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INTRODUCTION

The climate of the Paleocene-Eocene is well understood in mid-latitudes of North America however there is very little known about the paleoclimate at higher latitudes.

The Kootznahoo Formation contains an abundance of carbonate (Fig. 1) that occurs as concretions, cements, and spars. Oxygen isotope ratios, carbon isotope ratios, and isotopologue abundance can be used to study the conditions of carbonate formation and, more broadly, the paleoclimate of the region. In this case, the isotopic signatures from the carbonates also contain important information about the paleohydrology of the Kootznahoo suggesting that they are representative of a mixing of terrestrial and marine waters. Clumped Isotope Thermometry also suggests that the formation of these carbonates occurred under burial conditions influenced by igneous intrusions rather than at the surface. The combination of stable and clumped isotope geochemistry allows for a comprehensive investigation into the conditions of carbonate formation and how the Kootznahoo fits into the global climate patterns of the Paleocene-Eocene.

METHODS

Sampling

Samples of carbonate-bearing sediment (Fig. 1) were collected from four different geographic and stratigraphic locations within the Kootznahoo formation (listed in relative stratigraphic order from the bottom of the formation to the top): Hamilton Bay, Dakaneek Point, Big John Bay, and Kadake Bay (Fig. 1, Davidson et al., this volume). At Hamilton Bay and Dakaneek Point the samples were taken at intervals through the stratigraphy while at Big John Bay and Kadake Bay multiple samples were collected from a single carbonate-rich horizon. In all locations carbonate occurred in the form of cement, concretions and spar, and all of these types of carbonate were sampled for study.

Stable isotope analysis

Oxygen and carbon isotope ratios of 50 carbonate samples were measured at the Stable Isotope Facility of the University of Wyoming. This was done using
a Finnigan Delta Plus XP mass spectrometer. Ratios are presented using the ‘delta’ notation where \( \delta^{18}O \) or \( \delta^{13}C = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 = \%e \) and \( R \) equals the ratio of the heavy to light isotope (\(^{13}C/^{12}C\) and \(^{18}O/^{16}O\)). The PDB standard is used in the case of carbon and the SMOW standard is used in the case of oxygen.

**Clumped isotope analysis**

The abundance of CO\(_2\) isotopologues with an atomic mass of 47, or ‘clumped isotopes’ was determined for seven carbonate samples that represent each of the four different sampling locations and a few of the samples with outlying \( \delta^{13}C \) or \( \delta^{18}O \) values. This work was done at the California Institute of Technology and results are presented in the \( \Delta 47 \) notation where \( \Delta 47 \) is the abundance of CO\(_2\) isotopologues with an atomic mass of 47. This CO\(_2\) isotopologue becomes more abundant with lower temperatures of formation and this relation with temperature makes it possible to use the abundance of mass 47 isotopologues as a paleothermometer (typically referred to as the ‘clumped isotope paleothermometer’).

**RESULTS**

**Stable isotope ratios**

When \( \delta^{13}C \) is plotted against \( \delta^{18}O \), several patterns become apparent. Hamilton Bay samples form an array of values that exhibit a positive ‘curvilinear’ correlation between \( \delta^{13}C \) and \( \delta^{18}O \) (Fig. 2). Samples from all other sites exhibit a similar positive ‘curvilinear’ correlation between \( \delta^{13}C \) and \( \delta^{18}O \), but are characterized by lower \( \delta^{18}O \) such that values do not overlap with Hamilton Bay (Fig. 1). A group of the samples from Dakaneek Point and Big John Bay have much lower \( \delta^{18}O \) values than the samples from other sites (Fig. 2). No trends are discernable when the data is organized by carbonate phase (cement, concretion, or spar).

**Clumped isotope temperatures**

The temperature of carbonate formation inferred using clumped isotope paleothermometry for the

**DISCUSSION**

**Factors influencing \( \delta^{13}C \) and \( \delta^{18}O \) of carbonates**

The isotopic standards of PDB and SMOW are derived from marine sources, and according to the \( \delta \) equation, the closer the isotopic ratio of the sample is to that of the standard, the closer the \( \delta \)-value will be to zero. Therefore, isotopic ratios of carbon and oxygen from marine sources will be close to zero. The isotopic values of carbon and oxygen in most terrestrial settings are very different from the marine values due to mass-dependent isotopic fractionation (Sharp, 2007). The fractionation leaves the fresh groundwater depleted of the heavier isotope thereby giving it a negative \( \delta \)-value. Fractionation occurs in carbon due to the natural isotopic discrimination against the heavier \(^{13}C\) in plants, and because plants are typically the source of dissolved carbon in groundwater, most groundwaters carry roughly the same \( \delta^{13}C \) values (Fricke, 2004). Fractionation occurs in oxygen because the lighter \(^{16}O\) preferentially evaporates out of the ocean and as air masses move poleward they preferentially rain out the heavier \(^{18}O\).
resulting in greater $^{18}O$-depletion with further distance from the source (Koch, 1998). In order to find the $\delta^{18}O$ of precipitation, the fractionation value of $\delta^{18}O$ from calcite to water must be calculated using the equation:

$$1000 \ln \alpha = D(106/T) + E(103/T) + F$$

Where, $D = 2.780$, $E = 0.00$, $F = -2.89$, and the whole equation is temperature dependent (O’Neil et al., 1969; Friedman et al., 1977). The resulting value can be subtracted from the SMOW $\delta^{18}O$ value of calcite to infer the $\delta^{18}O$ of precipitation and ground water at the time of carbonate formation. The temperatures determined from clumped isotope analysis can be used in the fractionation equation above to more accurately determine the $\delta^{18}O$ of precipitation.

### Temperature of Carbonate Formation

Although the number of temperature estimates obtained for this study is limited, they are intriguing, because none of the temperatures reflect likely surface temperatures. A latitudinal gradient exists where temperature decreases from the equator to the poles and in the warmer Eocene the gradient was probably shallow. According to a preexisting Eocene gradient by Fricke and Wing (2004), the estimated mean annual temperature at this latitude is between 10 and 15°C.

In contrast to these estimates, the lowest clumped isotope temperature is 58.5°C and others as high as 120°C. These temperatures likely represent burial conditions with different degrees of influence from igneous intrusions in the area (Fig. 1, Davidson et al., this volume). For the purpose of this study we will assume that the lowest clumped isotope temperature of 58.5°C is representative of burial temperatures during carbonate formation for all the samples and that higher recorded temperatures were likely caused by hydrothermal circulation associated with igneous intrusions that ‘reset’ the clumped isotope system post-burial.

In addition to resetting clumped isotope temperatures, it is also likely that Miocene-aged igneous activity (Hauessler et al., 1992; Ancuta, this volume) impacted stable isotope ratios of some of the carbonate samples. For example, the isotope ratios of the samples that make up the two curvilinear trends in Figure 1 are interpreted to represent a temperature of formation of ~60°C during burial. Carbonate formation at higher temperatures would result in a smaller oxygen isotope fractionation between carbonate and water, and thus lower $\delta^{18}O$ values. In the case of Dakaneek Point there is direct evidence for such a link between higher temperature (120°C) and lower $\delta^{18}O$ (-25 per mil). For this reason all samples with low $\delta^{18}O$ that lie off of the curvilinear trends are interpreted to reflect the recrystallization of carbonate as a result of igneous/hydrothermal activity after burial.

### Mixing of Marine and Meteoric Fluids

The two curvilinear trends displayed by the isotopic ratios of the Kootznahoo data are classic examples of what would be expected if two fluids with different carbon and oxygen isotopic ratios and concentrations mixed together prior to carbonate formation (Faure, 1986; Ufnar et al., 2004). There is also reason to expect such a potential mixing in the study area since Kootznahoo sediments were deposited in a basin(s) adjacent to the ocean and, therefore groundwater in the basin likely had some marine, as well as terrestrial influence.

Isotopic ratios of groundwater that would exist as a result of mixing terrestrial surface water (from precipitation) with ocean water in the groundwater system can be inferred using a two-component mixing model. In turn, the results of this model can be compared with isotopic data from carbonates to test its validity. For this study, the following mixing model is used (Faure, 1986):

$$R_M = R_S X_f + R_P X_p (1 - f)$$

$$X_S f + X_p (1 - f)$$

where $R_M$ is the isotopic ratio of either carbon or oxygen for a given mixture (M) of the two end-member components (S for seawater and P for precipitation). Therefore, $R_S$ and $R_P$ are the isotopic ratios of
the element in each of the end-member solutions and \(X_s\) and \(X_p\) are the concentration (mmol/l) of the given element in each end-member solution. The aforementioned variables remain constant in the equation so that \(f\) is the only variable that changes the outcome of \(R\). The variable \(f\) is the proportion of one of the components in the mixture and values may range from 0 to 1. In this case, \(f\) is the proportion of the fluid mixture that is seawater.

Input values for \(R_s\), \(X_s\) and \(X_p\) for carbon were chosen to reflect modern values for terrestrial and marine environments. Similarly, input values for \(R_s\), \(X_s\) and \(X_p\) for oxygen were chosen to reflect likely marine environments of the Paleogene. \(R_p\) values (i.e. \(\delta^{18}O\) of precipitation) are unknown for the Paleogene, and for the purposes of this exercise they were chosen in order to best fit the data. Because there are two distinct curvilinear datasets, two separate mixing models with different \(R_p\) are used, one with \(R_p\) of -5‰ and one with \(R_p\) of -14‰ (Fig. 3). The mixing model curve fit to Hamilton Bay data also used isotopic ratios of 0‰ for \(\delta^{18}O\) and -1‰ for \(\delta^{13}C\) for the seawater end-member and a \(\delta^{13}C\) of -19‰ for the groundwater end-member. For the other curve, an isotopic ratio of 0‰ was used for both \(\delta^{13}C\) and \(\delta^{18}O\) in the seawater end-member and a value of -19‰ was used for \(\delta^{13}C\) in groundwater. Lastly, in order to compare the results of the mixing models to our carbonate data, it is necessary to assume a temperature of carbonate formation. On the basis of the clumped isotope analysis, a temperature of 58.5°C is assumed.

A comparison of the two mixing models with the carbonate isotope data suggest strongly that the curvilinear trends can in fact be explained by a mixing of terrestrial surface water and ocean water in the ground water system prior to carbonate formation (Fig. 3). This means that the \(\delta^{18}O\) of the carbonates formed in the Kootznahoo Formation probably do not provide a direct reflection of \(\delta^{18}O\) of precipitation. The degree of marine influence must be teased out before the \(\delta^{18}O\) of precipitation can be calculated.

Changes in Local Hydrology Over Time

In order to best fit all the isotopic data, it is necessary to use two separate mixing models that have very different assumed \(\delta^{18}O\) values of local precipitation (Fig. 3). The most likely explanation for such drastic difference in \(\delta^{18}O\) of local precipitation in the area is a shift in sources of air mass/precipitation over time. The end-member \(\delta^{18}O\) value of -5‰ from the oldest sediments (Hamilton Bay) could be high due to a localized evaporative source whereas the end-member of -14‰ from higher in the stratigraphic section at Dakaneek Point, Big John Bay, and Kadake Bay (Fig. 1, Davidson et al., this volume) could be from a more distal source, allowing it to lose more of the heavier isotope before reaching the Kootznahoo. This would be possible if the Kootznahoo region was receiving fewer air masses from distant global sources during the earlier deposition or lithification of the Hamilton Bay sediments; that is, the \(\delta^{18}O\) signature recorded in Hamilton Bay is likely controlled by a nearby, local hydrological cycle.

The shift of the \(\delta^{18}O\) groundwater end-member to -14‰ higher in the stratigraphic section is probably due to a dominant source change from local to dis-
tal. Because temperature largely affects the circulation of air masses, a similar latitudinal gradient to the one mentioned above exists for $\delta^{18}O$. When the value of -14‰ is plotted with other inferred $\delta^{18}O$ (of precipitation) values from different North American latitudes of the Eocene, it plots nicely along the shallow gradient (Fig. 4). This supports the hypothesis that the end-member $\delta^{18}O$ value is representative of a global/North American hydrological pattern. The global hydrological circulation became more prominent and likely overprinted any local water cycle that was responsible for the higher $\delta^{18}O$ values (-5‰).

**Importance of Temperature Constraints in Paleoenvironmental Interpretations**

If it had been assumed for this study that carbonates formed under surface conditions, then a temperature of 10-15°C would have been assumed for the formation of the carbonates. Such an assumption produces very different mixing models; in particular RS values of the model would be ~10 per mil lower. These large differences in inferred $\delta^{18}O$ of Paleogene precipitation highlight the critical influence of temperature, and should serve as a warning when making paleoenvironmental interpretations of isotopic data from authigenic carbonates.

**CONCLUSION**

The stable and clumped isotopes of the carbonates in the Kootznahoo Formation reveal important information relating to the history of their formation and the paleoclimatic history of the region. A fluid mixing model where seawater and meteoric water mix in the water column during the formation of carbonate explains the curvilinear trends displayed by the isotopic data (Fig. 2 and 3). The variables in the mixing model can be manipulated to help explain the environmental conditions during deposition of the Kootznahoo Formation. The $\delta^{18}O$ values in the groundwater end-members, -5‰ and -14‰, are taken to be the most accurate representation of precipitation with -5‰ being more representative of a Paleocene local hydrological cycle and -14‰ representing the Eocene global hydrological cycle. The $\delta^{18}O$ values are calculated using a temperature of 58.5°C and was chosen to represent burial temperature because it is the lowest of the clumped isotope temperatures. Clumped isotope temperatures higher than that were interpreted to be hydrothermally altered by Miocene igneous intrusions. The assumption of surface temperature (10-15°C) in the calculation of fractionation would have resulted in a ~10‰ difference of the inferred $\delta^{18}O$ of precipitation, resulting in a significantly different interpretation of the data, and is offered as a cautionary example when using stable isotopes for reconstructing past climate.

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**Figure 4:** The two $\delta^{18}O$ values for the ground-water end-member are plotted with $\delta^{18}O$ of precipitation values from other North American latitudes (Koch, 1995; Bowen et al., 2002; Fricke et al., 2004; Jahren et al., 2004; Bowen et al., 2008). The end-member value from the Hamilton Bay curve fits on the gradient but the end-member value from the other curve does not.

This change in hydrological ‘styles’ is interpreted to be the local reflection of the global climate change that occurs at the Paleocene-Eocene boundary. The Hamilton Bay samples are the oldest and thought to be Paleocene age while the overlying samples are Eocene in age. Globally, the Paleocene-Eocene boundary is marked by a distinct change in environmental conditions. Therefore, it is suggested here that a similar distinct environmental change also occurred in northern North America at the same time, one that was characterized by a change in atmospheric circulation patterns.
REFERENCES


