Evolution of the photosynthetic carbon isotope fractionation (ε_p) during the Late Paleozoic

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Photosynthesis is accompanied by a carbon isotope fractionation (ε_p) between the inorganic carbon substrate CO_2 and the assimilated organic compounds. In fossil marine sediments ε_p can be defined as the difference between the carbon isotopic compositions of phytoplankton biomass (δ_p) and dissolved CO_2 (δ_d). The magnitude of ε_p is dependent on (1) pCO_2 and pO_2 in the ocean-atmosphere-system, (2) cell-specific growth rate and (3) cellgeometry.

This study investigates ε_p in marine phytoplankton in a series of Late Paleozoic time windows. Compound-specific carbon isotope analysis of acyclic isoprenoids preserved in immature marine sediments enabled us to determine δ_p and carbon isotope data of well preserved brachiopod shells were used to calculate δ_d. While previous studies were limited to the calculation of ε_{TOC}, i.e. the carbon isotopic difference between total organic carbon (TOC) and carbonate carbon, our dataset provides the first genuine record of the Late Paleozoic evolution of ε_p.

Our results show that ε_p commonly varies by several permil within individual Late Paleozoic time windows. This spread can be ascribed primarily to varying phytoplankton growth rates, associated with locally differing nutrient availabilities, and/or regionally varying compositions of phytoplankton communities. Yet, the longterm evolution of ε_p reveals a steady increase form the Devonian (ca. 16 – 21.5‰) to the Late Pennsylvanian (ca. 19.5 - 25‰), followed by a slight decrease during the Permian (ca. 21 – 23.5‰). This secular trend is interpreted in terms of an interplay between the significant increase of pO_2 and the strong depletion of pCO_2 in the ocean-atmosphere-system from the Middle Devonian to the Permo-Carboniferous, as proposed by a number of published numerical models. Our results suggest that Late Paleozoic pO_2 variations had a stronger effect on ε_p than pCO_2.

Density parameters in thermodynamic surface complexation models

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Thermodynamic surface complexation models (TSCMs) can realistically describe ionic sorption if characterization of a mineral-water interface helps to constrain stoichiometry and coordination of surface complexes, areas of surface types, and densities of the available binding sites. How can such information be utilized in macroscopic TSCMs in a rigorous way?

1. Reference density Γ_o (in mol·m^{-2}) is to be taken the same for all mineral surface species. Then molar Gibbs energies G^o or equilibrium surface complexation constants K can be scaled to the same standard state if j-th surface species con- centration is defined as Γ_j/Γ_o (Γ_j is actual surface density), but not as "fractional surface coverage" $\theta = \Gamma_j/\Gamma_{max}$ or Γ_j/Γ_T. In that, the maximum Γ_{max} or total Γ_T (site) densities are taken as sample-specific properties of individual surface complexes or surface patches (types), respectively (Kulik, 2000; 2002).

2. While Γ_o takes part in standard state properties (G^o, log$K$), Γ_{max} (or Γ_T for species competing on a surface type) can be used only in surface activity terms (SAT) that suppress the species density Γ_j at $\theta \Rightarrow 1$. Coulombic terms in electrostatic TSCM also affect Γ_j of charged surface complexes as function of surface charge density Γ_η, which itself is a function of Γ_T.

3. In the linear adsorption region (close to the reference state at $\Gamma_j \Rightarrow 0$ and $\Psi \Rightarrow 0$), the densities Γ_j (and mole quantities x_j) of surface complexes depend only on G^o_j, chemical potentials in the system and the surface type area, but not on Γ_{max} (or Γ_T) parameters. Hence, if concentrations of mono-, bi-,… n-dentate surface complexes are referenced to the same species density at standard state (Γ_o) then their behaviour will differ only at approaching the site- or surface-type saturation.

4. Thus, Γ_{max} parameters and SAT equations (initially defined for monodentate surface complexes) must be re-derived for n- dentate surface complexes by careful interpretation of Γ_j, Γ_T and Γ_{max} parameters in terms of "available site density" and "species density". For that, statistical analysis of surface site geometry (following Benjamin, 2002) is promising, especially when enhanced by micro-spectroscopic molecular-scale data about the binding site types and their spatial distribution.

Some developments will be exemplified by comparing TSCMs for mono- and bidentate U^{VI} sorption on oxides, to conclude about usefulness of the new species-/site- density concepts in mechanistic model description of heterogeneous sorption, as well as in compilation of a uniform chemical thermodynamic database for surface complexes.

References
Benjamin M. (2002): *Environ. Sci. Technol.* **36**, 307-313.
Kulik D.A. (2000): *Geoch. Cosmoch. Acta* **64**, 3161-3179.
Kulik D.A. (2002): *Amer. J. Sci.* (in press).
Kulik D.A. (2002): *Radiochim. Acta* (in press).