

SECULAR CHANGE IN THE STABLE SULFUR ISOTOPE COMPOSITION OF CRUDE OILS RELATIVE TO MARINE SULFATES AND SULFIDES

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Secular changes in the stable sulfur isotope composition of seawater sulfate have been commonly inferred from that of evaporite minerals and from sulfate in carbonate shell matrices. The stable sulfur isotope compositions of marine sulfides follow a similar secular trend to that of sulfate, although substantially depleted in ³⁴S owing to fractionation via bacterial sulfate reduction. Few if any studies of secular changes in the stable isotope composition of organic matter have been attempted. This is in part because of the complexity of diagenetic pathways for the incorporation of sulfur into organic matter subsequent to biosynthesis (e.g. Werne *et al.*, 2003). However, given the range for the stable sulfur isotope composition of seawater sulfate (and resulting sulfide) during the Phanerozoic (~25 to 30‰), it is hypothesized that the magnitude of this isotopic variability will be generally reflected by marine organic matter, irrespective of diagenesis. Our approach is based on an initial observation by Thode (1981) that oils sourced from Ordovician age rocks were enriched in ³⁴S relative to Mississippian age oils, which in turn were enriched in ³⁴S relative to Pennsylvanian age oils, a trend that is consistent with that reported for seawater sulfate for these time intervals. Simulation studies by Amrani *et al.* (2006) also support previous observations that crude oils generally reflect the stable sulfur isotope composition of their source materials and that the effects of thermal maturation on the stable sulfur isotope composition of oils are much less than for kerogens.

The stable sulfur isotope compositions of fifteen nondegraded crude oils (containing 1-3% sulfur) ranging in source rock age from Neoproterozoic to Neogene were determined. For seven of the oils, the stable sulfur isotope compositions of their respective aromatic, NSO and asphaltene fractions were also determined. Except for the siliceous Monterey, the source rocks for the oils were all marine carbonates/marls of low to moderate maturity.

The secular changes for the stable sulfur isotope compositions of the oils tracked the sulfate curve (Fig. 1) having $\delta^{34}\text{S}$ values intermediate to those of sulfate and sulfide. The secular trend exhibited by the stable carbon isotopes of the oils is also shown. The stable sulfur isotope values for the aromatic, NSO and asphaltene fractions of the oils were within 1-2‰ of the whole oil values. Oils formed from source rock depositional environments exhibiting photic zone euxinia (PZE) based on the presence of abundant aryl isoprenoids,

biomarkers for green sulfur bacteria (Summons and Powell, 1987), were more depleted in ^{34}S than oils of similar ages from phytoplankton/bacterial dominated sources. Based on these initial findings, the stable sulfur isotope composition of crude oils may provide the first independent method to check the secular sulfur isotope curves presently based on marine sulfate and sulfide minerals.

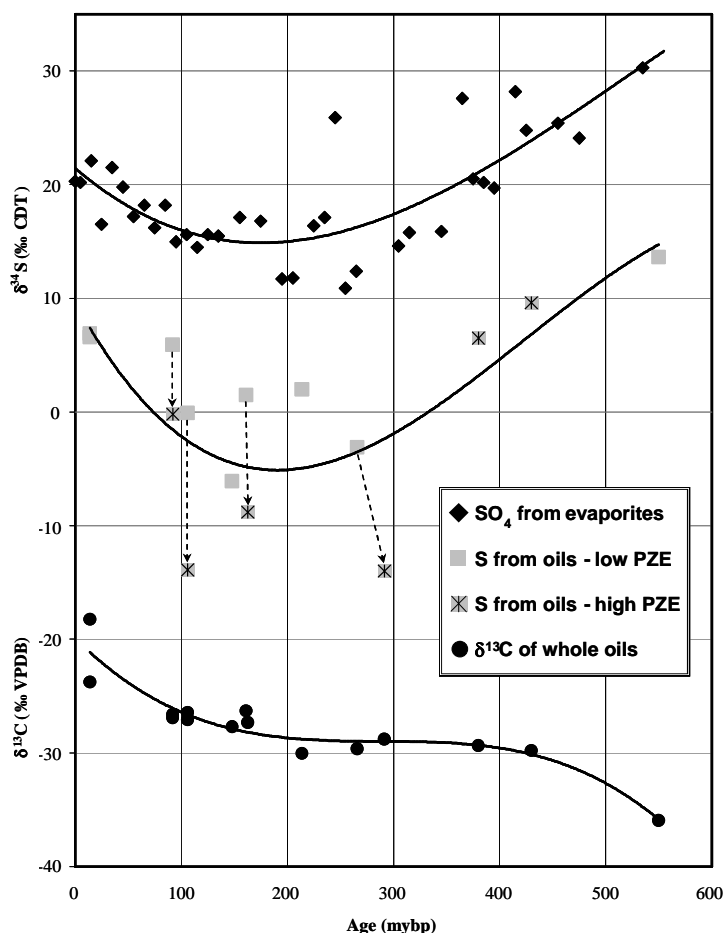


Figure 1. Stable isotope curves for sulfates (S; after Strauss, 1999) and crude oils (C,S).

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THE IMPACT OF ELEVATED CO₂ ON SOIL CARBON DYNAMICS IN A TROPICAL SAVANNA REGION

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Atmospheric carbon dioxide (CO₂) levels are rising and are expected to double present levels (~370 ppm) by the end of this century. This may significantly impact the environment, potentially altering plant growth, nutrient cycles and soil carbon dynamics. Much research has investigated the impact of elevated CO₂ on plant vegetation and above ground ecologies, but consequences for below ground biomass has received less attention.

The Australian free-air CO₂ enrichment (OzFACE) facility established near Townsville (N. Qld, Australia) in the year 2000 and decommissioned in late 2006 provided a unique opportunity to study the effects of elevated CO₂ on the root growth, microbial community and organic carbon pool dynamics of a savannah soil, with tropical wet summers and dry winters (rainfall = 1143 mm/annum). The open woodland vegetation has an understorey of perennial grasses consisting primarily of the C4 grasses *Themeda triandra*, *Chrysopogon fallax* and *Eriachne obtusa* (Stokes *et al.*, 2005). Separate plots were maintained at CO₂ concentrations of 370 ppm (i.e., ambient levels), 460 ppm and 550 ppm throughout the experiment. The common land practices of fertilisation via annual nutrient supplementation and grazing via regular clipping were also separately investigated at all CO₂ concentrations. Soil cores were taken to a depth of 10 cm and separated into the three depth intervals of 0-2 cm; 2-5 cm and 5-10 cm. These were then each separated into the following particle size fractions: a >53 µm particulate organic carbon (POC) fraction, representing the active pool and a <53µm passive pool. The POC fraction was further subdivided into a larger >200 µm fraction and a comparably finer 200-53 µm fraction, with the former representing the most labile pool of the active fraction. Surface soil and larger sized fractions, respectively, are expected to be most susceptible to changes in carbon input (Krull and Bray, 2005).

The δ¹³C of the larger >200 µm POC fractions had δ¹³C values in the range -16 to -23 ‰. The 0-2 cm depth data versus CO₂ concentration are shown in Figure 1. Corresponding values at 460 ppm were less than at ambient CO₂ concentrations for each treatment regime (i.e, control, fertilized and clipped) reflecting uptake of the industrially sourced carbon (δ¹³C of -25 ‰ compared to -8 ‰ of ambient air). The δ¹³C values at 550 ppm were typically also less than ambient values but significantly higher than 460 ppm values.

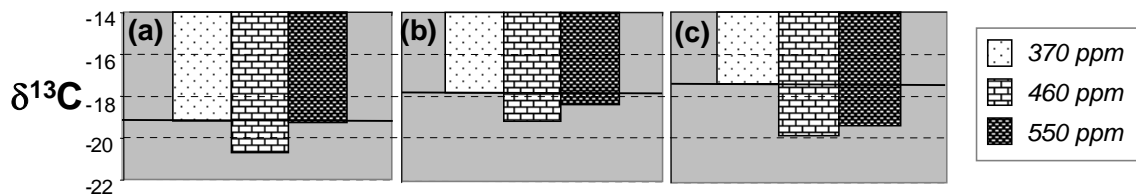


Figure 1. $\delta^{13}\text{C}$ data for mobile $>200\ \mu\text{m}$, 0-2 cm depth fractions versus CO_2 concentration for (a) control; (b) fertilised and (c) clipped soils.

The root biomasses, which generally increased with CO_2 concentration, showed a similar trend with the mass of some fractions less at 550 ppm than at 460 ppm. The $\delta^{13}\text{C}$ and root biomass data suggest the effective removal of the new (predominantly ^{13}C depleted) carbon at 550 ppm via increased microbial mineralization. A previous study of tallgrass prairie soils exposed to elevated CO_2 showed at least 55% of new carbon was mineralized (Williams et al., 2004). Previous research has also shown that an increased input of root exudates and dead root matter, possibly stimulated by increased CO_2 levels, can increase microbially activated CO_2 respiration and carbon mineralization. The $\delta^{13}\text{C}$ values might also be influenced by an increased contribution of ^{13}C enriched carbon inputs such as additional C4 grasses stimulated by enhanced CO_2 concentrations, clipping or fertilization, although this is not supported by the lack of appreciable TOC variation with CO_2 concentration or treatment.

Previous predictions have suggested at least 7-10 years of enhanced CO_2 concentrations would be needed to have any significant change on carbon pools (Smith., 2004). Co-incident increases of carbon inputs and mineralisation in the $>200\ \mu\text{m}$ labile POC pool fraction may contribute to no net change. The $\delta^{13}\text{C}$ analysis of the slow 53-200 μm and passive $<53\ \mu\text{m}$ fractions of the soils is presently underway. The sequestration of carbon in the more recalcitrant organic pools of the soil would have significant implications for global carbon cycles. Much further research is needed to fully understand the effects of CO_2 concentration on below (as well as above) ground carbon dynamics with important variables such as soil type, vegetation, climate and nutrient levels requiring particular attention.

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DIVERSITY OF INTACT POLAR LIPIDS IN ENVIRONMENTAL PROKARYOTES: AN EVOLVING DATABASE

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The characterization of inventories of intact polar membrane lipids (IPLs) of prokaryotes is typically motivated by biomedical research objectives and thus focuses on pathogens or compounds of potential pharmaceutical interest. Our interest is to develop these universal cell compounds further into chemotaxonomic tools for studies in microbial ecology in geologically relevant environments. In recent years, we have been assembling systematic information on the inventories of IPLs in prokaryotes of environmental relevance. To date, we have studied the composition of intact membrane lipids in ~100 prokaryotes (30 archaea, 70 bacteria) that were isolated from both continental and marine environments, including extreme habitats. The prokaryotes cover most major branches of the phylogenetic tree of life, enabling us to examine the data set in terms of evolutionary relationships of lipid composition between major phyla. At this point, we have exclusively focused on the determination of structural properties that are analyzable by HPLC-electrospray ionization-ion trap multistage-MS (cf. Sturt et al., 2004). Major distinctive features examined encompass the structures and distribution of polar headgroups, bond types between alkyl chains and glycerol, and the number of carbon atoms and degree of unsaturation in alkyl chains. Archaeal membrane lipids are dominated by mono- and diglycosidic archaeol and/or glycerol dialkyl glycerol tetraether. Phospholipids were observed in less than 50% of our archaeal cultures with phosphatidylethanolamine (PE) being the most common phosphorus-bearing headgroup. Among all prokaryotes, phosphatidylglycerol (PG; ~55% of studied species), PE (~50%), diphosphatidylglycerol (DPG, ~40%), and monoglycosyl derivatives (~40%) are most commonly expressed. The latter headgroup is particularly common among the archaea and the cyanobacteria. In combination, the examined structural features lead to valuable chemical

fingerprints that are taxonomically distinctive on the monospecific level. In environmental communities, however, the situation is more complex and IPL signatures represent ecosystem rather than species fingerprints. Our presentation will highlight the relationship between lipid composition and 16S rRNA-based molecular phylogeny. Results from selected ecosystems based on lipids are compared to those obtained from other techniques; strengths and weaknesses will be examined.

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FORMATION OF SULFUR AND NITROGEN CROSS-LINKED MACROMOLECULES UNDER AQUEOUS CONDITIONS

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Polysulfides and ammonia are abundant in young depositional environments and play an important role in the formation of macromolecular structures such as protokerogen and humics. In this work we study the co-incorporation of polysulfides and ammonia into simple carbonyl model compounds: octanal and *trans* 2-octenal in order to study their effect on the formation a cross linked macromolecule and suggested a feasible mechanism. The reactions performed in aqueous solutions, ambient temperature and pH~6 to 9 to simulate formation of S and N cross linked polymers in the natural environment. The complex S and N containing polymer studied by ¹⁵N enrichment of the polymer coupled to 2D NMR (¹H, ¹³C, ¹⁵N) techniques and chemical degradation (MeLi/MeI) of the S-S bonds with deuterium labeling followed by GCMS analyses. In addition we apply high-level molecular modeling techniques, Density Functional Theory at the DFT/B3LYP/6-31G** levels and water solvation effects, in order to provide theoretical interpretations and important molecular-level insights on the chemistry. The results shows that polysulfides out compete ammonia in the formation of Michael adducts while ammonia has been shown to compete well at the carbonyl position. The co incorporation of ammonia and polysulfides into carbonyls rapidly form N and S cross-linked polymer. The effect of ammonia and amines on the polymerization processes is via two means: (i) reaction with carbonyls through an imine functionality (Figure 1) and forming oligomers and polymers and (ii) catalysis of the reaction of sulfur nucleophiles on the carbonyl in the formation of *gem*-disulfide/dithiols, enhancing the rate of polymerization. Similar effects are observed when other amines (e.g., glycine) are used instead of ammonia. This catalytic effect achieved by incorporation of sulfur nucleophiles on the intermediate imine, reduces the Gibbs free energy as compared with direct addition to the carbonyl. DFT calculations of several possible transition barriers suggests that this catalytic effect can be also related to proton transfer assisted by the formation of six member rings with ammonia and

gem hydroxyl-thiol, resulting in the elimination of water and formation of the very active thioaldehyde. This mechanism is especially important under basic conditions that prevail in most marine environments. These results show that ammonia and amine are intimately involved with sulfur nucleophiles throughout the polymerization processes that occur at low temperatures and are, thus, suggested to be key reactants in the diagenetic formation of protokerogen and humics. This important role of nitrogen is enhances our understanding on the mechanisms at the early preservation stages of organic substances in natural depositional environments.

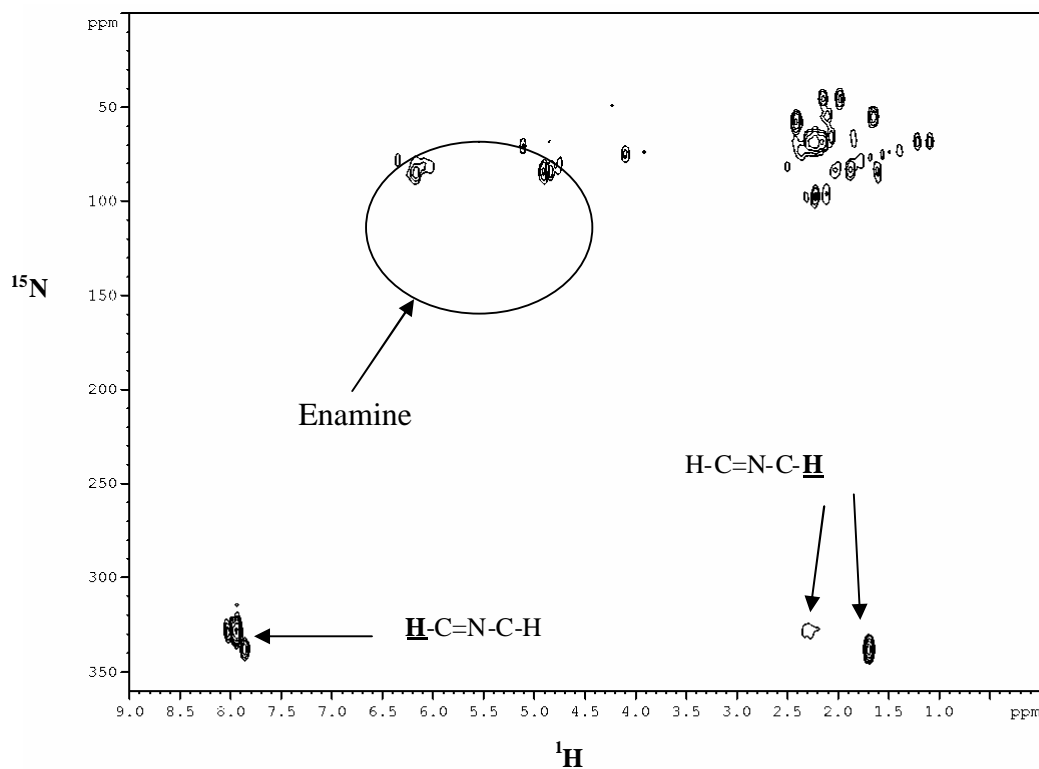


Figure 1. HMBC ^{15}N - ^1H NMR spectrum for the reaction products between $(\text{NH}_4)_2\text{S}_x$ and *trans* 2-octenal.