A probabilistic analysis of meteorically altered $\delta^{13}C$
chemostratigraphy from late Paleozoic ice age carbonate platforms

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ABSTRACT
The stratigraphic expression of meteoric diagenesis in carbonates is
glimpse into the weathering, fluid transport, and biological productive-
ty of the ancient near-surface terrestrial environment. To infer this
environmental information, we use a probabilistic approach to merge
an isotope-based reactive transport model with chemostratigraphic
data from carbonates that were subaerically exposed during an expan-
sion of the late Paleozoic ice age in the middle Carboniferous. The
rate of carbon flowing through the carbonate platform relative to the
rate of carbon reacting between mineral and fluid phases controls the
length scale, curvature, and magnitude of the diagenetic carbon iso-
tope profiles. The ratio of advection to reaction is determined for seven
stratigraphic sections, and the advection rate is used to estimate the
minimum carbonate weathering associated with each profile. These
carbonate weathering rates extrapolated over the expansive shallow
carbonate platforms of the middle Carboniferous indicate that gla-
coeustatic fall may have caused a 20%–50% increase in the dissolved
CaCO$_3$ flux to the ocean. The complex feedbacks among carbonate
weathering and accumulation, atmospheric $pCO_2$, glacioeustasy,
and passive margin subsidence may have played an unexplored role in
the glacial-interglacial climate dynamics of the late Paleozoic ice age.

INTRODUCTION
The sedimentary record of seawater chemistry forms a basis for our
understanding of the coevolution of the atmosphere, lithosphere,
and biosphere through deep time. Chemical sediments, such as carbonates,
precipitate from the water column and form layered archives from which
secular changes in seawater chemistry are inferred (e.g., Hayes et al., 1999;
Veizer et al., 1999). These carbonate sediments often are deposited in a
shallow environment that can be subjected to diagenetic reactions during
local sea-level fall or uplift (James and Choquette, 1984). Without proper
identification, this diagenetic window may lead to false inferences about
weathering, fluid transport, and biological productivity of the ancient
near-surface marine environment. To infer this environmental information,
we use a probabilistic approach to merge an isotope-based reactive trans-
port model with high-resolution isotopic data from carbonates that were
subaerically exposed during an expansion of the late Paleozoic ice age in
the middle Carboniferous. The rate of carbon flowing through the carbonate
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the glacial-interglacial climate dynamics of the late Paleozoic ice age.

FORWARD REACTIVE TRANSPORT MODEL
A representative forward model for meteoric diagenesis must capture
persistent isotopic exchange between mineral phases and a fluid flowing
through the pore space of the rock. In detail, this process depends on
fluid carbonate chemistry and small-scale fluid dynamics arising from
complex permeability networks. However, a simpler modeling approach
may be sufficient to capture the first-order isotopic expression of meteoric
diagenesis in the phreatic zone. The dissolution of carbonate minerals
in the upper vadose zone buffers the carbonate chemistry of the fluids
entering the phreatic zone, where isotopic exchange between fluids and
together clearly persists (Allan and Matthews, 1982; Lohmann, 1988; Swart
and Eberli, 2005). Modern pore-water chemistry suggests that this dia-
genesis occurs near or at equilibrium in the phreatic zone (Plummer et
al., 1976; Budd, 1988; Whitaker and Smart, 2007). These observations
justify a modeling approach where the diagenetic fluids have carbonate
chemistry near equilibrium, and the diagenetic reaction can be prescribed
as continuous small-scale dissolution-reprecipitation of CaCO$_3$.

The meteoric diagenesis model presented here contains a Cartesian
grid in two dimensions, where each cell represents a volumetric geometry
of 1 m$^3$ (Fig. 1A). In each grid cell, the mass and isotopic composition
of carbon, oxygen, and calcium are tracked for a fluid and rock phase
with constant porosity (Fig. 1B). With each step forward in time, the
mass and isotopic compositions of the fluid move between adjacent grid
cells according to a prescribed two-dimensional (2-D) divergence-free
flow field. During the same time step, mass and isotopic compositions
exchange between the rock and fluid phases at a prescribed reaction rate
(a free parameter inferred from the duration of exposure). The initial fluid
boundary conditions (carbon isotopic composition and concentration) are
set to observations from fluids at the top of phreatic zones in modern karst
systems (−8% $\delta^{13}C$ and 40 ppm total C; Zhao et al., 2015). The advection
of each fluid parcel is solved by the continuity equation (Equation 1) with
a forward marching Euler numerical scheme.

\[
C_{i+1} = C_i - v_i (dt / dy)(C_i - C_o) - u_i (dt / dx)(C_i - C_{i-1}),
\]

where $C_i$ is the property of interest, such as the $\delta^{13}C$ of the fluid, for a
single mesh cell at the current time step, and the i + 1 subscript represents
the property at one time step \((dt)\) forward. \(C_a\) and \(C_i\) correspond to the upstream boundary conditions for the mesh cell in the \(x\) and \(y\) directions, and \(u\) and \(v\) are the \(x\) and \(y\) components to the velocity field. The middle Carboniferous isotopic excursions analyzed in this paper have length scales of 10–100 m and likely formed over long time scales \(\left(10^5–10^6\ \text{yr}\right)\). Over these time and length scales, diffusion is negligible (Péclet number \(Pe\) and direction).

Step represents the dissolution of a small calcite particle followed by the reaction, which is described by the dissolution rate constant, \(k\). In the laboratory, the reaction rate constant is determined by the mass flux \((F)\) between the fluid and rock phases. The mass \((M)\) concentrations of carbon, oxygen, and calcium in the rock phase (denoted as subscript \(r\)) are set to a stoichiometric calcite composition, and the mass exchange between the rock and fluid is proportional to the mass of each element in the \(CaCO_3\) mineral (Equation 3). Essentially, the reaction step represents the dissolution of a small calcite particle followed by the reprecipitation of a new calcite particle of the same mass. The change in the isotopic composition \((\delta)\) in the fluid and rock is a function of the total mass exchange between the two phases and the fractionation factor \((\alpha)\) for each element \(j\) (Equations 4 and 5). An isotopic fractionation factor \((\alpha)\) for a given element that is equal to 1 corresponds to no isotopic fractionation between the fluid and the rock at equilibrium.

\[
(dM/dt)_{\text{rock}} = -(dM/dt)_{\text{fluid}} = F_i \delta_i - F_o \delta_o. \tag{2}
\]

\[
F_i = F_o = R \times M_{\text{rock}}. \tag{3}
\]

\[
(d\delta/dt)_{\text{rock}} = \left[F_i \delta_i + (\alpha_i - 1.0) \times 10^\gamma\right] - F_o \delta_o. \tag{4}
\]

\[
(d\delta/dt)_{\text{fluid}} = \left[F_i \delta_i + (\alpha_i - 1.0) \times 10^\gamma\right] - F_o \delta_o. \tag{5}
\]

As the infiltrating fluids react with the host rock, a transient reaction front develops and propagates in the direction of flow. This reaction front is the region over which the isotopic compositions of the host rock are transitioning between original isotopic composition and diagenetic fluid isotopic composition. The modeling of mass loss and fluid-rock interactions in porous media by Lichtner (1988) provides a physical basis for understanding the thickness of the reaction front. The thickness of the front is determined by the ratio of mass transport to the ratio of mineral dissolution (mass reaction). The isotope-based model presented in this work captures this phenomenon of a quasi-steady-state reaction front propagating through the rock with a shape that is determined by the ratio of the mass of a given element advecting through the pore space in a fluid to the mass of that same element moving between the fluid and rock phases (Fig. 1D). Regardless of the absolute values chosen for fluid composition, reaction rate, or advection rate, the dimensionless advection to reaction ratio for a specific element of interest (carbon) determines the curvature, magnitude, and length of the diagenetic reaction front for that same element along a single stream line.

**FREE PARAMETER ESTIMATION**

A probabilistic approach can extract quantitative information (including uncertainty) about the free model parameters from the isotopic data and hundreds of thousands of iterations of the predictive model. With Bayesian inference, probability distributions are provided for each free model parameter (mass advection rate, mass reaction rate, and total duration of diagenesis; see Fig. DR1 in the GSA Data Repository\(^1\)). The inference algorithm updates these distributions to posterior distributions based on the likelihood that the observations (isotopic data and stratigraphic height) could be generated by the predictive model (Metropolis et al., 1953; Hastings, 1970; Patil et al., 2010). Generally, this process involves comparing the observed data set to hundreds of thousands of realizations of the predictive model where the free parameters are selected from the full range of prior distribution values. When the data and model offer little information to constrain a free parameter, the prior and posterior distributions are nearly identical.

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\(^1\)GSA Data Repository item 2017034, Figure DR1 and a synthetic test of the Bayesian inference model, is available online at http://www.geosociety.org/pubs/R2017.htm or on request from editing@geosociety.org.
The only prior information about the free parameters for the middle Carboniferous isotopic data is the maximum duration of diagenesis at Arrow Canyon, Nevada (USA), that is constrained by the age difference in conodonts below and above the unconformity (Fig. 2B; 2.5 ± 1.5 m.y.; Bishop et al., 2009). To represent a lack of prior knowledge about reaction and advection rates, the prior distributions for these free parameters are uniform flat distributions covering five orders of magnitude (Figs. 2C and 2E; 10⁻¹⁻⁻¹⁰% reaction/m.y. and 10⁻¹⁻⁻¹⁰ m/yr). However, the length scale, curvature, and magnitude of the Arrow Canyon isotopic excursion are only generated by a narrow range of reaction and advection rates (Fig. 2E). In the remaining stratigraphic sections, there is no reliable prior information about the duration of diagenesis, so the posterior distribution for reaction rate inferred from the Arrow Canyon data set (Fig. 2D) is used as a prior distribution for reaction rate in the remaining inference simulations. The resulting posterior distributions of the advection to reaction ratio illustrate the range of values that can predict the chemostratigraphic data with this diagenetic model (Figs. 2A and 2E).

When the inferred duration of diagenesis and the advection to reaction ratio are considered jointly, the carbon isotopic observations from each stratigraphic section may reveal information about the local carbonate weathering. For example, Arrow Canyon has an advection to reaction ratio of ~8, so 8 times more carbon passed through the section than reacted between the fluid and rock. The carbon in this advecting fluid is a mixture of organic carbon (~25‰) and dissolved rock carbon (+2‰) from the overlying vadose and soil zone (Pearson and Hanshaw, 1970; Rightmire and Hanshaw, 1973). The isotopic composition of −8.0‰ δ¹³C for the initial fluid is based on observations in the upper portion of modern phreatic fluids in the karst terrain of southeastern China (37% of the carbon flux comes from dissolved carbonate; Zhao et al., 2015). This number certainly does not represent the full range of karst fluids in modern or ancient systems, but serves as an estimate of the dissolved carbonate load in terrestrial karst environments. In the Arrow Canyon example, a minimum of 3 m dissolves in the overlying vadose zone every 1 m.y. (37% times the advection to reaction ratio of 8). Therefore, the weathering fluxes from each section are proportional to the advection to reaction ratio, which is determined by the curvature of the isotopic excursion. The lowest inferred weathering rates are in the Strawberry Creek section of the Salt River Range (Wyoming, USA), where at least 0.5–1.5 m of limestone are dissolved per 1 m.y., and the highest weathering flux in Leadville (Colorado, USA; U.S. Geological Survey Core U956) corresponds to the dissolution of 19–80 m of limestone per 1 m.y. (Fig. 2E).

**LATE PALEozoIC GlACIAL-INTERGLAcIAL DYNAMICS**

High-precision U-Pb zircon ages from interbedded ash layers in late Paleozoic cyclic far-field stratigraphy suggest that ice sheet volume varied at the frequency of long-term eccentricity (400 k.y.; Davydov et al., 2012). Insolation changes at this frequency are small, so there must be a significant positive feedback amplifier that is insensitive to higher frequency insolation changes (<400 k.y.). The drawdown of pCO₂ from the dissolution platform carbonates during lowstands may be such a mechanism.

Carbonate accumulation in the modern interglacial ocean is estimated as 32 × 10¹² mol CaCO₃/yr (Milliman and Draxler, 1996), and is fixed on long time scales to the volcanic CO₂ input to the atmosphere. The change in carbonate weathering from sea-level highstand to sea-level lowstand can be estimated by extrapolating the dissolution rates calculated from the late Paleozoic carbon isotopic profiles across the entire surface area of shallow-water carbonate platforms. The magnitude of this change is negligible in the modern interglacial ocean (<1% change) because of the limited surface area of shallow-water carbonates (0.6 × 10⁶ km²; Walker et al., 2002). This conclusion is supported by observations that the carbonate compensation depth and carbonate accumulation rates did not change significantly from the Last Glacial Maximum through deglaciation (Catubig et al., 1998). However, shallow-water carbonate shelf area was much greater in the late Paleozoic (40 × 10⁶ km²; Walker et al., 2002). Consequently, the carbonate weathering flux to the late Paleozoic ocean may have increased 20%–50% whenever sea level fell significantly. If

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**Figure 2.** A: Carbon isotopic data from seven middle Carboniferous stratigraphic sections and cores spanning the western United States. Gray data represent all sections, pinned at 100 m to the regional unconformity surface (stratigraphic context and section locations reported by Dyer et al. [2015]). B: Prior and posterior distributions for the duration of diagenesis for the Arrow Canyon (Nevada, USA) data. C: Distributions for the advection to reaction ratio inferred from the Arrow Canyon data. D: Distributions for the reaction rate for each section. E: Distributions of the advection to reaction ratios inferred for each of the stratigraphic data sets depicted in A (colored accordingly).
carbonate accumulation in the ocean is less than the increased flux of dissolved CaCO$_3$, then carbon would move from the atmosphere to the ocean (Sigman and Boyle, 2000), and this loss in atmospheric pCO$_2$ would result in further cooling and a positive feedback with ice sheet expansion. Moreover, deep-sea carbonate deposition in the modern ocean is dominated by coccolithophores and pelagic foraminifera, which did not evolve until the Triassic, so the lowstand late Paleozoic ocean may have had a lower capacity to redistribute incoming carbonate weathering to the deep ocean (Ridgwell and Zeebe, 2005).

Subsidence or physical erosion of the newly exposed carbonate platforms will cause the carbonate weathering pulse to the ocean to gradually shut off during the lowstand as exposed shelf area decreases and carbonate accumulation and weathering return to steady state. For 100 m of sea-level fall, the carbonate platforms will be exposed for 100 k.y. (typical thermal subsidence rates are 1 mm yr$^{-1}$; Royden et al., 1980), and the additional drop in pCO$_2$ over this time scale may shield ice sheets from higher frequency orbital-driven changes in insolation. Therefore, the complex feedbacks among carbonate weathering, glacioeustasy, and subsidence may have had as-yet unknown roles in the climate variability during the late Paleozoic ice age.

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