

# Geosci 615 Organic & Biogeochemistry

225 Morrill-II; MWF 9:05-9:55

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In this course we will evaluate and discuss the composition, formation, destruction and transformation of organic matter in natural environments.

Topics covered include:

- global carbon cycles, short-term and long-term
- classification and chemical structure of biomarkers
- analytical techniques in organic geochemistry
- formation and biosynthesis of organic matter
- preservation: diagenesis, sedimentary organic matter, hydrocarbon generation
- biomarker relationships to phylogeny and physiology
- paleoenvironmental reconstructions using biomarkers

Each section of the course comprises a suite of lectures and a set of assigned readings of the primary literature. Grades will be awarded based on two term papers (40% each) and on contribution to discussion and critique of assigned readings (20%).

Midterm Term Paper - due 10/27/06, theme is:

***Biosynthetic controls on isotopic and molecular biosignatures***

Final Term Paper - due 12/15/06, theme is:

***Reconstruction of biological communities, past and present***

Recommended Text: *Introduction to Organic Geochemistry*, 2<sup>nd</sup> ed. (2005) Killips, S., and Killips, V., Blackwell Pub. 393 pp.

## **Section 1**

The global carbon cycle - short term and long term; coupled global biogeochemical cycles

## **Section 2**

Geologic record of OM; extraterrestrial and abiogenic OM

## **Section 3**

Stable isotopes - fractionation of C, H, N, S, O during biosynthesis and diagenesis

## **Section 4**

Chemical composition of organic matter

Biomarkers and biosynthesis - acetogenic lipids; isoprenoid lipids: acyclic, steroids, hopanoids, carotenoids; pigments; cellulose; lignin; complex biopolymers

## **Section 5**

Production, preservation and degradation of organic matter; kerogen and coal; hydrocarbon generation

## **Section 6**

Sedimentary biomarkers and reconstruction of paleoenvironments; archaeological and forensic organic geochemistry

## ***Organic and Biogeochemistry Reading List***

You are *not* responsible for reading every one of the following papers. The list should rather serve as a guide where to start probing the literature for detailed information on particular topics, to supplement lectures and material covered in the text. Select papers from this list will be assigned in class. It is highly recommended that you do *acquire* the majority of these papers for future reference.

### ***Section 1***

- Berner, R. A. (1989) Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over Phanerozoic time. *Palaeogeography, Palaeoclimatology, Palaeoecology* **75**, 97-122.
- Berner, R. A. (2003) The long term carbon cycle, fossil fuels and atmospheric composition. *Nature* **426**, 323-326.
- Falkowski, P. G., Scholes, R. J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N., Hibbard, K., Högberg, P., Linder, S., Mackenzie, F. T., Moore III, B., Pedersen, T. F., Rosenthal, Y., Seitzinger, S., Smetacek, V., and Steffen, W. (2000) The global carbon cycle: a test of our knowledge of Earth as a system. *Science* **290**, 291-296.
- France-Lanord, C. and Derry, L. A. (1997) Organic carbon burial forcing of the carbon cycle from Himalayan erosion. *Nature* **390**, 65-67.
- Hedges, J. I. (1992) Global biogeochemical cycles: progress and problems. *Marine Chemistry* **39**, 67-93.
- Jasper, J. P. and Hayes, J. M. (1993) Refined Estimation Of Marine And Terrigenous Contributions To Sedimentary Organic Carbon. *Global Biogeochemical Cycles* **7**, 451-461.
- Kasting, J. F. (1989) Long-term stability of the Earth's climate. *Palaeogeography, Palaeoclimatology, Palaeoecology* **75**, 83-95.
- Lasaga, A. C. (1980) The kinetic treatment of geochemical cycles. *Geochimica et Cosmochimica Acta* **44**, 815-828.
- Lasaga, A. C. and Ohmoto, H. (2002) The oxygen geochemical cycle: dynamics and stability. *Geochimica et Cosmochimica Acta* **66**, 361-381.
- Lovelock, J. E. and Kump, L. R. (1994) Failure of climate regulation in a geophysiological model. *Nature* **369**, 732-734.
- Royer, D. L., Berner, R. A., and Beerling, D. J. (2001) Phanerozoic atmospheric CO<sub>2</sub> change: evaluating geochemical and paleobiological approaches. *Earth-Science Reviews* **54**, 349-392.
- Van Cappellen, P. and Ingall, E. D. (1996) Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity. *Science* **271**, 493-496.

### ***Section 2***

- Anders E. (1989) Pre-biotic organic matter from comets and asteroids. *Nature* **342**, 255-257.
- Engel M.H. and Macko S.A. (1997) Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite. *Nature* **389**, 265-268.
- Hayes, J. M., Strauss, H., and Kaufman, A. J. (1999) The abundance of <sup>13</sup>C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Myr. *Chemical Geology* **161**, 103-125.
- Hedges, J. I. and Oades, J. M. (1997) Comparative organic geochemistries of soils and marine sediments. *Organic Geochemistry* **7/8**, 319-361.
- McCollom T.M. (2003) Formation of meteorite hydrocarbons from thermal decomposition of siderite. *Geochim. Cosmochim. Acta* **67**, 311-317.
- McCollom, T. M. and Seewald, J. S. (2006) Carbon isotope composition of organic compounds produced by abiotic synthesis under hydrothermal conditions. *Earth and Planetary Science Letters* **243**, 74-74.
- Schidlowski, M. (1988) A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature* **333**, 313-318.

Sherwood-Lollar, B., Westgate, T., Ward, J. A., Slater, G. F., and Lacrampe-Couloume, G. (2002) Abiogenic formation of alkanes in the earth's crust as a minor source for global hydrocarbon reservoirs. *Nature* **416**, 522-524.

### Section 3

- Beaumont, V. and Robert, F. (1999) Nitrogen isotope ratios of kerogens in Precambrian cherts: a record of the evolution of atmospheric chemistry? *Precambrian Research* **96**, 63-82.
- Boschker, H. T. S. and Middelburg, J. J. (2002) Stable isotopes and biomarkers in microbial ecology. *FEMS Microbiology Ecology* **40**, 85-95.
- Eglinton T. I., Benitez-Nelson B. C., Pearson A., McNichol A. P., Bauer J. E., and Druffel E. R. M. (1997) Variability in radiocarbon ages of individual organic compounds from marine sediments. *Science* **277**, 796-799.
- Freeman, K. H. and Hayes, J. M. (1992) Fractionation of carbon isotopes by phytoplankton and estimates of ancient CO<sub>2</sub> levels. *Global Biogeochemical Cycles* **6**, 185-198.
- Hayes, J. M. (2001) Fractionation of the isotopes of carbon and hydrogen in biosynthetic processes. pp.225-278 in John W. Valley and David R. Cole (eds.) *Stable Isotope Geochemistry, Reviews in Mineralogy and Geochemistry* Vol. 43. Mineralogical Society of America, Washington, D. C. (2001). pdf available at <http://www.nosams.whoi.edu/docs/biosynfracsjmh.pdf>. **pay particular emphasis to sections on " isotopic composition of carbohydrates" and " isotopic composition of lipids"**
- Huon, S., Grousset, F. E., Burdloff, D., Bardoux, G., and Mariotti, A. (2002) Sources of fine-sized organic matter in North Atlantic Heinrich Layers:  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  tracers. *Geochimica et Cosmochimica Acta* **66**, 223-239.
- Laws, E. A., Popp, B. N., Bidigare, R. R. Kennicutt, M. C., and Macko, S. A. (1995) Dependence of phytoplankton carbon isotopic composition on growth rate and [CO<sub>2</sub>]<sub>aq</sub>: Theoretical considerations and experimental results. *Geochim. Cosmochim. Acta*. **59**, 1131-1138.
- Pearson, A., McNichol, A. P., Benitez-Nelson, B. C., Hayes, J. M. and Eglinton, T. I. (2001) Origins of lipid biomarkers in Santa Monica Basin surface sediment: A case study using compound-specific  $\Delta^{14}\text{C}$  analysis. *Geochim. Cosmochim. Acta* **65**, 3123-3137.
- Sachs, J. P. and Repeta, D. J. (1999) Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events. *Science* **286**, 2485-2488.
- Schubert, C. J. and Calvert, S. E. (2001) Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition. *Deep-Sea Research I* **48**, 789-810.
- Sessions, A. L., Burgoyne, T. W., Schimmelmann, A. and Hayes, J. M. (1999) Fractionation of hydrogen isotopes in lipid biosynthesis. *Organic Geochemistry* **30**, 1193-1200.

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- Bates, A. L. and Hatcher, P. G. (1992) Quantitative solid-state <sup>13</sup>C nuclear magnetic resonance spectrometric analyses of wood xylem: effect of increasing carbohydrate content. *Organic Geochemistry* **18**, 407-416.
- Blokker P., Schouten S., de Leeuw J. W., Sinninghe Damsté J. S., and van den Ende H. (2000) A comparative study of fossil and extant algae using ruthenium tetroxide degradation. *Geochim. Cosmochim. Acta* **64**(12), 2055-2065.
- Blokker P., van Bergen P. F., Pancost R. D., Collinson M. E., Sinninghe Damsté J. S., and de Leeuw J. W. (2001) The chemical structure of *Gloeocapsomorpha prisca* microfossils: implication for their origin. *Geochim. Cosmochim. Acta* **65**, 885-900.
- Brocks, J. J., Logan, G. A., Buick, R., and Summons, R. E. (1999) Archean molecular fossils and the early rise of eukaryotes. *Science* **285**, 1033-1036.
- Cowie, G., Calvert, S., De Lange, G., Keil, R., and Hedges, J. (1998) Extents and implications of organic matter alteration at oxidation fronts in turbidites from the Madeira Abyssal Plain. *Proceedings of the Ocean Drilling Program, Scientific Results* **157**, 581-589.
- Derenne S. and Largeau C. (2001) A review of some important families of refractory macromolecules: composition, origin and fate in soils and sediments. *Soil Science* **166**, 833-847.

- Gelin F., Boogers I., Noordeloos A. A. M., Sinninghe Damsté J. S., Riegman R., and de Leeuw J. W. (1997) Resistant biomacromolecules in marine microalgae of the classes Eustigmatophyceae and Chlorophyceae: geochemical implications. *Org. Geochem.* **26**(11-12), 659-675.
- Goñi, M. A. and Hedges, J. I. (1990) Potential applications of cutin-derived CuO reaction products for discriminating vascular plant sources in natural environments. *Geochimica et Cosmochimica Acta* **54**, 3073-3081.
- Goñi, M. A. and Hedges, J. I. (1992) Lignin dimers: structures, distribution, and potential geochemical applications. *Geochimica et Cosmochimica Acta* **56**, 4025-4043.
- Goñi, M. A., Ruttenger, K. C., and Eglinton, T. I. (1997) Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. *Nature* **389**, 275-278.
- Goñi, M. A., Yunker, M. B., Macdonald, R. W., and Eglinton, T. I. (2000) Distribution and sources of organic biomarkers in Arctic sediments from the Mackenzie River and Beaufort Shelf. *Marine Chemistry* **71**, 23-51.
- Hernes, P.J. and Benner, R. (2006) Terrigenous organic matter sources and reactivity in the North Atlantic Ocean and comparison to the Arctic and Pacific Oceans. *Marine Chemistry* **100**, 66-79.
- Hoefs, M. J. L., Schouten, S., de Leeuw, J. W., King, L. L., Wakeham, S. G., and Sinninghe Damsté, J. S. (1997) Ether lipids of planktonic Archaea in the marine water column. *Applied and Environmental Microbiology* **63**, 3090-3095.
- Hoefs, M. J. L., Sinninghe Damsté, J. S., De Lange, G. J., and de Leeuw, J. W. (1998) Changes in kerogen composition across an oxidation front in Madeira Abyssal Plain turbidites as revealed by pyrolysis GC-MS. *Proceedings of the Ocean Drilling Program, Scientific Results* **157**, 591-607.
- Höld, I. M., Schouten, S., Van Kaam-Peters, H. M. E., and Sinninghe Damsté, J. S. (1998) Recognition of *n*-alkyl and isoprenoid alkanes in marine sediments by stable carbon isotopic analyses of pyrolysis products of kerogen. *Organic Geochemistry* **28**, 179-184.
- Kates M. (1993) Membrane lipids of Archaea. In *The Biochemistry of Archaea (Archaeobacteria)* (ed. M. Kates, K. D. J., and A. T. Matheson), pp. 261-295. Elsevier Science. **available at Amherst and Smith College libraries**
- Lichtfouse, É., Bardoux, G., Mariotti, A., Balesdent, J., Ballentine, D. C., and Macko, S. A. (1997) Molecular, <sup>13</sup>C and <sup>14</sup>C evidence for the allochthonous and ancient origin of C<sub>16</sub>-C<sub>18</sub> *n*-alkanes in modern soils. *Geochimica et Cosmochimica Acta* **61**, 1891-1898.
- Louchouart, P., Opsahl, S., and Benner, R. (2000) Isolation and quantification of dissolved lignin from natural waters using solid-phase extraction and GC/MS. *Analytical Chemistry* **72**, 2780-2787.
- Michaelis W., Seifert R., Nauhaus K., Treude T., Thiel V., Blumenberg M., Knittel K., Gieseke A., Peterknecht K., Pape T., Boetius A., Amann R., Jørgensen B. B., Widdel F., Peckmann J., Pimenov N. V., and Gulin M. B. (2002) Microbial reefs in the Black Sea fueled by anaerobic oxidation of methane. *Science* **297**, 1013-1015.
- Moldovan J. M., Dahl J. E. P., Huizinga B. J., Fago F. J., Hickey L. J., Peakman T. M., and Taylor D. W. (1994) The molecular fossil record of oleanane and its relation to angiosperms. *Science* **265**, 768-771.
- Nelson, P.N. and Baldock, J.A. (2005) Estimating the molecular composition of a diverse range of natural organic materials from solid-state C-13 NMR and elemental analysis. *Biogeochemistry* **72**, 1-34.
- Sinninghe Damsté J. S., Rijpstra W. I. C., Hopmans E. C., Prahl F. G., Wakeham S. G., and Schouten S. (2002) Distribution of membrane lipids of planktonic Crenarchaeota in the Arabian Sea. *Applied and Environmental Microbiology* **68**, 2997-3002.
- Sinninghe Damsté J. S., Schouten S., and van Duin A. C. T. (2001) Isorenieratene derivatives in sediments: possible controls on their distribution. *Geochim. Cosmochim. Acta* **65**, 1557-1571.
- Summons R. E. and Walter M. R. (1990) Molecular fossils and microfossils of prokaryotes and protists from Proterozoic sediments. *Am. J. Sci.* **290-A**, 212-244.
- Summons R.E. and Jahnke L.L., 1990, Identification of the methylhopanes in sediments and petroleum. *Geochimica et Cosmochimica Acta* **54**, 247-251.
- Talbot, H.M., Watson, D.F., Pearson, E.J., and Farrimond, P. (2003) Diverse biohopanoid compositions of non-marine sediments. *Organic Geochemistry* **34**, 1353-1371.

- Thiel V., Peckmann J., Seifert R., Wehrung P., Reitner J., and Michaelis W. (1999) Highly isotopically depleted isoprenoids: molecular markers for ancient methane venting. *Geochim. Cosmochim. Acta* **63**(23/24), 3959-3966.
- Thiel, V., Peckmann, J., Richnow, H. H., Luth, U., Reitner, J., and Michaelis, W. (2001) Molecular signals for anaerobic methane oxidation in Black Sea seep carbonates and a microbial mat. *Marine Chemistry* **73**, 97-112.
- Volkman JK (2003) Sterols in microorganisms. *Applied Microbiology and Biotechnology* **60**, 495-506.
- Volkman, JK, Barrett, SM, Blackburn, SI, Mansour, MP, Sikes, EL, and Gelin, F. (1998) Microalgal biomarkers: a review of recent research developments. *Organic Geochemistry* **29**, 1163-1179.
- Wakeham, S. G. and Beier, J. A. (1991) Fatty acid and sterol biomarkers as indicators of particulate matter source and alteration processes in the Black Sea. *Deep Sea Research* **38**, Supp. 2, S943-S968.

## Section 5

- Canfield, D. E. (1994) Factors influencing organic carbon preservation in marine sediments. *Chemical Geology* **114**, 315-329.
- Eglinton, T. I. (1994) Formation and diagenesis of macromolecular organic sulfur in Peru margin sediments. *Organic Geochemistry* **22**, 781-799.
- Hartnett, H. E., Keil, R. G., Hedges, J. I., and Devol, A. H. (1998) Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature* **391**, 572-574.
- Hatcher, P. G., Spiker, E. C., Szeverenyi, N. M., and Maciel, G. E. (1983) Selective preservation and origin of petroleum-forming aquatic kerogen. *Nature* **305**, 498-501.
- Hedges, J. I., Baldock, J. A., Gelin, Y., Lee, C., Peterson, M. L., and Wakeham, S. (2001) Evidence for non-selective preservation of organic matter in sinking marine sediments. *Nature* **409**, 801-804.
- Hedges, J. I., Hu, F. S., Devol, A. H., Hartnett, H. E., Tsamakis, E., and Keil, R. G. (1999) Sedimentary organic matter preservation: a test for selective degradation under oxic conditions. *American Journal of Science* **299**, 529-555.
- Hwang, J. and Druffel, E. R. M. (2003) Lipid-like material as the source of uncharacterized organic carbon in the ocean? *Science* **299**, 881-884.
- Keil, R. G., Montluçon, D. B., Prahl, F. G., and Hedges, J. I. (1994) Sorptive preservation of labile organic matter in marine sediments. *Nature* **370**, 549-552.
- Kennedy, M. J., Pevear, D. R., and Hill, R. J. (2002) Mineral surface control of organic carbon in black shale. *Science* **295**, 657-660.
- Kennedy, M., Droser, M., Mayer, L. M., Pevear, D., and Mrofka, D. (2006) Late Precambrian oxygenation; Inception of the clay mineral factory. *Science* **311**(5766), 1446-1449.
- Mayer, L. M. (1999) Extent of coverage of mineral surfaces by organic matter in marine sediments. *Geochimica Et Cosmochimica Acta* **63**(2), 207-215.
- Lewan M. D. (1997) Experiments on the role of water in petroleum formation. *Geochim. Cosmochim. Acta* **61**(17), 3691-3723.
- Price L. C. (1993) Thermal stability of hydrocarbons in nature: limits, evidence, characteristics, and possible controls. *Geochimica et Cosmochimica Acta* **57**, 3261-3280.
- Sinninghe Damsté, J. S., Kok, M. D., Köster, J., and Schouten, S. (1998) Sulfurized carbohydrates: an important sedimentary sink for organic carbon? *Earth and Planetary Science Letters* **164**, 7-13.
- Tegelaar, E. W., de Leeuw, J. W., Derenne, S., and Largeau, C. (1989) A reappraisal of kerogen formation. *Geochimica et Cosmochimica Acta* **53**, 3103-3106.
- Werne, J. P., Hollander, D. J., Behrens, A., Schaeffer, P., Albrecht, P., and Sinninghe Damsté, J. S. (2000) Timing of early diagenetic sulfurization of organic matter: a precursor-product relationship in Holocene sediments of the anoxic Cariaco Basin, Venezuela. *Geochimica et Cosmochimica Acta* **64**, 1741-1751.

## Section 6

- Copley, MS, Berstand, R, Mukherjee, AJ, Dudd, SN, Straker, V, Payne, S, and Evershed, RP (2005) Dairying in antiquity. Evidence from absorbed lipid residues dating to the British Iron Age. *Journal Archaeol. Sci* **32**, 485-503.

- Eglinton G. and Calvin M. (1967) Chemical fossils. *Scientific American* **261**, 32-43.
- Evershed, RP, Dudd, SN, Charters, S., Mottram, H, Stott, AW, Raven, A, van Bergen, PF, and Bland, HA (1999) Lipids as carriers of anthropogenic signals from prehistory. *Phil. Trans. Royal Soc. London B* **354**, 19-31.
- Joachimski, M. M., Ostertag-Henning, C., Pancost, R. D., Strauss, H., Freeman, K. H., Littke, R., Sinninghe Damsté, J. S., and Racki, G. (2001) Water column anoxia, enhanced productivity and concomitant changes in  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  across the Frasnian-Famennian boundary (Kowala - Holy Cross Mountains/Poland). *Chemical Geology* **175**, 109-131.
- Kuypers M. M. M., Blokker P., Erbacher J., Kinkel H., Pancost R. D., Schouten S., and Sinninghe Damsté J. S. (2001) Massive expansion of marine Archaea during a Mid-Cretaceous Oceanic Anoxic Event. *Science* **293**, 92-94.
- Kuypers, M. M. M., Blokker, P., Hopmans, E. C., Kinkel, H., Pancost, R. D., Schouten, S., and Damsté, J. S. S. (2002) Archaeal remains dominate marine organic matter from the early Albian oceanic anoxic event 1b. *Palaeogeography Palaeoclimatology Palaeoecology* **185**(1-2), 211-234.
- Kuypers, M. M. M., Pancost, R. D., and Sinninghe Damsté, J. S. (1999) A large and abrupt fall in atmospheric  $\text{CO}_2$  concentration during Cretaceous times. *Nature* **399**, 342-345.
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- Pagani, M., Arthur, M. A., and Freeman, K. H. (1999) Miocene evolution of atmospheric carbon dioxide. *Paleoceanography* **14**, 273-292.
- Powers, L. A., Werne, J. P., Johnson, T. C., Hopmans, E. C., Damsté, J. S. S., and Schouten, S. (2004) Crenarchaeotal membrane lipids in lake sediments: A new paleotemperature proxy for continental paleoclimate reconstruction? *Geology* **32**(7), 613-616.
- Schouten, S., Hoefs MJL and Sinninghe Damsté, JS (2000) A molecular and stable carbon isotopic study of lipids in late Quaternary sediments from the Arabian Sea, *Organic Geochemistry* **31**, 509-521.
- Simons, D.-J. H. and Kenig, F. (2001) Molecular fossil constraints on the water column structure of the Cenomanian-Turonian Western Interior Seaway, USA. *Palaeogeography Palaeoclimatology Palaeoecology* **169**, 129-152.
- Sluijs, A., Schouten, S., Pagani, M., Woltering, M., Brinkhuis, H, Sinninghe Damsté, JS, Dickens, GR, Huber, M, Reichert, GJ, Stein, R, Metthiessen, J, Lourens, LJ, Pedentchouk, N, Backman, J., and Moran, K. (2006) Subtropical Arctic ocean temperatures during the Paleocene/Eocene thermal maximum. *Nature* **441**, 610-613.
- Wing, SL., Harrington, GJ, Smith, FA, Bloch, JI, Boyer, DM, and Freeman, KH (2005) Transient floral change and rapid global warming at the Paleocene-Eocene boundary. *Science* **310**, 993-996.