Application of novel trace analysis methods for lignin and levoglucosan in flowstone samples from New Zealand during the Holocene

Anja Beschnitt✉, **Thorsten Hoffmann**✉

Department of Chemistry; Johannes Gutenberg University Mainz, Germany (anja.beschnitt@uni-mainz.de, ✉ hoffmant@uni-mainz.de)

Introduction

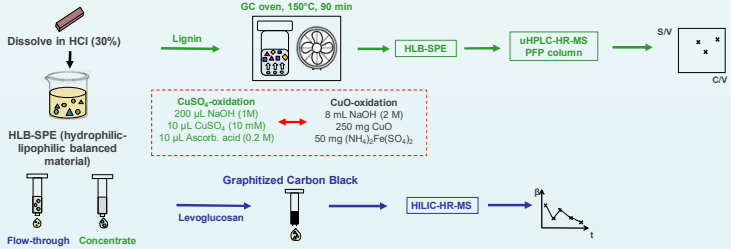
Speleothems are valuable climate archives, continuously growing for 1,000-10,000 years, they can be precisely dated back to 500,000 years.[1] Stable conditions in caves protect organic compounds from external influences, preserving them for several thousand years.

The biopolymer lignin is the second most abundant polymer after cellulose, consisting of three monomers. The monomer ratio depends on the type of vegetation. Lignin analysis in speleothems offers the possibility to draw conclusions on the amount and type of vegetation above a cave.[2] Since this vegetation is influenced by climate conditions like temperature and rainfall, lignin is a useful tool to study climate changes in the past.

Levoglucosan is an anhydrosugar formed by cellulose combustion (>300°C). It is a novel proxy used for determination of paleofire incidents. A new multi-analyte approach was established integrating lignin and levoglucosan analysis into one workflow. The lignin degradation workflow was replaced by a novel approach using $CuSO_4$ instead of the eco-toxic Cu(II)O, highly improving several aspects of *Green Chemistry*.[3,4]

Integration of analytical processes
In-situ measurements
No toxic reagents
Less waste
Direct analytical techniques
Minimal sample size
Minimized energy use
No derivatization
Increased operator safety
Chemicals from renewable sources
Multi-analyte method
Automation and miniaturization

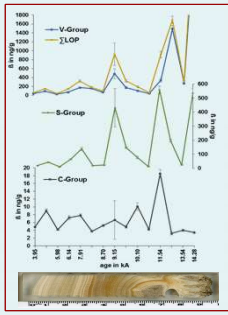
Experimental Design

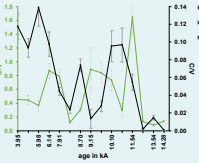


Hodges Creek Cave

Kahurangi National Park

Altitude: 940 m
Vegetation: beech forests, herbs, screes and rocks
Soil: well-drained, deep grykes
→ accumulated organic litter

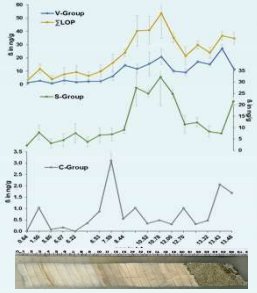




- Highest conc. among investigated caves
- **Correlation** of S- and V-group (*r=0.63*)
- 11.6-13.5 kA → **lateglacial reversal**
  cooler climate
  = less forest, more shrubs
  low S/V ratios (more coniferous species)
  low C/V ratios (more wooden plant material)

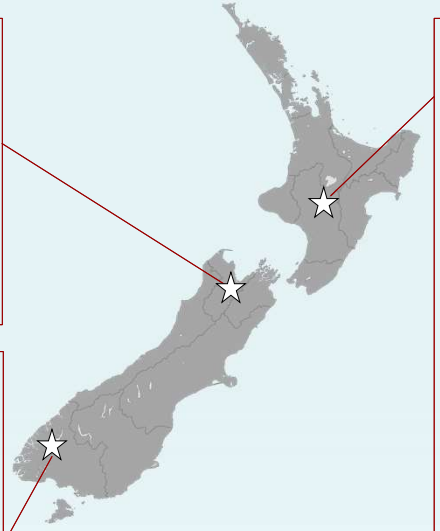
Daves Cave

Fiordland National Park



- Clear **concentration shift** according to colour of speleothem → correlation to TOC
- Low lignin concentrations according to expectations (low amount of vegetation, cold and dry conditions + high Mg^{2+} conc.)
- Correlation to Ba^{2+} → lignin transport influenced by **soil mobility** → transport through soil by **adsorption to particles**
- **Treeline** shifting depending on climate conditions → most significant influence of climate on lignin concentration

Altitude: 1450 m
Vegetation below treeline: temperate rainforest, mostly silver- and mountain beech, podocarp, shrubs, ferns
Vegetation above treeline: snow grasses (daisies, buttercups), tussock, native alpine plants
Soil: peaty organic rich soil, water-logging due to cold and wet conditions, thin earth layer → tree avalanches



Waipuna Cave

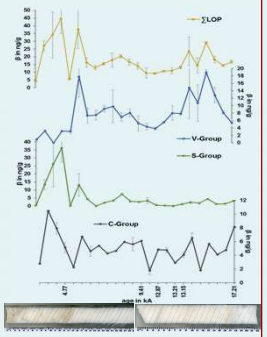
Waitomo District

Altitude: 80 m
Vegetation: lush podocarp forest, dense undergrowth of shrubs, ferns, and trees
Soil: deep (>1m), developed on rhyolitic volcanic ash deposits, exceptionally well-drained

- Most **dense vegetation**, exceptionally **well-drained soil**
- Expectation of high concentrations contradicts with results (100x lower than Hodges Creek)

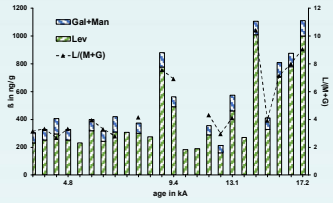
Possible explanations

1) Dry conditions? → not supported by analysed Mg^{2+} conc.
2) Low soil mobility? → no correlation to Ba^{2+} conc.
3) Degradation? → lignin is stable against microbial degradation
4) Disturbed transfer from plants into soil? → less lignin from leaves to soil to speleothem
5) Disturbed inclusion into the speleothem? → high drip rates, possibly slow lignin inclusion kinetics → **experiments in artificial caves possible**



Levoglucosan

- **Waipuna** concentrations > LOQ
- First levoglucosan data in a New Zealand cave
- **No correlation** to lignin → A) no input of levoglucosan by vegetation or B) **suppression** of levoglucosan by other organic content
- **Isomers galactosan and mannosan** are formed by hemicellulose combustion
- **L/(M+G)** describes source of emission by experimentally determined values
- Three forest fire related concentrations in sample 2, 4 (4.8 kA) and 7



Summary and Outlook

Development of a novel, multi-proxy analytical approach for lignin and levoglucosan in speleothems according to *Green Chemistry*

Application to speleothem samples from different caves in New Zealand

Successful proof-of-principle study → results generally agree with type of vegetation

New insights into lignin transport processes (adsorption to particles in dry conditions, transport by water in wet conditions)

Further method optimization especially for levoglucosan enrichment and a 2D-LC method

References:

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4. Anastas, P., Eghbali, N. (2010). *Chemical Society Reviews*, 39, 301-312