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04-02: Vibrational spectroscopy of pollen as a tool for reconstructing solar-ultraviolet irradiance

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Solar ultraviolet-B radiation (UV-B, 280-315 nm) has extensive impact on biological and ecological processes from the individual to the ecosystem level. Moreover, absorption of UV-B by ozone is also one of the primary heat sources to the stratosphere, so variations in UV-B have important relationships to the Earth's radiation budget. Unfortunately, there is limited understanding about the changes in UV-B radiation in the geological past because ground-based and satellite measurements of total ozone and surface UV-B only exist for the last two decades. Therefore, biological or geochemical proxies from sediment archives are needed to reconstruct UV-B irradiance received at the Earth surface beyond the experimental record. Fossil pollen grains are often not only the most abundant but also among the best preserved remains of plant species, thus providing crucial information for the reconstruction of past flora, population sizes and terrestrial communities. Recent studies have shown that the quantification of UV-B-absorbing compounds in pollen have the potential to provide a continuous record of the solar-UV radiation received by plants [1]. As a result, there is an increasing interest to develop this proxy in palaeoclimatic, and palaeoecological research.

Phenolic constituents (i.e. phenylpropanoids) of sporopollenins in the pollen grain wall protect pollen by effectively absorbing UV-B radiation and providing defence against DNA damage as well as quenching reactive oxygen species. Therefore, changes in the chemical composition of fossil pollen could constitute a possible means to reconstruct ancient UV-B irradiance. Thermally assisted hydrolysis and methylation with pyrolysis gas chromatography coupled to mass spectrometry (THM-GC-MS) has become the method of choice in qualitative and quantitative measurements of phenolics in pollen [2]. However, the method is time consuming and it requires a large number of pollen grains for a statistically significant measurement. Therefore, an alternative approach based on vibrational spectroscopy has been in development for the measurement of pollen chemistry.

In general, vibrational spectroscopies, comprising Fourier Transform Infrared (FTIR) and Raman spectroscopies, are complementary, non-destructive and highly sensitive biophysical methods that provide precise signatures of the overall biochemical composition of pollen. Thus, they can be used for a wide range of research, from biology, ecology, agronomy, and forestry, to medicine, forensics, geology and archaeology. Vibrational spectroscopy of pollen includes a broad range of measurement techniques, covering both bulk measurements (10^4-10^6 pollen grains per measurement) [3-7], as well as microspectroscopies on single pollen grains [7-10].

Both FTIR and Raman spectroscopies can be used for qualitative determination of phenolic constituents in pollen grain wall [7]. However, the disadvantage is that they can only achieve relative estimates in the quantification of UV-B absorbing compounds. Obtaining absolute quantification of the compounds is challenging and will require more studies on a broad

sample sets with direct measurement of UV-B irradiation as reference values. Moreover, microspectroscopy of single pollen grains face some specific challenges, such as strong Mie scattering in FTIR microspectroscopy that results in anomalous spectral features [8-11]. We have recently demonstrated that scatter-free FTIR spectra can be obtained by using an embedding matrix, and thus achieving identification of single pollen grains with unprecedented accuracy [8]. Here, we will present different approaches in measuring pollen chemistry, focusing on pollen chemistry as a tool for reconstructing solar UV-B irradiance. These approaches include vibrational spectroscopy studies conducted at NMBU, as well as numerical correction methods [10,11] and a number of experimental settings [7-9].

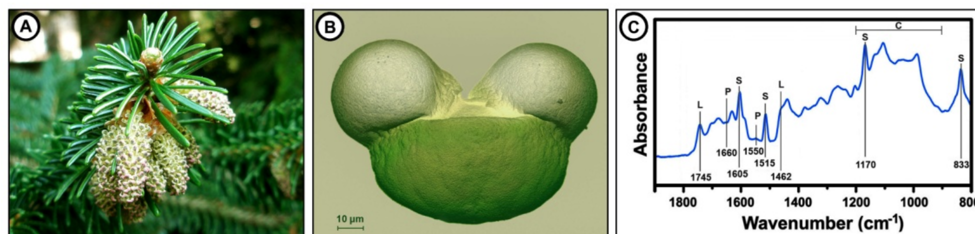

Fig. *Abies cephalonica* (Greek fir): **A**) Branch with male cones (strobili) during pollination. **B**) Scanning electron microscope image of pollen grain in equatorial view. **C**) FTIR spectrum of pollen; the marked vibrational bands are associated with lipids (L), proteins (P), sporopollenins (S) and carbohydrates (C).

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