

Similar fossil ferns having dissimilar organic geochemical preservation

A.D. CZAJA^{1,2,4*}, A.B. KUDRYAVTSEV², G.D. CODY³
AND J.W. SCHOPF^{1,2}

¹Dept. of Earth and Space Sciences, Univ. of California, Los Angeles, CA 90095-1567, USA

(*correspondence: aczaja@geology.wisc.edu)

²Center for the Study of Evolution and the Origin of Life (Inst. of Geophysics and Planetary Physics), Univ. of California, Los Angeles, CA 90095-1567, USA

(kudryavtsev@ess.ucla.edu, schopf@ess.ucla.edu)

³Geophysical Laboratory, Carnegie Inst. of Washington, Washington, DC 20015, USA (gcody@ciw.edu)

⁴Current address: Dept. of Geology and Geophysics, Univ. of Wisconsin, Madison, WI 53706, USA

The processes of organic maturation that occur during the permineralization of fossils and the detailed chemistry of the resulting products are incompletely understood. Primary among such processes is the geochemical alteration of organic matter to produce kerogen, such as that which comprises the cell walls of the fossils here studied: essentially unmetamorphosed Eocene-age plant axes (specimens of the fossil fern *Dennstaedtiopsis aerenchymata* cellularly permineralized in cherts of the Clarno Formation of Oregon and the Allenby Formation of British Columbia). The composition and molecular structure of the kerogens that comprise the cell walls of such axes were analyzed by ultraviolet Raman spectroscopy (UV-Raman), solid-state ¹³C-nuclear magnetic resonance spectroscopy (¹³C-NMR), and pyrolysis-gas chromatography-mass spectrometry (py-GC-MS).

Cellularly well-preserved fern axes from both geologic units exhibit similar overall molecular structure, being composed primarily of networks of aromatic rings and polyene chains that, unlike more mature kerogens, lack large polycyclic aromatic hydrocarbon (PAH) constituents. The kerogenous cell walls of the Allenby Formation specimens, however, are geochemically less altered than those of the Clarno chert, exhibiting more prevalent oxygen-containing and alkyl functional groups and comprising a greater fraction of rock mass.

This study represents the first demonstration of the effectiveness (and limitations) of the combined use of UV-Raman, ¹³C-NMR, and py-GC-MS to analyze the kerogenous cell walls of chert-permineralized vascular plants.

Absolute speleo-thermometry, using clumped isotope measurements to correct for kinetic isotope fractionations induced by CO₂ degassing

M. DAÉRON^{1*}, W. GUO², J. EILER², D. GENTY¹,
K. WAINER¹, H. AFFEK³, H. VONHOF⁴ AND D. BLAMART¹

¹Lab. des Sciences du Climat et de l'Environnement, France

²Geophysical and Planetary Sciences, Caltech, USA

³Geology and Geophysics, Yale, USA

⁴Faculty of Earth and Life Sciences, Vrije Universiteit Amsterdam, the Netherlands

(*correspondence: daeron@lsce.ipsl.fr)

Assuming that a given speleothem precipitates near thermodynamic equilibrium, quantitative interpretation of its ¹⁸O record in terms of physical parameters is generally hampered by the lack of robust methods for separating isotopic variations due to paleo-temperatures and those reflecting source water composition. Moreover, in many settings it appears likely that speleothems form out of equilibrium, due to kinetic isotopic fractionation caused by rapid CO₂ degassing, which further detracts from the reliability of paleo-environmental reconstructions.

By combining (1) an *ab initio* model of the kinetic isotopic fractionation associated with the degassing / precipitation, (2) “traditional” oxygen isotopic measurements and (3) “clumped-isotope” measurements of Δ₄₇ (a thermodynamic variable which quantifies the statistical overabundance of ¹³C-¹⁸O bonds in the carbonate crystal) [1, 2], it appears possible to determine quantitatively the precipitation temperature of an *a priori* out-of-equilibrium speleothem.

Initial testing of the method on modern, well-characterized speleothems from settings including the Villars cave (SW France) support the model's predictions. Additionally, significant variations in the amplitude of kinetic isotope effects were observed in different speleothems from the same setting.

[1] Eiler, J. (2007) Earth & Planet. Sc. Letters **262** 309–327.

[2] Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E., Schrag, D., Eiler, J. (2006) Geochim. Cosmochim. Acta **70** 1439–1456.