

Hyperspectral imaging: a novel, non-destructive method for investigating sub-annual sediment structures and composition

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Hyperspectral imaging offers a rapid and cost-effective way of generating records of sediment properties and composition at the micrometer-scale. Photopigments and clay minerals detected using this method can reflect temperature, precipitation or runoff and primary production in lake sediments.

The quest for maximizing the resolution of long paleoenvironmental data sets from sedimentary archives has prompted rapid developments in analytical methods and techniques. Non-destructive scanning techniques such as X-ray radiography and computer tomography of sediment structures and density, and scanning micro-X-ray fluorescence (μ XRF) to map elemental composition are now widely used. Other powerful, although still less well-known methods are digital image analysis and color codes (e.g. CIELAB color space; Debret et al. 2011), and scanning multi-channel reflectance spectroscopy in the visible and near infrared range (typically 380-1000 nm). These techniques are used to identify organic substances and minerals in sediments on the basis of their diagnostic color absorption properties.

Scanning techniques have a number of advantages: they do not require sub-sampling of sediments; are non-destructive; operate at (sub-)millimeter spatial resolution; are very cost effective; allow us to quickly produce long data series; and offer the opportunity to replicate data sets, which is often impossible or inefficient with analytical techniques. Disadvantages are that measured values are often not substance-specific and can be influenced by matrix effects (water content, porosity), thereby limiting the interpretation of results.

Reflectance spectroscopy VIS-RS

While μ XRF techniques are routinely used in many laboratories, the potential of reflectance spectroscopy in the visible range (VIS-RS, 380-730 nm) has only been demonstrated relatively recently. VIS-RS has been successfully applied to fresh sediment cores to measure carbonate content in marine sediments (Balsam and Deaton 1996), and on marine and freshwater sediments to measure clay minerals (mainly illite and chlorite; Rein and Sirocko 2002), Fe-species (Debret et al. 2011), organic carbon, sedimentary photopigments (mainly chlorophyll-a and diagenetic products) and sedimentary carotenoids (Rein and Sirocko 2002; Das et al. 2005; Rein et al. 2005; Wolfe et al. 2006; Michelutti et al. 2010; Trachsel et al. 2013).

Interpretation of the reflectance spectra remains challenging. However, spectral indices characteristic of lithogenic material and sedimentary pigments (e.g. the relative absorption band depth between 660-670 nm, $RABD_{660:670}$ indicative of chlorophyll-a and diagenetic

products) compare very well with analytical measurements (typical R^2 between 0.70 and 0.98).

Built on the rationale that the substances measured by VIS-RS (clay minerals, carbonate, pigments, etc.) contain a climate signal in certain lakes, recent studies have demonstrated that VIS-RS data measured on fresh sediment cores can be directly calibrated to meteorological data, which makes them powerful sources for high-resolution quantitative climate reconstruction. For example, VIS-RS indices diagnostic for photopigments (\approx algal productivity) and clay minerals (lithogenic influx) were calibrated to temperature or precipitation in organic sediments from eutrophic lakes in Central Chile, Patagonia and Tasmania (von Gunten et al. 2009, 2012; Saunders et al. 2012, 2013; Elbert et al. 2013; de Jong et al. 2013) and to inorganic sediments from the Swiss Alps (Trachsel et al. 2010).

Hyperspectral imaging

Here, we present the first results from the next generation measurement device, a hyperspectral core scanner that combines micro remote-sensing techniques with lake sediment analysis. The Specim Ltd. scanner (Fig. 1) consists of a hyperspectral camera and a sample tray that moves underneath an illumination

chamber and the camera slit. The camera takes reflectance spectra from the sediment surface in the range 400-1000 nm with a spectral resolution of 0.8 nm and a spatial resolution (pixel size) as small as $38 \times 38 \mu\text{m}$. One meter of sediment core is measured in ca. 15 min and produces ca. 45 GB of data. Data normalization and analysis is made using remote sensing software.

Figure 2 presents the first example of hyperspectral imaging using biochemical varves from Lake Żabińskie, a dimictic lake in the Masurian Lakeland, Poland. The varves are 3-4 mm thick and consist of a white calcite layer formed in early summer and a dark layer composed mostly of aquatic organic matter deposited from late summer until winter.

Figure 2c shows a high resolution $RABD_{660:670}$ profile covering a two year period. Each varve is represented by 40-60 data points depending on varve thickness. These data can be obtained from fresh sediment cores or from resin embedded polished sediment slabs. The measurements show low chlorin concentrations in calcite layers and high concentrations in dark organic layers. It remains to be tested whether the precise position of the $RABD_{660:670}$ peak actually represents the timing of the algal bloom in the summer season.

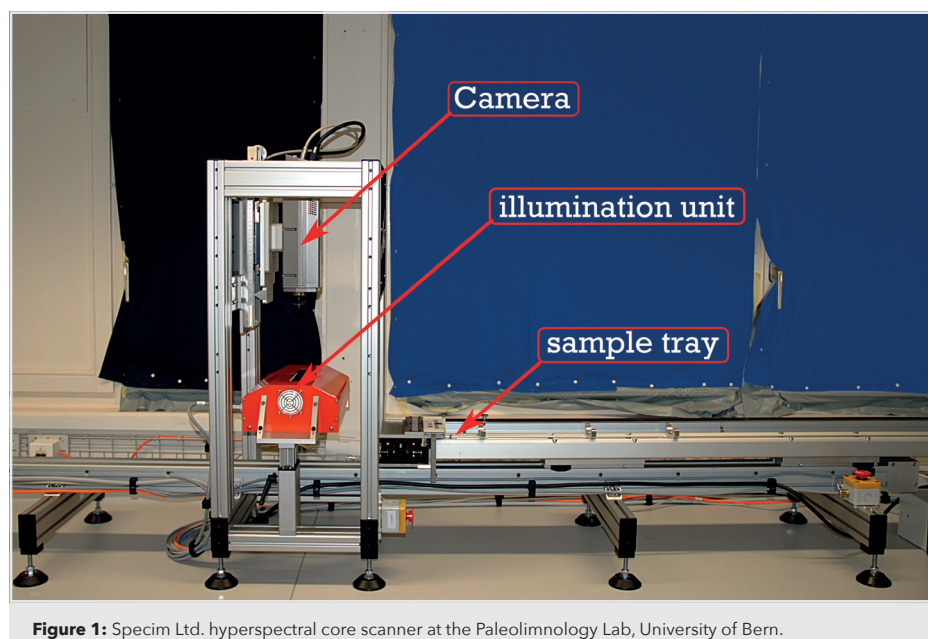


Figure 1: Specim Ltd. hyperspectral core scanner at the Paleolimnology Lab, University of Bern.

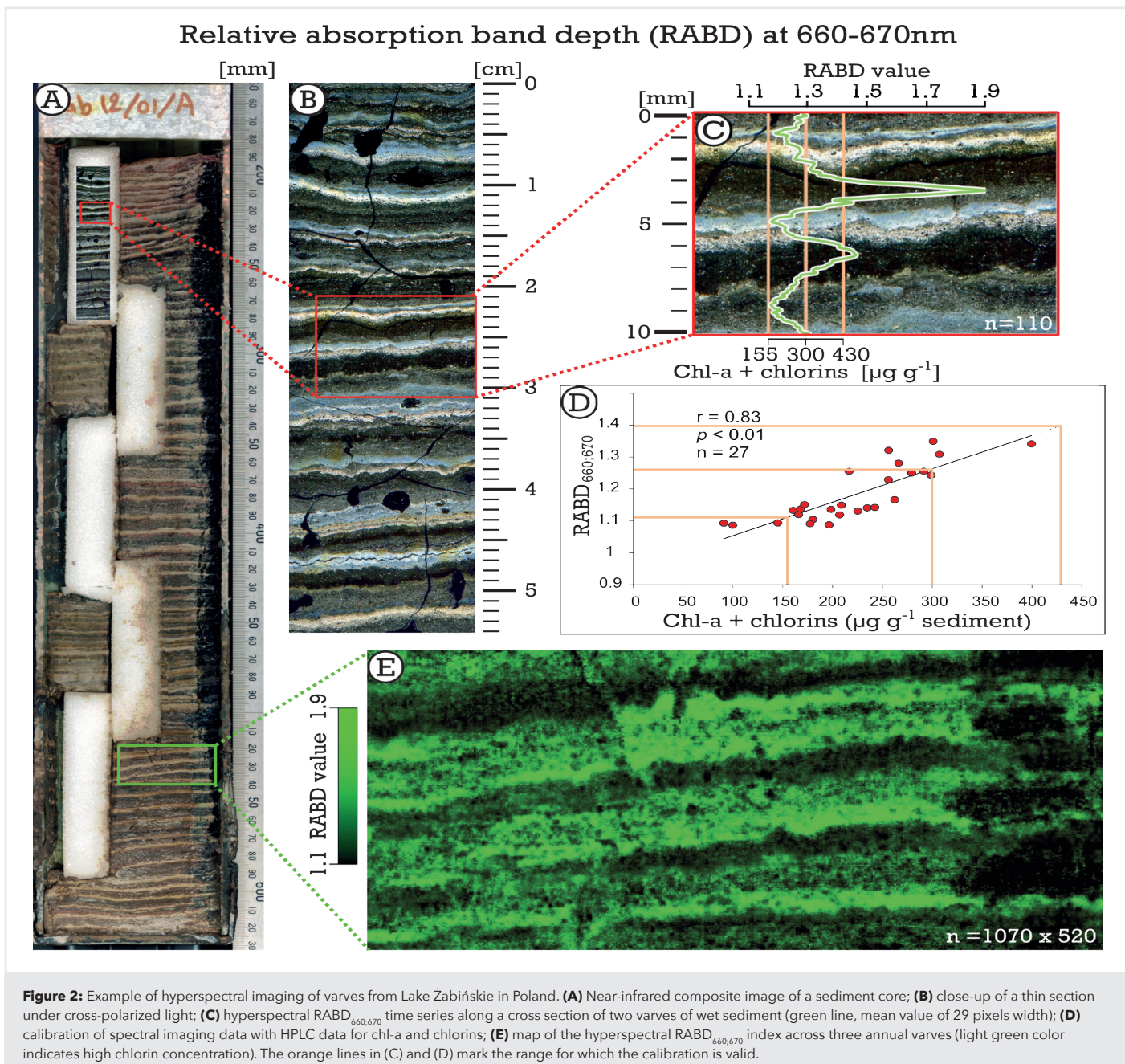


Figure 2d shows the regression between high-performance liquid chromatography (HPLC) measurements of photopigments in dry sediment (after pigment extraction) and $RABD_{660,670}$ measured on the wet sediment. This suggests that the spectral index used here represents chl-a and chlorins, and that it can be converted into concentration values ($\mu\text{g g}^{-1}$).

Figure 2e shows the same spectral index but now as a map of $RABD_{660,670}$ values with 1070 x 520 pixels (individual data points). The optically lighter calcite layers have low chlorin values and appear as darker areas while the green areas reflect the high chlorin concentrations found in the organic-rich layers.

Outlook

The example presented here demonstrates the rich potential of hyperspectral imaging as a relatively novel non-destructive sediment analysis. Further opportunities and challenges are found in the following areas:

- Higher spectral resolution (0.8 nm) potentially allows the detection and diagnosis of further substances and a more detailed speciation (e.g. separation of chl-a from chlorins);
- Very high spatial resolution (pixel size 38 μm) allows sub-varve scale investigation (e.g. seasonality of chl-a production) and the detection of sand-size grains (e.g. macro charcoal and fire history).
- The similar resolution as attained with μXRF scanning allows one to compare these two data types at very high resolution.
- Attributing the spectral properties of sediments to specific substances and minerals (proxy-proxy calibration) remains a great challenge since most of the pixels contain information from a mix of substances. Statistical techniques applied in remote sensing, such as pixel classification, end-member spectra, spectral unmixing, might help to improve the calibration between hyperspectral index data and the concentration

of specific substances in sediments. Making this step is fundamental for improving the interpretation of hyperspectral data.

In summary, hyperspectral imaging offers great opportunities for the analysis of lake sediments at the sub-varve scale. The method can also be applied to marine sediments, tree rings or speleothems.

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