

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

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PALEOENVIRONMENTAL RECORDS AND EARLY DIAGENESIS OF MARL LAKE SEDIMENTS: A CASE STUDY FROM LOUGH CARRA, WESTERN IRELAND

Faculty: *ANNA MARTINI*, Amherst College, *TIM KU*, Wesleyan University.

Students: *SARAH SHACKLETON*, Wesleyan University, *LAURA HAYNES*, Pomona College, *ALYSSA DONOVAN*, Amherst College.

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**PORE WATER AND SEDIMENT CARBON ISOTOPE GEOCHEMISTRY OF MARL LAKE
SEDIMENTS, LOUGH CARRA, IRELAND**

SARAH SHACKLETON, Wesleyan University

Research Advisor: Timothy Ku

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LAURA HAYNES, Pomona College

Research Advisor: Dr. Robert Gaines

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Research Advisor: Anna Martini

PORE WATER AND SEDIMENT CARBON ISOTOPE GEOCHEMISTRY OF MARL LAKE SEDIMENTS, LOUGH CARRA, IRELAND

SARAH SHACKLETON, Wesleyan University
Research Advisor: Timothy Ku

INTRODUCTION

Lake sedimentary records can provide a history of the aquatic ecosystem and surrounding watershed. Core records can document thousands of years and follow environmental changes from lake formation, or can be over shorter timescales and display signs of anthropogenic impact. Carbonate mineral $\delta^{13}\text{C}$ values reflect the $\delta^{13}\text{C}$ of a lake's dissolved inorganic carbon (DIC), and thus the processes that affect these values. $\delta^{13}\text{C}$ of carbonate and organic matter in marl lakes have been used as proxies to study changes in lake productivity, carbon input sources, algal compositions, and land use (McKenzie, 1985; Teranes and Bernasconi, 2005; Diefendorf et al. 2008). Unfortunately, the $\delta^{13}\text{C}_{\text{DIC}}$ of lake waters can be influenced by a variety of processes, and it is not always possible to isolate one from another.

Prior studies of Lough Carra, Ireland's largest marl lake located in County Mayo, found significant (2.5‰) down core increase $\delta^{13}\text{C}_{\text{CaCO}_3}$ of a 2.5-meter sediment core (Huang, 2003). The author proposed several potential explanations for this shift, including a decrease in productivity, a decrease in detrital carbonate input, and diagenetic alterations, but a definitive answer remained elusive with the available data.

Our study sought to build on the past research of this lake and 1) identify the cause of this significant $\delta^{13}\text{C}_{\text{CaCO}_3}$ shift and 2) determine if similar isotopic shifts occur throughout the lake. Our analyses focused on carbon isotope values of the sediment ($\delta^{13}\text{C}_{\text{CaCO}_3}$, $\delta^{13}\text{C}_{\text{OrgC}}$, and $\Delta^{13}\text{C}_{\text{carb-org}}$) and water ($\delta^{13}\text{C}_{\text{DIC}}$ and $^{13}\text{C}_{\text{CH}_4}$)

to examine the processes that influence marl lake $\delta^{13}\text{C}_{\text{CaCO}_3}$ values.

STUDY LOCATION

Lough Carra is a shallow marl lake located in the county of Mayo in Western Ireland. It covers an area of approximately 16.10 km², has an average depth of 1.8 meters and is part of the Corrib catchment. The lake has three basins: Castleburke Basin, Castlecarra Basin, and Twin Islands Basin and is fed by the North Basin, Mullingar, Clooneen, Ballintrobe and Partry rivers. Lough Carra outflows into the larger Lough Mask through the Keel River. The lake and its catchment area lie entirely over Carboniferous limestone. The lake has no significant concentrations of human population in its vicinity. The surrounding land is used predominately for sheep and cattle grazing (King & Champ 2000; Hobbs et al. 2005).

METHODS

This study will focus on three sites: 1) LC13, located in a deep portion of the Twin Island Basin, 2) LC15, located near the shoreline of the Twin Island Basin over a suspected spring, and 3) LC16, a shallow site at the southern end of the Castlecarra Basin that duplicates the sediment core described by Huang (2003). At each site, overlying waters were collected with a van Dorn bottle and sediment cores were collected using a UWITEC gravity core. Water column temperature, pH, and dissolved oxygen were measured in situ using a YSI Professional Plus instrument and Quatro cable. Sediment pore waters were obtained by centrifuge and sediments were

collected in 1-cm intervals. Waters were filtered (0.20-0.45 μm) and alkalinities were determined by Gran titration. Allotted aliquots were preserved for later cation (inductively coupled plasma atomic emission spectrophotometer), anion (ion chromatography), dissolved carbon (DIC and CH_4), and isotopic ($\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CH}_4}$) analyses. Sediments were dried and homogenized. Sediment total carbon was determined on a Thermo Flash 1112 Elemental Analyzer and inorganic carbon was measured on a UIC 5011 coulometer. Organic carbon was calculated as the difference between total carbon and inorganic carbon. $\delta^{13}\text{C}_{\text{CaCO}_3}$ was analyzed at the Stable Isotope Laboratory of UMass Amherst. $\delta^{13}\text{C}_{\text{OrgC}}$ samples were measured at the UC Davis Stable Isotope Lab after carbonate removal. All DIC and methane concentrations and isotopic compositions were determined at the UC Davis Stable Isotope Lab and all carbon isotope compositions are reported in standard delta notation relative to the VPDB standard.

RESULTS

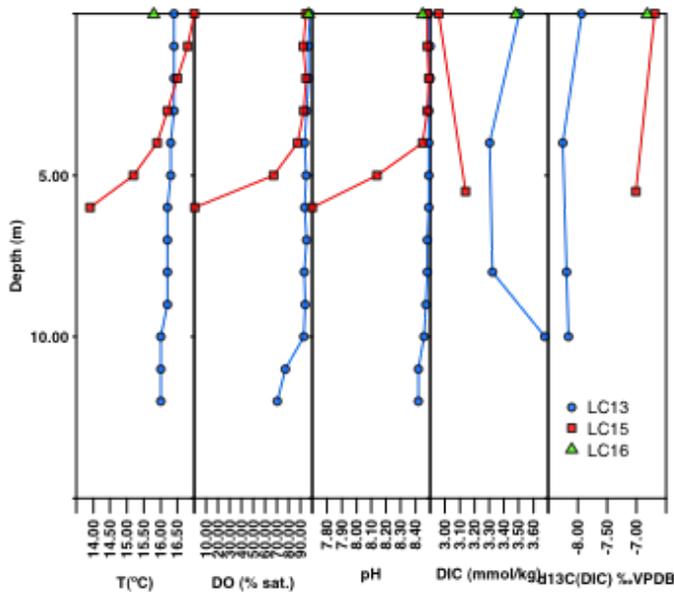


Figure 1 shows overlying water profiles of temperature (in Celsius), dissolved oxygen (in % saturation), concentration of dissolved inorganic carbon (DIC in mmol/kg), and $\delta^{13}\text{C}_{\text{DIC}}$ (in ‰ relative to the PDB standard), with increasing depth. Site LC16 was the shallow site of Huang's sediment core, so there is only one data point for this site.

Overlying Waters:

Water column profiles are presented in Figure 1. Water depth at LC16 is less than 1 m so only a surface water sample is shown. At site LC13, temperature, dissolved oxygen, and pH decrease slightly with increasing depth until about 10 m when these measurements decrease more sharply. This decrease in temperature, dissolved oxygen, and pH is more pronounced at LC15 where these shifts begin at around 4m and dissolved oxygen is completely depleted by 6m (Figure 1). Surface pH values from all sites are 8.4-8.5. DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ values for LC15 range from 3.0-3.1 mM and -7.9 to -8.2‰, respectively, and contrast with the higher DIC concentrations and more positive $\delta^{13}\text{C}_{\text{DIC}}$ values of LC13 and LC16 (3.2-3.7 mM and -6.7 to -7.0‰ (Figure 1).

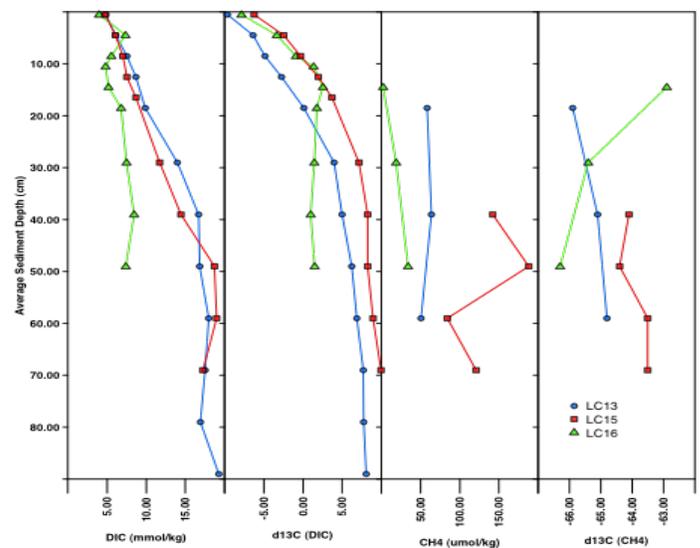


Figure 2 shows sediment core pore water DIC concentrations (in mmol/kg), $\delta^{13}\text{C}_{\text{DIC}}$ (in ‰ relative to the PDB standard), CH_4 concentrations (in mol/kg), and $\delta^{13}\text{C}_{\text{CH}_4}$ (in ‰ relative to the PDB standard) with increasing sediment depth for sites LC13, LC15 and LC16.

Pore Waters

Sediment pore water DIC, $\delta^{13}\text{C}_{\text{DIC}}$, CH_4 , and $\delta^{13}\text{C}_{\text{CH}_4}$ values for sediment cores are presented in Figure 2. Pore water DIC and $\delta^{13}\text{C}_{\text{DIC}}$ start at values similar to overlying waters, but with increasing core depth, there is a significant increase in both DIC and $\delta^{13}\text{C}_{\text{DIC}}$ values in each core. In cores LC13 and LC15 pore water DIC and $\delta^{13}\text{C}_{\text{DIC}}$ values increase steadily down core from 4.8 mM and -6.2 to -9.6‰ to about 19 mM and +8.1 to +10.0‰ at 70-90 cm depth. At site LC16, DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ values increase less and appear to remain relatively constant in the 20 to 50 cm depth (Figure 2). Dissolved methane concentrations ranged from 2.5 to 188 μM with the highest concentrations found in LC15 and the lowest concentrations in LC16. For all cores, methane carbon isotopic compositions ranged from -66.3 to -63.5‰.

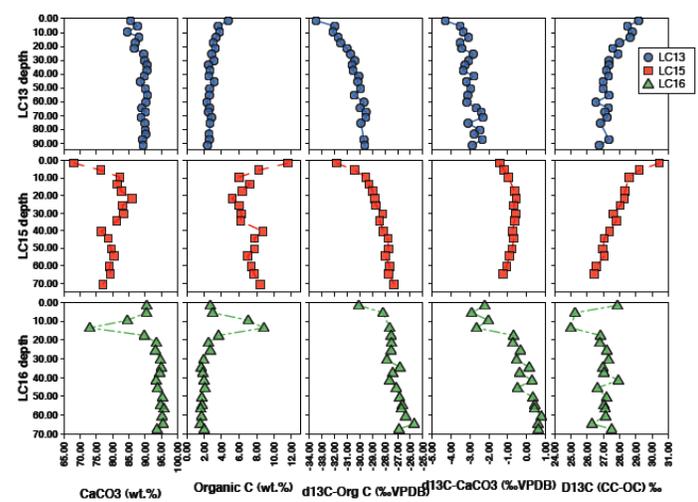


Figure 3 shows sediment CaCO_3 , organic carbon, $\delta^{13}\text{C}_{\text{CaCO}_3}$, $\delta^{13}\text{C}_{\text{OrgC}}$, and $\Delta^{13}\text{C}_{\text{carb-org}}$ (in ‰ relative to the PDB standard) for sediment cores at site LC13, LC15 and LC16.

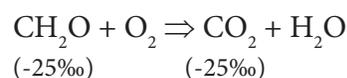
Sediment

Carbonate concentrations ranged from 68 to 95 wt.% and organic carbon concentrations ranged from 1.6 to 11.6 wt.% with LC15 having lower CaCO_3 concentrations and higher organic C concentrations compared to LC13 and LC16 (Fig. 3). $\delta^{13}\text{C}_{\text{OrgC}}$, $\delta^{13}\text{C}_{\text{CaCO}_3}$, and $\Delta^{13}\text{C}_{\text{carb-org}}$ (difference between sediment $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{OrgC}}$) top-core values vary greatly between coring sites (Fig. 3). $\delta^{13}\text{C}_{\text{OrgC}}$ values for LC13

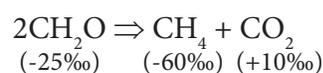
and LC15 consistently increase with increasing depth to about 30 cm, at which point the values appear to increase only slightly. LC16 $\delta^{13}\text{C}_{\text{OrgC}}$ values show a general increase, but with less consistent trends. Importantly, $\delta^{13}\text{C}_{\text{OrgC}}$ values for all three cores show very little overlap even though all have similar trends with depth. Top core $\delta^{13}\text{C}_{\text{CaCO}_3}$ values are 1.6-3.0‰ more positive than predicted calcite precipitated in equilibrium with overlying $\delta^{13}\text{C}_{\text{DIC}}$ (Deines et al., 1974). LC13 gradually increases in $\delta^{13}\text{C}_{\text{CaCO}_3}$ for a ~ 1.5 ‰ shift at depth. LC15 smoothly increases in $\delta^{13}\text{C}_{\text{CaCO}_3}$ values through 30 cm depth (~ 0.8 ‰) then $\delta^{13}\text{C}_{\text{CaCO}_3}$ values gradually decreases from 30 to 65 cm (~ 0.7 ‰). LC13 has less consistent down-core trends, but overall there is a ~ 2.5 ‰ positive shift going down core. LC13 $\Delta^{13}\text{C}_{\text{carb-org}}$ values at 1.5 cm depth start at 29.2‰ and decrease to ~ 27 ‰ at 30 cm depth then remains relatively constant to the bottom of the core (Fig. 3). In LC15, the surface $\Delta^{13}\text{C}_{\text{carb-org}}$ value is 30.4‰, this value decreases steadily with increasing depth. LC16 $\Delta^{13}\text{C}_{\text{carb-org}}$ values decrease sharply in the upper 13 cm then decrease steadily further down core. $\Delta^{13}\text{C}_{\text{carb-org}}$ values for all three cores are similar (~ 27 ‰) in the bottom parts of the cores (Fig. 3).

DISCUSSION

Water column parameters at the three sites show substantial differences between locations indicating that Lough Carra contains basins with different thermal structures and chemistries including different $\delta^{13}\text{C}_{\text{DIC}}$ (Fig. 1). Pore water DIC and $\delta^{13}\text{C}_{\text{DIC}}$ profiles can provide insight into reactions that occur after sediment deposition. Under aerobic conditions, organic matter decomposition can introduce ^{12}C -rich carbon by the following reaction:



Under suboxic or anoxic conditions, organic matter decomposition occurs through a sequence of redox pathways with methanogenesis being last. Methane production results in methane with low $\delta^{13}\text{C}$ and carbon dioxide with high $\delta^{13}\text{C}$:



Pore water $\delta^{13}\text{C}_{\text{DIC}}$ values can show if one, both or neither of these processes is occurring. This DIC has the potential to precipitate calcite when water are supersaturated resulting in higher $\delta^{13}\text{C}_{\text{CaCO}_3}$ values (Hu and Burdige, 2007, Walter et al. 2007).

From the pore water $\delta^{13}\text{C}$ data (Fig. 2), it is clear that methanogenesis is occurring. The extent of this process can be determined by changes in DIC and $\delta^{13}\text{C}_{\text{DIC}}$ values, as well as the amount of methane present in the pore waters, and appears to be dependent on the depth of the sediment, as well as the amount of organic matter available.

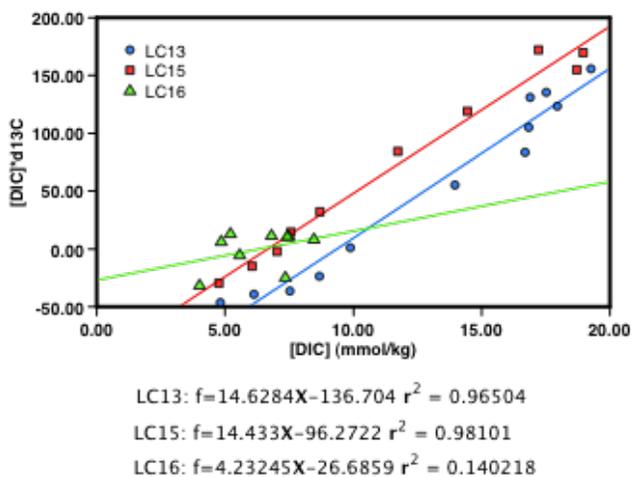


Figure 4 shows DIC pore water concentration (in mmol/kg) versus $[\text{DIC}] \times \delta^{13}\text{C}_{\text{DIC}}$. The linear regression of this plotted data is equivalent to the $\delta^{13}\text{C}$ value of the DIC added into the pore water (Hu and Burdige, 2007).

A graphical method to determine added $\delta^{13}\text{C}_{\text{DIC}}$ pore water values was established by Sayles and Curry (1988). Plotting the linear regression of $[\text{DIC}] \times \delta^{13}\text{C}_{\text{DIC}}$ versus DIC of the pore waters gives the carbon isotopic value of added DIC (Fig. 4). Linear regressions for LC13 and LC15 have both significant coefficients of determination ($r^2 = 0.96$ and 0.98 respectively) and demonstrate that the net carbon inputs to the DIC have similar and positive values ($+14.63$ and $+14.43$ respectively). These results indicate that added DIC for these sediment cores have a value of $\sim +14.5\%$. Along with the presence of bacterially produced methane, we may conclude that the DIC added into the system, post deposition, contains a high percentage of carbon from methanogenesis. LC16 has an insignificant coefficient

of determination ($r^2 = 0.14$) and a lower slope. Due to the shallow water depth, this core is more susceptible to physical disturbance via bioturbation and severe weather, so trends in pore water data may not be observed.

From bulk density calculations and sedimentation rates given in O'Reilly (2011), sediments in LC13 and LC15 may be 300 years old, but may be considerably younger. LC16 ages are much more difficult to assess due to the possibility of physical mixing. Analyzing $\delta^{13}\text{C}_{\text{CaCO}_3}$, $\delta^{13}\text{C}_{\text{OrgC}}$, and $\Delta^{13}\text{C}_{\text{carb-org}}$ together, along with overlying water and pore water data, we consider four potential explanations for the data, and their relative influences on the system.

First, changes in $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{OrgC}}$ signals in lake sediment often indicate changes in aquatic productivity (McKenzie, 1985). These isotopic values can be strongly influenced by plant photosynthesis and respiration. Over time, increases in plant productivity will deplete the lake of ^{12}C -DIC and the residual pool becomes ^{13}C -rich. Both $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{OrgC}}$ increase over time with increasing productivity. This process generally does not change $\Delta^{13}\text{C}_{\text{carb-org}}$ values, because the fractionation between these two pools will remain relatively constant as long as overall DIC concentrations remain stable (Diefendorf, 2008). However, in highly productive lakes, where the $\text{CO}_{2(\text{aq})}$ pool becomes limited, $\Delta^{13}\text{C}_{\text{carb-org}}$ values will decrease. Thus, the Lough Carra sediment records would show a decrease in productivity towards more recent times (Fig. 3). However, recent studies of lake health (McCarthy et al., 2000) and phosphorous input (Hobbs et al., 2005) indicate a consistent increase in lake productivity over time.

Second, early organic matter decomposition can influence $\delta^{13}\text{C}_{\text{OrgC}}$ values. Bacteria may preferentially utilize ^{12}C compounds in organic matter increasing values of residual $\delta^{13}\text{C}_{\text{OrgC}}$ (Meyers, 1993). This coincides with an increasing C/N ratio, as bacteria more rapidly decompose organic nitrogen (Lehmann, 2002). In our sediment cores, we see an increase in $\delta^{13}\text{C}_{\text{OrgC}}$ with increasing depth, but the C/N ratio of LC15 does not consistently increase with depth and this diagenesis process does not explain the increasing $\delta^{13}\text{C}_{\text{CaCO}_3}$ values with depth (Fig.3).

Third, pore water data shows that methanogenesis and subsequent calcite precipitation may add ^{13}C -rich calcite to the sediment (Fig. 2). Future $\delta^{13}\text{C}_{\text{DIC}}$ modeling using calcite saturation states and carbon inputs and outputs will examine this process in detail, but carbonate recrystallization does not explain the trends in $\delta^{13}\text{C}_{\text{OrgC}}$.

Fourth, the Suess Effect describes the global increase in ^{12}C enriched atmospheric CO_2 through the burning of fossil fuels since the industrial revolution in the late 19th century. CO_2 exchange at the air-water interface results in a lower $\delta^{13}\text{C}_{\text{DIC}}$ over this time period. If this atmospheric exchange is significant enough to affect $\delta^{13}\text{C}_{\text{DIC}}$ of overlying water values, it will manifest as decreasing $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{OrgC}}$ during this time. Increased atmospheric pressure of CO_2 due to fossil fuel burning also increases the overall concentration of DIC in water bodies through gas exchange. This increase in DIC input will increase $\Delta^{13}\text{C}_{\text{carb-org}}$ values, which is driven by more rapid changes in $\delta^{13}\text{C}_{\text{OrgC}}$ than $\delta^{13}\text{C}_{\text{CaCO}_3}$ due to the kinetic isotope effect of CO_2 fixation.

Our data shows effects of the Suess Effect. Decreasing $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{OrgC}}$ through much of the core and increasing $\Delta^{13}\text{C}_{\text{carb-org}}$ towards more recent sediments (Fig.3). Consistent with the Suess Effect, increases in $\Delta^{13}\text{C}_{\text{carb-org}}$ values from 30 cm and above is primarily dependent on changes in $\delta^{13}\text{C}_{\text{OrgC}}$, consistent with increased exchange with atmospheric CO_2 (Fig. 5). Further age models and carbon isotope modeling will help determine if the observed changes in sedimentary carbon isotope compositions are primarily from the Suess Effect or if other input/output processes play a significant role.

CONCLUSION

Water column, sediment, and sediment pore water data at three sites in Lough Carra show a clear difference between water and sediment chemistries across the lake and active methanogenesis produces very positive pore water $\delta^{13}\text{C}_{\text{DIC}}$. Down core trends in $\delta^{13}\text{C}_{\text{CaCO}_3}$, $\delta^{13}\text{C}_{\text{OrgC}}$, and $\Delta^{13}\text{C}_{\text{carb-org}}$ are consistent with the Suess Effect, though future carbon isotope modeling will determine the magnitude of this effect relative of other processes.

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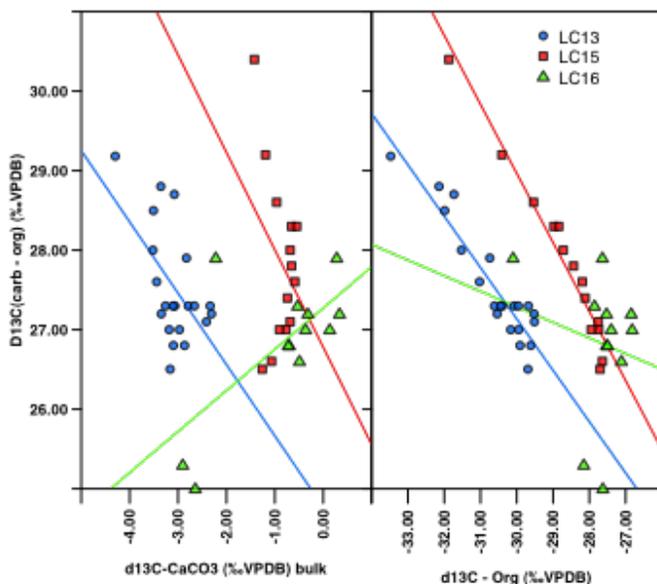


Figure 5 shows $\Delta^{13}\text{C}_{\text{carb-org}}$ plotted against $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{OrgC}}$ (in ‰ relative to the PDB standard) in order to determine which measurement had a greater impact on $\Delta^{13}\text{C}$.

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