HOLOCENE CLIMATE VARIABILITY IN WESTERN IRELAND: DO LACUSTRINE CARBONATE SEDIMENTS RECORD AMBIENT TEMPERATURE?

ROGER HUANG
Amherst College, Amherst
Sponsor: Anna Martini, Amherst College

INTRODUCTION

Oxygen and carbon isotopic compositions from carbonate lacustrine sediments have been used as temperature and productivity proxies in paleoclimate studies. Indeed, our current study of Holocene climate variability in western Ireland depends upon these records. It is assumed that precipitated carbonate sediment record the ambient temperature and that this record is preserved through post-depositional processes. Our purpose is to determine whether post-depositional processes such as dissolution and re-precipitation of calcite by groundwater influence this record and, if so, to model the extent of their influence on the isotopic temperature and paleoproductivity record.

Dissolution of calcite due to acidity is possible beneath the peat-marl interface, where organic acids from the overlying peat may flow downward into the underlying marl, dissolving some of the carbonate and re-precipitating it further down section. Dissolution and re-precipitation of carbonate of this type would alter the isotopic signature of the affected carbonates. Similarly, chemical exchange with porewaters in deposited carbonates and additional precipitation of carbonate below the water sediment interface and further down section may influence isotopic signatures of the marl.

To investigate these possibilities water samples were taken from rivers and lakes in the Lough Corrib and Lough Inchiquin drainage basins to gain an understanding of local hydrogeology and geochemistry. Push cores and pore waters were obtained from Lough Corrib and Lough Carra for analysis of modern depositional processes and the geochemical dynamics of the marl.

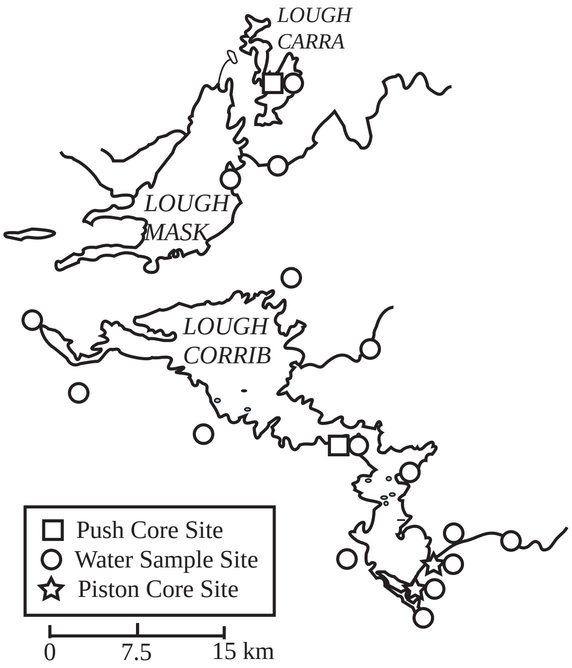

Figure 1. Lough Corrib catchment and sampling site map.

METHODS

pH and temperature of each lake and river sampled were measured with a Corning 313 pH/Temperature meter. Two samples of water were taken from each site and filtered with a 0.2 μm filter to remove particulate matter. One sample was acidified with hydrochloric acid to keep the cations in suspension and the other was left unacidified for alkalinity and anion analysis. The acidified sample was used for cation analysis with a Leeman Labs DRE-D Inductively Coupled Plasma Spectrophotometer (ICP) at Amherst College. The unacidified sample was used for alkalinity titration in the lab at the National University of Ireland, Galway and for anion concentrations using ion chromatography (IC) analysis with a Dionex DX 500 Chromatography system at Amherst.

Two push cores were obtained from Lough Carra (LCa PC 1 and LCa PC 2) and one from Lough Corrib (LC PC 1). The cores were extracted from submerged marl near the shoreline. Push cores were obtained using 5 cm diameter PVC tubes. The tubes were pushed vertically into the lake sediment, capped, and then pulled out, producing a vertical section of modern marl approximately 30-45cm deep. The cores were brought back

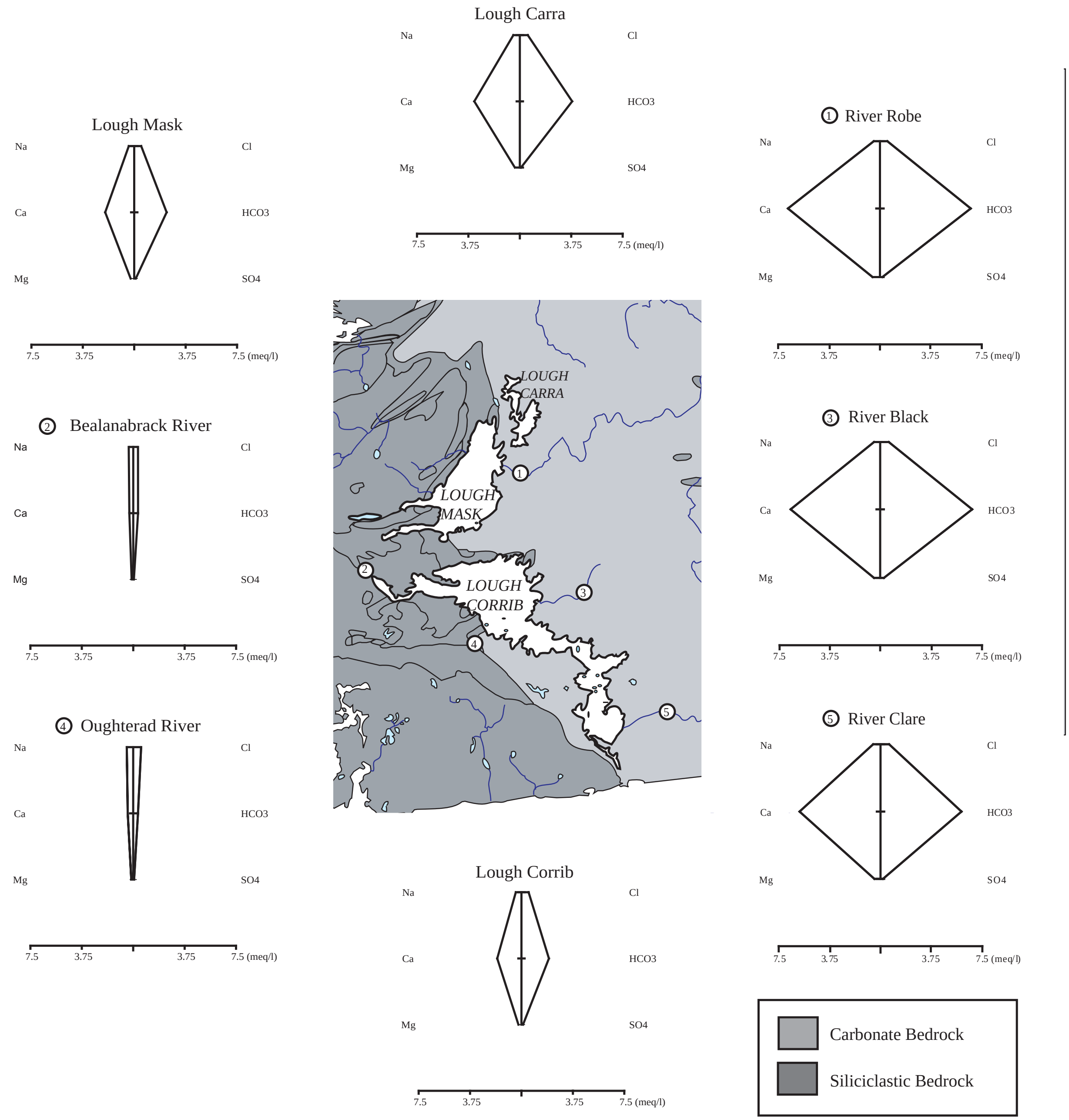

Figure 2. Stiff plots and simplified geologic map. Differences in bedrock show a strong control on the water chemistry of rivers in the Lough Corrib catchment. Rivers flowing over carbonate bedrock have high concentrations of Ca^{2+} and HCO_3^-. Rivers flowing over siliciclastic bedrock have much lower concentrations of dissolved species.

to NUI Galway, cut in 5cm sections and run through a centrifuge to extract the pore water. These pore waters were titrated for alkalinity and samples were bottled for ICP and IC analysis at Amherst and stable isotope analysis at the University of Saskatchewan, Saskatoon.

The geochemical computer models, Aquachem 3.7 and MacSOLMINEQ.88, were used to calculate calcite saturation states.

RESULTS

Our water sampling revealed a strong bedrock control on the chemistry of lake and river waters. The Lough Corrib catchment overlies two general types of bedrock: carbonate bedrock to the east, and non-carbonate bedrock dominating the west. Rivers flowing through the eastern carbonate bedrock have water chemistries dominated by dissolved calcium carbonate as indicated by stiff plots (Figure 1). The rivers flowing though the western siliciclastic terrains have far lower concentrations of dissolved species. This contrast in water chemistry and dissolved solids reflects the orders of magnitude difference in rates between carbonate and silicate dissolution.

The water chemistry of the lakes is also dominated by dissolved calcium carbonate, although to a lesser extent than that of the eastern rivers. This reflects a mixing of water chemistries from the eastern and western rivers.

Figure 2 shows changes in calcite solubility (log IAP/kT) and concentrations of Ca^{2+} and HCO_3^- with depth in each of the three push cores. In LCa PC 2 increasing concentrations of Ca^{2+} and HCO_3^- with depth and the change from undersaturation of calcite near the surface to increasing oversaturation with depth indicate that calcite is dissolving near the surface and re-precipitating deeper in the marl. The profiles of LCa PC 1 show that calcite is oversaturated throughout the column. This resembles the deeper half of LCa PC 2. The higher calcite saturation in LCa PC 1 versus LCa PC 2 may be explained by the fact that LCa PC 1 was extracted much closer to the lake margin than LCa PC 2, and the higher calcite saturation is a reflection of the warmer, shallower water and increased biogenic precipitation of calcite that is expected near the lake margins. The near surface portions of the LC PC 1 profiles resemble the upper portions of LCa PC 2; however, below 20 cm the Ca^{2+} and calcite saturation levels drop sharply. This may be the result of subsurface discharge of waters with low Ca^{2+} concentrations. Since this core is located on the western edge of the lake, the influence of

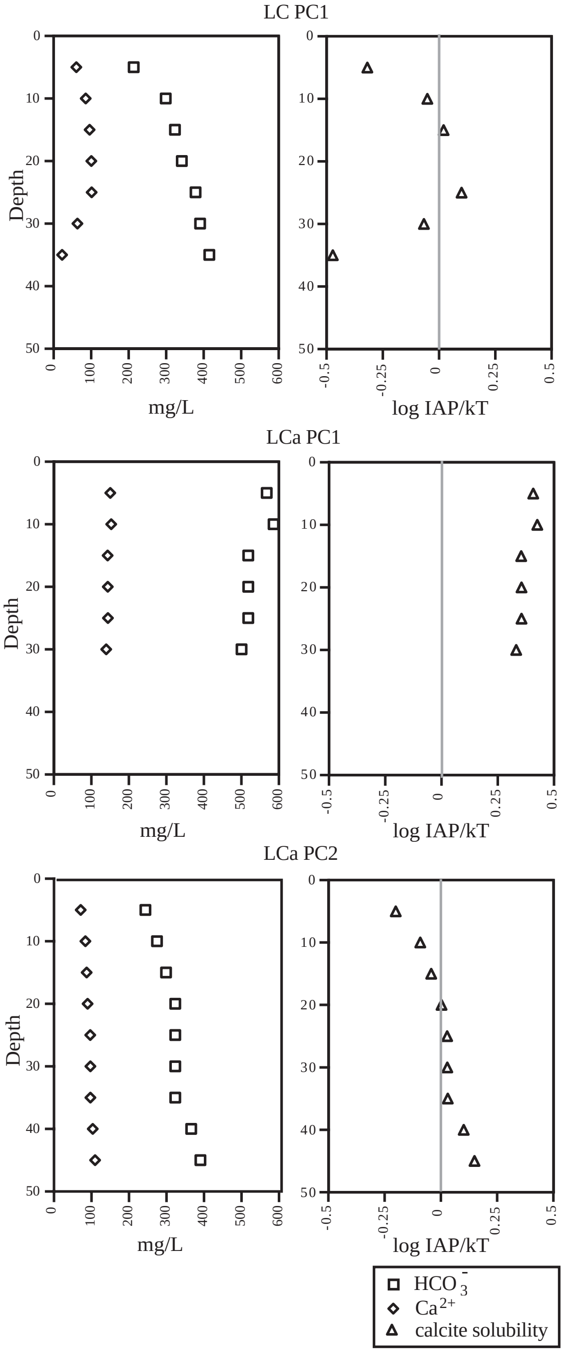

Figure 3. Profiles of Ca^{2+} and HCO_3^- concentration and calcite solubility (log IAP/kT) with depth in push cores.

groundwater from siliciclastic units may be important.

CONCLUSION

Our calcite solubility data confirms that post-depositional dissolution and re-precipitation is occurring in modern, near surface, carbonates. We will model the potential impact of these processes on the isotopic temperature and paleoproductivity records, as well as investigate other areas of potential post-depositional dissolution and re-precipitation such as the peat-marl interface.

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