

Paleoaltimetry from “clumped” ^{13}C - ^{18}O bonds in carbonates, Colorado Plateau

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The elevation history of Earth’s surface is a key element linking tectonic, geodynamic, climatic, and surface processes, but remains difficult to reconstruct from the geologic record. In contrast to conventional stable isotope paleoaltimetry approaches, the new “clumped” ^{13}C - ^{18}O paleothermometer independently determines carbonate growth temperature and the $\delta^{18}\text{O}$ of water from which the carbonate grew, potentially enabling the effects of altitude, climate, and seasonality to be distinguished. This approach has been successfully applied to paleosol nodules. Here, we examine what other materials may potentially access paleoelevation information using this technique, including gastropods, the bivalve *anomia*, oysters, barnacles, soil, marl, and limestone from Cretaceous to Pliocene deposits from and adjacent to the Colorado Plateau, southwestern USA.

The abundance of ^{13}C - ^{18}O bonds in diverse carbonate materials from related sediments records temperatures between 20-84°C and $\delta^{18}\text{O}_{\text{snow}}$ water values of -2 to 12‰. Temperature estimates for independent preparations of the same sample are reproducible to within ± 0.55 -2.2°C (2 s.e.), and average temperatures determined for different materials from the same deposit exhibit negligible variations (± 0.05 °C).

While samples at the lower end of the observed temperature range represent reasonable Earth surface conditions that may be interpreted in terms of paleoelevation, samples yielding temperatures in excess of ~33°C likely provide a record of carbonate recrystallization/replacement during burial metamorphism (‘resetting’). Clear examples of resetting include gastropod fossils in which original aragonite is completely replaced by calcite (yielding apparent temperatures of 76.5 \pm 1.7°C) and a suite of more cryptically reset Pliocene molluscs from tidal flat facies that yield temperatures of >42°C. Most apparently unreset samples are fine-grained (impermeable) micrites, which consistently yield temperatures within the plausible Earth-surface range. This suggests that resistance to diagenesis is grain size dependent – a promising result given the abundance of well preserved fine-grained lacustrine and marine carbonates found throughout the geologic record. Results for micritic carbonates from Middle Miocene to Pliocene age record reasonable spring to summer depositional temperatures and oxygen isotopic values relative to modern lake waters on the Colorado Plateau.

Simulations of dry-out and halite precipitation due to CO₂ injection

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Although CO₂ is not very soluble in supercritical CO₂, a continuous stream of CO₂ being injected into a formation, will result in a region around the injection well to dry out. As the water of the formation brine is continuously extracted, the irreducible water saturation may attain practically zero. Enhanced injectivity is the result in a low salinity brine environment. In formations saturated with highly saline brine (e.g. Northern German Basin) the outcome is opposite: injectivity is impaired. In this case, the brine becomes supersaturated as continuously H₂O evaporates into the CO₂ phase and salt (halite) precipitates in the pores. The porosity and permeability diminish, which can lead to the loss of a injection well.

We present simulations of these processes as an example of pre-injection study for a CO₂ injection and storage site. The simulation tool consists of a commercial compositional code used extensively in the oil and gas industry to simulate the flow of multiple phases (oil, water, gas) in porous or fractured media. The mutual solubility of CO₂ and H₂O with a correction for salinity is implemented as described in Spycher and Pruess (2005). The brine salinity is adjusted accordingly until the saturation threshold is reached and halite is precipitated. The severity of this process can be evaluated for a specific site and also remediation strategies (injection of dilute fluids) tested.

Reference

Spycher N. and Pruess, K. (2005), CO₂-H₂O mixtures in the geological sequestration of CO₂, II Partitioning in chloride brines at 12-100°C and up to 600 bar, *Geochim. Cosmochim. Acta* **69**, 13, 3309-3320.