Pairing high-resolution charcoal records with landscape models helps overcome an important limitation common to paleorecords: patterns of past change can be reconstructed, but the causal mechanisms responsible are difficult to determine.

Ecological modeling offers the distinct advantage of being able to isolate the interactive influences of climate, vegetation and/or human activity on fire regimes. Statistically comparing simulation output with reconstructed fire history then helps to evaluate competing hypotheses explaining past fire-regime dynamics. Brubaker et al. (2009) employed this approach to suggest that the impact of shifting vegetation was more influential on regional fire regimes in Alaska than the direct effects of climate change. Specifically, in a statistical comparison of charcoal-inferred and simulated fire regimes, a reconstructed increase in fire frequency at ca. 5.5 cal ka BP only matched simulations that combined the addition of highly-flammable black spruce with the fire-dampening effects of decreased temperature or increased precipitation.

Data-model comparisons are also instructive when evaluating human impacts on past fire regimes. Using a dynamic landscape vegetation model, Colombaroli et al. (in review) found that ignition frequency overrode climatic influences in determining area burned near the treeline in the Swiss Alps. Thus, an increase in the impact of fire on treeline vegetation during the last 4 ka was attributed to Bronze Age land-use intensification.

Conclusions and future directions

An improved understanding of sediment-charcoal records through process modeling has helped advance analytical techniques for inferring fire history over thousands of years. In conjunction with a proliferation of high-resolution charcoal records developed over the past several decades, paleofire records are increasingly used to untangle complex interactions between multiple drivers of historic fire regimes. Data-model comparisons in particular have and will continue to play an important role in these efforts. Although we focused here on how these comparisons help improve interpretations of sediment-charcoal records, the benefits of this integration are equally important to model development. Ultimately, landscape and larger-scale models can be validated using sediment records and thus more confidently applied to project fire regimes under anticipated future conditions.

Data

The empirical charcoal records reported in figures 1-2 are publicly available through the International Multiproxy Paleofire Database: http://www.ncdc.noaa.gov/paleo/impd/paleofire.html.

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Specific molecular markers in ice cores provide large-scale patterns in biomass burning

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Flammable vegetation releases distinct organic markers associated with smoke particles, and the presence of these compounds in ice cores across the globe provide information on changes in fire regimes through time.

International efforts to retrieve ice cores from both poles and every possible continent have resulted in a wealth of high-resolution climatic and environmental records. Methodological advances in measuring past atmospheric chemistry are revealing aerosols from both natural and anthropogenic biomass burning. Chemical markers in ice cores can measure past fire regimes including changes in spatial distribution, timing and fuel type (Conedera et al., 2009). Low-latitude ice cores primarily reflect regional fire and climate parameters, while polar ice cores reflect a global signal. The reconstruction of past wildfire occurrence through molecular markers in ice cores is a new field, one that requires further investigation; nonetheless, the global array of archived ice cores allows for future research into one of the least known aspects of the climate system.

Fire activity has varied in the past in response to climate, vegetation change and human land use. Recent aerosol emissions are a combination of anthropogenic particle emissions (e.g., oils, soot, synthetics) and vegetation burning (Simoneit, 2002). Biomass burning causes carbon dioxide emissions equal to 50% of those from fossil-fuel combustion and so is also highly likely to influence future climate change (Solomon et al., 2007). Here, we discuss four chemical groups that can be used as proxies for fire-history reconstruction from ice cores: (1) monosaccharide anhydrides (MA), (2) light carbolic acids, (3) polycyclic aromatic hydrocarbons (PAH), and (4) lignin burning products. Combining measurements of these four chemical groups can help determine the relative contributions of natural and anthropogenic emissions on regional and global scales.

Specific molecular tracers in smoke (MA)

Biomass burning injects particles with distinct signatures of organic matter into smoke and the global atmosphere (Simoneit, 2002). Important compounds from biomass burning include monosaccharide anhydrides (MA), where the most important tracer compound among them is levoglucosan and to a lesser degree galactosan and mannosan. These are specific molecular tracers because they can only be generated by combusting woody tissue at temperatures greater than 300°C (Simoneit, 2002). Among MA, levoglucosan has been considered an excellent tracer choice because it is emitted in large quantities and is globally pervasive. Levoglucosan is transported in smoke plumes and returns to the surface by wet and dry deposition. The presence of levoglucosan in ice cores can therefore be used as a smoke emission tracer (Simoneit, 2002). The University of Venice has pioneered a technique for the determination of levoglucosan flux in ice cores (Gambaro et al., 2008) and has measured past biomass burning tracers in ice from both Greenland and Antarctic (Fig. 1).

Global and regional burning (light carbolic acids)

Fresh smoke particles contain up to 1% organic acids, including formate, acetate and oxalate, which have been measured in polar snow and ice as a proxy for global and regional biomass burning (Barbante et al., 2003; Reid et al., 2005 and references within). Figure 2 depicts oxalate concentrations and the annual cycle (Na^+) in sixty-eight snow pit samples from Summit, Greenland (72°20'N; 38°45'W, 3270 m asl). Atmospheric oxalate can be formed through both biomass burning and vehicle emissions. The summer 1994 oxalate peak highlights a Canadian forest fire (Barbante et al., 2003). However, in areas with one snow accumulation season, such as the Himalaya, or in areas near a constant influx of vehicle emissions, such as the Alps, it may be more difficult to determine if oxalate is from natural or anthropogenic sources. Preliminary results conducted at the University of Venice show that levoglucosan flux replicates the oxalate measurements in the Summit Greenland snow samples. This reproduction of biomass burning proxies can be used to validate the two types of measurements as levoglucosan can only be produced by biomass burning (Gambaro et al., 2008).

Anthropogenic activity (PAH)

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous pollutants from fossil fuel or biomass incomplete combustive processes. Approximately 90% of recent PAH emissions are estimated to be anthropogenic (Yunker et al., 2002). Polar ice caps and mountain glaciers depict the historical environmental burden of PAH as a consequence of human activities. The low preindustrial quantities of these compounds have rarely been measured, but are present in ice cores because PAH can be transported over global distances by wind systems (Gabrieli et al., 2010). Wildfires comprise the largest PAH input from natural combustion but the compounds are not source specific. Once the presence of biomass burning versus hydrocarbon combustion PAH in ice cores has been established, greater specificity regarding the organic materials being burned can be obtained through analyzing vegetation sources.

Vegetation sources (aromatic alcohols + degradation products)

Recent advances in methodology now allow the determination of the major species of vegetation that were burned in the past, and current investigations are examining vegetation sources as recorded in ice cores (Condera et al., 2009). Source specific molecular tracers not only show that fires occurred in the past but also provide a chemical fingerprint that can be used to identify vegetation species or regional vegetation cover (Simoneit, 2002). Woody tissue contains three major aromatic alcohols that are present in differing proportions among the major plant classes. Grasses are enriched in p-coumaryl alcohol, softwoods contain primarily coniferyl alcohol and hardwoods include a high proportion of siapyl alcohol. When these three aromatic alcohols are burned, they produce degradation products that are emitted in different proportions based on different types of biomass (Fine et al., 2004). For example, resin acids were found in emissions from pine needle fires and *Sequoia* forest. Similarly, research shows that syringaldehyde is abundant in emissions from sagebrush, whereas vanillic acid is a conifer-specific biomass burning tracer (Fine et al., 2004).

Softwoods are the easiest plant class to determine through investigating molecular markers in smoke because the aromatic alcohols and degradation products are injected into smoke plumes in relatively large quantities. The proportion of oxygenated compounds from aromatic alcohols is less prominent in hardwood smoke and almost undetectable in grass smoke (Simoneit, 2002). Grass smoke can be defined through the ratios of the detectable aromatic alcohols and degradation products with levoglucosan. The presence of levoglucosan confirms biomass burning, and the determination of aromatic alcohols and their degradation products provides more specific insight into the type of vegetation burned.

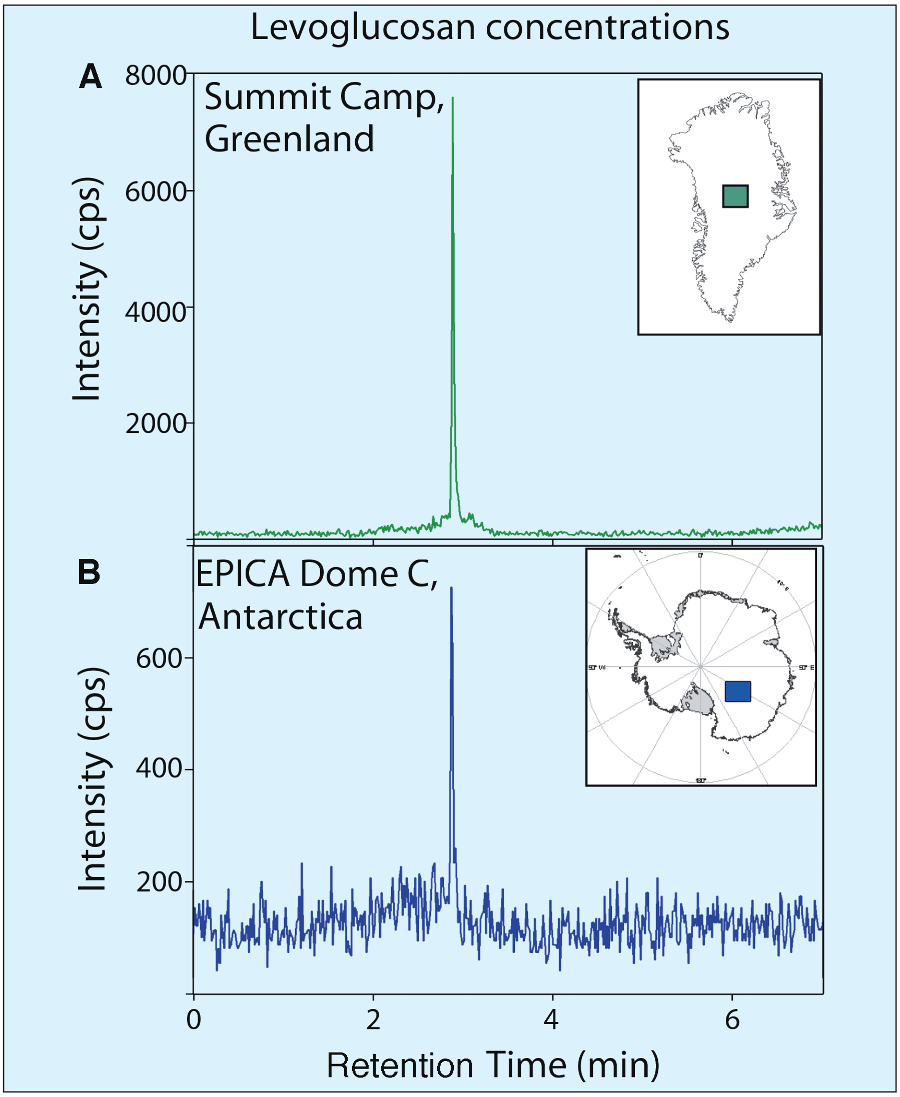

Figure 1: Chromatograms of levoglucosan (counts per second, cps) in ***A****) Greenland Summit Camp snow and* ***B****) the European Project for Ice Coring in Antarctica (EPICA) Dome C ice core (2682.9 m; 420.7 ka BP on EDC3 chronology, Parrenin et al., 2007). Levoglucosan is a monosaccharide anhydride produced by combustion of woody tissue at high temperatures (Simoneit, 2002) and can be used as a tracer of past biomass burning. The difference in levoglucosan concentrations in Greenland and Antarctica may reflect relative distance from smoke emission between the two sites. Figure modified from Zangrando, 2008.*

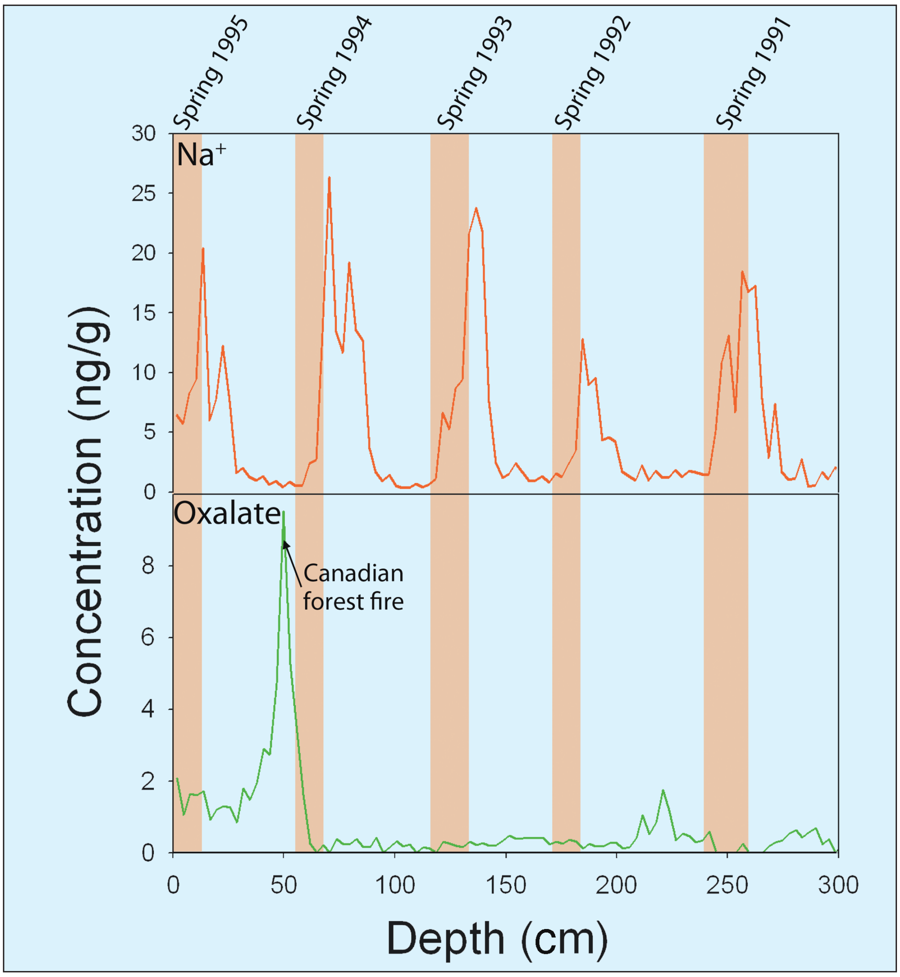

*Figure 2: Changes in Na$^+$ (**orange**) and oxalate concentration (**green**; ng g^{-1}) averaged from 68 central Greenland snow-pit samples, from the surface (June 1995) to 2.7 m (1991). Peaks in Na$^+$ are associated with boreal winters as increased cyclogenesis in the North Atlantic deposits greater concentrations of sea salts on the Greenland Ice Sheet. **Orange bars** indicate the position of spring snow accumulation. Figure modified from Barbante et al., 2003.*

Conclusion

Glaciers and ice sheets incorporate tracers of biomass burning into their ice layers resulting in a multitude of paleoenvironmental data within a single matrix. Molecular markers in ice cores provide insight into past fire occurrence, the type of material burned and the impacts of human activity. The global array of ice cores supplies high-resolution Quaternary proxy records that encompass six continents. The study of molecular markers of past fires in ice cores is still in its infancy and future work should also incorporate studies into the stability, durability and degradation mechanisms that may affect molecular markers under different conditions. Even with these caveats, the investigation of organic atmospheric tracers is expanding the limits of proxy information gleaned from ice cores and creates the possibility to couple fire activity, climate oscillations and human activity.

Data

The data from Figure 1 is available from Roberta Zangrandp (Rozangra@unive.it). Data presented in Figure 2 is available from Carlo Barbante (Barbante@unive.it).

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Global patterns of biomass burning during the last glacial period

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Sedimentary charcoal records covering the last glacial period provide information on the response of global biomass burning to rapid climate changes, such as those occurring during Dansgaard-Oeschger cycles.

The Global Palaeofire Working Group (http://www.gpwg.org/) has updated a database of over 700 individual sedimentary charcoal records worldwide (GCD_V2: Daniau et al., in prep). This database provides a powerful tool for studying changes of biomass burning at global and regional scale (Power et al., 2008; Power et al., 2010). A focused study of fire records covering the last glacial period (73.5-14.7 ka) allows examination of the response of biomass burning to the rapid climate changes (within 10-200 years) of large magnitude that occurred during Dansgaard-Oeschger (D-O) cycles (Steffensen et al., 2008). D-O cycles are characterized in Greenland ice-core records by a marked warming followed by a cooling. Herein, D-O warming events refer to the initial rapid warming (Sánchez-Goñi and Harrison, in press), Greenland Interstadials (GI) correspond with the D-O warm phase followed by the initial slow phase of cooling, D-O cooling events refer to the precipitous cooling at the end of GI, and Greenland Stadials (GS) correspond with the final cool phase.

Methodology

Sixty-seven sites (11 marine and 56 terrestrial; Fig. 1) that have records for some part of the last glacial period were extracted from the database and used to analyze changes in global biomass burning (Daniau et al., in press). These records were developed using a broad range of quantification methods and units. For the majority, charcoal counts were converted to charcoal concentration (number of particles cm^{-3} or per g of sediment), charcoal influx (number of particles cm^{-2} a^{-1}) or charcoal