

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

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**KECK GEOLOGY CONSORTIUM
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**Keck Geology Consortium: Projects 2012-2013
Short Contributions— Matanuska, Alaska Project**

GEOLOGY, PALEOECOLOGY AND PALEOCLIMATE OF THE PALEOGENE CHICKALOON FORMATION, MATANUSKA VALLEY, ALASKA

Faculty: *CHRIS WILLIAMS*, Franklin & Marshall College, *DAVID SUNDERLIN*, Lafayette College.

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USING STABLE ISOTOPE GEOCHEMISTRY TO RECONSTRUCT THE PALEOHYDROLOGY AND PALEOCLIMATE OF THE PALEOCENE-EOCENE CHICKALOON FORMATION, ALASKA

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INTRODUCTION

Climate was much different during the Paleogene period, with fossil and geochemical evidence showing a global greenhouse climate versus the icehouse climate of today (Zachos et al., 2008). Understanding the nature of greenhouse climate and hydrology during the Paleogene is important to understand the nature and impacts of predicted future climate change. There is critical need for climatic analogs of a mild, ice-free Arctic, due to unprecedented warming seen today in today's Arctic regions, where temperatures are rising by almost twice the rate as the rest of the world (ACIA, 2005, Eberle et al. 2010). Among the best time analogs for a greenhouse climate may be the late Paleocene-early Eocene (~55 Ma), and particularly the Paleocene-Eocene Thermal Maximum (PETM) when the Earth experienced a drastic increase in atmospheric CO₂, and a global temperature increase by as much as 5-8 °C (McInerney et al., 2011).

In association with higher global temperatures were very different global hydrological patterns. Climate and hydrologic patterns at high latitudes was particularly different during hothouse climates, with rivers and wetlands occupying areas now covered by ice and permafrost (Pagani et al., 2006). Paleobotanical records provide evidence that swampy, temperate rainforests existed in the Arctic. In south-central Alaska, during the early Eocene, for example, MAT (mean annual temperature) was 11–14.6 °C; significantly warmer than today (Sunderlin et al., 2011).

Much of our understanding of Paleogene climate and hydrology comes from stable isotope ratios of carbon

and oxygen from various forms of carbonate, and other materials. Changes in the isotopic composition of water within the water cycle provide a recognizable signature, recording different phases of the water cycle. The changes in isotopic composition of atmospheric waters, terrestrial groundwater, surface waters, and soils can be applied to hydrologic patterns and utilized to reveal paleo-climatological conditions.

A comprehensive investigation of hydrologic patterns and methanogenic processes can be studied using carbon and oxygen isotopes. Stable isotope geochemistry of carbonates provides insight into methanogenic processes that may have been occurring at high latitudes during the late Paleocene and early Eocene.

The Paleocene-Early Eocene Chickaloon Formation in South-Central Alaska has several well-exposed outcrops with carbonate concretions, cements, and calcite spar that offer the potential to reconstruct paleomicrobial activity and paleohydrology using carbon and oxygen isotopes. Therefore, the Chickaloon Formation provides an opportunity to study the Paleogene paleoclimate, North American hydrologic patterns, and possible soil carbon feedbacks on climate during this greenhouse climate.

GEOLOGIC SETTING

The Chickaloon Formation is a package of sediment currently located in the Matanuska Valley of south-central Alaska. Today, the structural and topographic basin is bordered to the north by the Castle Mountain Fault and to the south by the Border Ranges Fault. The volcanic Talkeetna Mountains lie to the north of the

basin, while the Chugach Mountains lie to the south of the basin. The Matanuska basin developed during the Cretaceous and Paleocene periods between a volcanic arc and an accretionary prism, in association with the subduction of the Kula and Farallon plates beneath the Wrangellia composite terrane (Trop et al., 2003). These basin-bounding highlands were the dominant source material for the formation. Paleocene to early Oligocene activity on these faults led to a fluvial basin infill sequence, as braided and meandering stream systems deposited sediment from metasedimentary and other source rocks from the Chugach accretionary complex to the south, and volcanics and volcanoclastics from the Talkeetna Mountains to the north (Sunderlin et al, 2011; Moore, 2013, this volume). These fluvial deposits make up the 1500 m thick Chickaloon Formation in the Matanuska Valley. This unit comprises a succession of sandstone, laminated siltstone, mudstone, carbonaceous shale, conglomerate, and coal beds. The westernmost extent of the Chickaloon formation shows deposits characteristic of a marine or estuary environment, making it likely that the basin was at low elevation throughout its depositional history. As the basin filled, coarser alluvial deposits prograded across the ancient valley, depositing the Wishbone Formation, which conformably overlies the Chickaloon Formation (Trop et al., 2003). Carbonate is found throughout the Chickaloon Formation as spar, cements and concretions.

Chickaloon Formation strata lie in an angular unconformable contact with the underlying Upper Cretaceous marine Matanuska Formation (Trop et al., 2003). At the Evan Jones Mine, the upper Chickaloon has been dated to an age of 54.8 ± 0.9 Ma, based on U-Pb geochronologic of 25 zircons from a volcanic ash layer in the outcrop, (Williams, personal communication). Based on these and other geochronology studies (e.g., Triplehorn et al., 1984), the formation appears to span the Paleocene-Eocene boundary at the Evan Jones mine outcrop.

There is an absence of well-supported paleolatitude data during deposition of the Chickaloon Formation. Stamatakis et al. (1989) provide paleomagnetic data that places the Matanuska valley at $48^{\circ}\text{N} \pm 11$ degrees during the Paleocene-Eocene transition. On the other

hand, it has been suggested that Chickaloon deposition may have occurred around 76°N (Wolfe, 1994). More recent analysis has suggested that no more than 500 km of tectonic displacement has occurred since 57 Ma (Cole et al., 2007). This is also supported by extrapolation from paleoclimate gradients from Fricke and Wings (2004) data. The MAT derived from leaf boundaries ($11-14.6^{\circ}\text{C}$) would correspond to a latitude of about 60°N . This extrapolation means the Matanuska Valley's current location (61°N) may be very close to the latitude where Chickaloon deposition was occurring (Sunderlin et al., 2011).

METHODS

To gain an understanding of the Chickaloon hydrology and conditions of carbonate formation, 42 carbonate samples were collected from five sites throughout the Matanuska Valley. These sample locations were based on accessibility and presence of carbonate. Each sample collected is tied to a measured stratigraphic section of the outcrop, so its stratigraphic location is constrained.

Samples were collected from two main outcrops, The Evan Jones Mine and Elephant Foot outcrop. Samples collected from ancillary localities (Coyote Late, The Pit, Chickaloon Road, Hicks Creek, and Moose Creek) located along the basin axis supplement these samples.

Outcrops at the abandoned and partially reclaimed Evan Jones Coal Mine in the Wishbone Hill district of the Matanuska Coal field contain the uppermost strata of the Chickaloon Formation. Exposures are excellent with approximately 90 m of vertical and 1 km of laterally continuous Chickaloon strata exposed at the main surface of the mine (Neff et al., 2011). A total of thirteen samples were collected from the Evan Jones Mine location. These samples may provide the most informative isotopic information because of existing age control at the site. A total of ten samples were gathered from the Elephant foot outcrop. This section has a total of 217 meters of vertical exposure.

A Dremel drill with a diamond-tipped bit was used to powder small parts of each sample in preparation of carbon and oxygen isotope analysis. Each drilled sample yielded about 30 mg of powder. These 42 samples were then analyzed at the Stable Isotope lab at

the University of Arizona.

RESULTS

The analysis provided $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for the carbonate samples with the standard VPDB scale,

$$\left(\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 1000 = \delta^{18}\text{C}$$

(Equation 1)

The VPDB values for $\delta^{18}\text{O}$ were then converted to standard mean ocean water (SMOW) using the formula (Sharp, 2007);

$$\delta^{18}\text{O SMOW} = 1.0309 \times (\delta^{18}\text{O PDB}) + 30.9$$

(Equation 2)

The SMOW scale is more convenient to work with for this topic of interest because the data are being used to infer the $\delta^{18}\text{O}$ of precipitation.

Carbon and oxygen isotopes data from the Chickaloon carbonate samples are presented in columns 1-6 in Table 1, and are illustrated in Figure 2, where $\delta^{13}\text{C}$ is on the y-axis plotted against $\delta^{18}\text{O}$ on the x-axis. Overall, the $\delta^{13}\text{C}$ values range from -10.34‰ to +13.69‰ (VPDB) with an average of -1.51‰. The $\delta^{18}\text{O}$ values range from -20.15‰ to -6.64‰ with an average of -14.96‰ (VPDB), and 10.13‰ to 22.11‰, with an average of 15.49‰ (SMOW).

In Figure 2, the difference in geographic and stratigraphic location is shown. When the samples are sorted by location, there is one strong isotopic grouping showing overlap between locations. Each location shares a similar pattern, however there are discernable $\delta^{13}\text{C}$ isotopic groupings between location, particularly between the two main data sets from Evan Jones Mine and Elephant Foot outcrop. They both have similar $\delta^{18}\text{O}$ values, but they show extremely different isotopic ratios of $\delta^{13}\text{C}$. Even given the differences, the data clearly shows one strong positive curvilinear pattern. This graph may also be interpreted as showing two major groupings of $\delta^{18}\text{O}$ values with variable $\delta^{13}\text{C}$ values.

DISCUSSION

1. Oxygen isotope ratios of groundwater

In order to calculate the isotopic ratios of groundwater, it requires the use of the appropriate isotopic fractionation factor and an estimate of the temperature of carbonate formation. For the former, fractionation

Table 1. Location	Sample Number	Sample Type	$\delta^{13}\text{C}$ (VPDB)	$\delta^{18}\text{O}$ (SMOW)
Evan Jones Mine	1.1	Cement	10.21	20.08
Evan Jones Mine	1.2	Spar	-4.44	13.64
Evan Jones Mine	2.1	Cement	7.61	19.64
Evan Jones Mine	2.2	Spar	0.62	15.74
Evan Jones Mine	3	Cement	-0.11	16.36
Evan Jones Mine	4	Cement	11.10	19.97
Evan Jones Mine	6	Cement	4.53	15.06
Evan Jones Mine	7	Cement	0.93	14.46
Evan Jones Mine	8	Cement	1.95	15.80
Evan Jones Mine	9.1	Cement	-4.78	13.04
Evan Jones Mine	9.2	Cement	2.91	14.02
Evan Jones Mine	9.3	Cement	-4.77	12.90
Evan Jones Mine	10	Cement	6.08	17.01
Evan Jones Mine	11	Concretion	4.35	14.15
Evan Jones Mine	13	Cement	0.07	15.41
The Pit	14	Concretion	13.69	22.11
The Pit	15	Cement	-1.07	17.42
The Pit	15.2	Spar	-8.39	15.16
Moose Creek	16	Cement	-7.12	13.41
Moose Creek	18	Cement	-1.52	10.13
Moose Creek	19	Cement	-1.99	10.18
Elephant Foot	21.1	Cement	-0.28	16.29
Elephant Foot	21.2	Cement	-2.25	15.86
Elephant Foot	21.3	Spar	-0.93	16.02
Elephant Foot	22.1	Cement	-3.14	15.61
Elephant Foot	22.2	Spar	-3.11	14.98
Elephant Foot	23	Cement	-0.19	13.72
Elephant Foot	24	Cement	-3.69	15.01
Elephant Foot	25	Cement	-5.45	13.82
Elephant Foot	26	Cement	-5.00	15.04
Elephant Foot	28	Cement	-6.32	13.84
Elephant Foot	29.1	Cement	-8.86	14.20
Elephant Foot	29.2	Cement	-10.34	14.04
Elephant Foot	30	Cement	-7.13	13.93
Elephant Foot	31.1	Concretion	-2.75	15.39
Elephant Foot	31.2	Concretion	-7.81	13.82
Coyote Lake	33	Cement	-9.79	15.05
Coyote Lake	34	Cement	-8.52	14.96
Coyote Lake	35	Cement	-4.24	15.13
Coyote Lake	36	Concretion	5.52	19.61
Chickaloon Road	37	Concretion	10.63	24.06
Chickaloon Road	38	Cement	-4.46	16.13
Chickaloon Road	39	Cement	-6.55	15.36
Chickaloon Road	40	Concretion	-5.41	13.41
Chickaloon Road	41	Cement	-7.58	16.02

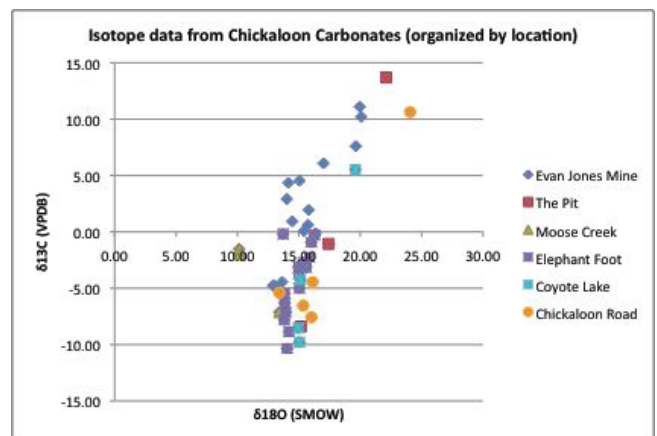


Figure 2. The isotopic data from carbonate is plotted with $\delta^{13}\text{C}$ plotted against $\delta^{18}\text{O}$. This isotopic data is organized by location. Notice the Curvilinear trend, and the large variety (many >5‰) of $\delta^{13}\text{C}$ values.

is calculated for sidente using the following equation (Carothers, 1988):

$$1000\ln \alpha = 2.780(10^6 / T^2) - 2.89$$

(Equation 3)

The temperature of carbonate cement formation is ambiguous in the absence of clumped isotope data. Not much is known for certain about how and when these cements formed. One possibility could be under near-surface conditions. In this case a temperature of 12.8°C (285.95°K) is used, which is the estimated average MAT for the Chickaloon during the Eocene (Sunderlin et al. 2011). However, recent clumped isotope work from the Kootznahoo Formation in Alaska suggests that carbonates form during burial at higher temperatures (~58.8°C). In the absence of clumped isotope data from the Chickaloon cements, two estimates of $\delta^{18}\text{O}$ of groundwater are made. One using surface temperature obtained using leaf physiognomic analyses, and the other made assuming that Chickaloon Cements formed at temperatures similar to Kootznahoo Cements (See Figure 3 and 4).

Using these temperatures, it is possible to estimate the amount of isotopic fractionation associated with carbonate formation and thus estimate isotopic ratios of groundwater that was in equilibrium with the minerals during formation. In order to calculate the $\delta^{18}\text{O}$ of groundwater fluids present during carbonate formation, the fractionation value is subtracted from the isotopic ratios of the carbonate (Affek, 2008).

The oxygen isotopic values preserved in the carbonate of the Chickaloon Formation are strongly depleted (-6.64‰ to -20.15‰ VPDB), and relatively invariant between locations. These strongly depleted compositions are consistent with North American paleolatitudinal trends, and may have been accentuated by globally increased precipitation due to an intensified hydrologic cycle during the “greenhouse-world” condition of the Paleocene-Eocene boundary.

The relatively constant and distinct ^{18}O composition of carbonates indicate that during formation, the $\delta^{18}\text{O}$ composition of ground water, as well as temperature remained relatively constant. Invariant $\delta^{18}\text{O}$ compositions have been interpreted as recording precipitation in stable shallow groundwater systems

at depths of a few meters, below which reasonable variability is buffered and only varies within a few degrees of MAT (Ludvigson et al., 1998, Matthes, 1982).

2. Carbon isotope ratios of groundwater and methanogenesis

Similar to $\delta^{18}\text{O}$ calculation, in order to calculate the $\delta^{13}\text{C}$ isotopic ratios of groundwater, the appropriate isotopic fractionation factor and an estimate of temperature of carbonate formation is needed. fractionation is calculated for sidente using the following equation (Carothers, 1988).

$$10000\ln \alpha = 0.8610(10^6 / T^2)$$

(Equation 4)

Carbon fractionation is less dependant on temperature than oxygen is, which is why there are different constants between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. This difference in constants results in a smaller fractionation value for $\delta^{13}\text{C}$. Knowing the temperature of carbonate cement formation is less important for $\delta^{13}\text{C}$ because fractionation is not very sensitive to temperature. Nonetheless, the $\delta^{13}\text{C}$ values of groundwater will be calculated using surface temperature and temperature of Kootznahoo Cement formation (See Figure 3 and 4).

What is striking about the Chickaloon Formation, particularly at the Evan Jones Mine site are the high $\delta^{13}\text{C}$ values. Interestingly, high $\delta^{13}\text{C}$ values are dominant at the Evan Jones Mine, whereas no high $\delta^{13}\text{C}$ are found at the Elephant Foot outcrop. This could be due to lateral shifts in environments, where lithofacies at Evan Jones Mine are primarily swampy mire environments, and Elephant Foot sediments are dominated by fluvial deposits. The Evan Jones Mine is a coalmine, indicating backswamp wetland environments were persistent enough to accumulate peat. These edaphic differences between location could explain the different CH_4 generation rates.

Non-marine carbonates have $\delta^{13}\text{C}$ values reflecting the isotopic compositions of the waters from which they precipitated. Typically $\delta^{13}\text{C}$ values in these environments are in the range -20 to +5‰ (Leng, 2005). The generally positive (>5‰) $\delta^{13}\text{C}$ values suggest formation in wetland paleosols under reducing

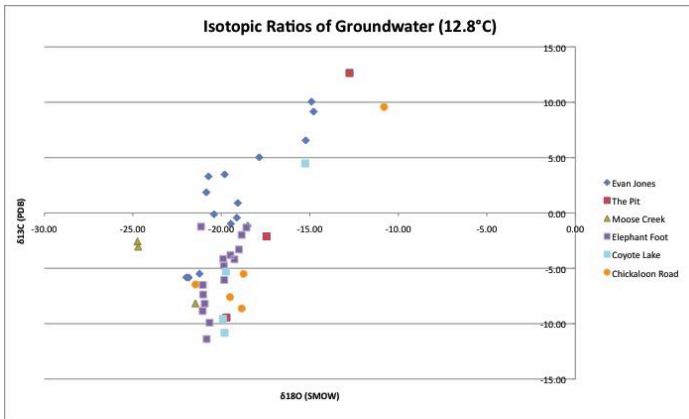


Figure 3. The inferred isotopic ratios of the groundwater plotted $\delta^{18}\text{O}$ against $\delta^{13}\text{C}$. Isotopic fractionation value calculated using a temperature of 12.8°C .

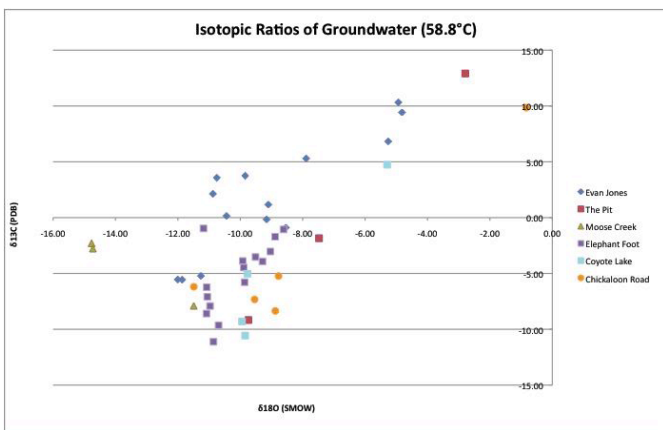
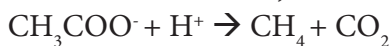


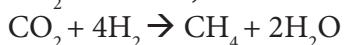
Figure 4. The inferred isotopic ratios of the groundwater plotted $\delta^{18}\text{O}$ against $\delta^{13}\text{C}$. Isotopic fractionation value calculated using a temperature of 58.8°C .

conditions in the methanogenic zone. Methane is generated by anaerobic methanogenic bacteria in anoxic sediments by two metabolic pathways (Whiticar et al. 1986, Schlesinger, 1997):

(1) Acetate fermentation,



(2) CO_2 reduction,



Although both pathways may operate simultaneously, CO_2 reduction is dominant in the sulfate-free marine environments, whereas acetate fermentation is the

dominant pathway in freshwater environments. Within temperate terrestrial environments, acetate formation accounts for $\sim 70\%$ of all methanogenesis (Whiticar and Faber, 1986).

Methane-producing soils have been found to contain CO_2 with $\delta^{13}\text{C}$ values higher than expected due to normal plant and soil respiration. During CO_2 reduction, the CO_2 present in the soil solution forms HCO_3^- which serves as an electron acceptor (Schlesinger, 1997). This involves fractionation of ^{12}C and ^{13}C . The methane generation process is kinetically controlled, enriching CH_4 in the light isotope (^{12}C) and the residual CO_2 in the heavy isotope (^{13}C). In turn, the residual HCO_3^- in pore fluids during carbonate precipitation becomes enriched with heavier ^{13}C , resulting in an enriched $\delta^{13}\text{C}$ value in the carbonates (Whiticar and Fabor, 1986).

Previous work describing high values of $\delta^{13}\text{C}$, has been used to infer methanogenesis from high latitude wetland soils during the mid-cretaceous (Ufnar et al., 2004, Ludvigson et al, 2008). Fossil sphaerosiderites from Canada and Alaska with $\delta^{13}\text{C}$ values as high as $+10.8\%$, were found, and interpreted as evidence for methanogenesis (Ufnar et al 2004). Methanogenesis has also been inferred in Eocene Arctic soils from high $\delta^{13}\text{C}$ values found in tree fossil carbonates from Axel Heiberg Island (Jahren et. al., 2004). Given the unusually high positive carbonate values seen at the Evan Jones Mine outcrop, these carbonates most likely resulted from methanogenesis. The $\delta^{13}\text{C}$ values are much higher than values expected due to plant and soil respiration, which would be similar to plant material being respired (Quade et al., 1989).

It has been suggested that during the early Eocene, a contributor to the global greenhouse climate was wetland-liberated methane. This resulted in a polar stratigraphic ice cloud that prevented severe winter cooling in the polar-regions (Sloan et al., 1992). This, as well as other factors, may have accounted for the reduced thermal gradient from the equator to the poles during the Eocene. Annual emissions of methane from the Chickaloon paleosols, as indicated by the high positive values of $\delta^{13}\text{C}$, may have been a contributing factor to the relatively warm Arctic climate during the early Eocene.

CONCLUSION

The stable isotopes of the carbonates of the Chickaloon Formation reveal important information regarding the paleoclimate history of the region. Due to high values of $\delta^{13}\text{C}$ (up to +13.69‰), it appears that methanogenesis was occurring in the Chickaloon paleosols. Methane in the atmosphere has been shown to be a powerful greenhouse gas (Lashof and Ahuja, 1990), and its oxidation is a significant source of water vapor in the stratosphere (Cicerone and Oremland, 1988). Annual emissions of methane from the Chickaloon soils, as indicated by the carbon isotope relationships in carbonate, may have been a contributing factor to the relatively warm high latitude climate during the Early Eocene.

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