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Published Version

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Peer-reviewed

### Citation for published item:

McClymont, E.L. and Pendall, E. and Nichols, J. (2010) 'Stable isotopes and organic geochemistry in peat : tools to investigate past hydrology, temperature and biogeochemistry.', PAGES news., 18 (1). pp. 15-18.

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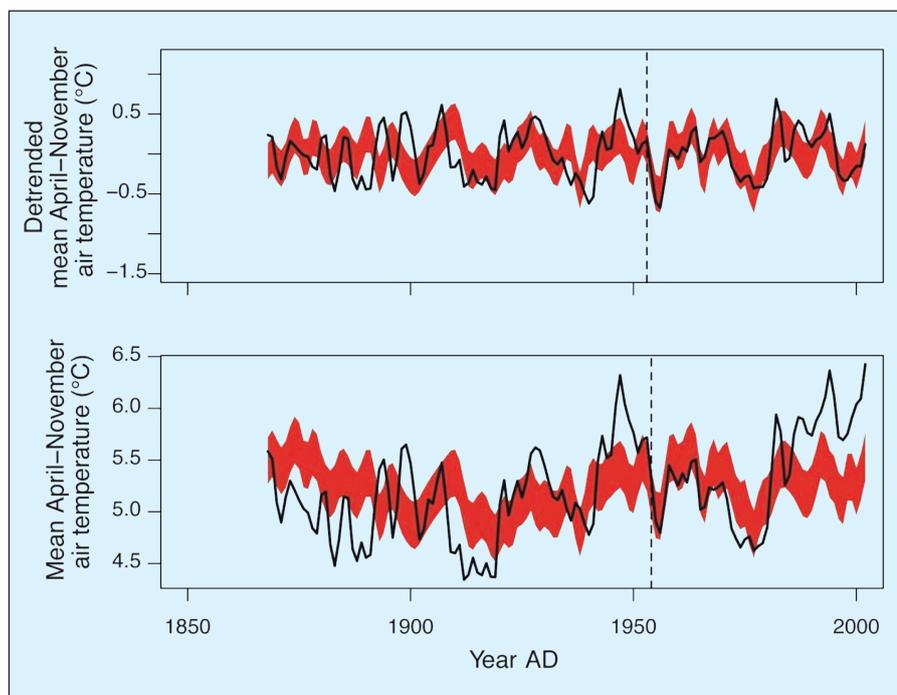


Figure 3: Confidence bands (95%) of detrended (upper panel) and non-detrended (lower panel) pollen-based warm-season temperature reconstructions (red) versus measured temperature (solid black line) during the instrumental period. Pollen picked up long-term (at least decadal-scale) temperature changes (e.g., 1900–1950). Time series were detrended to reduce the effects of human impact. Calibration period (AD 1954 onwards) and verification period (pre-AD 1954) are delineated by a dashed vertical line (modified from Kamenik et al. 2009).

tion. There is potential for scientists to use peatlands in mountain regions as archives of past climate change and landscape transformation. However, peatland ecology and the relationship between climate and peatland development needs to be better understood.

### Perspectives

The comparison of testate amoeba-inferred water table depth,  $\delta^{18}\text{O}$  data from *Sphagnum* stems, and instrumental climatic data revealed some interesting correlations. We now need 1) more high-resolution multi-proxy studies similar to that

from Mauntschas to determine if these patterns can also be observed elsewhere, and 2) manipulative experiments to assess the relative influences of temperature, precipitation and water table depth on testate amoeba communities and the *Sphagnum*  $\delta^{18}\text{O}$  isotopic signal. Such combined studies will help understand which factors most strongly control the development of alpine peatlands, how these peatlands can be fully exploited for inferring paleoclimatic and environmental signals, and how they may respond to ongoing and future climate changes.

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## Stable isotopes and organic geochemistry in peat: Tools to investigate past hydrology, temperature and biogeochemistry

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**Characterizing the stable isotope and biomarker geochemistry of peat cores enables reconstruction of key climatic and environmental variables in the past, including temperature, hydrology and the cycling of carbon.**

### Proxy targets and the value of geochemistry

Peatlands are valuable archives of terrestrial environmental change due to their sensitivity to the hydrological regime and the excellent preservation of organic matter. Peat geochemistry reflects the composition of the original peat-forming plant assemblage (which is itself dependent on air temperature and hydrology), and the subsequent transformation of that organic matter in the aerobic surface layer (the acrotelm) and the anaerobic catotelm (below the water table). Changes to air temperatures and water table depth are thus reflected in peat via changes to both

organic matter input and its subsequent degradation (Fig. 1). Precipitation and evaporation cause isotopic fractionation of hydrogen ( $\delta\text{D}$ ) and oxygen ( $\delta^{18}\text{O}$ ), so that the isotopic composition of the meteoric water used by peatland plants reflects a combination of precipitation source and peatland hydrology (Daley et al., in press). Stable carbon isotopes ( $\delta^{13}\text{C}$ ) give important information on carbon pathways, including fractionation during photosynthesis (White et al., 1994; Williams and Flanagan, 1996), and the recycling of organic matter and consumption of  $\text{CO}_2$  and methane by microbial activity (Pancost et al., 2000).

Humic acid formation during degradation of plant material (humification) is a proxy for peatland wetness (Yeloff and Mauquoy, 2006). Total carbon and nitrogen contents also indicate wetness (McClymont et al., 2008), since drier conditions cause the plant remains to spend a longer time in the acrotelm, where degradation preferentially releases nitrogen over carbon (Kuhry and Vitt, 1996). However, isolating whether changes to biomass and/or peatland hydrology drive the humification or bulk geochemistry signals recorded in peat cores makes environmental interpretations of such records difficult (Yeloff and Mauquoy, 2006). Here, we discuss the

potential for organic and stable isotope geochemistry analyses to determine more precisely the climatic and environmental evolution of peatlands (Fig. 1).

### Isotopic analysis of plant remains

Different peat-forming plants can have distinct chemical characteristics that reflect their different water sources and biochemical pathways (Fig. 1). For example, *Sphagnum* mosses contain higher carbon/nitrogen ratios than vascular plants (Kuhry and Vitt, 1996). The absence of functioning guard cells, which encircle the leaf pores used in gas exchange (stomata) and regulate the size of the stomatal opening, prevents control over water loss and gas exchange (Loader et al., 2007). Thus the isotopic composition of *Sphagnum* cellulose potentially records the isotopic composition of meteoric waters (Pendall et al., 2001). However, a bulk peat sample contains variable contributions from different plant sources, which limits efforts to isolate the controls over the signals recorded. Manually picking the remains of specific plants reduces such errors and yields a cleaner hydrological/climatic signal.

For example, White et al. (1994) exploited the differences in CO<sub>2</sub> uptake between *Sphagnum* and sedges, recorded in their  $\delta^{13}\text{C}_{\text{cellulose}}$ , to reconstruct Holocene atmospheric CO<sub>2</sub> concentrations, although temperature and humidity effects on  $\delta^{13}\text{C}$  had also to be considered. *Sphagnum*  $\delta^{13}\text{C}_{\text{cellulose}}$  has also been shown to be strongly related to mean air temperatures along a transect in SW Poland (Skrzypek et al., 2007). However, careful sample selection is required to minimize the impacts of inter- and intra-plant variability in *Sphagnum*  $\delta^{13}\text{C}$  (Loader et al., 2007).

A strong temperature signature in the  $\delta\text{D}$  of *Sphagnum* tissues in Patagonian peatlands has been paired with humidity reconstructed from  $\delta^{13}\text{C}$  in *Carex* (a sedge genus) fragments to provide a record of Holocene climate change that is independent of vegetation change as recorded in pollen (Pendall et al., 2001). *Sphagnum* cellulose  $\delta^{18}\text{O}$  from Walton Moss (UK) was dominated by the precipitation  $\delta^{18}\text{O}$  (Daley et al., in press). Given strong modern temperature controls over  $\delta^{18}\text{O}_{\text{precipitation}}$  in the UK and also in Nova Scotia, Daley et al. (2009; in press) used Holocene *Sphagnum* cellulose  $\delta^{18}\text{O}$  to reconstruct paleotemperatures. However, the influences of evaporation/peatland surface wetness (Daley et al., in press), and changing  $\delta^{18}\text{O}$  of the precipitation source (Daley et al., 2009) under different climate regimes complicated interpretations. Adoption of multi-proxy

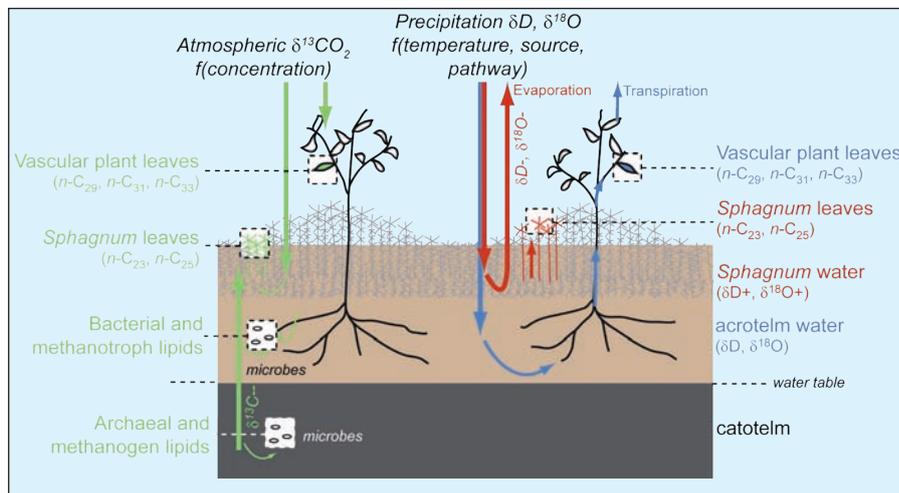


Figure 1: Conceptual model of water (blue, red) and carbon (green) pathways through the upper horizons of a peatland, including the isotopic fractionations associated with their utilization by *Sphagnum* (moss) and sedges ( $\delta+$  shows enrichment,  $\delta-$  shows depletion). The initial isotopic composition of water and CO<sub>2</sub> are functions (*f*) of a range of environmental factors as shown. Blue arrows follow the path of water used by sedges. Red arrows follow the path of water used by *Sphagnum*, which is affected by both precipitation (downward) and evaporation (upward). Fractionation also occurs along biosynthetic pathways. The impact of evapotranspiration on vascular plant isotopes is not shown because responses vary between cellulose and plant wax biomarkers. The aerobic acrotelm (light brown) occurs above the water table, at the peat surface. The anaerobic catotelm (dark brown) is found below the water table, and contains the peat archive of preserved organic material from which cores are taken. Adapted from Nichols et al. (2010).

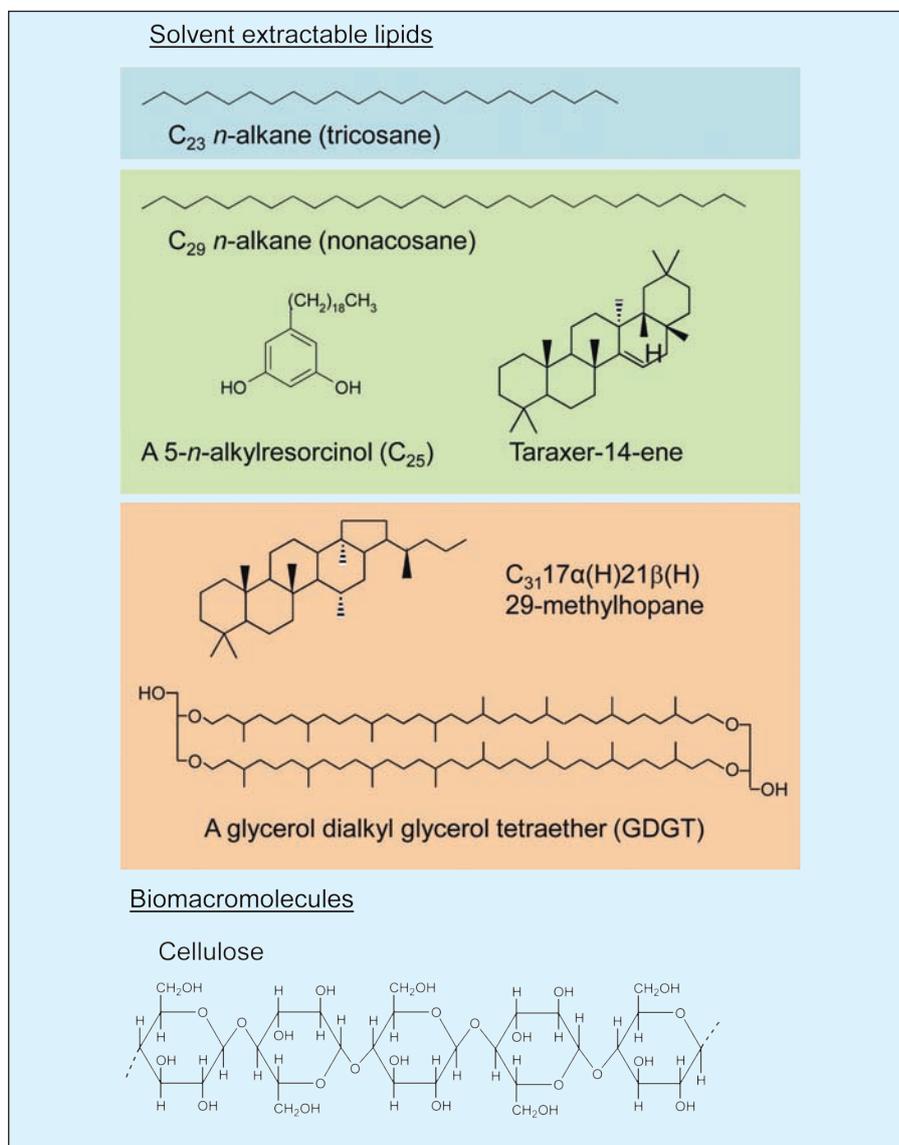


Figure 2: Chemical structures of selected biomarkers for either peat-forming plants, microbial activity, and/or diagenetic transformations of organic matter. Both solvent-extractable lipids and those requiring thermal degradation techniques for analysis (e.g., biomacromolecules) are shown. Only the partial structure of cellulose is shown. Lignin is also a common biomacromolecule, the structure of which is too complex to display clearly here. Blue shading = *Sphagnum* source; Green shading = vascular plant source; Orange shading = microbial source.

strategies can help disentangle these various factors.

## Development of biomarker proxies

Analyzing manually picked plant remains requires good preservation, which is not always characteristic of well-humified peats. Alternatively, organic geochemistry techniques can characterize bulk samples of peat, in cases where specific molecules or groups of compounds (biomarkers) are associated with particular peat-forming plants, microbial activity, or diagenetic transformations. Two principal methods have been employed in peats (Fig. 2): analysis of solvent-extractable lipids, and analysis of biomacromolecules via thermal degradation techniques (pyrolysis).

Compounds that are specific to particular peat-forming plants (Fig. 2) include the 5-*n*-alkylresorcinols (in sedges; Avsejs et al., 2002), a group of triterpenoids, the taraxeroids (in Ericaceae rootlets; Pancost et al., 2002), and a pyrolysis product of *sphagnum* acid, 4-isopropenylphenol

(Boon et al., 1986; van der Heijden et al., 1997). The most widely applied markers for peat-forming plants are the straight chain hydrocarbons from plant waxes, the *n*-alkanes, whose dominant chain-lengths differ between *Sphagnum* (usually C<sub>23</sub>, C<sub>25</sub>) and non-*Sphagnum* (>C<sub>29</sub>) species (Baas et al., 2000; Bingham et al., 2009; Nichols et al., 2006; Nott et al., 2000). These relationships and the post-depositional stability of the *n*-alkanes have enabled changing plant inputs to be detected (Fig. 3) (McClymont et al., 2008; Nott et al., 2000). Compound-specific stable isotope analysis also allows simultaneous generation of isotopic information for both *Sphagnum* and non-*Sphagnum* species.

Mechanisms of organic matter degradation have been determined and linked to Holocene water table depths because microbial activity and chemical transformations are controlled by oxygen and hydrogen availability. Biomarker records of degradation include the stereochemical transformations of hopanes and the presence of anaerobic and aerobic microbial

lipids in Holocene peats (McClymont et al., 2008; Pancost et al., 2003). Methanogenesis (formation of methane by microbes) in peats has been identified by the presence and  $\delta^{13}\text{C}$  signature of lipids derived from Archaea (Pancost et al., 2000). A pronounced increase in archaeal lipid concentration in the catotelm of Swedish peat supported this interpretation, and could potentially be used to assess water table depth (Weijers et al., 2004). The preferential degradation of plant macromolecules (e.g., polysaccharides, lignin) under aerobic and anaerobic conditions can also be detected (Schellekens et al., 2009). Applying these relationships down-core may offer insights into both changing water table depth and the biogeochemical response to such events.

## Application of compound-specific isotope analysis

Ombrotrophic peatlands contain two distinct plant groups that potentially draw water from different reservoirs and are distinguishable by different leaf wax biomarkers (Fig. 1). *Sphagnum* uses water from within water-retaining (hyaline) cells and that held among the leaves and branches, which may be strongly affected by evaporation and therefore enriched in deuterium (D) relative to precipitation. In contrast, vascular plants use water from below the surface in the acrotelm, protected from evaporation and representative of precipitation  $\delta\text{D}$  (Nichols et al., 2009). Further fractionation during biosynthesis leads to vascular plant cellulose being systematically enriched relative to *Sphagnum*, and this is also reflected in *n*-alkane  $\delta\text{D}$  (Menot-Combes et al., 2002). By measuring  $\delta\text{D}$  of both vascular plant (peatland water before evaporation) and *Sphagnum* biomarkers (peatland water after evaporation), and assuming that vascular biomarkers were not affected by evapotranspiration, Nichols et al. (2010) calculated Holocene evaporation in north America. This approach has also enabled both peatland wetness and precipitation seasonality to be determined in Holocene peats from Norway, and subsequently linked to the sea-surface temperatures in the Norwegian Sea (Nichols et al., 2009) (Fig. 3).

Two major factors affect  $\delta^{13}\text{C}$  of *Sphagnum* biomarkers: *Sphagnum* water content and the amount of recycled methane contributing to the CO<sub>2</sub> pool used by *Sphagnum* for photosynthesis. When *Sphagnum* is more saturated, the water film over the photosynthetic cells impedes the incorporation of CO<sub>2</sub> and thus the plant becomes less selective against <sup>13</sup>C

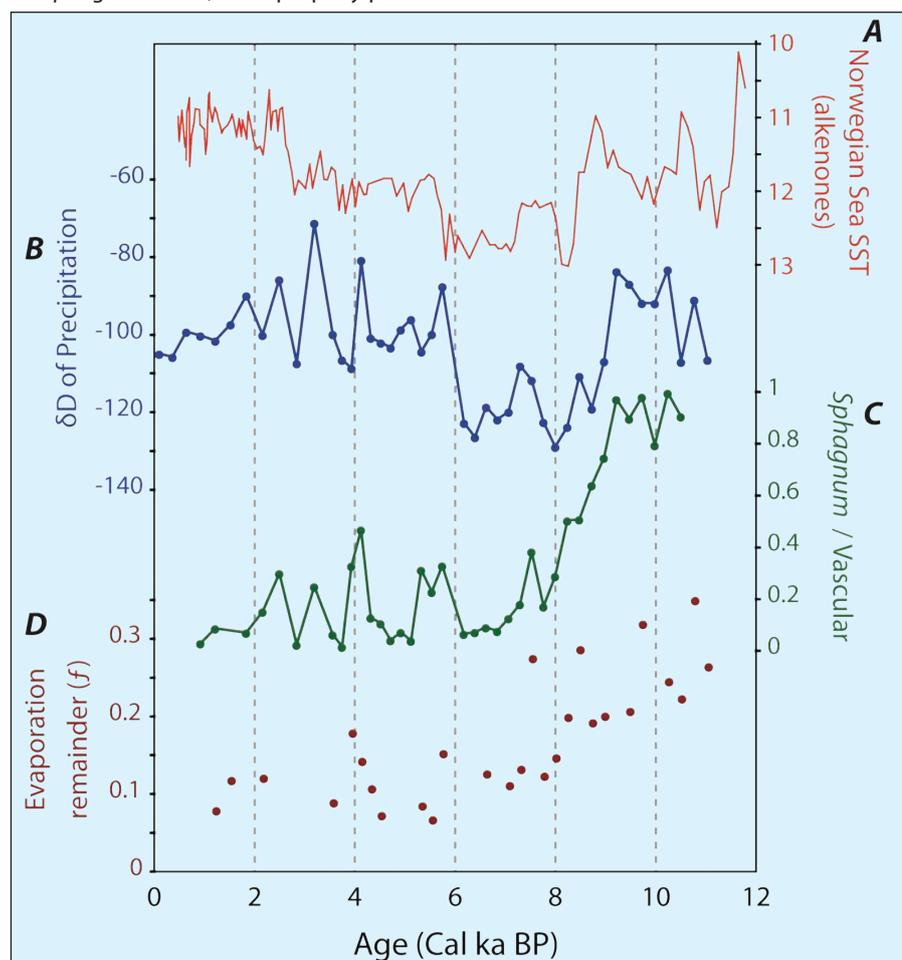


Figure 3: Biomarker records from a peatland on the Lofoten Islands of arctic Norway (modified from Nichols et al., 2009). **A**) Norwegian Sea Surface Temperature (SST) on inverse scale, plotted for regional context (Calvo et al., 2002). **B**)  $\delta\text{D}$  of precipitation derived from  $\delta\text{D}$  of the vascular plant biomarker, nonacosane. From ~9 ka to 6 ka, warm SSTs allowed for increased winter precipitation at the coastal Norway site, resulting in depleted annual average  $\delta\text{D}$  of precipitation. **C**) The *Sphagnum*/*Vascular* ratio is an *n*-alkane biomarker ratio indicating the relative contribution of *Sphagnum* and vascular plants to the peat. The contribution of *Sphagnum* to the peat declines rapidly with the decrease in summer precipitation at 9 ka. *Sphagnum* recovers at 6 ka, but not fully, indicating the region is drier during this period. **D**) “*f*” is the fraction of water remaining in *Sphagnum* after evaporation, based on the comparison of the  $\delta\text{D}$  of *Sphagnum* and vascular plant biomarkers. In this Norwegian peatland, evaporation increases as the region becomes cooler and drier.

( $\delta^{13}\text{C}$  increases) and vice versa (Williams and Flanagan, 1996). However, the effect of recycled methane on  $\delta^{13}\text{C}$  of *Sphagnum* biomarkers has the opposite relationship with moisture. When the peatland is wetter, more methane produced at depth is respired by methanotrophs that are symbiotic with *Sphagnum*, the resulting low- $\delta^{13}\text{C}$   $\text{CO}_2$  is assimilated by *Sphagnum* and recorded in lower  $\delta^{13}\text{C}$  of *Sphagnum* biomarkers. During drier conditions, the reverse occurs (Nichols et al., 2009; Raghoebarsing et al., 2005). These competing factors necessitate careful interpretation of *Sphagnum* biomarker  $\delta^{13}\text{C}$  measurements.

## Conclusions

Isotopic and organic geochemistry analyses of peats are valuable approaches for understanding past climatic and environmental change. The complexity of peatlands requires a multi-proxy approach to fully exploit the paleoenvironmental signatures contained within peat archives. Further research is also needed into the factors controlling the isotopic composition of different plant compounds (e.g., evaporative effects in plant waxes vs cellulose) to better understand the environmental signatures contained within them.

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# Peat cellulose isotopes as indicators of Asian monsoon variability

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**Stable isotopes in peat cellulose provide records of Asian monsoon variability in the Holocene and suggest persistent teleconnections between the Asian monsoons and North Atlantic climate variability.**

## Peat cellulose isotopes as proxy climate indicators

A practical proxy for climate reconstruction for the Holocene epoch should be able to span about 10 ka with decadal to centennial time resolution. Over the last 20 years oxygen and carbon isotope analysis of peat cellulose has been developed as a Holocene paleoclimate proxy (Brenninkmeijer et al., 1982; Hong et al., 2000, 2001; Ménot-Combes et al., 2002). Peat plant cellulose is a macromolecular polymer of interlinked dextroglucose molecules (Hong et al., 2009; and see McClymont et al., this issue), formed from oxygen atoms derived from the water used by the plant and carbon atoms derived from atmospheric  $\text{CO}_2$ . The stable isotopic composition of cellulose oxygen and carbon is influenced by different physical and chemical processes. Oxygen isotopes ( $\delta^{18}\text{O}$ ) in water molecules undergo temperature-dependent fractionation during condensation. Variations in  $\delta^{18}\text{O}$  of meteoric water are generally positively correlated with atmospheric temperature (Dansgaard, 1964). During photosynthesis, the  $\delta^{18}\text{O}$  signature of the source water is recorded in cellulose molecules. Source water for photosynthesis in many peatlands is primarily meteoric, although it may be enriched by evaporation. Vascular

plants respond to variations in water availability and relative humidity by regulating the opening or closing of leaf stomata. This leads to changes in the stable carbon isotopic composition ( $\delta^{13}\text{C}$ ) of atmospheric  $\text{CO}_2$  utilized in photosynthesis (Francey and Farquhar, 1982; Schleser, 1995). The amount of rainfall is also negatively correlated to the plant  $\delta^{13}\text{C}$  value; the larger the amount of rainfall, the smaller the  $\delta^{13}\text{C}$  value (Lee et al., 2005; Wang et al., 2008). Therefore, information on climatic changes is preserved in the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of peat plant cellulose. Finally, plant cellulose is highly resistant to decomposition. Both cellulose and its isotopes are highly stable over periods of approximately  $10^5$  years (Briggs et al., 2000). Peat plant cellulose isotopes therefore have significant potential as a bioindicator of paleoclimatic changes. Here we summarize the contribution of peat cellulose isotopes to the reconstruction of East Asian monsoon variability during the Holocene.

## Spatial variation of the EASM and peatland distribution

Recent advances in extraction and purification of cellulose from bulk peat samples have allowed application of peat cellulose isotopes (Hong et al., 2000, 2001) to reconstruct the history of the Asian summer

monsoon (e.g., Hong et al., 2009). Peat deposits of northern China are largely dominated by sedges, so the isotopic sig-

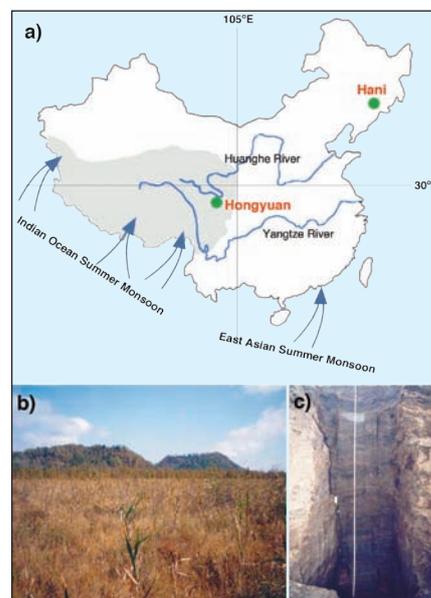


Figure 1: Hani and Hongyuan peatlands. **a)** Map of China showing the location of Hani and Hongyuan peatlands on the Chinese mainland and the monsoon systems. The Tibetan plateau region is indicated by the gray shading. **b)** The landscape and surface vegetation of the Hani peatland (42°13'N, 126°31'E). **c)** A profile of the drained Hongyuan peatland (32°46'N, 102°30'E), which consists of continuous herbaceous peat. Coloring on the uneven surface of the profile can quickly change in the process of excavation. This photograph shows the horizontal micro-layer structure consisting of brown alternating with grey-blue peat deposition, particularly for the fresher bottom portion of the profile.