemblages, ^{14}C-dated stratigraphies, known tephra layers derived from Icelandic ash falls, and by traditional ^{210}Pb, ^{14}C, and U-Th dating techniques on organic matter, carbonates, or bulk sediment (O'Connell et al., 1987; Swindles et al., 2011). Previous efforts to date sediments by ^{210}Pb from the shallow areas of lake were unsuccessful due to likely reworking of sediment though O'Reilly et al. (2011) was successful in obtaining sedimentation rates in Lough Carra's deeper basins (Keck 2003 Symposium). At this stage, preliminary dates are based on bulk density profiles, counting of laminations, and ^{14}C dates from plant and carbonate shells.

RESEARCH OBJECTIVES AND METHODOLOGY

Lough Carra is a shallow marl lake in County Mayo, Western Ireland, situated on Carboniferous limestone bedrock (Fig. 1). Its watershed encompasses ~104 km^2 and is underlain nearly entirely by the same Carboniferous Limestone bedrock with variable amounts of glacial till on top. It is fed by two principle rivers, the River Paltry and the River Annies, and drains into Lough Mask, to the south. Land use in the low-relief terrain surrounding the lake is predominantly grass production and sheep and cattle farming (King and Champ 2000).

The 2012 Keck field team included 2 professors, 3 Keck students as well as 2 undergraduate research assistants from Amherst College and 1 from Wesleyan University funded by university support. Water column measurements and water samples were collected from all sites. Short cores were collected using a gravity-

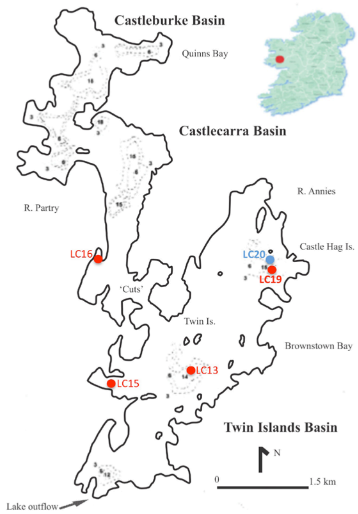

Figure 1: Lough Carra and sampling locations. Three gravity cores (LC 13,15 19) were taken in deeper water basins. One core (LC 16) was taken in shallow water (<1m) via push-core. LC 20 was extracted using a Usinger piston-corer and platform set-up in 8 meters of water. Inset shows location of Lough Carra in Ireland.

coring device from various deep-water sites across the lake. These below wave base sites are far more likely to record annual changes within the basin. During the previous Keck project to Lough Carra in 2003, only push cores from shallow sites were possible to collect. These have a distinct disadvantage as the fine-grained marl is easily resuspended in "white out" events throughout the year. We did collect a repeat core from one of these locations on this trip for comparison (LC 16).

Figure 2: a) Gravity core sampling on Lough Carra, b) Large Usinger piston coring platform, and c) Laminated sediments from core LC 20.

RESEARCH QUESTION AND APPROACH

For the Keck 2012 study group the 3 principle research objectives became the three student projects. The first, examining early diagenesis, grew from the previous sample trip-namely a shallow push core where $\delta^{13}C_{CaCO3}$ values consistently increased from -0.9‰ at the surface to +1.3‰ at a depth of 1.86m (Huang, 2003). The $\delta^{13}C$ value of autochthonous lacustrine carbonate reflects the carbon isotopic composition of dissolved inorganic carbon (DIC), which is controlled by three primary processes: input C sources, atmosphere exchange, and primary productivity. In many lakes, primary productivity largely determines the sedimentary $\delta^{13}C_{CaCO3}$ values because photosynthesis by aquatic plants preferentially removes ^{12}C from the DIC pool; thus, high primary productivity rates result in more positive $\delta^{13}C_{CaCO3}$ values (e.g. Leng and Marshall, 2004). If the nearly 2 meters of sediment only represents the past 100+ years, the changing atmospheric $\delta^{13}C_{CO2}$ due to the burning of fossil fuels may account for much of this isotopic shift. This would imply, however, very high sedimentation rates, as well as less reworking of the sediment at this shallow site than we had suspected. That the continuous increasing $\delta^{13}C_{CaCO3}$ trend with depth is present despite significant sediment reworking suggests a rapid diagenetic process if primary productivity or the lake $\delta^{13}C_{DIC}$ has not shifted over time. In the study by Diefendorf and others (2008; results from Keck 2002 project) the $\delta^{3}C_{CaCO3}$, $\delta^{13}C_{org}$, and $\delta^{13}C$ record from nearby Lough Inchiquin was examined. Here the interpretation found large (>10‰) positive down core changes in both $\delta^{13}C_{CaCO3}$ and $\delta^{13}C_{org}$ from 16.8 to 8.5 kyr B.P. The authors interpreted this trend as resulting from changing input carbon sources as the regional landscape transitioned from barren limestone just after glaciation to a forested ecosystem. The same cannot be true for Lough Carra, as the sediments are much younger (upper parts contained ^{210}Pb and rough extrapolation of deep water sedimentation rates would give an age of ~1500 years at 1.8m depth), and landscape vegetation has not changed *as dramatically* over this time period. While variations in primary productivity may cause the shift in $\delta^{13}C_{CaCO3}$, diagenetic processes linked to microbial metabolisms (both sulfate reduction and methanogenesis) leading to rapid carbonate recrystallization (dissolution – precipitation) may also be important. To examine this possibility, pore water samples were collected for methane and DIC $\delta^{13}C$ values and the role of diagenesis in determining $\delta^{13}C_{CaCO3}$, $\delta^{13}C_{org}$, and $\delta^{13}C$ values was examined by Sarah Shackleton of Wesleyan University.

The second objective was to see if the Lough Carra marl recorded the land use changes and airborne anthropogenic pollution over the last few hundred years. For the most recent (~25 years) we will be examining the rate of nutrient loading to the lake, and projecting these changes into the future. Like many shallow marl lakes, Lough Carra is extremely susceptible to eutrophication, mainly in the form of nitrates and phosphates entering the catchment via agriculture and cattle ranching (King and Champ, 2000). Over the course of 30 years surveillance, the lake has gone from oligotrophic to mesotrophic classification (Donohue et al., 2010). To study the cultural eutrophication and wider anthropogenic effects in Lough Carra, Alyssa Donovan of Amherst College, measured sedimentary Hg, phosphorus pools, and carbonate associated metals.

The third objective was to examine the long-term paleoclimate and paleoproductivity record of Lough Carra. In 2012, we obtained an 8 meter sediment core containing well-preserved laminations (Fig. 2b). Laura Haynes of Pomona College examined the sedimentology, age-depth model (^{14}C), sediment chemistry (CHNS), $\delta^{13}C_{CaCO3}$, and $\delta^{18}O_{CaCO3}$ of this core (Fig. 2c).

STUDENT PROJECTS

Laura Haynes (Pomona College) *The Paleoclimate Record of Lough Carra:* Using $\delta^{13}C$ and $\delta^{18}O$ of carbonate marl sediments from the ~8m core taken from the south basin of Lough Carra, a record of climate and productivity changes for the region have been described. A fascinating transition from massive, unlaminated gray marl occurs at ~1.5 m, wherein the rest of the core has distinct laminations. This change occurs during late 1700 to 1900, when population, farming, livestock as well as the industrial revolution all occurred. Accurate dating of the core (^{14}C, ^{210}Pb, ^{137}Cs, lamination examinations) is critical for close examination of some of these stratigraphic transitions.

Sarah Shackleton (Wesleyan University) *Carbonate Diagenesis of Marl Lake Sediments*. Lake water, pore water and sediment incubation measurements ($\delta^{13}C_{DIC}$, Ca^{+2}/Cl^-, DIC, P_{CH4} $\delta^{13}C_{CH4}$) provide ways to evaluate early organic matter decomposition pathways and carbonate recrystallization processes that influence $\delta^{13}C_{CaCO3}$ and $\delta^{13}C_{orgC}$ values in Lough Carra sediments. Methanogenesis was found to be a key process that determines pore water $\delta^{3}C_{DIC}$ and carbon isotope mass balance modeling helps quantify the significance of this process in determining sedimentary $\delta^{13}C_{CaCO3}$. Processes that explain upcore trends of decreasing $\delta^{13}C_{CaCO3}$ and $\delta^{13}C_{org}$ and increasing $\delta\delta^{13}C_{carb-org}$ are also examined.

Alyssa Donovan (Amherst College) *Metal and Nutrient Loading in Lough Carra.* Carbonate chemistry has been used to document both land-use changes (Fe:Ca ratios), mercury deposition (both as a global containment and use as a secondary timeline for dating cores), calcite recrystallization, and eutrophication (total phosphorus). As in the stratigraphy of the long core, the interval from 1700-1900 A.D. is strongly associated with highly variable metal concentration, and spikes in Fe:Ca ratios correlate with other changes in the lamination patterns (thickness and color).

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