Clumped Isotope Paleoaltimetry of the Northwestern Colorado Plateau

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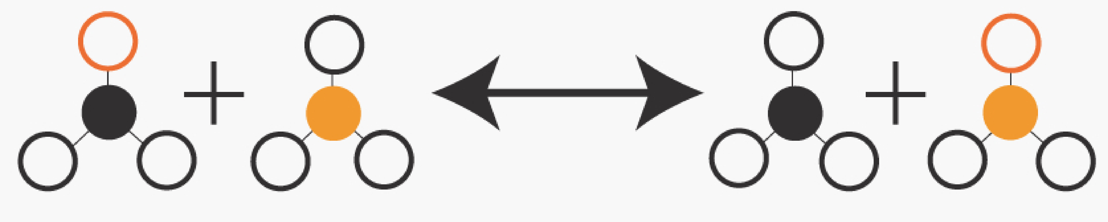
Abstract

A technique for estimating paleoevelation is based on isotopic measurements of δ018 of carbonate minerals; however, the technique is limited by the need to assume a δ018 value of the ancient water. The relatively new "clumped isotope" method is capable of measuring paleotemperatures without the need for assuming the δ018 value of the original water, but due to the technique's youth, it hasn't been shown to work for bulk rocks with ages much greater than 10 million years. The goal of this study is to use the clumped isotope thermometer on lacustrine carbonate rocks from the northwestern portion of the modern Colorado Plateau, with samples dating from the Eocene back to the Cretaceous. The data shows that the majority of samples have temperatures that are hotter than would be expected to represent surface temperatures, thus the influence of diagenetic alternation in the sample suite is great. Despite this, there are a few samples that have temperatures that are representative of surface or near-surface temperatures. In this group, there is a single sample from the Paleoeocene-Eocene Colton Formation that suggests that the northwestern Colorado Plateau was at a high elevation as early as 53 Ma, which would have major implications on the accepted history of the rise of the Colorado Plateau, which is currently thought to have gained much of its present elevation in the last 10 million years.

Carbonate 'Clumped' Isotope Thermometry



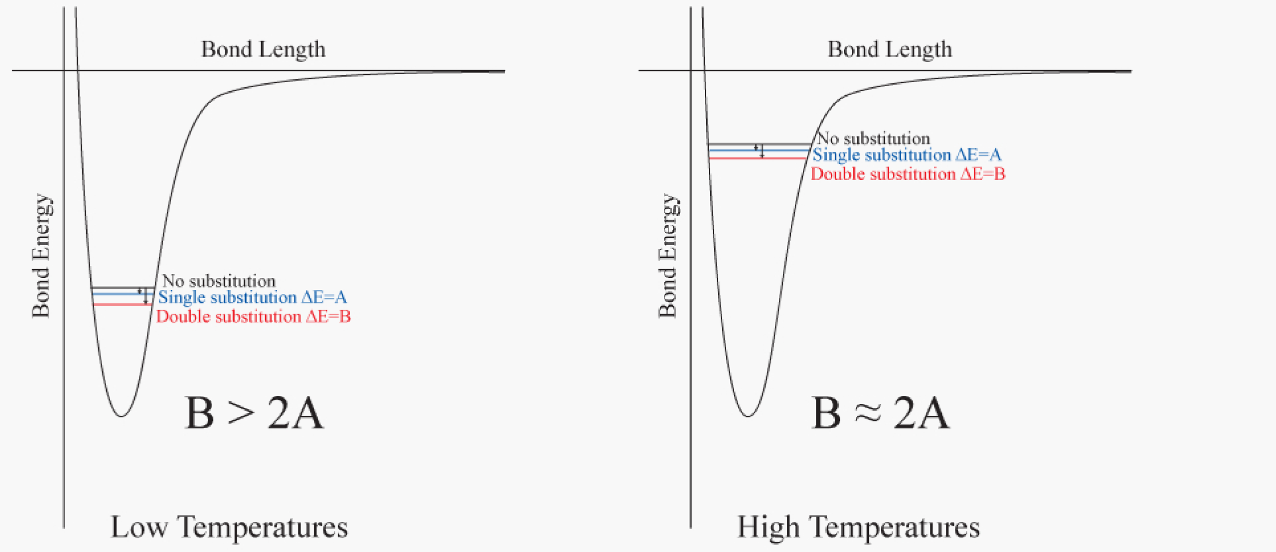
Carbonate exchange reaction (calcium excluded):

^{12}C ● ^{16}O ○

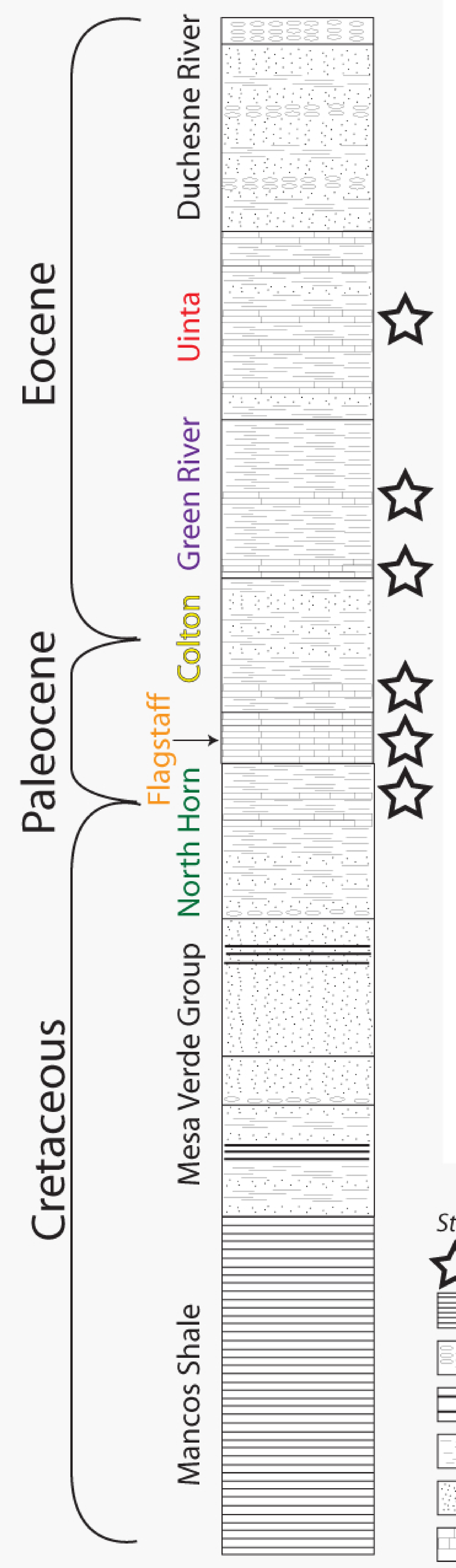
^{13}C ● ^{18}O ○

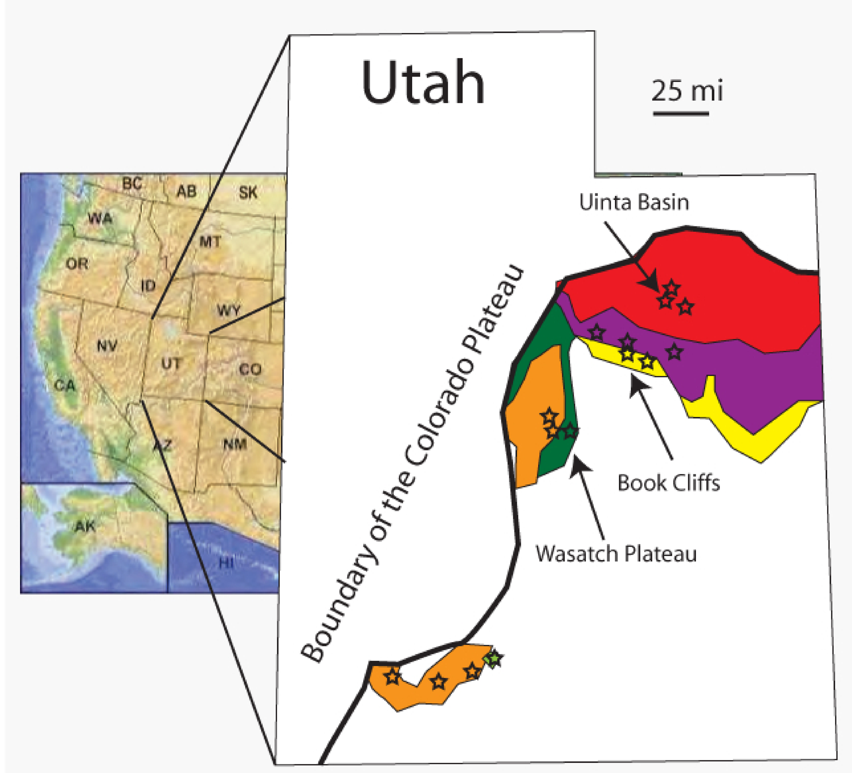
$$Ca^{13}C^{16}O_3 + Ca^{12}C^{18}O^{16}O_2 \leftrightarrow Ca^{13}C^{18}O^{16}O_2 + Ca^{12}C^{16}O_3$$

The carbonate clumped isotope themometer determines the temperature of a carbonate sample based on the relative 'clumping' of heavy isotopes into doubly substituted carbonate molecules. There are two general explanations for clumping; a thermodynamic and a statistical arguemnt. The thermodynamic arguement is as follows. At low temperatures, the 'clumped' molecules are thermodynamically favorable; that is, the internal energy of the molecules dominate compared to the pressure, volume, and entropy contributions. When a system is taken to high temperatures, the internal energy changes due to clumping become small compared to the influence of the temperature term, making clumping not thermodyanically important. The statistical mechanics is shown in the figures to the right. Each diagram is an Morse potential, which approximates the vibrational energy of a molecule as a simple harmonic oscillator. At low temperatures, the molecule will reside low in the energy well, while at higher temperatures it will jump to higher vibrational states, in effect moving up the energy well. Substituting higher mass isotopes into the molecule will reduce the vibrational energy. At low temperatures, the drop in energy for a doubly substituted molecule is more than twice that of a singly substituted molecule; at high temperatures this is not the case. Thus, at low temperatures, the clumping of heavier isotopes into single molecules is prefered as it lowers the vibrational energy of the molecule, making it more stable.



Stratigraphy and Sample Locations





Shown in this panel is the general stratigraphy and location of the samples collected for this study. All the samples are micrite limestone collected from beds that are lacustrine in nature. From the generalized stratigraphic column, it is clear that many of the beds are limited in their total thickness, thus offering constraints on the approximate burial depth of the samples. All of the samples that have been analysed so far in this study have originated from the northern set of samples, collect from the Uinta Basin, Book Cliffs, and Wasatch Plateau regions of Utah. Colors of the units on the map of Utah match the colors of the units in the stratigraphic column (units with names in black are not drawn on the map for clarity).

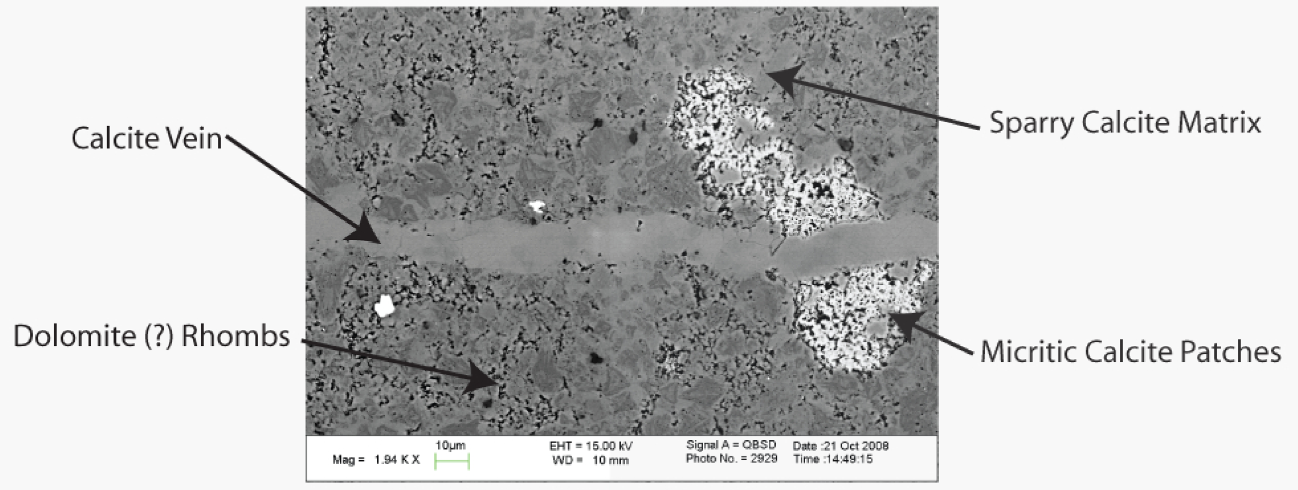
Stratigraphic Column Key

- ☆ Sample Collected from this unit
- Marine black shales
- Conglomerate
- Coal/organic material present in the unit
- Nonmarine shales
- Nonmarine sandstones
- Limestone, primarily lacustrine. May be interbedded with ss, shales

Sample Characteristics

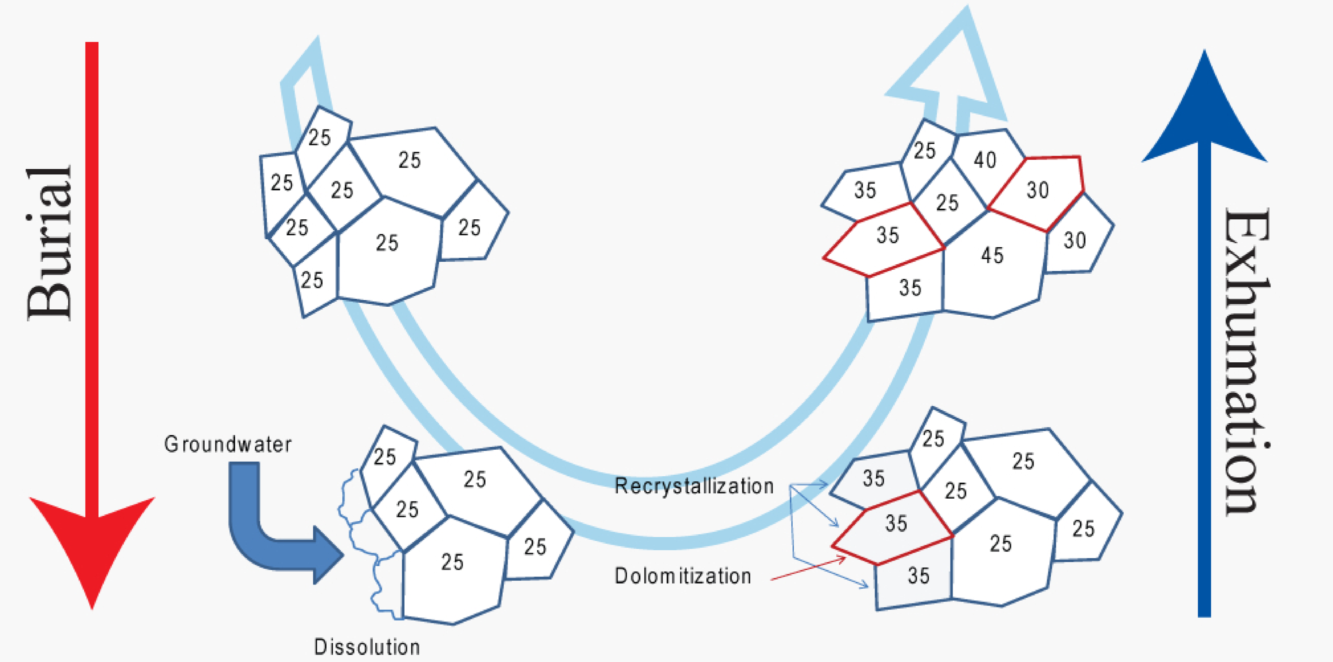
Limestone outcrop in Uinta Basin, near Duschnse, Utah.

To the left is a picture representing the standard outcrop style, with complete beds of micritic, grey-white limestone. In hand-sample, the limestone looked nearly uniform in texture and material. Once back from the field, a more rigorous analysis of some of the samples revealed a much more complex history to the limestone than would be determined just from a hand-sample. For example, the SEM image shows several textural and compositional difference, as well as late-stage veining within a sample described in the field as a pure, grey micrite. Generally, microscopic analysis of the rocks indicated several stages of diagenesis upon burial.



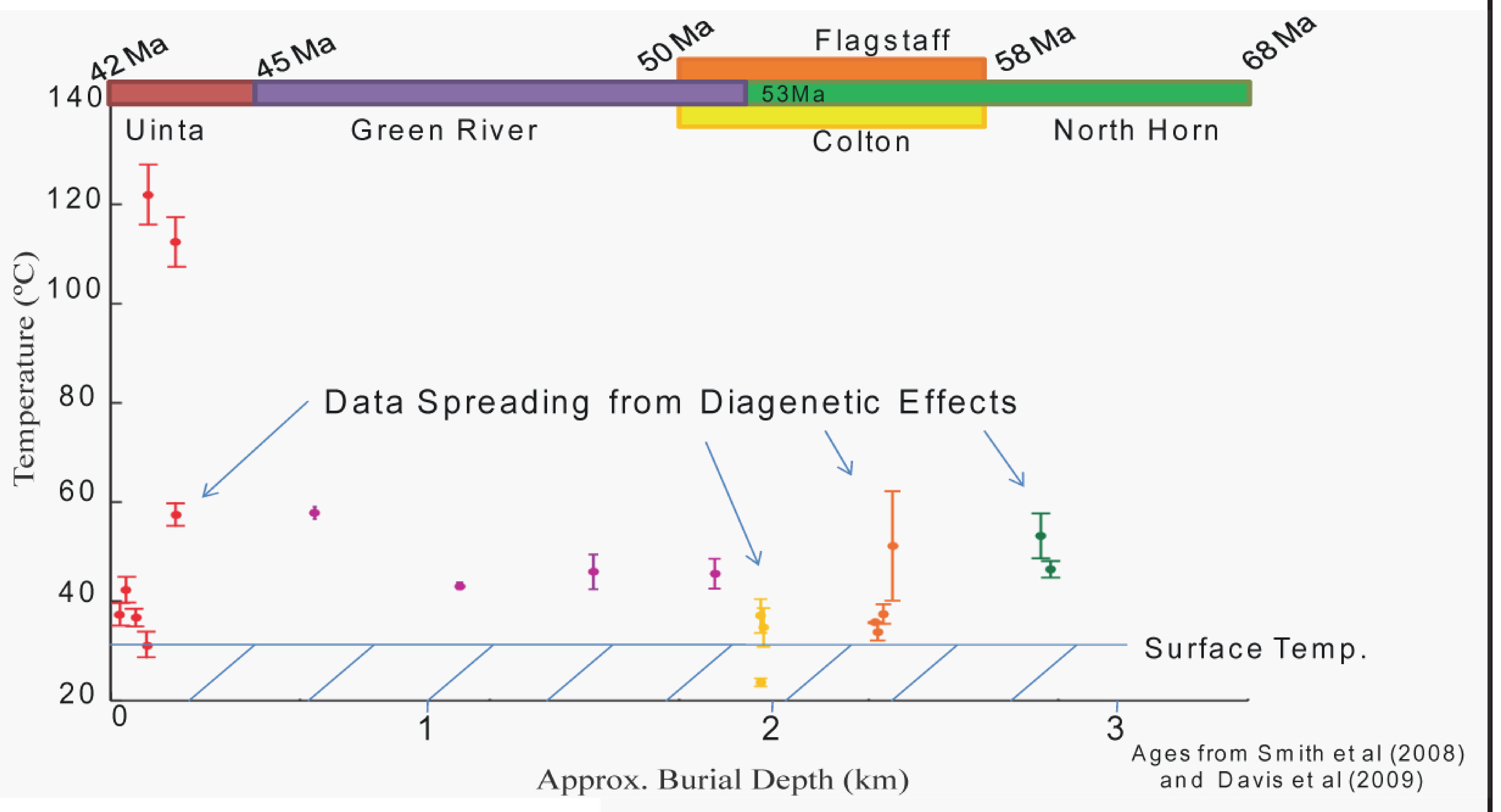
SEM image of sample JT-01-08, Colton Formation.

Diagenetic Effects on Temperature

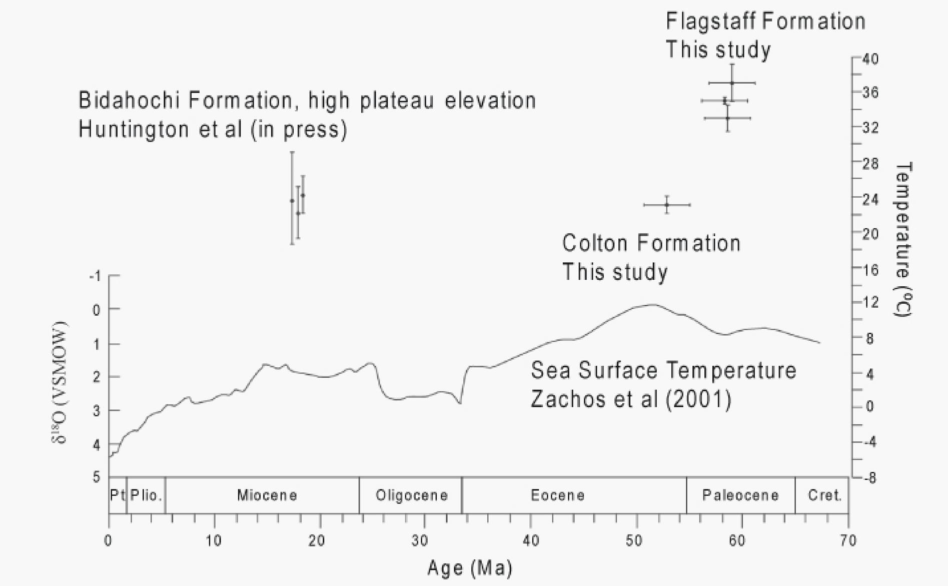


Shown above is a schematic diagram of the effects of diagenesis on the temperatures recorded within a cluster of carbonate crystals based on the clumping of heavy isotopes. The first cluster is one that has formed at surface conditions (25 °C), which is shown in the temperatures of all the crystals. Upon burial, it is likely that the carbonate is exposed to groundwater, which dissolves some (but very importantly, not all) of the crystals. The carbonate then recrystallizes at the higher temperature, and perhaps is replace with dolomite, but dolomite records temperature in the clumping of heavy isotopes in the same fashion are calcite, so this does not invalidate the analysis. Upon an extended period of burial and subsequent exhumation, the cluster can have crystals that are representative of a large range of temperature. Work in John Eiler's laboratory suggests that the crystals do not reset to lower temperatures upon exhumation, meaning that any preserved low temperatures are primary (Bonifacie, Bergmann, unpublished data). Due to the rarity of doubly substituted isotopologues, large sample sizes (8-10 mg) are necessary for the clumped isotope thermometer. This means that each sample will likely be a combination of primary and secondary temperatures; however, there is no evidence that diagenetic effects reduces the temperature signal seen in the samples. Thus, a low temperature analysis is taken to be indicative of a true formation temperature, and cannot be easily explained through diagenetic processes, the easiest of which would be recrystallization upon exhumation.

Results



Above, all the data collected for this study. Error bars represent 1-standard error of the mean temperature value. Right, the summary figure for the results with tectonic implications. The coldest Flagstaff Formation and Colton Formation temperatures are shown compared to samples of the Miocene Bidahochi Formation, from the southwestern Colorado Plateau, which Huntington et al (in press) interpret as being evidence of high elevation of the Colorado Plateau. A sea-surface temperature curve is plotted to show that the Colton Formation sample, which matches the temperature of the Bidahochi Formaiton, cannot be explained by climatic variability. This single data point suggests that the northwestern Colorado Plateau had reached substantial elevation by the early Eocene.



Conclusions

*Temperature data is largely not representative of surface (i.e. formation) temperatures, as all but two samples fall above 30 °C

*Diagenetic effects are hard to quantify, but suggest that low temperatures are indicative of formation or near-formation temperatures

*There is a possible uplift signal in Paleocene-Eocene Colton Formation, but the spread of data makes any interpretation based on a single (but reproducible!) data point from the Colton Formation

References and Acknowledgments

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