# TRACE ELEMENT GEOCHEMISTRY OF HOLOCENE LAKE MARL: PALEOCLIMATE ANALYSIS OF LOUGH CARRA, COUNTY MAYO, IRELAND

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## INTRODUCTION

The trace element chemistry of carbonate lake sediments has been shown to reflect temperature and precipitation levels during deposition. As carbonate precipitates from lake water, metals including magnesium, strontium, and manganese can substitute for calcium in the crystal lattice, and certain climatic conditions favor these substitutions. When combined with other chemical and paleontological data, such as carbon/nitrogen ratios, oxygen and carbon isotope numbers, and mollusk and gastropod population data (see Phelps, this volume), trends in trace metal concentrations aid in developing a picture of the environmental history of the lake.

Lough Carra is a shallow marl lake (average depth 1.75 m) of 14.38 $km^2$ (King and Champ 2000) in County Mayo, Western Ireland, situated on Carboniferous limestone bedrock. Carra was chosen for this paleoclimatic study because of its exposure to the North Atlantic and its almost pure-carbonate sediments. Variations in Mg/Ca, Sr/Ca, and Mn/Ca ratios throughout the cores reflect changes in lake conditions over the past 2000 or more years.

## Core and Site Descriptions

Five push cores, up to 2.5 meters in length and including surface material, were taken from different locations around Lough Carra; this study focuses on the trace metal content of four of these cores. Core LCa1, 187 cm long, was taken from ~0.3-m-deep water in a very low energy area with sparse reeds. Core LCa2, 128-cm long, was taken in ~1 m of water, 5 to 10 meters from the tip of an exposed rocky peninsula with moderately abundant reeds and bottom grasses. Core LCa3, 80-cm long, was taken from a calm marl shelf with abundant reeds and 0.6-m-deep water, along a rock-free point of land. Core LCa5, 218-cm long, was taken in 0.6-m-deep water in an area of marl without reeds near a rocky island.

## Methods

### Preparation and Physical Analysis

Within 24 hours after collection, cores were divided into 1-cm segments, stored in plastic. Loss on ignition (LOI) data was obtained in Dr. Anna Martini's environmental geochemistry lab at Amherst College by igniting 1-$cm^3$ plugs, taken at 5-cm intervals, for an hour each at 550°C and then at 1000°C, weighing after each ignition. The mass lost during ignition at 550°C was taken to represent the organic carbon, while mass lost at 1000°C represents inorganic carbon, removed as $CO_2$ (leaving residual CaO, lime).

### Elemental Analysis

Subsamples for elemental analysis were taken from dried (not yet ignited) plugs and stored in foil. These samples were analyzed for carbon and nitrogen content in Dr. Tim Ku's lab at Wesleyan University.

### Isotope Data

Stable isotopes of carbon and oxygen were analyzed at 5-cm intervals in Cores LCa1-3 in the Isotope Lab at the University of Saskatchewan.

### Trace Metal Analysis

Samples for chemical analysis were dried at 60°C and powdered after removal of large shells. Cores LCa1, LCa2, LCa3 and LCa5 were then analyzed, at 5 cm intervals, in Dr. Frank Dunnivant's environmental chemistry lab at Whitman College. For each segment analyzed, 0.1 g of dry sediment was weighed into a 125-mL HDPE sampling bottle, and 1 mL of 30% $H_2O_2$ was added to oxidize organic matter. Then the sample was dissolved in 25 mL of ~2.5% pesticide-grade nitric acid and filtered through a glass fiber filter. Ca, Mg, Sr, and Mn analyses were performed on a Perkin-Elmer 1100B Flame Atomic Absorption Spectrometer (FAAS). Samples for Ca and Mg analysis were diluted in 2.5% $HNO_3$ (1:253 for Ca, 3:53 for Mg), with addition of $LaCl_3$ $7H_2O$ at ~0.25% (also added to Ca and Mg standards).

## RESULTS

The metal analyses confirm that the cores are composed primarily of calcium carbonate, with calcium averaging 35 weight percent in all samples analyzed. This suggests a carbonate content of approximately 88% and is roughly supported by the LOI data, which indicates an average inorganic carbon content of 11.2%, corresponding to 93% carbonate.

All cores showed an overall trend of decreasing Mg/Ca, Sr/Ca, and Mn/Ca ratios with depth (Figure 1), despite consistent or slightly decreasing calcium concentrations with depth. This trend of decreasing trace metal concentrations suggests less substitution of these elements into precipitating $CaCO_3$.

Generally, the concentrations of Mg and Sr seem to vary together in the cores, with aligning peaks and troughs, while Mn is less predictably correlated. However, Core LCa3 shows correlation between all three trace elements. Coordinated trace metal peaks also occur at 70-80 cm and 162-180 cm in LCa1, at 12-30 cm and 70-90 and 108-120 cm in LCa2, and at 70-85 cm and 210-215 cm in LCa5.

Ratios of organic carbon/nitrogen (OrgC/N), a measure of lake productivity, were calculated from elemental analysis, using LOI data to calculate organic carbon content. These ratios

and percent inorganic carbon (not taken for LCa3) do not seem to correlate well enough with the trace element data or with each other to enable interpretation, although the two values do seem to vary inversely.

Isotope data is expressed as _$^{13}$C and _$^{18}$O, comparing marl values with those of ocean water (set at 0). Like the trace metal ratios, _$^{13}$C increases with depth, sometimes apparently correlating with Mn/Ca values (see LCa1 130-170 cm, LCa2 110-120 cm), and first crosses into positive values at around 80 cm in LCa1 and 60 cm in LCa2 (where data collection began). _$^{18}$O values show no overall trend with depth, but appear to often vary inversely to the _$^{13}$C values.

## DISCUSSION

The patterns of substitution of trace metals into calcite and aragonite are dictated by water conditions, primarily temperature and ion concentrations. Kinsman (1969) concluded that Sr substitution into $CaCO_3$ (as represented by the distribution coefficient for the substitution) decreases linearly with increasing temperature. Muller and Wagner (1978) then correlated increased levels of Mg and Sr substitution into carbonates with decreased precipitation (and lake water) levels, and thus with increased salinity.

Considering these observed trends, the largely correlated decreases in Mg and Sr in the analyzed cores from Lough Carra should represent warmer and/or wetter conditions, while increases in these two elements should indicate periods of cooler and/or drier climate. Such environmental trends reflect the local environment of the lake, and may also reflect larger regional or global trends, due to Ireland's exposure to the globally influential North Atlantic Ocean.

_$^{18}$O and _$^{13}$C values are also the result of environmental variation, which affects isotopic fractionation. Fractionation of oxygen is generally correlated with effects of precipitation. Rainwater is $^{18}$O-depleted compared to seawater, and becomes more so with decreasing temperature. Thus, a cooler and wetter climate is correlated with decreased _$^{18}$O in precipitated $CaCO_3$, assuming
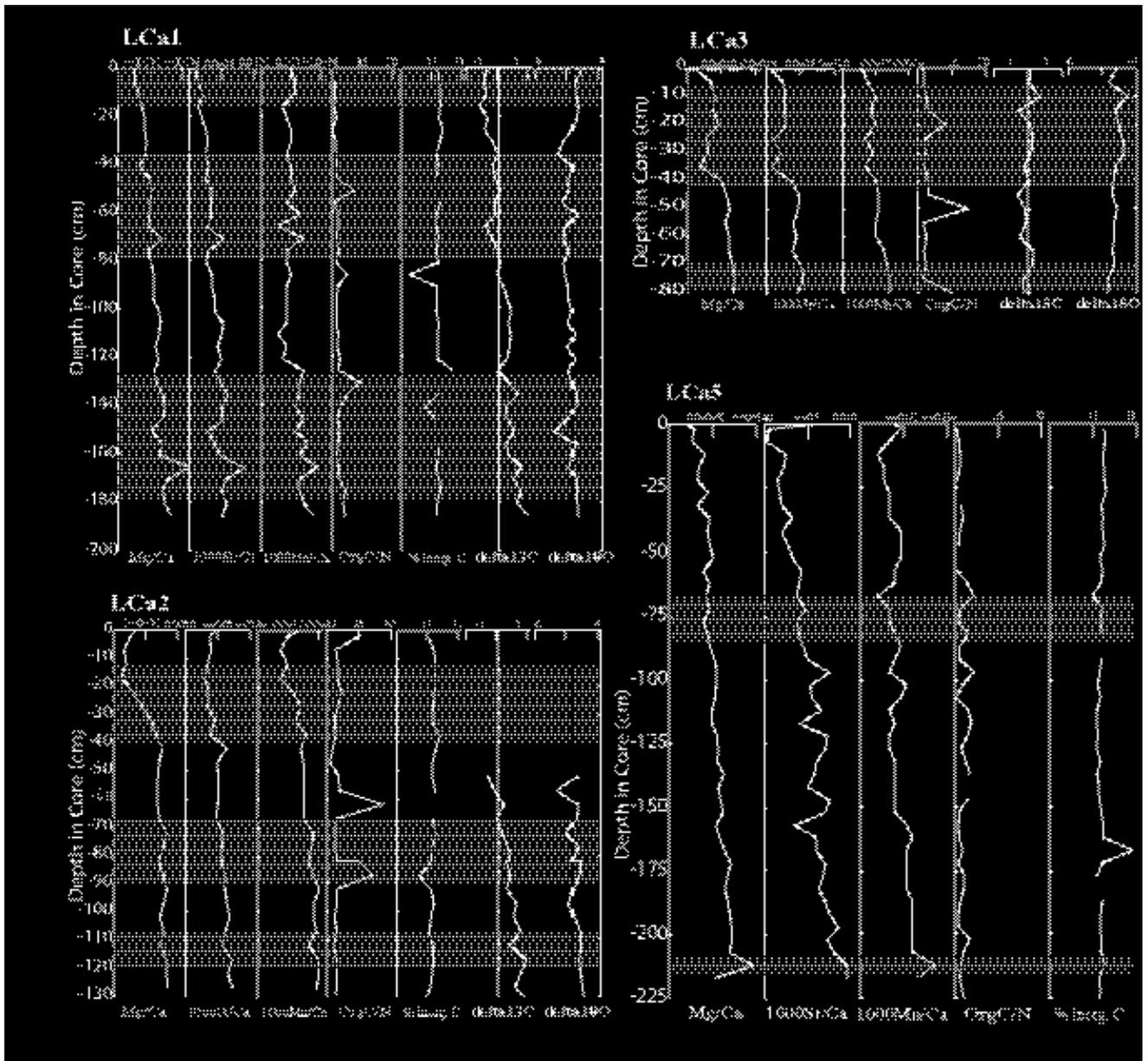
precipitation at isotopic equilibrium with the lake water. (Ralska-Jasiewiczowa, 2003)

Carbon isotope content in marl relies on complex relationships between dissolved and authigenic carbon sources, each with distinct $\delta^{13}C$ values. Ralska-Jasiewiczowa, et. al. (2003) also observed an inverse correlation between $\delta^{13}C$ and $\delta^{18}O$, also often seen in the Lough Carra cores, and attributed this to climatically-controlled processes of carbonate dissolution by groundwater.

In order to reconstruct the paleoconditions of Lough Carra, it is necessary to correlate depth with age of deposition and to correlate depths between cores. Rough dating can be made using approximate carbonate sedimentation rates. A rate of 0.059 cm/year (17.0 years per

centimeter) was estimated for other Irish lakes by Diefendorf (2002) consulting O'Connell et. al. (1999).

This estimate can be used as a starting point for dating of these cores, although the distinct conditions at different coring sites can be expected to lead to different sedimentation rates. It can be hypothesized that LCa1 and LCa3 represent the least disturbed record of recent carbonate precipitation, due to their localities' low- energy environments and distances from sources of clastic sediments.

Considering first the past 1000 years, and assuming 17 years per cm of marl, the Little Ice Age (300-600 B.P.) would encompass depths of 20-50 cm in these marl cores (Mann, 1998). LCa3 shows high trace metal

variability and distinct troughs in this interval, with patterns that are more subtly echoed in LCa1. $\_^{18}O$ values also vary in this interval, suggesting the environmental variability of the period, although they do not definitively indicate an overall cooling trend.

The general trend of decreasing ionic substitution and increased $\_^{18}O$ in the top 10 cm of LCa1 and LCa3 may represent increased regional precipitation and increased temperatures during the recent centuries, following the Little Ice Age.

The opposite trend, that of increasing ionic substitution, exhibited at the top of LCa2, could be an indication of net nondeposition or erosion occurring at this now high-energy site. Patterns in the upper portion of this core seem to align best with other cores if it is assumed that the top of LCa2 correlates with a depth of approximately 20 cm in cores LCa1 and LCa3, from what are now lower-energy sites. This 20-cm differential is also suggested by the location of the transition from negative to positive $\_^{13}C$ values in the two cores.

The upper portion of LCa5 also shows a zone of high trace metal variability, roughly but inconclusively correlating with that observed in LCa3. The lack of isotope data from this core further impedes correlation, however.

Moving farther down in the cores and into the second and possibly third millennium B.P., two zones of particular variability in ionic substitution occur in LCa1, at approximately 60-80 cm (~1100-1300 years B.P.) and 140-180 cm (~2400-3000 B.P.). Both of these zones include a distinct peak seen in all trace metals, possibly indicating a period of cooler, drier climate. The ~165 cm peak correlates with a trough in $\_^{18}O$, further suggesting a cooler climate.

LCa5 also shows high variability of strontium content, and shows some vague correlation between Sr and Mg in the zone of 100-180. However, the most distinct peak in this core occurs at the very bottom, with a peak preliminarily suggesting dry cooling, correlated with a subtle peak in $\_^{18}O$ that could also correspond to decreased precipitation.

## CONCLUSIONS

The trace metal data, combined with other chemical and physical data for these cores, indicates periods of variable conditions at Lough Carra during the past 2 to 3 millenia. These trends seem to roughly correlate between cores and with recognized climatic trends, and may be corroborated and elucidated by further data on paleontological populations within the cores.

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