

## VARIATIONS IN CYANOBACTERIAL POPULATIONS ASSOCIATED WITH ENVIRONMENTAL CHANGES DURING THE EARLY APTIAN OCEANIC ANOXIC EVENT

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2-Methylhopanoids have been widely reported in sedimentary rocks (Fig. 1a) and provide a signature for cyanobacterial contributions to organic matter (OM) (1). Their prevalence in sediments deposited during oceanic anoxic events (OAEs) suggests that the environmental conditions during OAEs favored cyanobacteria among the phytoplankton community (2, 3). This contribution aims to explore molecular (i.e., the 2-methylhopanoid index or 2-MHI) and isotopic (i.e.,  $\delta^{15}\text{N}$ ) markers as measures of cyanobacterial populations during the Early Aptian OAE (OAE1a; 120 Ma) at Shatsky Rise in the Pacific. We examine relationships among variations in cyanobacterial signatures and changes in depositional environment, especially water-column oxygenation, assessed using biogeochemical proxies. Temperature records reconstructed using  $\text{TEX}_{86}$  for these ancient sediments (4) further permit evaluation of evidence for linkages between cyanobacterial populations and climate.

The abundance of 2 $\beta$ -methylhopanoids (Fig. 1b) recorded by high 2-MHI values (Fig. 1a) in OAE1a sediments reflects substantial cyanobacterial contributions to OM. Low  $\delta^{15}\text{N}$  values ( $< -2\text{‰}$ ) indicative of nitrogen ( $\text{N}_2$ ) fixation by cyanobacteria occur throughout the OAE1a interval (5), whereas 2-MHI values increase during time intervals characterized by cooler sea surface temperatures (4) and oxygenated waters. Thus, environmental changes during OAE1a appear to have affected cyanobacterial populations. In the modern ocean, higher temperatures are known to favor filamentous, non-heterocystous,  $\text{N}_2$ -fixing cyanobacteria, and exclude heterocystous species, whereas low  $p\text{O}_2$  environments seem to favor species of unicellular cyanobacteria (6,7). Therefore, temporal fluctuations in the populations of  $\text{N}_2$ -fixing cyanobacteria accompany episodes of carbon cycle perturbation such as OAE1a. Our results illustrate the viability of using biogeochemical proxies (i.e., 2-MHI), to infer variations in cyanobacterial speciation coupled to environmental changes during OAEs, and prompt assessment of similar phenomena at other times in Earth history.

### REFERENCES

1. Summons, R.E., Jahnke, L.L., Hope, J.M. & Logan G.A. (1999) *Nature* **400**, 554–557.
2. Kuypers, M.M.M., van Breugel, Y., Schouten, S., Erba, E. & Sinninghe Damsté, J.S. (2004) *Geology* **32**, 853-856.
3. Dumitrescu, M. & Brassell, S.C. (2005) *Org. Geochem.* **36**, 1002-1022.

4. Dumitrescu, M., Brassell, S.C., Schouten, S., Hopmans, E.C. & Sinninghe Damsté, J.S. (2006) *Geology* **34**, 833-836.
5. Dumitrescu, M. & Brassell, S.C. (2006) *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **235**, 168-191.
6. Staal, M., Meysman, F. J. R. & Stal, L. J. (2003) *Nature* **425**, 504-507.
7. Tomitani, A., Knoll, A.H., Cavanaugh, C.M. & Ohno, T. (2006) *Proc. Natl. Acad. Sci. USA* **103**, 5442-5447.

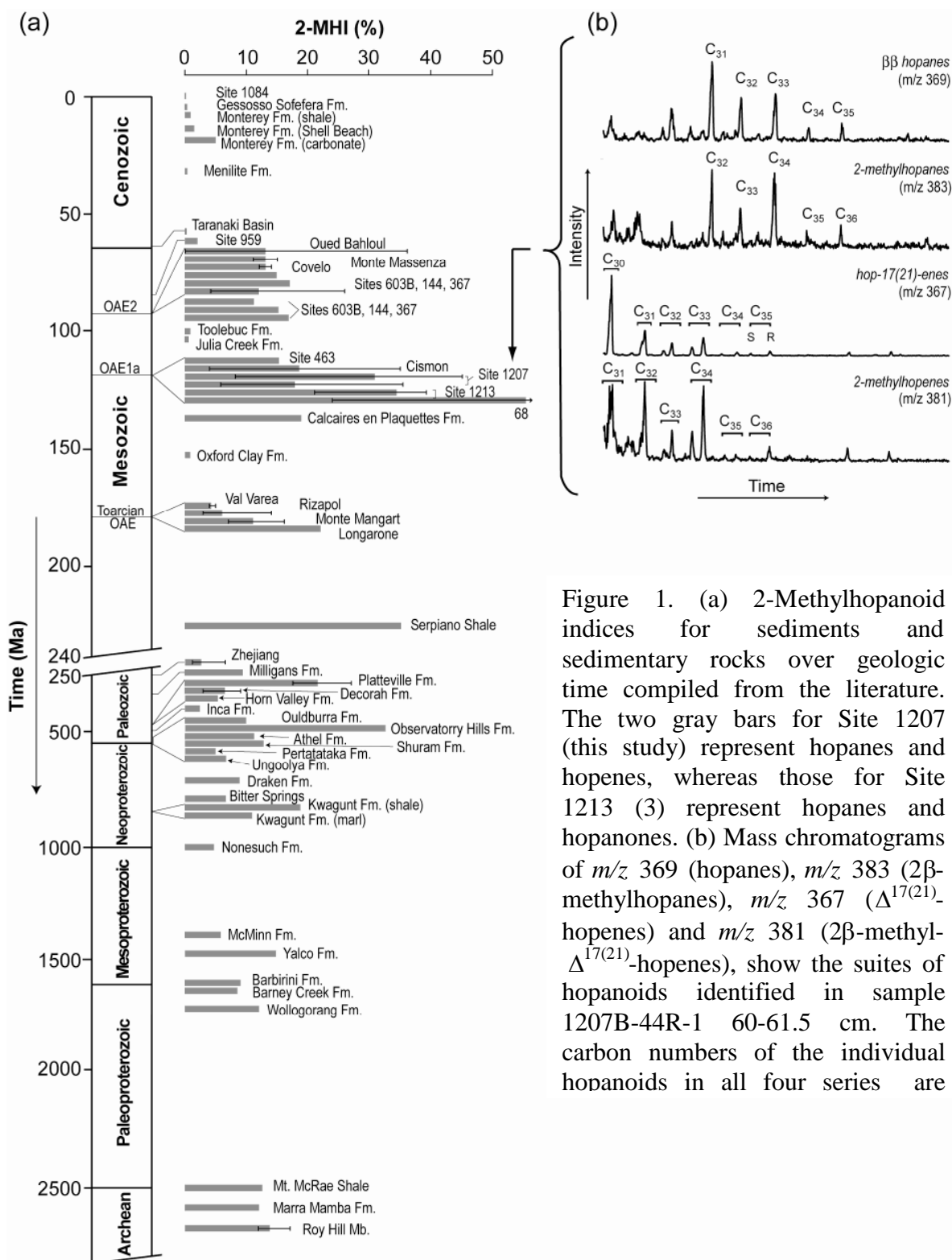


Figure 1. (a) 2-Methylhopanoid indices for sediments and sedimentary rocks over geologic time compiled from the literature. The two gray bars for Site 1207 (this study) represent hopanes and hopenes, whereas those for Site 1213 (3) represent hopanes and hopanones. (b) Mass chromatograms of  $m/z$  369 (hopanes),  $m/z$  383 ( $2\beta$ -methylhopanes),  $m/z$  367 ( $\Delta^{17(21)}$ -hopenes) and  $m/z$  381 ( $2\beta$ -methyl- $\Delta^{17(21)}$ -hopenes), show the suites of hopanoids identified in sample 1207B-44R-1 60-61.5 cm. The carbon numbers of the individual hopanoids in all four series are

## CONTRASTING LIPID BIOMARKER COMPOSITION AND $^{14}\text{C}$ AGES IN SURFACE SEDIMENTS OFF THE FIVE GREAT RUSSIAN ARCTIC RIVERS

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Numerical climate models forecast an amplified warming in the Arctic continental region (e.g., Zwiers, 2002), making it reasonable to expect that substantial effects of global warming will be first observed here. This will involve effects on the huge amounts of ‘old’ organic matter stored in Siberian soils. However, existing studies are inconclusive whether there is currently a climate-warming induced release of ‘new’ old carbon from the land. In addition, the availability of important detailed molecular data of the OM entering the Eurasian Arctic is limited or only available for single river systems. Therefore, surface sediments off the five Great Russian Arctic Rivers (GRARs), spanning 140 deg longitude, were investigated for their lipid biomarker composition to elucidate compositional distinctions of the exported OM across this continent-scale climosequence of the Siberian Arctic. In addition, high molecular weight (HMW) *n*-alkanes and *n*-alkanoic acids were isolated and used for compound-specific radiocarbon analysis (CSRA) to obtain information on the  $^{14}\text{C}$ -based reservoir age of the OM currently released from the Russian-Siberian permafrost.

The solvent extracts from all sediments are dominated by terrestrial biomarkers such as HMW *n*-alkanols, *n*-alkanoic acids and *n*-alkanes, branched glycerol dialkyl glycerol tetraethers, sterols (mainly  $\beta$ -sitosterol) and triterpenoids (Fig 1.). These estuarine sediments host only minor contributions of marine biomarkers (e.g., the ratio of terrestrial HMW to marine low molecular weight *n*-alkanes was between 17 and 80), further confirmed by the total organic carbon (TOC) to total nitrogen ratio (10 to 16), the  $\delta^{13}\text{C}_{\text{TOC}}$  (-25.0 to -27.4 ‰), and the branched and isoprenoid tetraether (BIT) index (0.88 to 0.92).

A large contribution of  $\text{C}_{23}$ - $\text{C}_{25}$  *n*-alkanes to the total HMW *n*-alkanes, particularly in the Ob estuary sediment, suggests substantial contribution of *Sphagnum*-derived OM. The  $\text{C}_{23}$ - $\text{C}_{25}$  contribution decreases from the west (Ob) to the east (Kolyma; Fig. 1), possibly indicating a decrease in the contribution of *Sphagnum* or, alternatively, a shift within the *n*-alkane distribution of the *Sphagnum* species, due to more arid conditions in the east. Another distinction in OM composition across the climosequence is the higher concentrations of *n*-alkanoic acids and  $\beta$ -sitosterol, in the Indigirka and Kolyma estuaries, compared to the more

western estuarine sediments (Fig. 1). Furthermore, the ratio of long-chain *n*-alkanoic acids to long-chain *n*-alkanes exhibits a west-to-east continent-scale trend (Fig. 1). This suggests that the OM exported by the eastern rivers are experiencing less degradation, which is consistent with increasing permafrost and a shorter annual thaw period from west to east along the Siberian Coast.

Taken together, this benchmark study suggests resolvable large-scale trends in OM lipid biomarker composition across the west-east set of the five GRARs, which reflects both differences in vegetative cover and climate. The resolved OM compositional differences may assist in predicting how the composition and decomposition of Arctic river-exported OM may change if the climate in the eastern Russian-Arctic region becomes more like the current state in the western part. In addition, CSRA of the isolated HMW *n*-alkanes and *n*-alkanoic acids will provide information which will contribute towards the understanding to what extent old carbon is now remobilized from the long-term repository represented by the Russian-Siberian permafrost and transported to the Eurasian rim of the Arctic Ocean; a scenario which would have major implications for the global carbon cycle and climate.

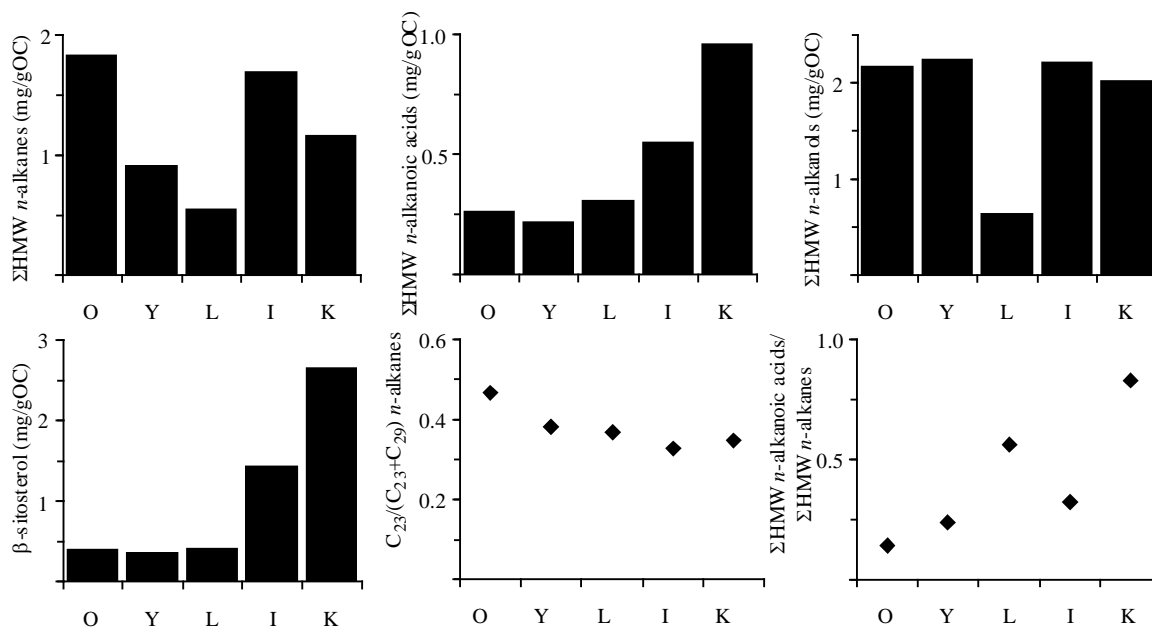


Figure 1. Abundances of terrestrial biomarkers and the ratios of C<sub>23</sub> *n*-alkanes to the sum of C<sub>23</sub> and C<sub>29</sub> *n*-alkanes and the summed concentrations of the *n*-alkanoic acids to the *n*-alkanes along the Eurasia-Arctic climosequence. The rivers in order from west to east: Ob (O), Yenisey (Y), Lena (L), Indigirka (I), Kolyma (K).

## REFERENCES

Zwiers, F.W., 2002. Climate change - The 20-year forecast. *Nature*, 416, 690-691.

## **GAS GEOCHEMISTRY OF MOBILE BAY: THERMAL CONTROLS ON GAS COMPOSITION AND IMPLICATIONS FOR RESERVOIR CONNECTIVITY**

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The Mobile Bay gas field is located offshore Alabama in the northern Gulf of Mexico. Production is from eolian dunes of the Jurassic-Age Norphlet sandstone at depths exceeding 6,100 meters and temperatures greater than 200°C. Reservoir connectivity and compositional variation, including the distribution of non-hydrocarbon gases (H<sub>2</sub>S and CO<sub>2</sub>) are critical factors in production strategy. To help understand the controls on compositional variation and connectivity, detailed molecular and isotopic analyses were conducted for 29 wells.

Fluid inclusion volatiles analysis, which measures rough abundances and compositions of fluids trapped in mineral cements suggest that the field was originally filled with oil that was subsequently cracked to gas. A paleo-oil-water contact was detected above the current gas-water contact, and pyrobitumen occurs above this paleo-contact.

Both hydrocarbon and non-hydrocarbon gas contents vary significantly. Hydrocarbon-normalized wet-gas contents (C<sub>2+</sub>) range from less than 0.1% to over 15%. Although carbon isotopic ratios of methane show only minor variation ( $\delta^{13}\text{C} = -36\text{‰}$  to  $-39\text{‰}$ ), carbon isotopic values of wet-gas components vary dramatically, becoming progressively heavier as gas compositions become drier. Hydrogen sulfide contents range from trace amounts to 10%, with highest concentrations in the Aloe Bay (AB) and Mary Ann (MA) portions of the field (Figure 1). Higher levels of H<sub>2</sub>S are generally associated with lower wet-gas contents, except where reservoir iron has scrubbed H<sub>2</sub>S. Sulfur isotopic compositions for H<sub>2</sub>S are similar to those for local evaporites ( $\delta^{34}\text{S} = +15\text{‰}$  to  $+16\text{‰}$  CDT). These observations suggest that thermochemical-sulfate reduction (TSR) of hydrocarbons is responsible for the formation of H<sub>2</sub>S and alteration of C<sub>2+</sub> hydrocarbon compositions.

Additional evidence for TSR alteration comes from condensate analyses which show that 90%+ of the liquid yields are composed of diamondoids. The distribution of specific diamondoid hydrocarbons appears to be controlled by the extent of TSR. For example, "carbonate" signatures in the diamantanes (Schultz, et al., 2001) increase with increasing TSR, suggesting that exposure to reduced sulfur governs selective destruction of the 3,4 isomer.

In contrast to hydrocarbon and H<sub>2</sub>S contents, CO<sub>2</sub> compositions are relatively constant throughout the field, averaging 3.5 mole percent. Carbon isotopic ratios for CO<sub>2</sub> parallel those for wet gas hydrocarbons but are heavier than expected for CO<sub>2</sub> originating from hydrocarbon oxidation via TSR. The narrow range of CO<sub>2</sub> contents and heavy isotope ratios suggest that CO<sub>2</sub> is also regulated by water-rock equilibration and calcite precipitation. Two distinct trends are evident for CO<sub>2</sub> isotopes; one trend may be affected by secondary fluid migration along Fault A (NWG1,2,3; Figure 1), while the second trend shows no fault-related migration effects (NCG2, MA, BSB). A transitional character for samples from NCG1 may reflect reduced levels of migration along Fault A as displacement decreases to the east.

Gas molecular and isotopic compositions help define reservoir compartments that are generally consistent with present-day gas-water-contact distributions. In some cases, gas compositional compartments may be baffled between dunes. Lack of communication between dune-sets may reflect inter-dune sealing lithologies. Similarly, the wide range of observed gas compositions and interpreted range in extent of TSR may reflect variations in within-dune or inter-dune (evaporite) lithologies.

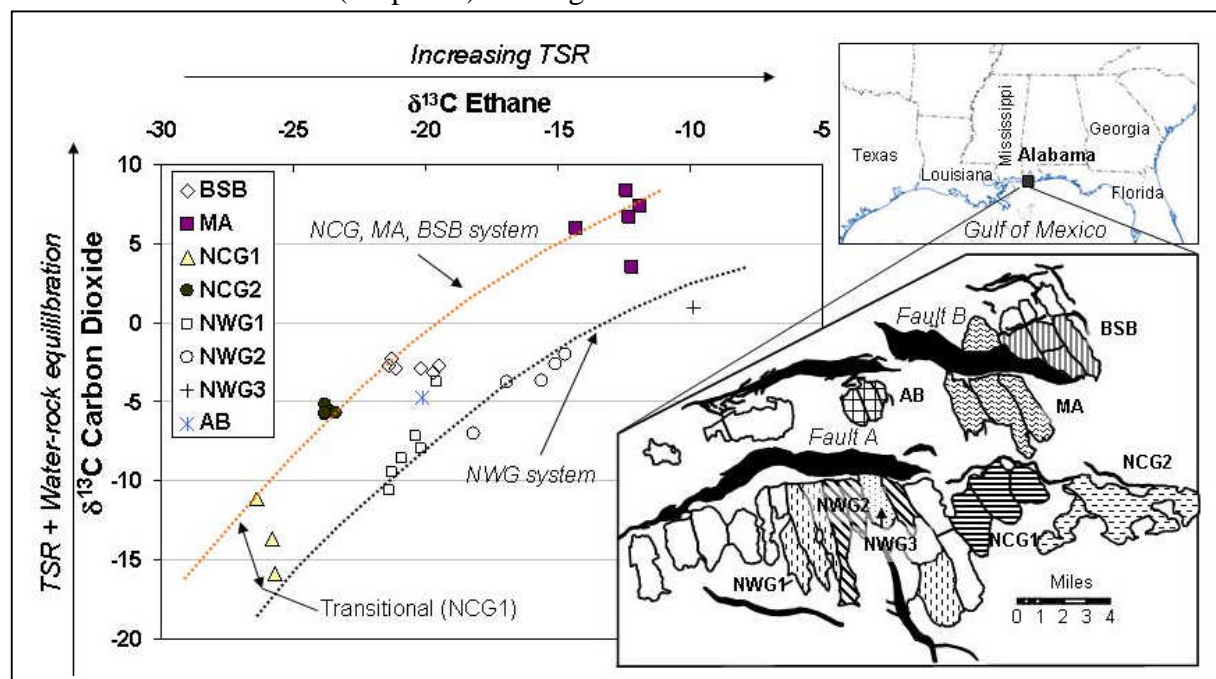


Figure 1. Plot of the carbon isotope ratios of ethane and CO<sub>2</sub> for sampled wells in the Mobile Bay field with adjacent map showing locations of gas families with similar compositions.

Eight gas families are identified: three in the Northwest Gulf (NWG), two in the North-Central Gulf (NCG), and the Bon Secour Bay (BSB), Maryann (MA), and Aloe Bay (AB) families. Additionally, two possible CO<sub>2</sub> systems are interpreted from δ<sup>13</sup>C of CO<sub>2</sub>.

## REFERENCES

Schulz, L.K., A.Wilhelms, E. Rein, and A.S. Steen. 2001. Application of diamondoids to distinguish source rock facies. *Organic Geochemistry* 32, 365-375.

## TIMESCALES OF TERRESTRIAL ORGANIC CARBON EXPORT TO THE OCEANS

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Great strides have recently been made in our understanding of the composition of organic matter discharged from rivers to the oceans, as well as its subsequent fate in the marine environment. In contrast, we know relatively little about the timescales over which vascular plant-derived organic carbon is stored in terrestrial reservoirs, moves between these reservoirs, and is discharged the oceans. This information is crucial if we are to develop accurate models that mimic carbon cycling in the environment as well as predict the impacts of anthropogenic perturbations of the natural system. Accurate interpretation of terrestrial and marine proxy records from continental margin sediments also depends upon knowledge of the temporal relationships between these signals.

Radiocarbon provides an effective tool to constrain residence and transport times of organic matter, and prior studies have revealed that the World's rivers discharge particulate and dissolved organic matter that varies markedly in radiocarbon age. However, a major impediment to the interpretation of these radiocarbon ages in terms of residence time is the unknown and potentially variable contributions of sedimentary rock and other non-vascular plant sources of organic matter to bulk phases. This complication can be obviated by targeting biomarker compounds specific to vascular plants for radiocarbon analysis.

We have performed compound-specific radiocarbon analysis on sediments recovered from fluvial deposits at the termini of several river systems spanning a range of drainage basin types, sizes, and bedrock lithologies, as well as varying in terms of climate (hydrology, temperature) regime. A first-order relationship appears to exist between terrestrial organic matter residence time and latitude, implying a strong influence of temperature on the rate of organic matter cycling within, and export from, watersheds.

In order to more tightly constrain residence times of the most active pools of terrestrial organic matter, detailed down-core molecular-level radiocarbon measurements have been made on terrestrial marker compounds preserved in anoxic marine basins adjacent to tropical and temperate drainage basins. We trace the atmospheric radiocarbon "bomb-spike" from its initial incorporation into vascular plant biomass to the downstream sedimentary sink. Lags

between the known date of the bomb-spike and its manifestation in vascular plant biomarkers preserved in sediments can be interpreted in terms of residence times of terrestrial organic matter within the corresponding drainage basin. These measurements suggest vascular plant-derived organic matter exported to the oceans involves at least two components – one that is rapidly transported (< 20 years) together with a pool of slower cycling “pre-aged” material (soil). Findings from the above studies will be discussed in terms of the controls on the export of particulate materials from rivers to the oceans and the sensitivity of terrestrial discharge to anthropogenic and climate perturbations.

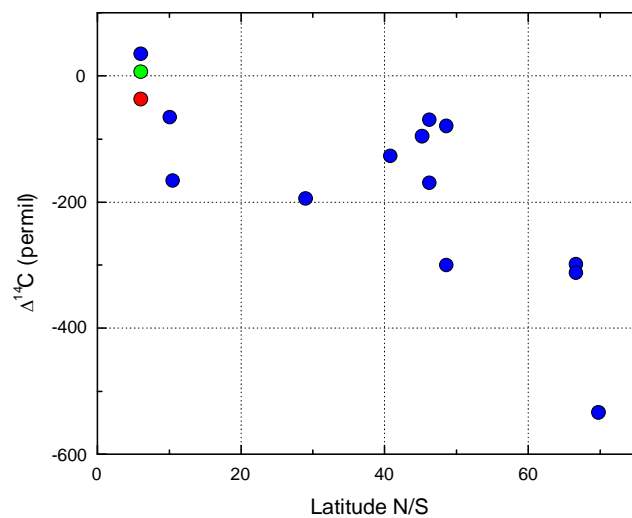


Figure 1.  $^{14}\text{C}$  content (expressed as  $\Delta^{14}\text{C}$ , permil) of plant wax-derived long-chain ( $\geq \text{C}_{24}$ ) lipids from sediments collected at the termini of river drainage basins plotted as a function of latitude (blue circles = n-alkanoic acids; green circles = n-alkanols; red circle = n-alkanes).