

EFFECT OF CLAY MINERALS ON THE DECOMPOSITION OF ALGAL LIPIDS IN OXIC AND ANOXIC SEDIMENTS

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Clay minerals play an important role in the transport and protection of many organic compounds by adsorption thus affecting the decomposition and preservation of organic matter during early diagenesis in marine sediments. In this study, we examined the effects of two clay minerals, montmorillonite and kaolinite, on the decomposition of the green algal *Chlorella. sp* in marine sediments under both oxic and anoxic conditions. The laboratory incubation experiments were conducted for 240 days and changes in total organic content, carbon isotopic composition ($\delta^{13}\text{C}$), and both “free” and “bound” algal fatty acid concentrations were analyzed with incubation time.

Our results indicate that when excess clay minerals were added to the sediment, the algal organic matter decomposed much slower than when no clays were added and showed no significant differences in decomposition rate under both oxic and anoxic conditions. During the decomposition process, $\delta^{13}\text{C}$ values of total organic matter decreased slightly in comparison to the original value but also showed no differences under both oxic and anoxic conditions. Among the detectable fatty acids, 14:0, 16:0, 16:1, 18:1, and 20:5 were the major compounds present. In most cases, the decomposition of “free” fatty acids exhibited a general pattern of a rapid decrease in the initial 10 weeks, followed by a much slower decline. During the decomposition, concentrations of bacterial fatty acids (15:0, 17:0) increased in association with a decrease in algal fatty acid levels. The decomposition of algal fatty acids occurred more rapidly under the oxic condition than the anoxic condition. Using a simple early diagenetic model, we calculated the decomposition rate constant for the fatty acids. Our values ranged from 0.018 to 0.059 d^{-1} and were much lower than those reported in previous laboratory studies in which no clay minerals were added to the incubated sediments. This suggests that the decomposition of fatty acids was protected by adsorption of clay minerals. The adsorption of fatty acids onto both montmorillonite and

kaolinite appeared to be a very rapid process as detected by dramatic increase in “bound” fatty acid levels. In general, mono- and polyunsaturated fatty acids had a higher degradation rate constant than that of saturated fatty acids in both oxic and anoxic sediments, indicating that double bonds play an important role in molecular lability. Our study suggests that in natural sediments, environmental factors such as mineralogy, redox condition, bacterial activities and molecule structure all play important roles in controlling the decomposition dynamic and pathway of organic matter.

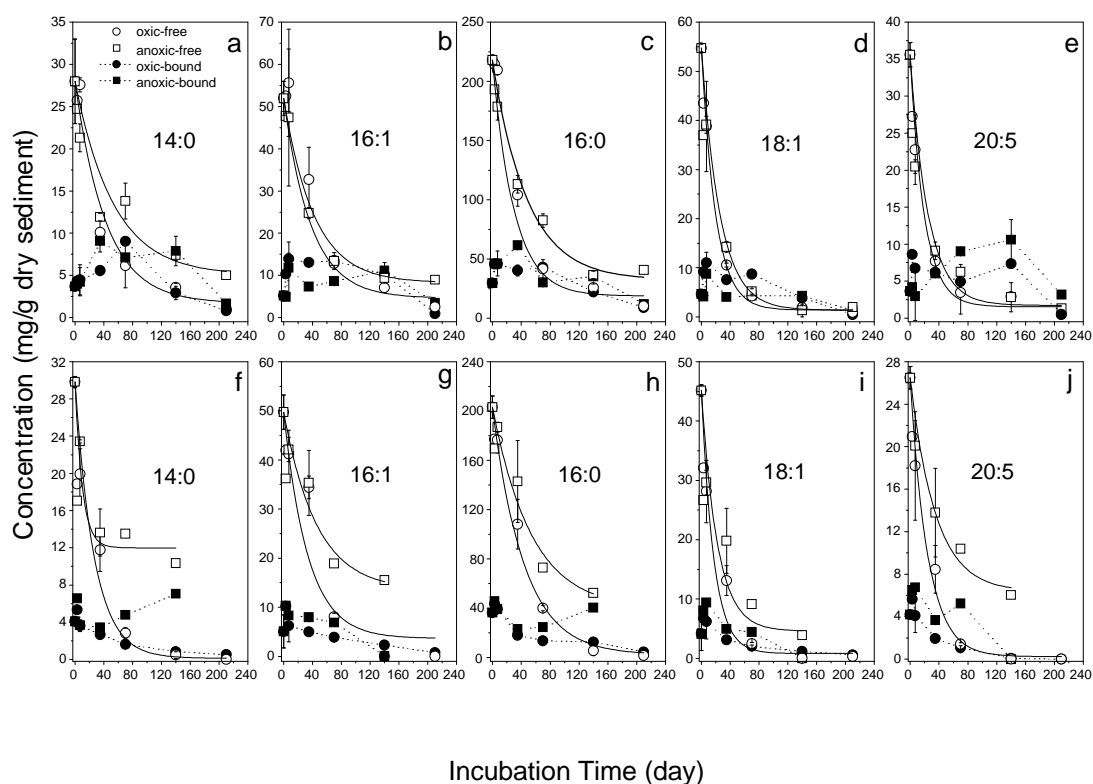


Figure 1. Plot of concentration changes in “free” and “bound” fatty acids during the decomposition in oxic and anoxic sediments with montmorillonite (a-e) and kaolinite (f-j) added. (○) and (□) are “free” fatty acids in oxic and anoxic sediments; (●) and (■) are “bound” fatty acids in oxic and anoxic sediments. The solid lines are model fits to the data.

**A DIRECT TEST OF THE RELATIONSHIP BETWEEN ORGANIC MATTER
REACTIVITY AND PARTICLE ASSOCIATIONS IN MARINE SEDIMENTS**

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Organic matter cycling through marine sediments represents an important component of the global carbon cycle. Despite numerous studies, our understanding of the factors dictate the degradation or preservation of organic matter remains limited. Two key recent observations that impinge on this issue are (i) the importance of organic matter-mineral associations as a crucial factor in preservation, and (ii) that organic matter deposited on the sea floor can be readily resuspended and laterally transported prior to its ultimate burial. Evidence for the latter process stems from natural abundance ^{14}C measurements on individual organic compounds isolated from sediments which have revealed that organic matter can be substantially pre-aged prior to, and during transport to its ultimate site of deposition (e.g., Ohkouchi et al., 2002; Mollenhauer et al., 2005).

In this study, we seek to examine the interrelationships between organic matter-mineral particle association, lateral transport and organic carbon burial in continental margin sediments. We exploit the age differences between freshly synthesized phytodetritus deposited from overlying surface waters and pre-aged algal residues supplied laterally on particles (e.g., in nepheloid layers). We seek to confirm the hypothesis that, due to the formation of an intimate association with detrital mineral phases, laterally advected organic matter will be less prone to degradation during diagenesis relative to freshly phytoplankton detritus (Mollenhauer & Eglinton, 2007).

In order to test this hypothesis, sediment from the Jordan Basin in the Gulf of Maine (an area of focusing and deposition of fine-grained sediments) was incubated under aerobic conditions for up to one year and the concentrations and ^{14}C natural abundances in lipid biomarkers (alkenones, fatty acids) were determined. We predict that the ^{14}C content of alkenones will decrease during the course of the experiment as young, labile alkenones are preferentially degraded over their pre-aged advected counterparts. Results from this study will be discussed in terms of our understanding of the controls on organic matter degradation in aquatic sediments.

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**ORGANIC MATTER DEGRADATION IN A “FRESHWATER OCEAN”
– A SEDIMENT TRAP STUDY IN LAKE BAIKAL**

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Lake Baikal offers the unique opportunity to study water column processes in a freshwater system with conditions similar to oceanic systems. With a maximum water depth of ~1640 m, Lake Baikal is the deepest lake on Earth and due to efficient vertical mixing, oxygen concentrations are high throughout the water column (Weiss et al. 1991). Investigations on sediment trap material provide information on the early stages of organic matter degradation in the water column. The data set we present is unique with regard to the environmental setting and the high spatial resolution of the sampling intervals.

Sediment trap material from 18 different water depths has been analysed for bulk organic matter parameters (concentrations of total organic carbon (TOC) and total nitrogen (TN), C/N-ratios, organic carbon and nitrogen isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$), chlorin concentrations, and Chlorin Indices (Schubert et al. 2005)). A detailed study will be presented, which focused on the concentration and composition of total hydrolysable amino acids (THAA), amino acid stereochemistry (D- and L-isomers), and the characterization of the fatty acid fraction.

The extent of organic matter degradation in the water column of Lake Baikal is reflected in the fluxes of TOC, TN, chlorins, THAA, and fatty acids at different water depths. All these parameters strongly decreased within the upper 500 m, indicating efficient degradation of settling organic matter in the upper water column. In line with earlier studies (e.g. Cowie and Hedges 1994), the labile compounds represented by chlorins, THAA, and fatty acids, were preferentially degraded over bulk organic carbon. A wide range of diagenetic indicators has been applied to assess the diagenetic stage of the sediment trap material. They all showed consistent trends, indicating that the diagenetic stage of the sediment trap material increased with increasing water depth. In particular, the Chlorin Index increased, the contributions of amino acid carbon to TOC (%T_{AA}C) and of amino acid nitrogen to TN (%T_{AA}N) decreased, the ratio of non-protein amino acids and their respective protein precursors increased, and the amino acid based degradation index (Dauwe et al. 1999) decreased with increasing water depth. Based on the distribution of D-amino acids, it was possible to estimate the contribution of peptidoglycan amino acids to THAA. This

contribution increased along with the increasing diagenetic stage of the sediment trap material, indicating that a relative accumulation of bacterial cell wall material can already be traced at the early stages of organic matter degradation and transformation.

In summary, this study of sediment trap material from Lake Baikal provided interesting insights in organic matter degradation in this unique aquatic system. It showed the applicability of different diagenetic indicators for studies of freshwater systems and at early stages of organic matter degradation. Furthermore, it was possible to trace the accumulation of bacterial organic matter during reworking and degradation in the water column of Lake Baikal.

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DOWNSLOPE TRENDS IN NITROGEN ISOTOPES FROM SURFACE SEDIMENTS ON THE PERU MARGIN

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Nitrogen isotope trends of bulk sediments deposited under the oxygen minimum zone on the Peru Margin were studied in samples from deck-deployed box cores and push cores acquired by submersible on two transects at 12° and 13.5° from 75 to 1000m water depth. Previous work of Arthur et al., (1998) has shown that organic matter is more poorly preserved than would be expected despite the low-oxygen conditions (<5 µmol/kg). This is attributed to constant advection of low concentrations of dissolved oxygen, activity of organisms, and resuspension and downslope transport of organic matter by strong bottom currents up to 30 cm/s. These processes extend exposure time to oxidant (dissolved oxygen or nitrate) which progressively degrades surface and suspended organic matter. Bulk nitrogen isotope values average 7.5 permil and range from 4.0 to 10.9 permil. The average of 7.5 permil is typical for modern upwelling zones where denitrification is the dominant suboxic autotrophic metabolism within the oxygen minimum zone. The variability in nitrogen isotope values reflects the influence of resuspension and downslope movement of sediment. Nitrogen isotope and pyrolysis hydrogen index values decrease down-slope are positively correlated while atomic C/N ratios increase. This suggests that increasing exposure times to oxidant and removal of labile nitrogen results in decreasing nitrogen isotope values. This trend is contrary to normal isotope degradation kinetics which typically drive nitrogen isotope values higher but could be achieved through selective degradation of ¹⁵N-enriched proteins and amino acids which has been observed where denitrification is occurring (van Mooy et al., 2002).

BIOMOLECULAR EVIDENCE FOR THE FORMATION OF AN EXTENSIVE TAR LAYER GENERATED DURING A VOLCANIC EVENT ON MONTSERRAT

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The island of Montserrat comprises four volcanic centres of which only the Soufrière Hills, at over 900 m, remains active (Harford et al., 2002). On 26th December 1997 a volcanic event occurred where the flank rocks of the edifice and dome talus on the south-western side failed, due to hydrothermal weakening of the edifice rocks. A subsequent blast generated a pyroclastic density current (PDC) that covered and devastated 10 km² of southern Montserrat and of the area was covered by a black 'tar' layer of 1-4 mm thick. Investigation of the layer indicated that the tar formed over a surface that had been already striated and grooved prior to deposition and it was postulated that a cloud of heated organic material had combusted to form the tar layer nearly synchronously as the hot current inundated the area (Sparks et al., 2002). This investigation tested the above hypothesis through comparative analyses of organic compounds (both molecular and macromolecular) extant in the tar and its putative sources, i.e. the local vegetation (grass) and soil.

The major biomolecular components of the tar were isolated then analysed by GC and GC/MS, classes investigated included: lipids (hydrocarbons, *n*-alkanols, *n*-alkanoic acids, sterols), carbohydrates and lignin (CuO oxidation). Analysis of freely extractable lipids revealed that despite the high temperatures associated with the PDC a lipid signature, indicative of an origin from the grass *and* soil, was still extant within the tar layer. The distribution of major *n*-alkanes in the hydrocarbon fraction extracted from the tar correlated remarkably well with those of the vegetation and soil indicating that organic matter from one or both of these materials constituted an important fraction of this sample. Investigation of other functionalised acyclic lipids enabled additional clarification concerning the source of organic matter. The *n*-alkanol fraction derived from the tar exhibited a wide range of homologues as observed for the soil. However, the C₂₂ and C₃₂ homologues were present at a higher concentration, relative to the peripheral components, than observed in the soil thereby indicating that there had also been a contribution from the grass.

Application of ^{13}C CP/MAS NMR corroborated findings obtained from the molecular analyses. The spectra obtained for tar MVO342 exhibited a large aromatic signal that maximised at 128 ppm in contrast to the grass and soil which generated a predominant O-alkyl signal mainly attributable to carbohydrates (76842 and 3874 mg^{-1}TOC total hydrolysable carbohydrates, respectively). This was indicative of naturally charred materials (Simpson and Hatcher, 2004) whilst the O-alkyl signal was greatly diminished paralleling the almost total loss of carbohydrates (93 mg^{-1}TOC , total hydrolysable carbohydrates). Additionally, there was a much larger alkyl carbon component that correlated with the occurrence of a large unresolved complex mixture (UCM) in the hydrocarbon fraction of the sample. With an integral of over 50% the signal relating to aromatic carbon was even more dominant relative to other carbon environments in the spectra obtained for tar MVO662 thereby attesting to the even greater amount of thermal alteration that been undergone by this sample (Simpson and Hatcher, 2004).

These findings suggest that the organic matter constituting the tar had been heated in excess of 300°C , thereby correlating with additional reflectance data indicating minimum temperatures of $325\text{--}370^\circ\text{C}$ and up to 425°C .

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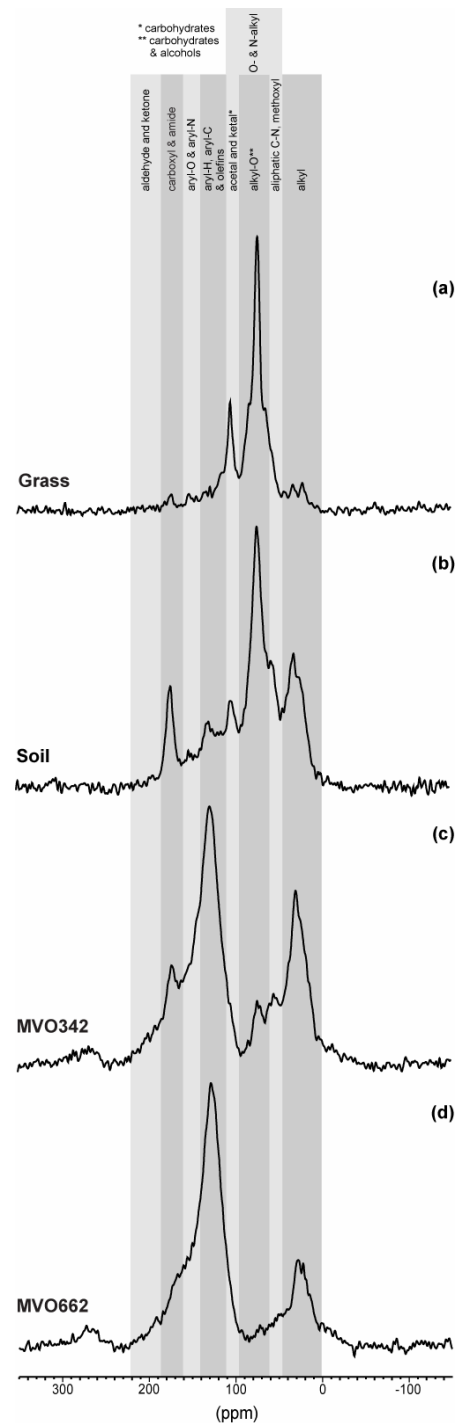


Figure 1. Solid state ^{13}C NMR spectra of (a) grass, (b) soil, (c) MVO342 and (d) MVO662

BIOMOLECULES PRESERVED IN MIDDLE JURASSIC FOSSIL CONIFER WOOD

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The oldest polar terpenoids are known from Cretaceous resinites (Alonso *et al.* 2000) and a few Cretaceous gymnosperm remains, such as *Sphenolepis* (Otto *et al.* 1999) and *Tritaenia* (Otto *et al.* 2002b). In all these cases only minor amounts of ferruginol and other unaltered terpenoids were detected. Here, we report the occurrence of relatively high concentrations of ferruginol derivatives and other polar diterpenoids as well as their diagenetic products in a fossil wood sample identified as a species of *Protopodocarpoxylon* Eckhold and *Xenoxylon phyllocladoides* Gothan from the Middle Jurassic (Bathonian) of the Polish Jura, south-central Poland and Middle Jurassic (Callovian) of the eastern part of the Polish Lowland.

The state of preservation of the wood fragments differs among specimens. Generally, they are either coalified and/or permineralized. The quality of preservation of the wood structure depends mainly on the time of permineralization after burial. Most of the wood samples display some bacterial attack on the cell walls, although the specimens studied as prepared peels have all diagnostic xylogenetic features. Thus, it can be hypothesised that, after a short drift and residence in salt-water, the woody fragments sank to an oxygen-poor sea-bottom, where they were rapidly buried in sediment. Mineralization processes began immediately after deposition.

The vitrinite reflectance (R_r) measurements, conducted on the Bathonian and Callovian wood samples, gave the values 0.25 – 0.35 %, however some exceptions with the higher R_r values (0.45 – 0.50 %), caused by secondary oxidation processes, were also noted.

The solvent extract of the best chemically preserved samples contains aliphatic lipids, diterpenoids, triterpenoids and steroids (Fig. 1). The aliphatic lipids are composed of long-chain (C_{24} - C_{29}) *n*-alkanols and *n*-alkanoic acids. The predominant compound is the secondary alcohol *n*-nonacosan-10-ol accompanied by four *n*-nonacosanediols (10,13-diol, 7,13-diol, 5,10-diol and 7,10-diol). Major constituents of the extract are diterpenoids of the abietane,

labdane, and totarane classes which are known as common constituents of conifer resins. With the exception of simonellite and labdanoic acid, most of the diterpenoids are unaltered, preserved biomolecules as observed in extant plants, especially conifers. Comparable compositions of polar biomarkers were hitherto reported only from much younger geological samples, namely fossil plants, resins and coals of Tertiary or Cretaceous ages. The excellent preservation of polar molecules is caused by the limited biodegradation of natural product compounds in the resin due to the presence of antimicrobial phenols and/or the rapid burial of the wood in anaerobic sediments.

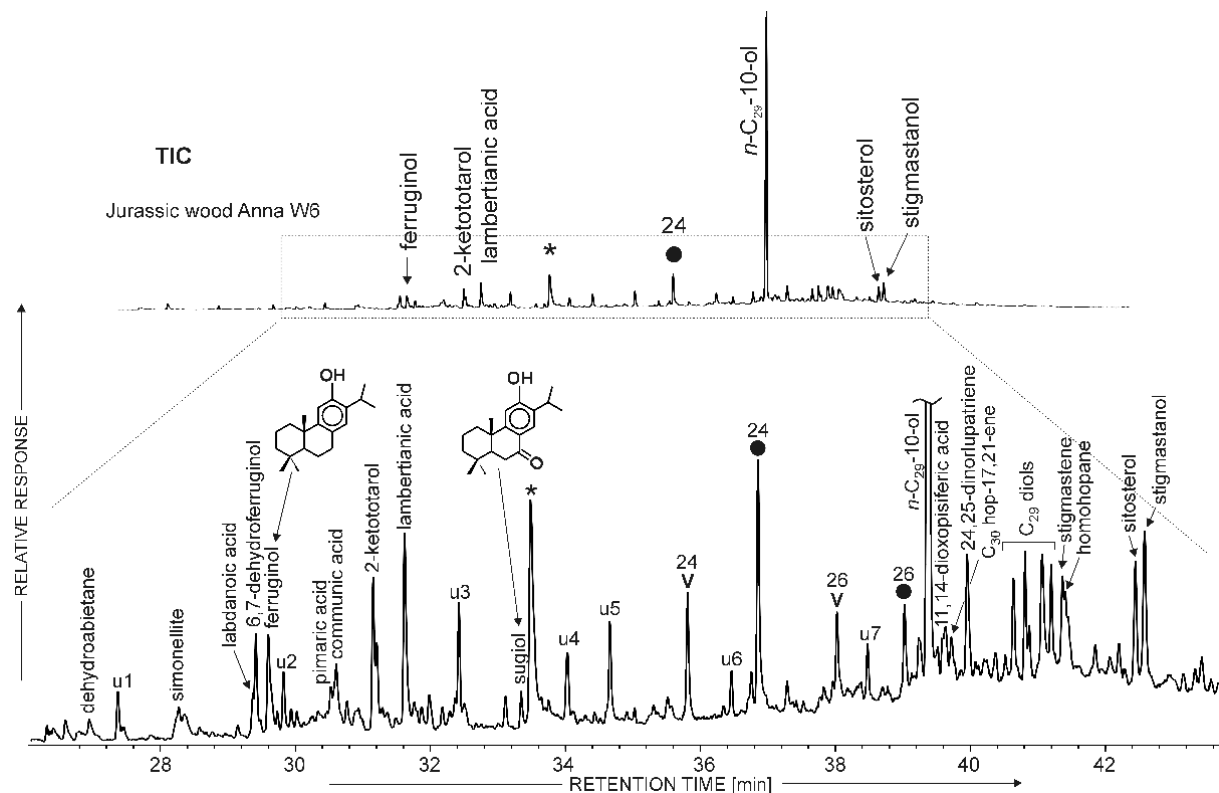


Figure 1. Mass chromatogram (TIC) of the silylated total extract (TMS derivatives) of the Jurassic *Xenoxylon phyllocladoides* wood from Poland. * = contamination, v = *n*-alkanols, • = *n*-alkanoic acids, u1-u7 = unknown compounds. Numbers indicate the number of carbons in the aliphatic lipid series.

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**BIOLOGICAL AND GEOCHEMICAL CHANGES IN LIGNOCELLULOSIC
SUBSTRATES DURING THE SOLID STATE FERMENTATION OF *PLEUROTUS
OSTREATUS***

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White-rot fungi are the most effective biotic degraders of lignin due to their suite of extracellular enzymes and mycelial growth habit. Their activity represents a key step in the global carbon cycle since it influences the forms in which carbon is released from lignocellulosic macrostructures such as tree trunks and grass stems as well as the pathways that the carbon will subsequently follow. This release of carbon is a biotic process that varies over time as the fungi grow, colonise substrates and express enzymes, suggesting that research will benefit from an approach that monitors multiple variables over time and that allows links to be made between the variables. Previous work in our laboratory (e.g. Vane et al. 2001a,b) has investigated time-dependent changes in lignin degradation products occurring during the breakdown of wheat straw lignin by white-rot fungi.

A model system with *Pleurotus ostreatus* growing on unamended wheat (*Triticum aestivum*) straw, common ash (*Fraxinus excelsior*) wood or Sitka spruce (*Picea sitchensis*) wood under solid-state fermentation conditions was used to investigate changes occurring during growth of this white-rot fungus. Sampling took place at regular intervals over 12 weeks. Lignin degradation was investigated using thermochemolysis in the presence of tetramethylammonium hydroxide (TMAH) which allowed identification of a suite of degradation products and changes in their relative abundances. Calculation of acid/aldehyde (e.g. 3,4-dimethoxybenzoic acid to 3,4-dimethoxybenzaldehyde) and side chain scission (e.g. 3,4-dimethoxybenzoic acid to 1,2-dimethoxy-4(1,2,3-trimethoxypropyl)benzene) ratios allowed lignin oxidation to be monitored. Changes in amounts of the fungal biomarker ergosterol were used as a proxy for fungal biomass. The activity levels of the extracellular enzymes were determined using targeted assays of the extracellular fluid removed from the solid state fermentation system. The ligninolytic enzymes manganese peroxidase and laccase were assayed, plus β -glucosidase which catalyses the breakdown of glucose oligomers.

Figure 1 a, b and c show the enzyme activity levels measured when *Pleurotus ostreatus* was grown on wheat straw; similar patterns were observed on ash and Sitka spruce. Of the two ligninolytic enzymes, laccase activity peaked one week earlier and subsequently declined more than manganese peroxidase activity. β -Glucosidase activity increased rapidly

in the first week but then remained relatively constant; the highest activity was measured in week 7. The pattern of enzyme activity contrasts with wheat straw lignin oxidation which displayed a time-lag of three weeks before the maximum rate of lignin oxidation (steepest gradient in plot) was observed (Figure 1d, in a separate experiment) and continued to increase throughout the incubation. Ergosterol concentration, and thus fungal biomass on wheat straw, also displayed a three-week time-lag before the maximum rate of increase was observed. These results indicate that enzyme production precedes fungal growth as well as lignin oxidation. Thus, the fungus probably devotes the highest proportion of its resources to producing ligninolytic enzymes when initiating lignin oxidation.

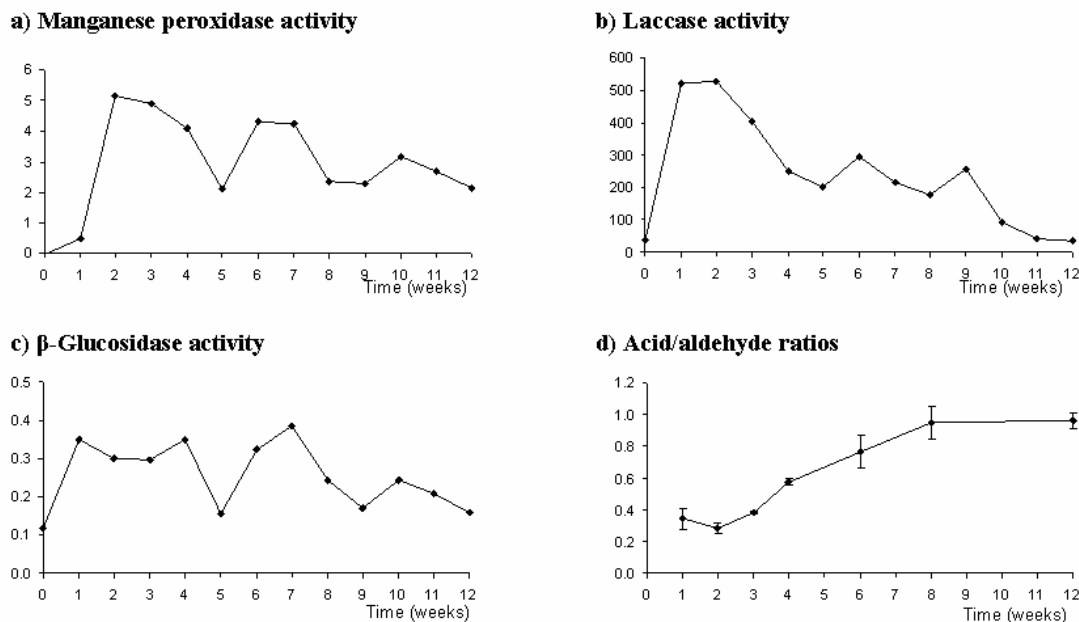


Figure 1:

- Total extractable manganese peroxidase activity (manganese peroxidase assay units/g of dry straw) levels during 12 week solid state fermentation of wheat straw (*Triticum aestivum*) with *Pleurotus ostreatus*
- Total extractable laccase activity (laccase assay units/g of dry straw) levels during 12 week solid state fermentation of wheat straw with *Pleurotus ostreatus*
- Total extractable β -Glucosidase activity (β -Glucosidase assay units/g of dry straw) levels during 12 week solid state fermentation of wheat straw with *Pleurotus ostreatus*
- Guaiacyl acid/aldehyde ratios (GCMS peak area ratios of 3,4-dimethoxybenzoic acid/3,4-dimethoxybenzaldehyde) indicating lignin oxidation during 12 week solid state fermentation of wheat straw with *Pleurotus ostreatus*. Data from a separate experiment to a), b) and c)

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**DEGRADATION OF BOTANICAL REMAINS IN ARCHAEOLOGY:
OPTIMIZING FOR PRESERVATION *IN SITU***

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Concerns about the degradation of the archaeological record with subsequent loss of information have led to initiation of research to establish guidelines for the optimal preservation of common materials found at archaeological sites, because this record is neither regenerable nor replaceable. Hitherto, research has focused on metal, bone and wood, but the research on botanical remains, such as plant seeds, has so far been scarce and is in need of further development. The results of this study should lead to a recommendation on the optimal approach to preserve our archaeological heritage *in situ*.

Botanical remains are an important component of many archaeological sites. The information contained within this type of material provides important information about human activities and environmental conditions in the past. The preservation of this material is henceforth an important issue, especially at sites where, in accordance with modern international concepts of archaeological heritage management, such preservation is done *in situ*.

The objective of the presented study is to develop an assessment system for the preservation potential of sites in wetland areas. To obtain an insight into the natural variation of the chemical composition of botanical remains, seeds from a wide variety of plant species commonly encountered at archaeological excavations were analyzed using Pyrolysis-GC/MS. Currently a library has been built up covering a selection of over 60 species (see Table 1). Additionally TMAH thermochemolysis has been applied to a large subset for additional information on the chemical composition of these plant species.

The application of factor analysis on the Py-GC/MS results allows for identification and observation of changes in the chemical composition reflecting degradation. By referencing soil parameters such as the presence or absence of water and oxygen, pH and the

buffer capacity of the soil from the corresponding excavation sites it can be determined which parameters cause the largest changes in the chemical composition, and therefore preservation state of botanical remains. With this information, guidelines can be established to develop long-term strategies for the *in situ* preservation of sites; and to develop techniques and methods to monitor protected sites; as well as to contribute to a theoretical basis for the sustainable management of our archaeological heritage.

<i>Atriplex patula/prostrata</i>	Common Orache / Spear-leaved Orache	<i>Persicaria maculosa</i>	Persicaria / Red Shank
<i>Avena</i>	Oat	<i>Phragmites australis</i>	Common Reed
<i>Bidens tripartita</i>	Trifid Bur-marigold	<i>Polygonum aviculare</i>	Knotgrass
<i>Bolboschoenus maritimus</i>	Sea Club-rush	<i>Potentilla anserina</i>	Silverweed
<i>Brassica rapa</i>	Turnip	<i>Prunus avium</i>	Gean / Wild Cherry
<i>Calluna vulgaris</i>	Heather / Ling	<i>Prunus domestica</i>	Bullace
<i>Cannabis sativa</i>	Hemp	<i>Prunus persica</i>	Peach
<i>Centaurea cyanus</i>	Cornflower	<i>Ranunculus acris/repens</i>	Meadow Buttercup / Creeping Buttercup
<i>Ceratophyllum demersum</i>	Rigid Hornwort	<i>Ranunculus sardous</i>	Hairy Buttercup
<i>Chenopodium album</i>	Fat-hen	<i>Raphanus raphanistrum</i>	Wild Radish
<i>Cirsium arvense/palustre</i>	Creeping Thistle / Marsh Thistle	<i>Rosa</i>	Rose
<i>Cladium mariscus</i>	Great Sedge / Saw-sedge	<i>Rubus idaeus</i>	Raspberry
<i>Corylus avellana</i>	Hazel	<i>Rumex acetosella</i>	Sheep's Sorrel
<i>Fagopyrum esculentum</i>	Buckwheat	<i>Rumex crispus</i>	Curled Dock
<i>Fallopia convolvulus</i>	Black Bindweed	<i>Rumex maritimus/ palustris</i>	Golden Dock/Marsh Dock
<i>Fragaria vesca</i>	Wild Strawberry	<i>Sambucus nigra</i>	Elder
<i>Galeopsis speciosa/ tetrahit</i>	Large-flowered- / Common Hemp-nettle	<i>Scleranthus annuus</i>	Annual Knawel
<i>Hordeum vulgare</i>	Six-row Barley	<i>Secale cereale</i>	Rye
<i>Juglans regia</i>	Walnut	<i>Solanum nigrum</i>	Black Nightshade
<i>Lamium album/ maculatum</i>	White Dead-nettle / Spotted Dead-nettle	<i>Sonchus arvensis</i>	Corn Sow-thistle/ Per. Sow-thistle
<i>Leontodon autumnalis</i>	Autumnal Hawkbit	<i>Stellaria media</i>	Chickweed
<i>Linum usitatissimum</i>	Cultivated Flax	<i>Suaeda maritima</i>	Annual-seablite
<i>Mentha aquatica/arvensis</i>	Water Mint/Corn Mint	<i>Thlaspi arvense</i>	Field Pennycress
<i>Myrica gale</i>	Bog-myrtle / Sweet Gale	<i>Triglochin maritima</i>	Sea Arrowgrass
<i>Nuphar lutea</i>	Yellow Water-lily	<i>Triticum aestivum</i>	Bread Wheat
<i>Oenanthe aquatica</i>	Fine-leaved Waterdropwort	<i>Urtica dioica</i>	Stinging Nettle
<i>Persicaria hydropiper</i>	Water-pepper	<i>Urtica urens</i>	Annual Nettle
<i>Persicaria lapathifolia</i>	Pale Persicaria	<i>Vitis vinifera</i>	Grape-vine

Table 1. Overview of the plant species for which Py-GC/MS traces were obtained of their seeds found during archaeological excavations.