

Marine Organic Geochemistry Course Review (Eglinton)

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Methods – Extraction, chromatography: principles & types

- Bulk vs. molecular-level measurements: advantages vs disadvantages.
- Considerations re. sampling, storage, contamination etc.
- General scheme for extraction and separation of lipids
- Extraction types: soxhlet, ultrasonic, SFE, ASE
- Chromatographic separation: principles, analytical vs. semi-preparative etc.
- Adsorption vs partition chromatography
- Factors influencing chromatographic efficiency
- Column chromatography
- Thin-layer chromatography
- HPLC: reverse vs. normal phase; detectors; gradient vs isocratic
- GPC
- Gas chromatography- components: injectors, columns detectors
- GC resolution, column efficiency, retention indices, HETP; stationary phases, quantitation methods, derivatization.
- Typical recipes for molecular analysis (lipids, PLFA, pigments, HOCs)

Analytical Methods-II Characterization of macromolecular organic matter, mass spectrometry

Characterization of macromolecular organic matter

- Methods of characterization (spectroscopy, chemical and thermal degradation)
- Organic matter concentration (demineralization) techniques
- Chemical degradation (chemolysis) methods
 - Characterization of polysaccharides
 - Characterization of proteins
 - Characterization of lignin
- Thermal degradation (pyrolysis).

Mass Spectrometry

- Components of a mass spectrometer (source, mass analyzer, detector)
- Ionization methods: EI, CI, electrospray etc.; soft vs hard ionization methods
- Mass analyzers and detectors: magnetic sector, quadrupole, Ion Trap, FT-ICR, TOF.
- Important features of mass spectra: molecular ion, fragments, base-peak.
- Mass spectral resolution: definition, accurate mass measurement
- Inlets to mass spectrometers
- Gas chromatography-Mass Spectrometry: selected ion monitoring, mass chromatography/fragmentography as tools to study complex mixtures.
- MS-MS for structural elucidation studies.
- MS methods for high mass compounds
- LC-MS of polar lipids
- Isotope ratio mass spectrometry, Irm-GC-MS, AMS.

Introduction to Molecular Markers

- Definition of molecular markers/biomarkers
- Molecular characteristics: structural uniqueness, distributional uniqueness (incl. 13C)
- Information content vs preservation potential
- Lipids: occurrence, function, structural types (ketide, isoprenoid)
- Polyketide lipids:
 - Compound classes, CPI, OEP, ACL
 - Biosynthetic pathways.
 - Fatty acids, Fatty alcohols, ketones, Hydrocarbons
 - Esterified lipids (di/triglycerides, wax esters, phospholipids)
- Polyisoprenoid lipids
 - Mono-, di-, tri-, tetraterpenes etc..
 - Isoprenoid linkages/configurations (head-tail, head-head, tail-tail)
 - Biosynthesis
 - Pentacyclic triterpenoids (hopanoids) - nomenclature
 - Tetracyclic triterpenoids (steroids)
 - Archaeal isoprenoid lipids
 - Carotenoids
 - HBI alkenes
- Biomarker properties (structure, abundance, isotopic composition)
- Integration of lipid biomarker and molecular biological approaches

Stable carbon isotopes

- Nomenclature & Notation
- Processes controlling isotopic composition of sedimentary organic matter.
- Isotope fractionation effects.
 - Equilibrium isotope effects
 - Kinetic isotope effects.
 - Fractionation in single vs multicarbon substrates.
- Isotope fractionation during photosynthesis
 - C₃, C₄ and CAM photosynthesis
 - Environmental conditions favoring different photosynthetic pathways.
 - Isotopic fractionation in aquatic photoautotrophs.
 - Anoxygenic bacterial photosynthesis
 - Isotopes as indicators of carbon flow, source etc.
- Additional considerations
 - Influence of heterotrophic activity
 - Isotopic differences between biochemicals
 - Isotopic differences within molecules related to biosynthetic pathways

Terrestrial organic carbon-I

- Potential significance of terrestrial OC in marine sediments
- Margins as loci for the majority of OC burial in the oceans.
- Approaches for assessment of source inputs:
 - Bulk d¹³C of TOC and Corg./N ratios: advantages and limitations
 - Concentration of terrestrial biomarkers (plant waxes, lignin)
- Estimates of loss of terrestrial OC during delivery (OC/SA vs d¹³C relationships)
- Biomarkers as tracers of terrestrial OC
 - Plant waxes
 - Lignin phenols
 - Compositional parameters derived from vascular plant biomarkers (CPI, Ad/Al, d¹³C)
 - Isotopic analysis of biomarkers.
- Evidence for terrestrial OC in marine sediments
 - Case study of Washington Margin and Gulf of Mexico sediments:
 - Biomarker concentrations along a river mouth-ocean transect
 - Spatial and temporal variations in the isotopic compositions of terrestrial OC
 - Measurement of lignin phenol and plant wax d¹³C.
 - Relationship between biomarker composition and bulk properties (d¹³C, C/N)
 - Effect of grain size/hydrodynamic sorting processes on OM composition

Terrestrial organic carbon-II

- Binary mixing models of marine and terrestrial carbon.
- Eolian inputs of terrestrial organic carbon.
- Evidence for significant C4 terrestrial OC inputs.
- C3/C4 vegetation inputs through geologic time.
- ^{14}C age of POC carried by rivers to the oceans.
- Importance of small, mountainous tropical rivers.
- Influence of riverine OC inputs to the Arctic ocean.
- Isotopic mass balance and the importance of constraining isotopic composition of marine and terrestrial end-members

Molecular markers - alkenone paleothermometry

The alkenone story – birth of a new paleoceanographic tool

- First identification in sediments
- Recognition as biological markers of Haptophyte algae
- Structural elucidation – unusual trans double bond config.
- Various structures (C#, ethyl/methyl, degree of unsatn) & related compounds (alkenoates, alkenes)
- Identification in sediments pre-dating emergence of *E. hux.*
- Recognition of relationship between unsaturation and growth temperature,
- Birth of a new proxy for paleoceanography, and of “molecular stratigraphy”
- Definition of UK37' parameter
- Methods of analysis
- Temperature calibration based on cultures, natural *E. hux* popns, POMsusp, sediment core-tops.
- Calibration at cold temperatures
- Assumptions, limitations and sources of potential error.
 - Alkenones in *Gephyrocapsa oceanica*
 - Seasonal variations, nutrient influences.
 - Water depth of alkenone prodn
 - Influence of differential degradation
 - Influence of sediment redistribution

Geochemistry of Radiocarbon in Organic Matter

- Formation of ^{14}C , abundance & half-life
- Measurement, systematics, notation, and use as a tracer & for mass balance
- Factors influencing ^{14}C abundance
 - Atmospheric variations
 - Suess effect, Bomb-spike
 - Calibration of ^{14}C ages
- Radiocarbon as a tool to examine OC cycling
- Bulk OC profiles in sediments
- ^{14}C variations in size fractionated sediments.
- ^{14}C variations between different biochemical classes
 - ^{14}C age order matches reactivity order (THAA \approx TCHO $<$ lipids \approx acid-insoluble OC).
- ^{14}C measurements at the molecular level
 - Methods
 - Application to pre-bomb/post-bomb sediments from the California Borderland Basin

Organic Phosphorus Guest lecturer: Ben Van Mooy

- P exhibits no redox chemistry in the sea.
- Phosphoric acid is the sole inorganic form.
- Sinking particulate P is more labile than sinking POC or PON? Unclear.
- DOP more labile than DOC? Probably.
- P in organic matter occurs in three different bonding environments: monoesters, diesters, and phosphonates.
- Plankton contain monoesters and diesters exclusively.
- Sinking particles contain greater amounts of phosphonate P at greater depths (similar for organic P in sediments).
- HMWDOP contains a fixed ratio of ester:phosphate.
- RNA, DNA and phospholipids are the primary biochemical reservoir of P in plankton (they all contain primarily diester bonds, some monoester).
- RNA, DNA and phospholipids are potent biomarkers.

Old carbon in the modern environment/black carbon

- Possible origins of old OC
 - Delivery of pre-aged terrestrial OC
 - Relict OC from sedimentary rock erosion
 - *Sediment redistribution*
 - *Black Carbon*
- Evidence for sediment redistribution
 - Coupled molecular and microfossil ^{14}C measurements
 - Relationship between algal biomarker ^{14}C and TOC ^{14}C
 - Other lines of evidence
- Black Carbon
 - Estimates of modern BC production and sources
 - Forms of BC & modes of analysis
 - Significance and sources of BC in marine sediments
 - Molecular proxies for combustion inputs
 - Historical records of combustion

Introduction to organic chemicals of environmental concern (C. Reddy)

- PCBs, DDT, and PBDEs are industrially-produced organic compounds made in the last century. They were useful compounds but too stable. When released into environment, they have persisted.
- Chlorinated dioxins and furans were never purposely manufactured by the chemical industry. They were trace impurities in the herbicide mixture “Agent Orange” but also can be produced during the combustion of organic matter in the presence of chloride. A few congeners likely have a natural source.
- PCBs, DDT, PBDEs, and the chlorinated dioxins and furans are hydrophobic compounds that have a tendency to partition into fats and organic media in the environment.
- Since the production history of the above compounds is relatively well-known, the presence of these compounds in sediment cores can be used to date distinct layers...much like ^{137}Cs .
- Most organic contaminants are analyzed by gas chromatography. Be aware of data that is approx. two decades old or older. It may have been run on a packed-column and not a capillary column. The former has much less resolution than the latter and may be less accurate (due to co-eluting compounds).
- There are three sources of polycyclic aromatic hydrocarbons: combustion of organic matter (pyrogenic), petroleum (petrogenic), and natural sources.
- While local areas can be impacted by petrogenic PAHs, combustion of organic matter is the largest source of PAHs to environment.
- Natural sources of PAHs are limited to only a few compounds (retene and perylene).
- In many urban areas, pyrogenic and petrogenic PAHs are apportioned by comparing the ratios of alkylated to parent PAHs (such as methyl phenanthrenes to phenanthrene). These ratios are larger for petrogenic sources. Lower formation temperatures (120°C) like what occurs for petroleum are more likely to have alkyl PAHs than pyrogenic PAHs, which are formed at higher temperatures (1000°C).
- The water solubility, vapor pressure, Henry's Constant, and octanol-water partition coefficient of organic compounds can be used to predict their fate in the environment, develop analytical methods, and focus sampling efforts to the most ideal media.

The Geological Fate of Organic Matter/ Organically-bound Sulfur

- Sedimentary sulfur cycle, sulfur species and oxidation states
- Sedimentary sinks for sulfur
- Elemental and isotopic evidence for "in-growth" of organic sulfur
- Conditions favoring organosulfur formation
- Types of organosulfur compounds observed
- Evidence for abiotic controls on sedimentary organic sulfur content
- Mechanism for formation of OSC: inter vs intramolecular addition
- Biochemicals most susceptible to reaction with sulfur
- Carbon skeletons of sulfur containing compounds
- Absolute and relative (w.r.t. pyrite fm) timing of sulfur incorporation into OM
- Relationship between degree of crosslinking and molecular size
- Tools for analysis of macromolecularly-bound sulfur:
 - Chemical degradation
 - Pyrolysis
 - X-ray absorption spectroscopy
- Potential of sequestration of organic compound via rxn w/ sulfur to bias molecular stratigraphic records.