# TERRA NOSTRA

### Schriften der GeoUnion Alfred-Wegener-Stiftung 2009/3



Annual meeting of the German Association of Stable Isotope Research (GASIR

#### **TERRA NOSTRA** – Schriften der GeoUnion Alfred-Wegener-Stiftung

Verlag **Publisher** eoUnion Alfred-Wegener-Stiftung GeoUnion Alfred-Wegener-Stiftung Arno-Holz-Str. 14, 12165 Berlin, Germany Tel.: +49 (0)30 7900660, Fax: +49 (0)30 79006612 Email: infos@geo-union.de Schriftleitung Christof Ellger **Editorial office** GeoUnion Alfred-Wegener-Stiftung Arno-Holz-Str. 14, 12165 Berlin, Germany Tel.: +49 (0)30 79006622, Fax: +49 (0)30 79006612 Email: Christof.Ellger@gfe-berlin.de Annual meeting of the German Association of Stable Isotope Research, Heft 2009/3 Abstract Volume and Program, Potsdam, Germany, October 5–7, 2009 Vol. 2009/3 Bernhard Chapligin, Hanno Meyer Herausgeber AWI – Alfred Wegener Institute for Polar and Marine Research **Editor** Research Unit Potsdam Telegrafenberg A43, D-14473 Potsdam Email: bernhard.chapligin@awi.de Redaktion Diedrich Fritzsche, Wolf-Dieter Hermichen, Holger Deckelmann **Editorial staff** AWI – Alfred Wegener Institute for Polar and Marine Research Brandenburgische Universitätsdruckerei und Verlagsgesellschaft Druck Potsdam mbH **Printed by** 

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ISSN 0946-8978

GeoUnion Alfred-Wegener-Stiftung, Berlin, September 2009

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Gain knowledge of the location and the surrounding. *from page 5 on* 

_		r	
	Monday, Oct. 5	Taesday, Oct. 6	Wedneeday, Oct. 7
14		Isotopes in Polar Regions	Isotopes in Polar Regions
10.00		Coffee	Break
1146			
9126		Matter Fluxes	Nutrition, Medicine,
91.68		in Ecceystems	Doping & Forensics
1018			
12.45		Isotope Award of the Karleugen-Habfast-	Award: Best Poster & Talk
12.66		Foundation	
12.24			
10.00		Luici	Ereak
10.00	Climate Change &		
10.00	<b>Climate Reconstruction</b>		Telegrafenberg
15.66		Analytics &	
18.04	Coffee Break	Quality control	
15.46			
18.66	Matter Fluxes		
18.00	in Ecosystems	Contee break	
12.45			
12.44		Poster Session II	
	Poster Session I		
1.0			
19.65			
18.24			
10.45			
20.00			
20.00			
20.00	User Meeting	Contenence Dinner	
2.00			
2.00			
2.4			
20.00			

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Abstracts & Adresses
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### Stable Isotopes & Research Chemicals

Stable Isotopes Chemical Standards Radiochemicals NMR Products Research Chemicals

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#### Herzlich willkommen zur ASI Tagung

Das Organisationskomitee der diesjährigen Jahrestagung der Arbeitsgemeinschaft Stabile Isotope e.V. (ASI) heißt Sie recht herzlich in Potsdam willkommen. Die ASI-Tagung findet vom 5.-7. Oktober 2009 am Alfred-Wegener-Institut für Meeres- und Polarforschung in Potsdam statt. Die Anwendung und Analytik stabiler Isotope ist am Alfred-Wegener-Institut fester Bestandteil der Forschung und wurde seit 1992 an der Forschungsstelle Potsdam aufgebaut. Ein Schwerpunkt der diesjährigen Tagung wird daher auf der Anwendung stabiler Isotope in den Polargebieten liegen. Daneben werden - nach bewährter Tradition der ASI - insbesondere auch Beiträge zur Analytik und aus dem gesamten Spektrum der Anwendungsgebiete stabiler Isotope vertreten sein. Die Tagung ist in folgende fünf Sessions unterteilt: Isotope in Polarregionen, Klimaänderung und Klimarekonstruktion, Ernährung, Medizin, Doping und Forensik, Analytik und Qualitätskontrolle, Stoffkreisläufe in Ökosystemen. Die Kurzfassungen aller Vortrags- und Poster-Beiträge, sowie wichtige Informationen zum Tagungsort finden Sie in diesem Tagungsband. Das Organisationskomitee möchte all denen danken, die zum Gelingen dieser Konferenz beigetragen haben.

Willkommen in Potsdam! Ihr Lokales Organisationskomitee.

#### Welcome to the ASI Conference

The Organising Committee of the annual meeting of the German Association of Stable Isotope Research (ASI/GASIR) welcomes you in Potsdam. The GASIR conference will be held from 5-7 October, 2009 at the Alfred Wegener Institute for Polar and Marine Research, Research Unit Potsdam. The application and analysis of stable isotopes at the Alfred-Wegener-Institute has been established since the foundation of the Research Unit in 1992. Hence, a major focus of this year's meeting will be on the application of stable isotopes in polar areas. Following a long tradition of the GASIR meetings, specific contributions to method development of stable isotope analysis as well as to the complete spectrum of stable isotope applications will be presented. The conference will be subdivided into the following five sessions: Isotopes in polar regions, Climate change and climate reconstruction, Nutrition, medicine, doping and forensics, Analytics and quality control, Matter fluxes in ecosystems.

Abstracts of all oral and poster presentations as well as background information to the conference location can be found in this abstract volume. The organising committee would like to thank all those who have contributed to the success of this conference.

Welcome in Potsdam! Your local Organising Comitee.

#### Scientific organising committee

Gerhard Strauch Matthias Gehre Annette Giesemann Gerhard Gebauer Rolf Siegwolf Michael E. Boettcher



#### Local organising committee

Hans-Wolfgang Hubberten Hanno Meyer Bernhard Chapligin Diedrich Fritzsche Holger Deckelmann Wolf-Dieter Hermichen Lutz Schönicke Conrad Kopsch Gabriela Schlaffer

#### Nachruf: Dr. Karleugen Habfast



Unser langjähriges Mitglied und Ehrenmitglied der Arbeitsgemeinschaft Stabile Isotope e.V., Dr. Karleugen Habfast, Vorsitzender der gleichnamigen Stiftung zur Förderung des wissenschaftlichen Nachwuchses, ist am 5. April 2009 in Bremen verstorben.

Dr. Karleugen Habfast hat in mehr als 4 Jahrzehnten die Massenspektrometrie technisch und theoretisch maßgeblich mit beeinflusst. Unter seiner fachlichen Leitung wurdenmassenspektrometrische Messsysteme in der "Bremer Fachschmiede" entwickelt, verbessert, neu konzipiert. Immer wurde Wert darauf gelegt, dem Nutzer der Massenspektrometrie ein Instrument bereitzustellen, das den steigenden Anforderungen an Präzision, Reproduzierbarkeit und Eleganz der Messung von stabilen Isotopen gerecht sein möge.

In unzähligen Diskussionen mit Fachkollegen hat Herr Dr. Habfast sein "Steckenpferd" zum Nutzen der Isotopenforscher zu immer größeren Leistungen gebracht. Er vertrat die Ansicht, dass Wissenschaftler und Praktiker, deren Arbeitsgebiet die Anwendung stabiler Isotope ist, nicht so recht in das übliche Schema wissenschaftlicher Fach-Vereinigungen passen, denn fast jeder setzt diese Methodik in einem anderen Fach ein. Daher war er ein steter Befürworter und Förderer einer Fachvereinigung, die die verschiedensten Interessengebiete zusammenbringt, um methodische Erfahrungen zu diskutieren – eben unserer Arbeitsgemeinschaft Stabile Isotope.

Es war ihm in den letzten Jahren zunehmend wichtig geworden, jüngere Fachkollegen anzuspornen, auf dem Gebiet der Isotopenforschung höchste Leistungen anzustreben. Zusammen mit seiner Familie hat Karleugen Habfast dazu ein Forum – die Dr. Karleugen Habfast-Stiftung – gegründet, um wissenschaftliche Leistungen in der Isotopenforschung gebührend zu würdigen. Der von dieser Stiftung ausgelobte Isotopenpreis wird jährlich im Rahmen der Tagung der Arbeitsgemeinschaft Stabile Isotope verliehen.

Herr Dr. Habfast wusste, dass stete Aufmerksamkeit und Referenz notwendig sind, um in Fachkreisen mitreden zu können. Seinem Engagement für eine höhere Bekanntheit unserer Arbeitsgemeinschaft Stabile Isotope und damit der Isotopenforschung in Deutschland ist es zu verdanken, dass die Arbeitsgemeinschaft ihre erste Internetplattform bekam. Bis zuletzt arbeitete Herr Habfast an unserer ASI-Homepage mit.

Viele von uns werden Dr. Karleugen Habfast mit seinem stets offenen Ohr für Diskussionen und Fachgespräche, Ratschläge und Hinweise vermissen. Im Gedächtnis vieler Isotopenforscher hat er sich einen Platz geschaffen.

Wir werden unserem Ehrenmitglied, Herrn Dr. Karleugen Habfast, in der Arbeitsgemeinschaft Stabile Isotope ein würdiges Andenken bewahren.

Der Vorstand der Arbeitsgemeinschaft Stabile Isotope e.V.

Dr. Gerhard Strauch Dr. Rolf Siegwolf Dr. Matthias Gehre

#### Nachruf: Prof. Dr. Dr. h.c. mult. Hubert Ziegler



Kurz nach dem Tod des Ehrenmitglieds Dr. Karleugen Habfast hat die Arbeitsgemeinschaft Stabile Isotope e.V. den Verlust eines weiteren langjährigen und bis zuletzt aktiven Mitglieds und Förderers zu beklagen.

Am 17. April 2009 ist Prof. Dr. Dr. h.c. mult. Hubert Ziegler im Alter von 84 Jahren in München verstorben.

Hubert Ziegler war einer der herausragenden deutschen Botaniker in der 2. Hälfte des 20. Jahrhunderts und ein Pionier bei der Anwendung stabiler Isotope in der Ökophysiologie der Pflanzen.

Nach dem Studium der Fächer Biologie, Chemie und Geographie für das Lehramt an Gymnasien, der Promotion und der Habilitation an der LMU München lehrte er als Professor für Botanik von 1959 bis 1970 an der TH Darmstadt und von 1970 bis 1992 an der TU München.

Seine wissenschaftlichen Interessen in der Botanik waren von ungewöhnlicher Breite. Sie erstreckten sich von der Biophysik bis zur Ökophysiologie von Pflanzen und der Umweltforschung. Er verfasste ca. 400 wissenschaftliche Publikationen und war Autor zahlreicher Lehrbücher.

Frühzeitig erkannte Hubert Ziegler auch das Potential stabiler Isotope bei der Aufklärung pflanzlicher Stoffwechselprozesse und bei der Herkunftskontrolle von Lebensmitteln. Seine ersten Publikationen zur Kohlenstoff-Isotopendiskriminierung bei Pflanzen mit CAM-Photosynthese stammen aus dem Jahr 1975 – und das war zwei Jahre vor Gründung der Arbeitsgemeinschaft Stabile Isotope.

Bereits 1977 publizierte er über die Verwendung stabiler Isotope zur Herkunftscharakterisierung von Honig. Im Physiologieteil des Lehrbuchklassikers der Botanik "Strasburger" führte er erstmalig den Begriff "stabile Isotope" als Mittel zur Differenzierung pflanzlicher Photosynthesewege ein. Später richtete er bei der Verwendung von stabilen Isotopen ein besonderes Augenmerk auf die Differenzierung von Stoffflüssen zwischen Parasiten - etwa der Mistel - und ihren Wirtspflanzen.

Den Tag seiner Emeritierung beging Hubert Ziegler 1992 bei der Jahrestagung der Arbeitsgemeinschaft Stabile Isotope in Bayreuth. Barry Osmond widmete damals seinen Hauptvortrag den frühen Beiträgen Hubert Zieglers zur modernen Ökophysiologie der Pflanzen unter Verwendung stabiler Isotope (C.B. Osmond (1993) Isotopenpraxis Environ. Health Stud. 29: 3-8).

Auch nach seiner Emeritierung blieb Hubert Ziegler der Arbeitsgemeinschaft Stabile Isotope aktiv verbunden. Bis zuletzt war er Mitglied im Editorial Board des Publikationsorgans der ASI "Isotopes in Environmental and Health Studies" und Gutachter zur Vergabe des Isotopenpreises der Dr. Karleugen Habfast-Stiftung.

Wir werden Herrn Prof. Hubert Ziegler in der Arbeitsgemeinschaft Stabile Isotope ein würdiges Andenken bewahren.

Im Auftrag des Vorstandes der Arbeitsgemeinschaft Stabile Isotope e.V.

Prof. Dr. Gerhard Gebauer, Bayreuth

#### Einsteintower

#### For Visitors

An Excursion is offered at the end of the conference, see details on page 16

#### **Building H: Conference location and cantine**

Entrance Hall: Conference office Oct. 5–7 Lecture Hall: Oral Sessions and awards Foyer: Poster sessions and coffee breaks







A45: AWI building Offices Labs: Wet chemistry, Sediment, Pollen, Microbiology



A43: AWI building Seminar Room Offices Stable Isotope Laboratory (Cellar)

#### Potsdam

Die brandenburgische Landeshauptstadt hat als ehemalige Residenzstadt der preußischen Könige eine Vielzahl historischer Attraktionen für Ihren Aufenthalt in Potsdam zu bieten. Die berühmteste Sehenswürdigkeit und zugleich das Wahrzeichen der Stadt ist das Schloss Sanssouci mit seiner weitläufigen Parkanlage, zahlreichen Gebäuden, Pavillons und Skulpturen. Die Mitte des 18. Jh. im Stil des Rokoko erbaute Sommerresidenz des Preußenkönigs Friedrich der Große ist ein Höhepunkt für Besucher aus aller Welt.



Die preußischen Herrscher ließen von den besten Architekten und Landschaftsplanern entlang der Havel eine einzigartige Kulturlandschaft mit zahlreichen Schlössern, Gärten und Parkanlagen schaffen. Große Teile Potsdams wurden daher von der UNESCO 1990 als Weltkulturerbe anerkannt. Dazu gehören neben dem Schloss Sanssouci und dem umgebenden Park auch die Parkanlagen Neuer Garten, Glienicke und Babelsberg mit ihren Schlössern sowie Schloss und Park Sacrow mit der Heilandskirche.

Without a doubt, Potsdam is one of the most beautiful cities in Germany. Adding to the cultural ambience, the capital city of the State of Brandenburg is a natural destination to satisfy varied interests and demands. Potsdam's most popular site is the Schloß Sanssouci palace, located in the park to which it gives its name. The former summer residency of prussian King Frederick the Great was built in the 18th century. Not only the palace and the surrounding Sanssouci park make your visit worthwhile. Great parts of the city of Potsdam have been recognised as UNESCO world's heritage in 1990. The Alexandrowka, the Holländisches Viertel (the Dutch Quarter) and the Weavers' Quarter - the historic sections of the city - provide the flair of a city steeped in European tradition. The Babelsberg Filmpark and the Biosphäre nature experience exhibit, are all special attractions which will make your visit to Potsdam a very pleasurable experience.

#### Wegbeschreibung zum Conference Dinner

#### Gaststätte Prinz Eisenherz - Mittelalterliche Erlebnisgastronomie im Filmpark Babelsberg

Zum Filmpark gelangen Sie am besten mit dem öffentlichen Nahverkehr:

Nehmen Sie die S-Bahn von Potsdam Hbf und steigen an de nächsten Haltestelle "Babelsberg" aus. Von dort bringen Sie Busse der Linien 601, 619 und 690 direkt vor den Eingang des Filmparks.

Take the S-Bahn from Potsdam

Hbf to the next station "Babelsberg". From there the busses 601, 619 and 690 get you to the Filmpark.





Time	Monday, Oct. 5	Tuesday, Oct. 6	Wednesday, Oct. 7
9:20			
9:40		Isotopes in Polar Regions I	Isotopes in Polar Regions II
10:00			
10:20		Coffee	Break
10:40			
11:00	Registration		
11:20		Matter Fluxes	Nutrition, Medicine,
11:40	Monday: 11.00 - 18:00 Tuesday: 8:00 - 18:00	in Ecosystems II	Doping & Forensics
12:00	Wednesday: 8:00 - 14:00		
12:20		Isotope Award of the	Award: Best Poster & Talk
12:40		Karleugen-Habfast-	Closing Ceremony
13:00		Foundation	
13:20	Opening & Keynote Lecture		
14:00		Lunch	Break
14:20	Climate Change &		
14:40	<b>Climate Reconstruction</b>		Option: Excursion
15:00		Analytics &	Telegrafenberg
15:20	Coffee Break	Quality control	
15:40			
16:00	Metter Eluves		
16:20	in Ecosystems I	Coffee Break	Rooms
16:40			All scientific sessions take place
17:00			Coffee breaks are in the foyer,
17:20	Poster Session I	Poster Session II	lunch breaks are hosted in the cantine of building H.
17:40			Other locations are mentioned in the table.
18:00			
18:20	Annual Meeting of the		
18:40	GASIR Members		
19:00			
19:20			
19:40			
20:00	Thermo Fisher	Conference Dinner	
20:20			
20:40	User meeting	(Prinz Eisenherz, Filmpark	
21:00	(Duilding LL contine)	Babelsberg; see page 9)	
21:20			
21:40			
22:00			
Gene	eral Programme 📃 Breaks	Poster Sessions	Oral Sessions

#### Monday, Oct. 5, 2009

#### Opening and keynote lecture, 13:00 - 14:00

#### Lecture hall (Building H)

Miller, H. Monday, Oct. 5, 13:30 – 14:00 Alfred Wegener Institute, Bremerhaven, Germany

Isotope und Eisbohrkerne (for details see abstract page 60)

#### Session A: Climate Change and Climate Reconstruction, 14:00 – 15:00

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#### Lecture hall (Building H)

Chair: H.-W.Hubberten (Potsdam)

- 14:00 14:20 A-1 <u>C. Mangili</u>, A. Brauer, B. Plessen Palaeoclimate reconstruction of the Piànico Interglacial (400 ka old) by means of stable isotope analyses on endogenic calcite
- 14:20 14:40 A-2 <u>A. Giesemann</u>, C. Balko Can  $\delta^{13}$ C values serve as an early indicator for drought tolerance of potato genotypes?
- 14:40 15:00 A-3 <u>R. Siegwolf</u>, M. Saurer, O. Sidorova Variability in tree ring stable C and O isotopes as a response to increasing CO<sub>2</sub>

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#### Coffee Break, 15:00 - 15:40

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Session B1: Matter Fluxes in Ecosystems I, 15:40 – 17:00

#### Lecture hall (Building H)

Chair: H.W.-Hubberten (Potsdam)

15:40 – 16:00 B1-1	<u>A. Vieth</u> , M. Gabriel and H. Wilkes Application of compound-specific carbon and hydrogen isotope ratios to evaluate alteration processes in petroleum reservoirs
16:00 – 16:20 B1-2	<u>M. Tichomirowa</u> , C. Heidel, M. Junghans, F. Haubrich Identifying water sources and the impact of decreasing $\delta^{18}$ O values of sulfate from precipitation in the region of Freiberg, Southeastern Germany
16:00 – 16:40 B1-3	<u>M.E. Böttcher</u> , O. Dellwig, T. Max Isotope biogeochemistry of dissolved sulfate and sulfide in the water column and surface sediments of the Black Sea

16:40 – 17:00 B1-3	U. Herzschuh, S. Mischke, H. Meyer, B. Plessen, C. Zhang Lake nutrient variability inferred from isotopic ( $\delta^{13}$ C, $\delta^{15}$ N) analyses of aquatic plant macrofossils
	Poster Session I, 17:00 - 18:00
See	e details on the poster presentation on page 17-18
Annua	I Meeting of the GASIR Members, 18:00 – 19:20
	Lecture hall (Building H)
Die Tagesord	nung für die jährliche Mitgliederversammlung umfasst die folgenden Punkte:
- Bericht de - Diskussior Habfast-S - Wahl des - Festlegen 2012; Voi	s Vorstandes und des Schatzmeisters nen zu den Berichten und über den Isotopenpreis der Dr. Karleugen tiftung neuen Vorstandes der Austragungsorte der ASI-Tagung 2010 und der JESIUM rstellung der Kandidaten
Т	hermo Fisher User Meeting, 19:20 – 22:00
	Lecture hall (Building H)
Tuesday, Oct.	6, 2009
Sessio	on C1: Isotopes in Polar Regions I, 9:20 – 10:20
	Lecture hall (Building H) Chair: M.E. Boettcher (Warnemünde)
9:20 – 9:40 C1-1	<u>M. Haupt</u> , T. Böttger, M. Friedrich, Y. Kononov Mathematisch-Statistische Aspekte bei der Erstellung von langjährigen Isotopenchronologien aus zeitlich unterschiedlich aufgelösten Sequenzen von Baumjahrringen am Beispiel einer <i>Pinus Sylvestris</i> -Chronologie (Halbinsel Kola, NW-Russland)
9:40 - 10:00 C1-2	<u>P. Quillfeldt</u> , R. McGill, R. W. Furness, C.C. Voigt, J.F. Masello Small pelagic seabirds in polar waters - stable isotopes reveal migration and foraging patterns
10:00 - 10:20 C1-3	<u>H. Meyer</u> , A. Dereviagin, T. Opel, G. Schwamborn, L. Schirrmeister, HW. Hubberten

Permafrost ice – a Quaternary climate archive

#### Coffee Break, 10:20 - 11:00

#### Session B2: Matter Fluxes in Ecosystems II, 11:00 – 12:20

#### Lecture hall (Building H)

Chair: M.E. Boettcher (Warnemünde)

11:00 – 11:20 B2-1	<u>C.F. Stange</u> , R. Russow Messung und Simulation der Entstehung der N-Gase durch Nitrifikation und Denitrifikation mittels eines <sup>15</sup> N-Markierungsversuches
11:20 – 11:40 B2-2	<u>N.Wannicke</u> , F. Korth, M. Voss Incorporation of diazotrophic fixed N <sub>2</sub> by mesozooplankton species - Case studies in the southern Baltic Sea using <sup>15</sup> N-stable isotope tracer addition
11:40 – 12:00 B2-3	<u>M. Voss</u> , B. Deutsch, I. Liskow, M. Pastuszak, U. Schulte, S. Sitek Nitrogen retention in the Oder lagoon, Baltic Sea
12:00 – 12:20 B2-4	<u>M. Stöckel</u> , C. Meyer, G. Gebauer Zwischen Grün und Weiss-Zusammenhang zwischen dem Chlorophyllgehalt der Blätter und dem Grad der Mykoheterotrophie bei der Orchidee <i>Cephalatera Damasonium</i>

#### .....

Isotope Award of the Dr. Karleugen-Habfast-Foundation, 12:20 – 13:20

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#### Lecture hall (Building H)

12:20 – 13:20 Der Isotopenpreis der Dr.-Karleugen-Habfast-Stiftung wird an herausragende (junge) Wissenschaftler verliehen, die sich der "Anwendung stabiler Isotope" widmen. Der diesjährige Preisträger wurde durch eine dreiköpfige Jury ausgewählt und zur Nominierung vorgeschlagen. Die Verleihung des Isotopenpreises 2009 wird auf der Jahrestagung der Arbeitsgemeinschaft Stabiler Isotope e. V. in Potsdam erfolgen.

The Isotope Award of the Dr.-Karleugen-Habfast-Foundation will be granted to outstanding (young) scientists, who are devoted their work to the application of stable isotope methods. This year's winner was selected and nominated by a jury of 3 persons. The ceremony of the Isotope Award 2009 will be held in the frame of the GASIR conference in Potsdam.

### Lunch Break, 13:20 - 14:20

#### Session D: Analytics and Quality Control, 14:20 – 16:00

#### Lecture hall (Building H)

Chair: M. Gehre (Leipzig)

- 14:20 14:40 D-1 <u>B. Chapligin</u>, H. Meyer, H. Friedrichsen, H.-W. Hubberten Oxygen isotopes of biogenic silica – calibration studies for using a remotelyoperated laser-fluorination based mass spectrometry unit and new methods for removing the hydrous layer
- 14:40 15:00 D-2 <u>M. Boner</u>, P. Bliznakov Möglichkeiten der Hochtemperatur-pyrolyse zur Stabil-Isotopen-Messung unter Einsatz von Temperaturen über 1600° C in Kombination mit der Siliciumcarbid-Einrohr-Technik
- 15:00 15:20 D-3 <u>D. Hatscher</u>, O. Kracht, A. Hilkert, J. Schwieters Advances in automated multi-isotopic fingerprint analysis using Thermo Scientific Elemental Analyzers
- 15:40 16:00 D-5 <u>A. Hilkert</u>, C.B. Douthitt Multicollectors in isotope ratio MS

Coffee Break, 16:00 - 16:40

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Poster Session II, 16:40 - 18:00

see details on the poster presentation on page 17-18

Conference Dinner, 19:00 - ca. 22:00

see details for location and travel on page 9

#### Wednesday, Oct. 6, 2009

#### Session C2: Isotopes in Polar Regions II, 9:20 – 10:20

#### Lecture hall (Building H)

Chair: G. Strauch (Leipzig)

- 9:20 9:40 C2-1 <u>M. Behrens</u>, L. Möller, H. Fischer Carbon isotopic studies on methane in polar ice cores as a clue to past methane sources
  9:40 – 10:00 C2-2 <u>J. Landsberg</u>, K. Holmen, E. Isaksson, D. Romanini, H.A.J. Meijer, E. Kerstel Continuous on-line water vapor isotope measurements in Antarctica
- 10:00 10:20 C2-3 <u>T. Opel</u>, D. Fritzsche, H. Meyer Late holocene climate change in the eurasian arctic – Evidence from Akademii Nauk Ice Core (Severnaya Zemlya)

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#### Coffee Break, 10:20 - 11:00

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#### Session E: Nutrition, Medicine, Doping & Forensics, 11:00 – 12:20

#### Lecture hall (Building H)

Chair: G. Strauch (Leipzig)

11:00 – 11:20 E-1	<u>M. Greule</u> , F. Keppler Schnelle und präzise Bestimmung der Isotopenverhältnisse pflanzlicher Methoxygruppen - Methode und Anwendung
11:20 – 11:40 E-2	<u>U. Flenker</u> , B. Linster, V. Gougoulidis, F. Hülsemann, W. Schänzer Possible absence of lipid <sup>13</sup> C depletion in sterols and steroids from eukaryotes
11:40 – 12:00 E-3	<u>F. Hülsemann</u> , U. Flenker, M. Machnik, I. Schenk, C. Zinner, J. Mester, Wilhelm Schänzer Identifizierung von Bicarbonat-Applikation bei Mensch und Pferd per IRMS
12:00 – 12:20 E-4	<u>T. Piper</u> , U. Flenker, W. Schänzer Determination of <sup>13</sup> C/ <sup>12</sup> C ratios of endogenous urinary steroids excreted as sulphates: Methods validation and reference population

#### Award Best Poster and Talk & Closing Ceremony, 12:20 – 13:20

#### Lecture hall (Building H)

12:20 – 13:20 Auch 2009 in Potsdam werden, einer langen Tradition der ASI-Tagungen folgend, der beste Vortrag und das beste Poster während der Tagung prämiert. Die Auswahl erfolgt durch Mitglieder des ASI-Vorstandes und die Session-Chairs.

Following a long tradition of the GASIR meetings, the best oral and poster presentations will be awarded during the conference by a jury comprising members of the ASI executive committee and the session chairs.

#### .....

#### Lunch Break, 13:20 - 14:20

.....

#### Excursion: Tour to Telegrafenberg, 14:20 – 15:20

#### Meeting in front of Building H

Leader: Diedrich Fritzsche, Potsdam

14:20 – 15:20 Die Führung ist ein etwa einstündiger Spaziergang über den historisch bedeutsamen Telegrafenberg. Dieser Park beherbergt eine einzigartige Mischung verschiedener wissenschaftlicher Gebäude, deren Bau um 1870 begonnen wurde. Namens gebend ist eine optische Telegrafenstation, die Berlin und Koblenz verbinden sollte. Die wissenschaftlichen Aktivitäten haben auf dem Telegrafenberg eine lange Tradition, insbesondere in den Bereichen Astrophysik, Geodäsie und Erforschung des Schwerefeldes der Erde. Im astrophysikalischen Observatorium wurde 1881 von Albert Michelson sein berühmtes Experiment durchgeführt. Das Sonnenobservatorium wurde 1924 fertig gestellt, um Einsteins Relativitätstheorie zu belegen. 1890 wurde das Königlich-Preußische Institut für Geodäsie nach Potsdam verlegt und das meteorologisch-geomagnetische Observatorium gegründet, das damals zahlreiche Expeditionen in die Arktis und Antarktis logistisch unterstützte.

> It will be an easy walk through the Telegrafenberg area for about one hour of duration. The park landscape and architecture of a unique collection of scientific facilities whose construction began in the 1870's and continue up to today will be the topics of this tour. The Telegrafenberg is named after a station of an optical telegraph line built to link Berlin with Koblenz via Potsdam. Research has a long tradition here and is characterized by activities in the fields of astrophysics, geodetic surveying and gravitation research. When the first special astrophysical observatory in the world was founded in 1874 it was the birth of the research site on Telegrafenberg hill. In 1924 the solar observatory in the Einstein tower on Telegrafenberg hill was completed which was to provide evidence for the predicted effects resulting from Einstein's general theory of relativity.

#### Poster Presentations, Oct. 5–7, 2009

#### Foyer Building H

I.K.U. Adam, G. Gebauer

Wie hoch ist der Gewinn an organischem C und N durch mykoheterotrophe Pflanzen in 1 ha Buchenwald? - Von der relativen Isotopenhäufigkeit zu absoluten Zahlen

B. Aichner, U., H. Wilkes

 $\delta^{13}$ C and  $\delta$ D values of lipid biomarkers in aquatic macrophytes, surface sediments and in a sediment core from Koucha Lake (Eastern Tibetan Plateau)

- E. Annweiler<sup>1</sup>, A. Probst<sup>1</sup>, <u>Th. Huber</u> Extraktion von Vanillin aus Lebensmitteln und Analyse mittels GC-C-IRMS
- G. Battipaglia, <u>P.Linke</u>, V. De Micco, W.A Brand, G. Aronne, P. Cherubini Assessing climate sensitivity of mediterranean plants by combining dendro-ecology, isotope composition and QWA
- <u>M.E. Böttcher</u>, A.M. Al-Raei, M. Segl, N. Volkenborn Seasonal impact of logworms (Arenicola Marina) on biogeochemical processes and carbon isotope geochemistry of intertidal surface sediments: Results from an in-situ experiment

W.A. Brand, H. Geilmann, E.R. Crosson, C.W. Reila Cavity ringdown for H<sub>2</sub>O isotopic analysis; The contamination issue

J. Bünning, V. Winde, O. Dellwig, U. Struck, N. Kowalski, M. Labrenz, M.E. <u>Böttcher</u> Stable isotope and trace element partitioning in a recent carbonate-precipitating stream, Rügen Island

<u>M. Czymzik</u>, A. Brauer, B. Plessen, P. Dulski, U. von Grafenstein Stable oxygen and carbon isotope data of detrital carbonates in annually laminated sediment from Lake Ammersee (Southern Germany) as a proxy for flood events

<u>F. Fernandoy</u><sup>1</sup>, H. Meyer<sup>1</sup>, C. Olivares<sup>2</sup> and M. Cartró<sup>3</sup> Stable water isotope characteristics of the recent hydrological system of the northern antarctic peninsula - implications for ice and firn core interpretation

<u>C. Frey</u>, C. Fellerhoff, F. Korth, I. Liskow, M. Voß Uptake of dissolved organic nitrogen of plankton communities in the Baltic Sea

<u>R. van Geldern</u>, V. Becker and A. Myrttinen, J.A.C. Barth A method for the simultaneous analysis of DIC concentration and carbon isotopic composition in continuous flow mode

C. Heidel, M. Tichomirowa

Confirmation of the incorporation of dissolved molecular oxygen into sulphate during abiotic pyrite oxidation experiments

- <u>K. Isensee</u>, S. Hille, O. Dellwig, R. Blake, M.E. Böttcher Zur Sauerstoff-Isotopen Biogeochemie von Phosphat in brackischen Nebenmeeren: I. Das Schwarze Meer
- K. Isensee, S. Hille, M. Nausch, O. Dellwig, R. Blake, M.E. Böttcher Zur Sauerstoff-Isotopen Biogeochemie von Phosphat in brackischen Nebenmeeren: II. Die Ostsee

- <u>Z.E. Kayler</u>, E.W. Sulzman, A.C. Mix, B.J. Bond Steady-State and non steady-state of soil respired δ<sup>13</sup>CO<sub>2</sub> in a douglas fir forest, Oregon, USA
- <u>K. Knöller</u>, A. Seebach and I.Baneschi Are meromictic lakes potential bioreactors for natural attenuation in mining landscapes?
- <u>P. Königer</u>, S. Möhring, A. Mulch, H. Wiederhold Stabil-Isotopenuntersuchungen in der ungesättigten Zone zur Bestimmung der Grundwasserneubildung auf der Nordseeinsel Borkum
- J. Köpp, G. Gebauer

Produktion und Konsumption der klimarelevanten Spurengase  $\rm N_2O$  und  $\rm CH_4$  in einem sauren Niedermoor

- <u>R. Langel</u>, L. Szwec, L. Schwendenmann, J. Dyckmans Methodische Aspekte bei der Messung von δ<sup>13</sup>C in DOC am LC IsoLink
- <u>T.C.W. Moerdijk-Poortvliet</u>, H.T.S. Boschker, P. van Breugel, M. Houtekamer, J.J. Middelburg Analysis of carbohydrate concentrations and stable carbon-isotope ratios in natural and <sup>13</sup>C enriched samples using liquid chromatography coupled to isotope ratio mass spectrometry (LC-IRMS)
- <u>Y. Oelmann</u>, U. Hensler, C. Valarezo, Wolfgang Wilcke The vertical distribution of δ<sup>13</sup>C values to predict mineralized N in soil in a tropical montane rain forest in Ecuador
- J. Sommer, K.W. Dixon, M.I. Bidartondo, G. Gebauer Myco-heterotrophy in a selection of Western Australian orchids
- M. Stöckel, V. Merckx, G. Gebauer

C and N isotope signatures of myco-Heterotrophic plants associated with arbuscular mycorrhiza from a tropical rain forest - A new facet of nutrient exchange between fungi and plants

- <u>R. Well</u>, H. Flessa Can isotopic signatures of soil-emitted  $N_2O$  be used as indicators of  $N_2$ -fluxes?
- <u>S. Wetterich</u>, H. Meyer, B. Plessen, L. Schirrmeister Stable isotopes in (sub-)arctic freshwaters and ostracod calcite

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♣ +49 (0) 21 59 / 69 42-10

info@iva-analysentechnik.de www.iva-analysentechnik.de

#### Wie hoch ist der Gewinn an organischem C und N durch Mykoheterotrophe Pflanzen in 1 ha Buchenwald? - Von der relativen Isotopenhäufigkeit zu absoluten Zahlen

#### I.K.U. Adam<sup>1</sup>, G. Gebauer<sup>1</sup>

<sup>1</sup> BayCEER-Labor für Isotopen-Biogeochemie, Universität Bayreuth, 95440 Bayreuth, Germany

Corresponding author: iris.adam@uni-bayreuth.de

Fast alle krautigen Pflanzen nutzen die Symbiose zu VA-Mykorrhizapilzen, um bodenbürtige anorganische Stickstoffverbindungen noch effektiver erschließen zu können. Von einer Reihe an Pflanzen insbesondere aus der Familie der Orchidaceae aber auch der Ericaceae ist jedoch bekannt, dass sie in eine Pilzsymbiose intervenieren, die eigentlich den Waldbäumen vorbehalten ist - die Ektomykorrhiza. Solche Pflanzen ernähren sich teilweise oder vollständig auf Kosten der Pilzassoziation und werden daher als partiell bzw. vollständig mykoheterotroph bezeichnet. Mykoheterotrophe Pflanzen sind über das Pilzmycel indirekt mit den Baumwurzeln verbunden. Die Pilzpartnerschaft hat entscheidende Vorteile für die mykoheterotrophe Pflanze. Neben der Erschließung anorganischer Stickstoffverbindungen - wie bei den vollständig autotrophen Pflanzen - haben sie sowohl Zugang zu organischen Kohlenstoffverbindungen aus der Photosyntheseleistung der Bäume als auch zu organischen Stickstoffverbindungen, die der Pilz mithilfe von Exoenzymen im Boden erschließt. Diese heterotrophe Ernährung über den Pilz führt dazu, dass diese Pflanzen eine Isotopie ähnlich dem des Pilzsubstrates aufweisen und aufgrund von Fraktionierungen im <sup>13</sup>C und <sup>15</sup>N gegenüber den Bäumen und der autotrophen Begleitvegetation charakteristisch angereichert sind. Diese Kenntnis hat man sich bereits zunutze gemacht, um den prozentualen Gewinn an C und N durch mykoheterotrophe Ernährung einzelner Pflanzen abzuschätzen. Offen war jedoch die Frage wie hoch dieser Gewinn auf Bestandesebene tatsächlich ist.

Ziel dieser Untersuchung war daher die Bestimmung der jährlichen über den Pilzpartner gewonnenen Masse an C und N aller mykoheterotrophen Pflanzen auf einem Hektar Buchenwald in Oberfranken (Bayern). Zur Quantifizierung des C- und N-Gewinns aus mykoheterotropher Ernährung wurden zum ersten Mal die biometrischen Daten von repräsentativen Pflanzen von vier partiell mykoheterotrophen Arten (*Cephalanthera damasonium, Cephalanthera rubra, Epipactis atrorubens* und *Orthilia secunda*) sowie zwei vollständig mykoheterotrophen (*Monotropa hypopitys* und *Neottia nidus-avis*) in Beziehung zu deren über EA-IRMS ermittelten Isotopendaten gesetzt. Durch eine Kartierung aller mykoheterotrophen Pflanzen dieser Arten des Untersuchungsgebietes konnte die Quantifizierung auf die Bestandesebene erweitert werden.

Im Ergebnis zeigte sich, dass von dem Gesamttrockengewicht von 346 g  $\cdot$  ha<sup>-1</sup>  $\cdot$  a<sup>-1</sup> der insgesamt 2361 partiell mykoheterotrophen und 127 vollständig mykoheterotrophen Pflanzen 103 g C (30%) und 6 g N (2%) aus der Pilzpartnerschaft stammten.

Die Analyse der relativen Isotopenhäufigkeiten von <sup>13</sup>C und <sup>15</sup>N in den Pflanzenproben ermöglichte somit einen quantitativen Einblick in den C- und N-Fluss besonders angepasster Pflanzen eines Waldbiotops. Ein Rückschluss auf die ökologische Relevanz dieser Ernährungsweise wird nun möglich.

## δ<sup>13</sup>C and δD values of lipid biomarkers in aquatic macrophytes, surface sediments and in a sediment core from Koucha Lake (Eastern Tibetan Plateau)

#### <u>B. Aichner<sup>1</sup></u>, U. Herzschuh<sup>1</sup>, H. Wilkes<sup>2</sup>

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Telegrafenberg A43, D-14473 Potsdam, Germany <sup>2</sup>GeoForschungsZentrum, Telegrafenberg B228, D-14473 Potsdam, Germany

Corresponding author: Bernhard.Aichner@awi.de

With a set of surface sediment samples and corresponding aquatic macrophytes from the eastern Tibetan Plateau we show that aquatic macrophytes are significant contributors to the sedimentary organic matter in lakes in this region. Submerged species like Potamogeton pectinatus turned out to show wide ranges of  $\delta^{13}$ C values both in bulk organic matter (-6.0‰ to -23.3‰) and in n-alkanes (e.g. -16.6‰ to 28.0‰ for  $nC_{23}$ ) due to bicarbonate metabolism.  $\delta D$  measurements reveal that *n*-alkanes record the hydrogen isotope signal of summer precipitation and that lipids in samples derived from the most humid locations (southeastern Tibetan Plateau), show an isotopic fractionation factor of ca -160 to meteoric water (OIPC-data [1]), which is in the range of reported fractionation factors [2]. In contrast, sediment and submerged plant samples derived from dry locations (e.g. from the northeastern Tibetan Plateau or the Qaidam Basin) show a less negative fractionation factor between lipids and source water, which can be explained by deuterium enrichment of the source water due to increased lake water evaporation and soil and leaf water evapotranspiration at these arid sites.

In a sediment core from Koucha Lake (Fig. 1) we found before 8 cal ka BP a congruence between curves of total organic carbon (TOC) contents, total amounts of aquatic macrophyte derived n-alkanes (e.g.  $nC_{23}$ ) and  $\delta^{13}$ C values of TOC and *n*-alkanes. This suggests that the lake was macrophyte dominated during that period.  $\delta$ D values of  $nC_{23}$  and terrestrial n-alkanes (e.g.



Fig. 1. Bulk parameter (\* derived from Mischke et al. 2008),  $\delta^{13}$ C and  $\delta$ D values as well as concentrations of lipid biomarkers in the sediment core from Lake Koucha, plotted versus age. Shaded areas indicate assumed cool periods (\*\*), deduced from low concentrations and  $\delta^{13}$ C values of biomarkers, and a period of reduced effective moisture availability (\*\*\*), inferred from ostracod and pollen transfer functions as well as  $\delta$ D values of the  $nC_{23}$ -alkane.

 $nC_{31}$ ), gradually decrease from the Late Glacial until the Early Holocene, giving evidence for an increase of precipitation amounts due to an intensification of the summer monsoon. Then, at the beginning of the Holocene,  $\delta D$  values of especially nC23 shifted to higher levels. This could be interpreted with respect to an increase of evaporation caused by higher temperatures during the monsoonal maximum which lead to higher  $\delta D$  values of the lake water. These results are in agreement with inferences from biological proxies (such as ostracods and pollen) which deduced a low effective moisture availability during that period, when increasing evaporation due to higher temperatures possibly have outweighed increasing precipitation amounts. At ca 7.2 cal ka BP, effective moisture increased again and the lake basin opened [3], as visible at a drop of reconstructed electric conductivity (derived from an ostracod transfer function). A variety of algal and bacterial biomarkers such as hopanoids and isoprenoids can be found in this transition period, of which especially phytane, pentamethylicosane (PMI), moretene and diploptene show relatively high abundances. Phytane and PMI have different isotopic signals ( $\approx$  -18‰ and  $\approx$  -28‰, respectively) which indicates that they are derived from different precursors. Phytane was possibly derived from cyanobacteria, while methanogenic archaea might be the source of PMI. The isotopic depletion of diploptene and moretene  $(\approx -60\%)$  indicates the presence of methane-oxidizers. From ca 6 cal ka BP on, a saturated C<sub>20</sub> HBI is the dominant compound in the sediment, which indicates a strong presence of algae or cyanobacteria. About 1000 years later an unsaturated C<sub>25</sub> HBI, which is a specific biomarker for diatoms, appeared. These results suggest that the lake was phytoplankton dominated during the last 6000 years. Short-term shifts towards low concentrations of bacterial (hopanoids, including moretene and diploptene) and terrestrial  $(nC_{31})$  biomarkers at 5.9, 3.1 and 1.9 cal ka BP are in phase with reported cool episodes from other locations in Tibet. These drops are accompanied by isotopic shifts towards more negative  $\delta^{13}$ C values of lipid compounds, which is especially pronounced for moretene.

A primary productivity induced shift towards very positive  $\delta^{13}$ C values (up to +8‰) of the total inorganic carbon (TIC) in this period is

reflected by the  $\delta^{13}$ C values of  $nC_{21}$ ,  $nC_{23}$  and  $nC_{25}$ , which reach values up to -12.6‰. We conclude that those *n*-alkanes could be excellent recorders of carbon-limiting conditions, which lead to the assimilation of isotopically-enriched carbon species by aquatic organisms such as macrophytes. The limitation of carbon sources could be a localized phenomenon occurring in dense plant stands (as in the older section of the core), or it may be induced by high primary productivity (as in the younger section).

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### Extraktion von Vanillin aus Lebensmitteln und Analyse mittels GC-C-IRMS

E. Annweiler<sup>1</sup>, A. Probst<sup>1</sup>, <u>Th. Huber<sup>1</sup></u>

<sup>1</sup>Chemisches und Veterinäruntersuchungsamt Freiburg, Bissierstr. 5, 79114 Freiburg

Corresponding author: Eva.Annweiler@cvuafr.bwl.de

Die Geschmacksrichtung Vanille kann durch den Einsatz unterschiedlicher Aromen erzielt werden. Zu unterscheiden sind hierbei:

- Natürliches Vanillearoma, das durch Extraktion aus der Vanilleschote gewonnen wurde (mit der Hauptaromakomponente Vanillin).
- Auf biotechnologischem Wege gewonnenes Vanillin aus natürlichen Ausgangsstoffen.
- Chemosynthetisch hergestelltes Vanillin, z.B. aus Sulfitablaugen der Papierindustrie.

Wird in der Bezeichnung eines Lebensmittels auf "Vanille" hingewiesen und werden dekorative Abbildungen von Vanilleblüten oder -schoten auf den Verpackungen angebracht, lässt dies erwarten, dass die zur Geschmacksgebung eingesetzten Zutaten auch von der Namen gebenden Vanille stammen. Kommen die erheblich preisgünstigeren, synthetischen oder biotechnologisch hergestellten Vanillearomen zum Einsatz, sollte dies für den Verbraucher erkennbar sein. Für bestimmte Produktgruppen wie z.B. Puddingerzeugnisse ist eine Kenntlichmachung von synthetischem Vanillin durch die Angabe "mit Vanillegeschmack" z.B. durch die Leitsätze des Deutschen Lebensmittelbuchs verlangt. Der Nachweis des verwendeten Aromas kann über die Bestimmung der sogenannten Verhältniszahlen erfolgen. Dazu wird das Konzentrationsverhältnis spezieller Aromakomponenten eines Vanilleextrakts oder Vanillearomas ermittelt und anhand bestimmter Richtwerte beurteilt [1]. Jüngere Untersuchungen weisen jedoch darauf hin, dass auch authentische Extrakte diesen Beurteilungs-kriterien nicht entsprechen [2]. Von den Richt-werten abweichende Verhältniszahlen wurden zudem bei der Anwendung alternativer Extraktionsverfahren beobachtet. Auch chemische oder biochemische Reaktionen im aromatisierten Lebensmittel können die Verhältniszahl verändern[3].

Als alternative Nachweismöglichkeit bietet sich die Stabilisotopenanalyse an. Das Kohlenstoffisotopenverhältnis von Vanillin erlaubt eine eindeutige Bewertung der Art des im Lebensmittel eingesetzten Vanillearomas. Vanillin, das aus der Vanilleschote gewonnen wurde, unterscheidet sich anhand seiner Kohlenstoffisotopensignatur deutlich von Vanillin, das auf anderem Wege gewonnen wurde.

Die Stabilisotopenanalyse von Vanillin in Aromen, Aromenzubereitungen und Lebensmitteln erfolgt üblicherweise mittels Gaschromatographie-Isotopenverhältnismassenspektrometrie (GC-c-IRMS). Dazu muss ein reiner, für die Gaschromatographie geeigneter Extrakt gewonnen werden, der eine ausreichende Konzentration an Vanillin aufweist [4]. Alternativ wurde die Isolierung von Vanillin aus Lebensmitteln zur Bestimmung mittels EA-IRMS beschrieben[5]. Das hierbei isolierte Vanillin muss in ausreichender Menge als Reinsubstanz vorliegen. Generelle Bedingung ist, dass das Kohlenstoffisotopenverhältnis durch die umfangreichen Aufarbeitungsschritte nicht beeinträchtigt wird.

Die Isotopenanalyse von Vanillin mittels GC-c-IRMS wurde bisher überwiegend für Aromenextrakte und Konzentrate beschrieben, die höhere Konzentrationen an Vanillin aufweisen. Gegenüber der Analyse von Aromenzubereitungen müssen die Extrakte aus Lebensmitteln für die GC-c-IRMS-Analyse stärker angereichert und aufgereinigt werden.

Bei der hier beschriebenen Methode handelt es sich um eine Aufarbeitungsmethode, die die direkte Analyse des Extrakts mittels GC-c-IRMS ermöglicht. Sie beruht auf der Flüssigflüssig Extraktion der geklärten Probe mit einem *n*-Propanol-Wasser-Gemisch.

Die Probe wird mit n-Propanol und Wasser versetzt und extrahiert. Durch die Zugabe von Carrez-Lösungen erfolgt die Klärung der Probe. Der gewonnene Extrakt wird nach Zugabe von Kochsalz mit n-Propanol extrahiert, durch Aussalzen erfolgt eine Phasentrennung. Der organische Extrakt wird über einer Silica Gel - Festphasensäule gereinigt, bei Bedarf eingeengt und mittels GC-c-IRMS bestimmt. Zur Bestimmung der Konzentrationsverhältnisse von Vanillin zu seinen charakteristischen Minorkomponenten, kann vor der Aufreinigung über die Festphasensäule ein Aliquot für die HPLC-Analyse abgenommen werden. Bei der beschriebenen Methode lag der Einfluss der Aufarbeitung auf den δ13C-Wert des Vanillins im Bereich der Messunsicherheit. Dotierungsversuche und Extraktionen reeller Matrices ergaben eine gute Präzision und Reproduzierbarkeit der Analysen. Die Optimierung der Methode erfolgte bezüglich der Stabilität des δ13C-Werts von Vanillin und nicht bezüglich der Wiederfindung. Mit dem beschriebenen Verfahren wurden Milcherzeugnisse, Speiseeis-Proben aus loser

Abgabe, Puddingerzeugnisse, Sojazubereitungen und Vanillezuckerproben analysiert. Die Ergebnisse unterschieden sich für die jeweiligen Produktgruppen deutlich (Abb. 1).

Die Auslobungen bezüglich natürlicher Vanille waren bei Milchprodukten und Speiseeisproben häufig nicht gerechtfertigt. Während Puddingerzeugnisse, Vanillezuckerproben und Sojadrinks oder -desserts fast ausschließlich korrekt gekennzeichnet waren.

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Abb. 1. Kennzeichnung des Vanillearomas bei Milch- und Puddingerzeugnissen

### Assessing climate sensitivity of Mediterranean plants by combining dendro-ecology, isotope composition and QWA

G. Battipaglia<sup>1</sup>, <u>P.Linke<sup>2</sup></u>, V. De Micco<sup>3</sup>, W.A Brand<sup>2</sup>, G. Aronne<sup>3</sup>, P. Cherubini<sup>1</sup>

<sup>1</sup>WSL Swiss Federal Institute for Forest, Snow and Landscape Research, CH-8903 Birmensdorf, Switzerland <sup>2</sup>Max Planck Institute for Biogeochemistry, Box 100164,07701, Jena, Germany <sup>3</sup>Dept. Arboriculture, Botany and Plant Pathology, University of Naples Federico II, via Università 100, I-80055 Portici (Naples), Italy

Corresponding author: giovanna.battipaglia@wsl.ch

#### INTRODUCTION

Mediterranean ecosystems are water limited; longer and more severe drought periods are expected in the near future for them (IPPC, 2007). So far, the response of local vegetation to changes in the climatic regime remains uncertain and the information on the relationship between environmental factors and wood growth is still scarce (Cherubini, 2003).

We believe that the combination of classical dendrochronology with isotopic analysis and quantitative wood anatomy is an emerging method with promising perspectives in treerings and climate change research, particularly in the Mediterranean environment where woody species develop specific adaptations to water stress. In particular shrubs and trees may form intra-annual density fluctuations (IADF), also called "false rings" or "double rings" (Tingley 1937; Schulman 1938) as a consequence of sudden drought events, occurring during the vegetative period. Thus, allowing intra-annual resolution, they may provide detailed information at a seasonal level, as well as species-specific sensitivity to drought.

The main aims of this study were 1) to characterize the anatomical features, especially the formation of annual ring boundaries of Mediterranean species; 2) to determine whether the relationships between IADF formation were related to climate or individual characteristics and 3) to test and standardize a novel method to assess climate sensitivity of Mediterranean species by combining dendro-ecology, isotopic analysis and quantitative wood anatomy (QWA).

#### METHODS

For our aims we selected two study sites on the island of Elba, western coast of Italy, charac-

terized by different soil moisture (around 40%) and identified as "mesic site" and "xeric site". The mesic site was located in the Nivera Valley at 460 m a.s.l. (42°46'N, 10°11'E), while the xeric site was placed on Monte Perone at 420 m a.s.l. We selected and sampled three species *Arbutus unedo L., Erica Arborea L.*, and *Quercus ilex*.

#### **Tree-ring data**

For each species a total of 10 trees were destructively sampled in both sites and 3 disks from base of each plant were cut and air-dried. Density fluctuations were identified in each disk for both sites; sub-samples from each disk were transversally sectioned with a sliding microtome and the stem cross sections were studied under a light microscope (Olympus BH-2) equipped with a photo-microadapter (Olympus OM-Mount) and a camera (Olympus OM101) for slide printing.

The position of the IADFs within the annual ring was precisely determined and they were classified according to that in: Type 1 (a) when the IADF was located at the beginning of the annual ring; Type II (b) when it was placed in the middle of the annual ring and Type III when it was formed at the end of the ring (Figure 1).



Fig. 1. Micro-photographs of wood cross sections of *A. unedo* showing different types of IADFs.

In addition to identification of IADFs, tree ring measurements were manually taken using a LINTAB linear table and a micrometer to a precision level of  $\pm$  0.001mm. The program COFECIA (Holmes 1983) was run to validate the crossdating and measurements and to find potential errors.

#### Quantitative wood anatomy

Quantitative wood anatomy was analyzed in 20 tree-rings per species, selecting both rings with Type-II IADFs and without fluctuations. Three transects per each ring were observed under a light microscope (BX 60, Olympus) equipped with a digital camera (CAMEDIA C4040, Olympus) and analysed with the AnalySIS® (Olympus) software. Several parameters were measured, including area, ECD (Equivalent Circle Diameter), maximum, mean and minimum Feret diameters, aspect ratio, elongation, sphericity, shape factor and convexity (De Micco and Aronne 2009). Data obtained from the three transects were pooled and included in graphs which were superimposed to the microphotographs to check the correspondence of possible trends in data with the position of the identified IADF.

#### Isotope measurement

The isotopic information was provided with the traditional method, distinguishing between earlywood, latewood and transition wood, after the cellulose extraction according to the methods described in Loader et al. (1997), and modified according to Battipaglia et al. (2008).  $\delta^{13}$ C was also measured by combustion in an elementalanalyser (Carlo Erba 1112 Flash EA) connected in continuous-flow mode to an isotope-ratio mass-spectrometer (MS-Delta-Plus, Finnigan, Bremen, Germany). Moreover, to address very narrow temporal windows, we used an isotoperatio-mass-spectrometer (Nd:YAG 266 nm UV Laser, Merchantek New Wave, Fremont, Calf. Coilped to Finnigan Delta+XL) as described in detail by Schulze et al. (2004). Profiles of  $\delta^{13}$ C were measured only on 3 trees per species and limited to the last 4 rings (2007-2004).

#### PRELIMINARY RESULTS

The figure 2 shows an example of the values of wood  $\delta^{13}$ C from different intra-annual sections (EW-earlywood), IADF and LW-latewood) in *A. unedo*. It is shown the seasonal  $\delta^{13}$ C pattern in

the growth rings (Helle and Schleser 2004) with the IADF wood isotopically the heaviest or the lightest according to the type of fluctuation.



The same  $\delta^{13}$ C pattern is evident in the figure 3 where the  $\delta^{13}$ C profile from laser ablation is synchronized with the rings boundary. The high resolution of the measurement allows the identification of the ring boundary and the quantification of the isotopic signals.



The figure 4 reports an example of a section of *E. arborea* showing a Type-II IADF: a graph showing the trend of vessel lumen size (area) is superimposed. A decrease of vessel lumen area occurs in correspondence with the IADF, suggesting that sudden drought regulated the formation of vessels resulting in narrower conduits We believe in a possible link between the position of IADF in the wood and climate, especially drought stress during vegetation period; this hypothesis will be tested in the future correlations of isotope and QWA data with precipitation and temperature information.

This work indicate that, although this multidisciplinary approach is still at an early stage of development and is time consuming, it deserves



Fig. 4. Vessel size in the IADF region reaches values similar to those in latewood.

to be further explored and developed since it shows potential for inferring drought impact at the intra-annual level.

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### Carbon isotopic studies on methane in polar ice cores as a clue to past methane sources

M. Behrens<sup>1</sup>, L. Möller<sup>1</sup>, H. Fischer<sup>2</sup>

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Am Alten Hafen 26, D-27568 Bremerhaven, Germany <sup>2</sup>Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland

Corresponding author: melanie.behrens@awi.de

Methane is recognised as an important greenhouse gas that contributes ~15 % to the current anthropogenic warming. With the help of isotopic analysis the contributions of different sources and sinks to the atmospheric burden can be estimated. Air enclosures in ice cores are the only direct paleoatmospheric archive and allow an assessment of natural changes of methane in the past. Ice core reconstructions of atmospheric methane concentrations show significant increases for both glacial/interglacial transitions as well as for rapid warming events (Dansgaard/Oeschger events). Due to the different carbon isotopic signature of different methane sources high-precision measurements of  $\delta^{13}CH_{A}$  in ice cores supply clues about the global methane cycle.

We developed a highly automated (continuous-flow) gas chromatography combustion isotope ratio mass spectrometry technique (GC/C/IRMS) for ice core samples of  $\sim 200$  g. The methane is melt-extracted using a purge and trap method, then separated from the main air constituents, combusted and measured as CO<sub>2</sub> by a conventional isotope ratio mass spectrometer. A CO<sub>2</sub> working standard, a  $CH_{4}$  and two air reference gases are used to identify potential sources of isotope fractionation within the entire sample preparation process and to enhance the stability, reproducibility and accuracy of the system. We show the performance of our set-up and data from the Antarctic EDML ice core.

#### Möglichkeiten der Hochtemperatur-Pyrolyse zur Stabil-Isotopen-Messung unter Einsatz von Temperaturen über 1600° C in Kombination mit der Siliciumcarbid-Einrohr-Technik

#### M. Boner<sup>1</sup>, P. Bliznakov

<sup>1</sup>TÜV-Rheinland Agroisolab GmbH, Karl-Heinz-Beckurt-Str. 13, 52428 Jülich

#### Corresponding author: m.boner@de.tuv.com

Die Hochtemperaturpyrolyse zur Messung der stabilen Isotope von Wasserstoff und Sauerstoff aus organischen und anorganischen Materialien ist in den letzten Jahren erheblich weiterentwickelt worden. Die Entwicklung reicht dabei von Einrohrtechniken bei niedrigen Arbeitstemperaturen bis zu 1300° C, über die Zweirohrtechnik mit einem Carbonrohr in Kombination mit einem Keramikrohr bis hin zum Einsatz hochinerter, sauerstofffreier Rohrmaterialien, vor allem Siliciumcarbidrohre, die bis heute bei Temperaturen von derzeit bis zu 1500° C verwendet werden.

Insbesondere der Einsatz von kovalent gebundenen Siliciumcarbidrohren in der HTPyrolyse eröffnet gute Möglichkeiten mit niedrigen Backgrounds die <sup>18</sup>O/<sup>16</sup>O und D/H Isotopenverhältnisse zu bestimmen.

Diese Siliciumcarbidrohre waren derzeit in ihrer Anwendung auf eine Temperatur von maximal 1500° C begrenzt. Dies war eine Einschränkung aufgrund der in der Länge limitierten Rohre, die es nicht ermöglichten, Hochtemperaturöfen mit Temperaturen oberhalb von 1500 °C einzusetzen.

Nun können deutlich kompaktere Hochtemperaturöfen zur Verfügung gestellt werden und ermöglichen die Durchführung von Pyrolysen bei bis zu 1600 °C. Im Vergleich der verschiedenen Temperaturintervalle von 1400 °C über 1500 °C bis zu 1600 °C zeigt sich, dass sich die Pyrolysequalität signifikant bei 1600 °C verbessert, so dass im Vergleich hohe Reproduzierbarkeiten der D/H und <sup>18</sup>O/<sup>16</sup>O Isotopenverhältnisse erreicht werden können. Dies gilt ebenfalls für organische Verbindungen, vor allem Proteine, die einen hohen Anteil von Stickstoff bzw. Schwefel enthalten. Durch die hohe Temperatur ist es ebenfalls denkbar, die D/H, <sup>15</sup>N/<sup>14</sup>N und <sup>18</sup>O/<sup>16</sup>O Isotopenverhältnisse von organischen Substanzen in einem Run zu vermessen.

Auch erzielen die hohen Temperaturen von 1600 °C neue Möglichkeiten, die Isotopenverhältnisse hochgeglühter, anorganischer Substanzen, z.B. Eisenoxid zu bestimmen, ohne dass Pyrolysezusätze in Form von Halogeniden genutzt werden müssen.

In der Summe erweist sich gerade die Kombination der hohen Temperatur von 1600 °C und der Siliciumcarbid-Einrohr-Technik als ein effektives Routineverfahren für große Probendurchsätze zur Bestimmung der Wasser und Sauerstoffisotopenverhältnisse.

### Isotope biogeochemistry of dissolved sulfate and sulfide in the water column and surface sediments of the Black Sea

M.E. Böttcher, O. Dellwig, T. Max

Leibniz Baltic Sea Research Institute, Seestr. 15, D-18119 Warnemünde

Corresponding author: michael.boettcher@io-warnemuende.de

The modern Black Sea offers the opportunity to study the fundamental processes in the sulfur cycle of natural euxinic systems. The Black Sea is the largest permanently euxinic system on Earth and provides, as a 'type system', the geochemical references for the interpretation of past marine anoxia preserved in the fossil sedimentary record. In the low-temperature sulfur cycle, sulfur and oxygen isotope discrimination have been found to be of particular value for evaluation of fundamental biogeochemical process mechanisms and rates.

We have analyzed the concentrations and stable sulfur isotope compositions of dissolved and solid sulfur species (sulfide, sulfate, FeS, CrII-reducible sulfur (S° and pyrite)) and the oxygen isotope composition of sulfate in the water column and Holocene surface sediments, recovered during Leg M72-5 of RV Meteor.

Results are compared to measurements from previous cruises. As a synthesis, we present the first data set for the sulfur isotope composition of sulfide for the complete (deep) Black Sea.

The magnitude of sulfur isotope discrimination between dissolved sulfate and sulfide in the anoxic water colum is close to 60 per mil that decreases in the upper part close to the pelagic redoxcline. Isotope discrimination is by far higher than observed in previous batch experiments with pure cultures of sulfate-reducing bacteria, indicating very low cellular activities probably dominated by strains, not isolated so far. The lowered overall isotope effect below the redoxcline accompanied by a steep gradient in dissolved sulfide is caused by the oxidation of dissolved sulfide at the redoxcline. Sulfur isotope discrimination in the water column is close to results from the surface sediments, indicating similar processes leading to the overall isotope discrimination. Disproportionation of sulfur intermediates may play a role close to the pelagic redox-cline but can be neglected in the surface sediments below anoxic bottom waters.

The oxygen isotope composition of dissolved sulfate below the redox-cline is enriched in the heavier isotope compared to open Ocean seawater. This indicates enhanced turnover in the sulfur system. In the sediments further <sup>18</sup>O enrichment is associated with net sulfate reduction and reaches isotope exchange equilibrium with pore water at higher depths.

## Seasonal impact of logworms (*Arenicola marina*) on biogeochemical processes and carbon isotope geochemistry of intertidal surface sediments: Results from an in-situ experiment

M.E. Böttcher<sup>1,2</sup>, A.M. Al-Raei<sup>1</sup>, M. Segl<sup>3</sup>, N. Volkenborn<sup>4</sup>

<sup>1</sup>Max Planck Institute for Marine Microbiology, Bremen, Germany
 <sup>2</sup>Leibniz Institute for Baltic Sea Research, Warnemünde, Germany
 <sup>3</sup>RCOM Center and Geoscience Department, Bremen University, Germany
 <sup>4</sup>AWI, Wadden Sea Research Station, Sylt, Germany

Corresponding author: michael.boettcher@io-warnemuende.de

Organic matter (OM) is mineralized in marine intertidal sediments by microbial activity using oxygen, sulfate, and metal oxides as major electron acceptors. The oxidation produces carbon dioxide that is a strong green-house gas and may be liberated from the sediments into the overlying water and the atmosphere. OM mineralization in the intertidal zone may be influenced by the activity of bottom dwelling organisms, as the lugworm Arenicola marina, causing bioturbation and bioirrigation of sediments. The isotopic composition of dissolved inorganic carbon (DIC) is a useful tracer for biogeochemical transformation of different carbon sources and was used in this study to identify the key reactions in the carbon-sulfur cycle of intertidal surface sediments. Variations in biogeochemical processes (e.g., sulfate reduction rates, pore water accumulation of metabolites and nutrients) and the carbon isotopic composition of DIC were measured in an intertidal area of Königshafen (Sylt island, North Sea) at lugworm-inhabited control sites and 'exclusion' sites that were free from lugworm activity due to the in-situ introduction of a 1mm mesh net at 10 cm depth on areas of 400 m<sup>2</sup> (Volkenborn & Reise, 2007).

Pore waters from experimental plots were sampled in the top 10 cmbsf (exclusion sites) and 20 cmbsf (control sites) using pore water lances. Water and sediment samples were analyzed for a number of (bio)geochemical parameters such as grain sizes distribution, temperature, TOC, TIC, DIC, microbial sulfate reduction rates, salinity, pH, sulfate, sulfide, pyrite, AVS, reactive Fe\* and Mn\*, and the carbon isotopic composition of DIC. Analytical methods include radio tracer incubation, ion chromatography, spectrophotometry, ion-selective electrodes, extraction and titration methods, and C-irmMS.

In the surface sediment, OM was mainly oxidized by oxygen and sulfate reduction (de Beer et al., 2005; Al-Raei et al., 2009, in prep.). Highest sulfate reduction rates were found in the top 10 cm and during summer time. No effects of lugworm presence/absence on SRR was detected. Correspondingly, enhanced accumulation of DIC and light carbon isotope signatures in DIC were found during summer months (down to -5.5 per mil vs. V-PDB). Due to the reduced exchange of pore waters with bottom waters, DIC at the exclusion sites was isotopically enriched in C-12 compared to the control sites.

Acknowledgements: The research is supported by Max-Planck Society, Leibniz IO Warnemünde, Sylt Wadden Sea Station, and partly by Deutsche Forschungsgemeinschaft (JO 307/4-2; BO 1584/4-3).

#### Stable isotope and trace element partitioning in a recent carbonateprecipitating stream, Rügen Island

J. Bünning<sup>1</sup>, V. Winde<sup>1</sup>, O. Dellwig<sup>1</sup>, U. Struck<sup>2</sup>, N. Kowalski<sup>1</sup>, M. Labrenz<sup>1</sup>, M.E. Böttcher<sup>1</sup>

<sup>1</sup>Leibniz Baltic Sea Research Institute, Seestr.15, 18119 Warnemünde <sup>2</sup>Museum für Naturkunde, Berlin

Corresponding author: michael.boettcher@io-warnemuende.de

Processes in the carbonate system at the surface of the temperate climate zone are in particular sensitive to variations as soil activity, humidity, temperature etc. associated with climate change. Calcium carbonate-saturated ground waters that emerge from springs may lose dissolved carbon dioxide to the atmosphere due to degassing. This leads to supersaturation of the aqueous solution with respect to several carbonates, including calcite. Stable isotope and trace element fractionation are of particular value to link these non-equilibrium processes to the formation mechanisms of calcite and the hydrodynamics of flowing streams. These are influenced by the ground water formation rate, temperature, and the CO<sub>2</sub> partial pressure of the atmosphere.

An example linking the past and present terrestrial and marine carbon cycles is found at the cliff coast line of Rügen Island, Baltic Sea: Fossil marine calcium carbonate that forms the cliffs, is nowadays dissolved on the Island by CO<sub>2</sub>-loaded soil solutions reaching saturation with respect to calcite in the water-saturated zone. When these ground waters emerge as springs, their dissolved carbonate system is in dis-equilibrium with respect to the recent Earth atmosphere. By following the chemical changes downstream it is found, that two regions of stream water evolution can be differentiated: After an induction period, where only CO<sub>2</sub>-degassing takes place, a second stage is observed where calcite begins to form from the highly supersaturated solutions. In this stage the carbonate system of the stream water is controlled by both, degassing and carbonate precipitation. At the bottom of the cliff, the carbonate stream water is finally entering the Baltic Sea mixing with the brackish coastal waters.

In the present study, trace element and stable isotope (C, O) isotope fractionation was followed in several carbonate-precipitating streams. Major, minor and trace element concentrations and  $\delta^{13}$ C and  $\delta^{18}$ O values of carbonate solids and aqueous solutions where analyzed as a function of the flow path. In addition, marine and older travertine carbonate samples were analyzed for a comparison with recent precipitates.

Sr<sup>2+</sup> and Mg<sup>2+</sup> were found to be depleted in the newly formed calcite compared to the aqueous solution. The partition coefficients are larger than previous experimental close-to-equilibrium calibrations and indicate relatively fast calcite precipitation rates. The spring carbon isotopic composition indicates ground water evolution under conditions, essentially closed with respect to a carbon dioxide gas phase. The  $\delta^{13}C$ values of DIC increased along the flow path, due to preferential degassing of <sup>12</sup>CO<sub>2</sub>. Travertin samples displayed a slight enrichment in <sup>13</sup>C compared to the solution which is consistent with experimental and theoretical studies. Some seasonality in the composition of the spring waters carbonate system as well as the degassing efficiency from the stream waters, however, can not be completely ruled out and require further investigations. Finally, the  $\delta^{18}O$ values preserved in the carbonates indicate influence of precipitation kinetics.

#### Oxygen isotopes of biogenic silica – calibration studies for using a remotely-operated laser-fluorination based mass spectrometry unit and new methods for removing the hydrous layer

B. Chapligin<sup>1</sup>, H. Meyer<sup>1</sup>, H. Friedrichsen<sup>2</sup>, H.-W. Hubberten<sup>1</sup>

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Research Unit Potsdam, Telegrafenberg A43, D-14473 Potsdam, Germany <sup>2</sup>MS-Analysentechnik, Aßmannshauser Str.12, D-14197 Berlin, Germany

Corresponding author: Bernhard.chapligin@awi.de

The analysis of oxygen isotopes from diatom silica in sediment cores has obtained importance for reconstructing the palaeoclimate and is especially valuable in noncarbonated lakes of cold regions, or in deeper oceans where no other bioindicators are available. A new approach for samples in the sub-mg range has been developed to provide a better chronological resolution and to expand the method to periods where little biogenic silica is available.

After extracting the diatoms from sediment cores with various preparation steps including wet chemistry, sieving and heavy liquid separation, a minimum of 700 µg fine material from 5 g of wet sample is obtained and the degree of purity assessed.

As diatoms consist of an isotopically homogenous inner Si-O-Si layer and a less dense, hydrous layer forming Si-OH bonds, this layer has to be removed from the sample prior to analysis. Three methods have been accepted so far to perform this step: Controlled Isotopic Exchange (CIE) followed by fluorination, Stepwise Fluorination (SWF) and inductive High-Temperature carbon reduction (iHTR). The former method of vacuum dehydration (VD) proved to be unable to remove all exchangeable oxygen.

CIE is both time-consuming and work-intense, SWF is impractical for this setup due to the high pressure increase during dehydration. Therefore, a new, efficient and fast method was developed to remove the hydrous layer before using the laser-fluorination process.

Two approaches were tested to remove the Si-OH layer and the impact on  $\delta^{\rm 18}O_{\rm si}$  was assessed by performing tests on internal standard materials of marine and lacustrine biogenic silica and of quartz. For vacuum bead melting (VBM), a minimum of 1.5 mg of pure sample is melted to a bead with a defocused laser to eliminate the hydrous outer layer and to reduce the surface. After the bead has formed it is transferred into the reaction chamber to be completely reacted with a focused laser under BrF<sub>5</sub> atmosphere and subsequently analysed on-line.

The second method, Helium flow dehydration (HFD) is an improvement of the outdated VD technique. The sample is heated to 1050°C in a He flow transporting away any removed exchangeable oxygen immediately and thus, not allowing it to re-react with the sample.

A remotely-operated laser-fluorination based mass spectrometry unit is used for the analysis.



Fig. 1. To prepare, the sample is heated at 1050°C under a He flow to remove the Si-OH layer by Helium Flow Dehadration (HFD). Through the use of a CO<sub>2</sub> laser, the sample is vaporized and under BrF<sub>5</sub>, the O<sub>2</sub> is released and the non-oxygen gas is trapped in the cold trap. The oxygen is transported to the molecular sieve. It is then transferred to the mass spectrometer for isotope measurement.

The silica is reacted with a  $CO_2$  laser in a BrF<sub>5</sub> atmosphere and oxygen is then transferred to and analysed in a mass spectrometer. The non-oxygen gas components are trapped in a -150°C cold trap, whereas oxygen passes on to a molecular sieve and is subsequently transferred to a PDZ Europa 20-20 for the analysis. Specially designed software and a video camera are used to survey and record the process in the reaction chamber, allowing an automised, remote operation. This guarantees maximum safety as the mass spectrometer is installed in a room separated from the reagent (BrF<sub>5</sub>), the

reaction chamber, and the laser unit arranged under a hood. The fluorination periphery is directly coupled to the mass spectrometer, making an online analysis possible.

VBM has difficulties to fully remove the hydrous layer, which results in comparatively low  $\delta^{18}$ O values. The HFD generated similar data than SWF in other labs with a high repeatability and accuracy (standard deviation <0.2 ‰). An inter-laboratory comparison is running right now. It will compare all existing methods for removing the hydrous layer and reference new, so far internal, biogenic standards.

#### Stable oxygen and carbon isotope data of detrital carbonates in annually laminated sediment from Lake Ammersee (Southern Germany) as a proxy for flood events

M. Czymzik<sup>1</sup>, A. Brauer<sup>1</sup>, B. Plessen<sup>1</sup>, P. Dulski<sup>1</sup>, U. von Grafenstein<sup>2</sup>

<sup>1</sup>GFZ German Research Centre for Geosciences, Section 5.2 Climate Dynamics and Landscape Evolution, Telegrafenberg, 14473 Potsdam, Germany

<sup>2</sup>Laboratoire des Sciences du Climat et de l'Environnement, UMR CEA-CNRS, Orme des Mersiers, 91191 Gif-sur-Yvette, France

Corresponding author: czymzik@gfz-potsdam.de

Lakes as sediment traps within the landscape accumulate continuous long-term records of climate and environmental change in their catchment. Especially from annually laminated lake sediment records detailed seasonal information can be obtained. Flood triggered short-term sediment fluxes of catchment derived detrital (carbonate) material into the lake result in event layers which can be dated by their microstratigraphic position within a varve with seasonal precision. Detrital contamination is a well-known bias in stable carbon ( $\delta^{13}$ C) and oxygen ( $\delta^{18}$ O) isotope data from lake sediments. This case study aims on using this effect for the reconstruction of a flood time series.

Therefore, we combined stable  $\delta^{13}$ C and  $\delta^{18}$ O analyses on bulk carbonate samples with micro-facies analyses and high-resolution element scanning ( $\mu$ -XRF) for the examination of two short varved sediment cores from Lake Ammersee (Southern Germany) covering the last 450 years. The non-detrital annual varve

structure in Lake Ammersee consisting of calcite/organic layer couplets makes this record an ideal archive for deciphering detrital carbonate contamination from the climate controlled isotope signal deduced from endogenic precipitated carbonates.

We identified peaks of distinct heavier  $\delta^{13}$ C and  $\delta^{18}$ O isotope values in samples containing detrital material coinciding with detrital microfacies (layers) and positive excursions of detrital element data, all supporting the interpretation of these layers as flood triggered. This interpretation is further strengthened by (1) the proximal-distal pattern of flood layer thickness indicating the main tributary River Ammer as source of the detrital material and (2) the agreement of our flood record with measured Ammer runoff and local precipitation data.

#### Stable water isotope characteristics of the recent hydrological system of the northern antarctic peninsula - implications for ice and firn core interpretation

F. Fernandoy<sup>1</sup>, H. Meyer<sup>1</sup>, C. Olivares<sup>2</sup> and M. Cartró<sup>3</sup>

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Potsdam Germany (AWI) <sup>2</sup>Antarctic Department of the Chilean Army (DAE) <sup>3</sup>Sciences Faculty, Autonomous University of Barcelona, Spain

Corrsponding author: Francisco.Fernandoy@awi.de

The Antarctic ice-sheet represents the biggest reservoir of fresh water in the world, covering an area of more than 13 million km<sup>2</sup>. The stability of ice shelves around Antarctica reacts faster to the climatic change than previously believed. In Antarctica several nations are presently carrying-out climatic monitoring programs. However, these observations comprehend a restricted temporal (50 years) and geographical distribution. Based on geochemical analysis, ice-cores have been used to extend the meteorological data available into the past. Water (ice) stable isotope composition is mainly linked to mean annual air temperature (MAAT) and sea surface conditions, but the interpretation of the isotope composition variations requires a detailed characterization of local and regional hydrological conditions. Here, we focus on the north of the Antarctic Peninsula region, where a lack of glaciological and geochemical information of snow and ice exits. A drilling of a medium-depth icecore is planned.

In this work stable isotope data of samples collected during the last summer campaign in Antarctica and over the year in 2008 are presented, including snow pits, shallow firn cores and precipitation samples retrieved near by the Chilean Antarctic O'Higgins Station (OH) (63°19'15''S, 57°53'57''W) and on King George Island (KGI), South Shetlands (62°02'S, 58°21'W). All samples were analyzed at AWI facilities (Potsdam) by mass spectrometry using the gas equilibration technique and a Finnigan-MAT Delta S spectrometer, as described in Meyer et al. (2000).

Both sample areas display small differences in MAAT (-1.1°C for KGI and -2.6°C for OH in 2008), also reflected in the stable isotope data of both data sets. Various isotope (such as seasonal, altitude and latitude) effects are visible in our data. An altitude effect was detected for the snow pits recovered from the KGI ice cap (FP-SP 1 - 700 m a.s.l. and FP-SP 2 - 400 m. a.s.l) with an isotope gradient of -0.3‰/100 m. This effect is only found above 400 m and not visible in the OH data so far. Mean  $\delta^{18}$ O of OH precipitation (taken at sea level) is with -9.6‰ similar to snow pit data at 400 m a.s.l.. Comparing FP and OH snow pits (at 400 m a.s.l.), a negative isotope gradient can be observed in southward direction. The potential moisture sources were investigated running a backward trajectory analysis. For this purpose, the atmospheric circulation model Hysplit from NOAA was used. The most common paths (98% of the trajectories) approach the South Shetlands Islands and the Antarctic Peninsula from the South Western Pacific, with year-round relatively stable conditions, most probably representing the main moisture source for this region. Local meteoric water lines (LMWL) are similar for both sites (OH:  $\delta D=7.8*\delta^{18}O+0.7\%$  and KGI:  $\delta D=7.7^*\delta^{18}O=0.6\%$ ), which reinforces the assumption of common evaporation/condensation conditions in the whole region, slightly deviating from the Global MWL ( $\delta D=8*\delta^{18}O+10\%$ ). In spite of evident melting processes in the firn/ ice column of both regions, OH shows the most suitable conditions, to recover an ice core in future, since the annual isotopic signal from snow pits and firn core is well preserved here.

### Possible absence of lipid <sup>13</sup>C depletion in sterols and steroids from eukaryotes

U. Flenker<sup>1</sup>, B. Linster, V. Gougoulidis<sup>1</sup>, F. Hülsemann<sup>2</sup>, W. Schänzer<sup>1,3</sup>

<sup>1</sup>Deutsche Sporthochschule Köln, Manfred-Donike-Institut für Dopinganalytik

<sup>2</sup>Deutsche Sporthochschule Köln, Momentum – Deutsches Forschungszentrum für Leistungssport <sup>3</sup>Deutsche Sporthochschule Köln, Institut für Biochemie

Corresponding author: u.flenker@biochem.dshs-koeln.de

In a variety of organisms it can be observed that lipids are significantly depleted in <sup>13</sup>C vs. total biomass. This phenomenon has been attributed to isotope effects during the decarboxylation of pyruvate. This metabolic step yields acetyl-CoA, the universal precursor of lipids, including isprenoids such as sterols and steroids.

By contrast, in the human, urinary steroids exhibit  ${\rm ^{13}C/^{12}C}$  ratios close to those of the total diet ( $\delta^{13}C_{_{VPDB}}$  ca. -18‰ to -25‰, depending on dietary C-4 plant proportion). At the same time, plasma free fatty acids show the familiar pattern and are significantly depleted in  ${\rm ^{13}C}$ . Practically, this steroid isotope anomaly is the basis for the detection of lilicit administration of synthetic steroids in sports. The latter significantly fall below the abovementioned  $\delta^{13}C_{_{VPDB}}$  values of natural hormones.

Baker's yeast (*Saccharomyces cervisiae*) was employed as model organism to investigate stable carbon isotopes during biosynthesis of lipids. *S. cerevisiae* is an eukaryotic organism and features lipid pathways similar to those of mammals. In particular, sterols were investigated. Steroid hormones biochemically are immediately derived from cholesterol, the most important sterol in animals. S. cerevisiae was grown under controlled conditions where glucose ( $\delta^{13}C_{VPDB}$  ca. -12.4‰) was the only source of carbon. Consistent with the well known trophical shift, total biomass as well as sterols initially exhibited  $\delta^{13}C_{VPDB}$  values slightly larger than those of the glucose (ca. -10.5‰). Following the exponential growth phase, sterols became slightly but significantly depleted in <sup>13</sup>C. Total biomass exhibited an opposite trend. Fatty acids obtained from sterol esters exhibited  $\delta^{13}C_{VPDB}$  values around -27‰ and thus showed a very pronounced <sup>13</sup>C depletion.

These observations possibly rule out the decarboxylation of pyruvate as an explanation for the <sup>13</sup>C depletion of lipids. Otherwise comparable values should be observed for fatty acids and sterols. Our results rather suggest a mechanism which is associated mostly with the biosynthesis of fatty acids. This at least may apply to eukaryotes where pyruvate decarboxylation is performed within the mitochondria. Complete pyruvate conversion within this compartment will prevent observable isotope fractionation even if a corresponding isotope effect is present mechanistically.

### Uptake of dissolved organic nitrogen of plankton communities in the Baltic Sea

C. Frey<sup>1</sup>, C. Fellerhoff<sup>1</sup>, F. Korth<sup>1</sup>, I. Liskow<sup>1</sup>, M. Voß<sup>1</sup>

<sup>1</sup>Baltic Sea Research Institute-Warnemuende (IOW), Rostock, Germany

Corresponding author: claudia.frey@io-warnemuende.de

The anthropogenic production of combined nitrogen nowadays exceeds the natural production and has led to eutrophication in aquatic ecosystems (Vitousek et al., 1997; Gruber and Galloway, 2008) with drastic negative effects like increasing hypoxia (Diaz and Rosenberg 2008). Nevertheless nitrogen is a limiting factor of productivity in marine environments. Nitrogen in the marine environment exists in particulate (PN) and dissolved forms (DN). The dissolved pool consists of inorganic (DIN; NH<sup>+</sup>, NO<sup>-</sup> and NO<sub>2</sub><sup>-</sup>) and organic nitrogen (DON). Dissolved organic nitrogen is divided into a low molecular fraction (<1kD) consisting of i.e. urea, dissolved free amino acids and a high molecular fraction (>1kD) including proteins, dissolved combined amino acids and humic substances (Bermann et al., 2003). The concentrations of DON exceed DIN concentration by a multiple (Bermann et al., 2003).

The role of DON for the nutrition of bacteria, or as an N- and P- Source for autotrophs in aquatic ecosystems is not yet well understood. Conventionally research on N uptake focused on dissolved inorganic nitrogen while organic nitrogen was usually ignored as a potential N source. However, studies on DON uptake and turnover by autotrophy and heterotrophs over the last years show that dissolved organic nitrogen is an important N source for many different aquatic organisms (Antia et al., 1991; Bronk, 2002; Zehr et al., 2002; Berman et al., 2003).

In the Baltic Sea DON occurs in high concentrations. Since the drainage area with a population of 85 million people, is four times larger than the sea surface (400.000km<sup>2</sup>) the Baltic Sea receives high amounts of fresh water and nitrogen loads originating from human activities but also from natural sources. The nutrient loads have tripled since the 1970s and 80s (Nausch et al., 1999) and since then stayed rather constant in the open sea part, but further increased in coastal waters (Voss et al. 2005, HELCOM 2009). The input today is approximately one million tons N per year. The average amount of DON can be up to 70% with concentrations varying between 14 and 20µmol/I (Feistel et al 2008). The main sources of DON are riverine inputs (Stepanauskas et al. 1999) which is reflected in higher DON concentrations close to estuaries and within coastal areas.

So far there have only been a few studies in the Baltic Sea quantifying the importance of DON as a potential source of N (Poder et al. 1999; Stepanauskas et al., 1999; Veuger et al., 2004). Some have shown that the uptake of urea by phytoplankton exceeds the uptake of bacteria (Cho et al., 1996; Lomas et al., 2002) and others, like Tamminen et al. (1996) demonstrated a higher uptake rate of urea for bacteria compared to phytoplankton in the Gulf of Finland. The latter findings are consistent with a study of Jørgensen et al. (1999) who found higher uptake rates for phytoplankton off the Danish coast.

Bacteria are still assumed to be the main consumer of DFAA. However, researches found phytoplankton to possess cell-surface enzymes (Mullholland et al., 1998), that enable them to take up DFAA, thus DFAA consequently contributes to plankton nutrition as well (Bronk et al., 2007).

In this study the DON concentrations and uptake rates of labile DON compounds (urea and DFAA) in estuarine, coastal and open waters of the Baltic Sea were investigated by means of stable isotope experiments with <sup>15</sup>N as tracer. We want to gain a sound understanding of the role of DON as a nutrient source in different plankton communities. We therefore examined the uptake of urea and DFAA into different size fractions to quantify under which conditions uptake is dominated by bacteria or phytoplankton. In short-term uptake experiments <sup>15</sup>N-labelled
urea and a <sup>15</sup>N-labelled algal derived amino acid mix were added to the water collected at different sites; in the open Baltic Sea, the Warnow River and at a coastal time series station Heiligendamm. Experiments were terminated by size fractionated filtration. First results show that DON concentrations are 2 fold higher in the Warnow River (48.61 +/-5.68 µmol/l) compared to the open Baltic (23.3 +/-3.35 µmol/l). However, in the open Baltic DON contributes 79% of total nitrogen where as in the Warnow River DON contributes only 57% to total nitrogen. The concentration of DON of the coastal station (21.8 +/-4.43 µmol/l) as well as the contribution to the total nitrogen pool (75%) are within the range of the open Baltic.

In conclusion DON seems to make a significant contribution to primary production. A management of DIN input for the Baltic Sea has been established by HELCOM (HELCOM, 2005), but DON remains to be considered in loading budgets.

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## A method for the simultaneous analysis of DIC concentration and carbon isotopic composition in continuous flow mode

R. van Geldern<sup>1</sup>, V. Becker<sup>1</sup> and A. Myrttinen<sup>1</sup> and J.A.C. Barth<sup>1</sup>

<sup>1</sup>Geozentrum Nordbayern, University of Erlangen-Nuremberg, 91054 Erlangen

Corresponding author: robert.van.geldern@uni-erlangen.de

Over the last decades several methods for the quantitative analysis of dissolved inorganic carbon (DIC) in water samples and the carbon stable isotope composition  $\delta^{13}C_{(DIC)}$  were published (for a review see e.g. Atekwana and Krishnamurthy, 2004). Some of these methods require dual inlet mass spectrometry with off line samples preparation while other need a special instrument set up for online measurements (e.g. St. Jean, 2003). We invented a method for the simultaneous determination of the DIC concentration and carbon isotopic composition using a standard CF-IRMS setup with a Gasbench II coupled to Delta *plus*XP mass spectrometer.

The motivation for this method arose from sampling campaigns for formation water in the CLEAN (www.clean-altmark.org) and CO<sub>2</sub>SINK (www.co2sink.org) projects. Due to technical reasons and limited sample amounts the planned in-situ titration could not be carried out. The water samples were filled directly into gas bags to avoid contact with the atmosphere and were stabilized with HgCl<sub>2</sub> for the subsequent stable isotope analysis. However, no quantitative DIC information was available at this stage.

Since the area of the sample peaks in a chromatogram from a CF-IRMS analysis is directly proportional to the  $CO_2$  generated by the reaction of the water with  $H_3PO_4$ , this information can be used to determine the DIC concentration in the sample. We prepared a set of standards with known DIC content by mixing  $Na_2CO_3$  with DIC free water. The concentration ranged from 200 to 3500 micromol C liter<sup>-1</sup>. This "calibration set" was included in every sequence analyzed with the Gasbench CF-IRMS system. The standards were treated in the same way as the samples. For accurate determination the exact amount of water in the vial and the density of the sample need to be known. This requires weighing of each vial before and after injection of the water sample. This method allows analyzing samples with highly different DIC concentrations since the required signal height for the stable isotope analysis can be adjusted by the sample amount.

Reproducibility and accuracy of the quantitative analysis of the dissolved inorganic carbon were checked by independent control standards, treated as samples.

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# Can $\delta^{13}$ C Values serve as an early indictor for drought tolerance of potato genotypes?

A. Giesemann<sup>1</sup>, C. Balko<sup>2</sup>

<sup>1</sup>Johann Heinrich von Thünen-Institut (vTI), Institut für Agrarrelevante Klimaforschung, Bundesallee 50, 38116 Braunschweig

<sup>2</sup>Julius Kühn Institut (JKI), Institut für Resistenzforschung und Stresstoleranz, R.-Schick-Platz 3, 18190 Groß Lüsewitz

Corresponding author: anette.giesemann@vti.bund.de

With regard to the climate change, the occurrence of drought periods will probably increase even in Middle Europe. Hence agricultural crops have to cope with water shortage. New cultivars which are adapted to such drought stress conditions are necessary and breeding is one approach to find such drought tolerant plants.

In order to easily characterise breeding relevant genotypes indirect selection criteria which are easily accessible at early developmental stages are desirable and need to be looked for.

The potato belongs to the crops responding relatively sensitive to drought stress. Different potato genotypes are available, characterized as either drought tolerant, or drought sensitive. One important physiological character of crop plants with regard to drought stress is their water use efficiency (WUE), for which the  $\delta^{13}$ C value is an integrative measure as the C isotopic composition of plants is different under different water regimes. The C isotopic composition integrates the concentration of CO<sub>2</sub> in the intercellular spaces over the time of tissue formation. Under sufficient water supply, stomata are wide open. Gas exchange is ensured and <sup>13</sup>C discrimination is high. Following drought stress conditions, stomata are (more or less) closed and the discrimination against <sup>13</sup>C is reduced.

Our aim was to find out the response of the C isotopic discrimination in various parts of the potato plant (leaves, stem, stolons, tuber, roots) under drought stress after different cultivation times after onset of the water stress in order to determine which plant part harvested at which time of growth can be used best to forecast their drought stress response.

Different potato genotypes (Desiree – drought tolerant; Katahdin - drought tolerant; Alegria

 assumed to be tolerant to drought; Norchip
 assumed not to be tolerant to drought; Pirol
 sensitive to drought) were grown until final harvest. Water consumption, yield, WUE and C isotopic composition of above ground biomass were analyzed.

As assumed, water use efficiency and  $\delta^{13}$ C values differed between the potato genotypes even under well watered conditions. Katahdin was the most efficient genotype with respect to WUE. The C isotopic composition changed with all genotypes under drought conditions. Katahdin showed a high shift in  $\delta^{13}$ C value.

Correlation of WUE and  $\delta^{13}$ C values under drought conditions was high (r = 0.76) showing that Katahdin gives the best WUE at the highest C isotope fractionation and hence was used for the experiment to find out which part of the plant could be used as early as possible to forecast good drought tolerance.

The C isotopic composition of the potato plant tissue (leaflets, stipes, internods) changed with plant growth. Under well watered conditions, the  $\delta^{13}$ C values shift by and by from about -27.5 ‰ in the oldest leaves to a minimum of -30‰ in about leaves No 15 (counted from bottom to top of the plant) followed by a turn to more positive values. Under drought stress conditions, a shift towards less negative  $\delta^{13}$ C values became obvious (about -27.5‰ to a maximum of -26.5‰). All plant compartments under evaluation showed a similar trend with time. Tubers, stolons, flowers, berries and the corresponding stipes reacted likewise. Differences became more obvious after 4 and 6 weeks of cultivation after onset of water stress.

A correlation of plant dry weight and  $\delta^{13}$ C values showed that the water stress reduced dry weight while  $\delta^{13}$ C values became more positive.

The adaptation to water stress is expressed as a reduction in water consumption which also went along with a shift in  $\delta^{13}$ C values and a better WUE under drought stress is confirmed by the positive correlation of WUE and  $\delta^{13}$ C values.

Fig. 1 shows the  $\delta^{13}$ C values of all leaves present at Katahdin plants either under well watered conditions or water stress after six weeks of cultivation from the onset of the stress treatment. As many as 20 leaves had been developed within four weeks after the onset of the stress.

Our results point out that a young, fully grown leaves harvested four weeks after onset of cultivation under drought stress (leaves numbers 18 to 20) seemed to serve best to forecast drought tolerance using the  $\delta^{13}$ C values of potato leaves (at least in the genotype Katahdin).



C isotopic composition of potato leaves (cv Katahdin) harvested six weeks after onset of water stress

# Schnelle und präzise Bestimmung der Isotopenverhältnisse pflanzlicher Methoxygruppen - Methode und Anwendung

<u>M. Greule<sup>1</sup></u>, F. Keppler<sup>1</sup>

<sup>1</sup>Max-Planck-Institut für Chemie, Joh.-Joachim-Becher-Weg 27, D-55128 Mainz, Deutschland

Corresponding author: m.greule@mpic.de

Bei der Bestimmung von Isotopenverhältnissen wird bisher meist die Gesamtheit eines Elements innerhalb eines Moleküls erfasst. Der konsequente, nächste Schritt ist, die Stabilisotopenverhältnisse einzelner Atome aus einem betreffenden Molekül zu bestimmen. Auf einfache Weise ist dies mit Methoxygruppen durchführbar, die sich mittels Iodwasserstoffsäure (HI) abspalten lassen. Diese von Zeisel entwickelte Methode (1) führt zu gasförmigem Jodmethan (CH<sub>3</sub>I), welches dann mittels GC-IRMS auf die <sup>13</sup>C/<sup>12</sup>C- und <sup>2</sup>H/<sup>1</sup>H-Isotopenverhältnisse untersucht werden kann (Abbildung 1).



Abb. 1. Abspaltung von Methoxygruppen mittels HI nach der "Zeisel-Methode"

Unter Anwendung dieser Methode konnten Keppler et al. (2) bereits zeigen, dass pflanzliche Methoxygruppen, wie sie vor allem in Pektin und Lignin vorkommen (Abbildung 2), relativ zur Gesamtbiomasse deutlich abgereicherte  $\delta^{13}$ C-Werte aufweisen.



Abb. 2. Beispiele von Molekülen pflanzlichen Ursprungs mit Methoxygruppen. Pflanzliche Methoxygruppen stellen auch eine Quelle für klimarelevante C1-Spurengase wie Methan und dessen Halogenide dar. Studien anhand der Isotopensignatur der Methoxygruppen können hierbei wichtige Informationen über Bildung, Quellen und emittierte Mengen dieser Gase liefern.

Die chemische Struktur der Methoxygruppe gewährleistet, dass deren Wasserstoffatome nicht mit anderen Protonen austauschen, auch nicht während der Reaktion mit HI zu Jodmethan. Die Analyse der  $\delta^2$ H-Werte lässt somit Rückschlüsse auf die Isotopensignatur zum Zeitpunkt der Biosynthese der jeweiligen Methoxygruppe zu, dies erlaubt z.B. Klimastudien an Baum-Jahresringen. Zudem kann mittels Isotopenanalyse pflanzlicher Methoxygruppen Herkunftsanalytik betrieben werden, indem man sich die global unterschiedlichen Muster der stabilen Wasserstoffisotope im Niederschlag zunutze macht.

Vorraussetzung ist allerdings eine detaillierte Validierung der Methode, um Isotopendiskriminierungen während der Aufarbeitung und Analyse auszuschließen; die hierzu durchgeführten Messungen und deren Ergebnisse werden vorgestellt (3, 4). Zudem werden anhand von Messungen an Baumbohrkernen sowie Analysen zur Authentizitätsbewertung von Vanillin die Potentiale der Methode veranschaulicht.

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### Mathematisch-Statistische Aspekte bei der Erstellung von langjährigen Isotopenchronologien aus zeitlich unterschiedlich aufgelösten Sequenzen von Baumjahrringen am Beispiel einer *Pinus Sylvestris*-Chronologie (Halbinsel Kola, NW-Russland)

M. Haupt<sup>1</sup>, T. Böttger<sup>1</sup>, M. Friedrich<sup>2,3</sup>, Y. Kononov<sup>4</sup>

<sup>1</sup>Helmholtz Zentrum für Umweltforschung - UFZ, Theodor-Lieser-Str. 4, D-06120 Halle (Saale)
 <sup>2</sup>Institut für Botanik, Universität Hohenheim, D-70593 Stuttgart
 <sup>3</sup>Heidelberger Akademie der Wissenschaften, Karlstraße 4, D-69117 Heidelberg
 <sup>4</sup>Institut für Geografie, RAS, Moscow, 29 Staromonetny per, Moscow 119017, Russia

Corresponding author: marika.haupt@ufz.de

Ein Ziel des EU-Projektes MILLENNIUM\* ist die Erstellung 1000-jähriger Isotopendendrochronologien ( $\delta^{13}$ C;  $\delta^{18}$ O) aus der Jahrringzellulose von Kiefern (*Pinus sylvestris*), gewachsen im Chibin- Gebirge der Halbinsel Kola (NW Russland), und die daraus ermittelte Rekonstruktion klimatischer Verhältnisse in jährlicher Auflösung.

Die in dieser Region wachsenden Bäume sind durch sehr enge Jahrringe gekennzeichnet, sodass häufig die Abtrennung einzelner Ringe für die Isotopenanalyse nicht möglich ist, oder keine für die Zellulosepräparation ausreichende Menge Holz aus jährlich geschnittenen Proben gewonnen werden kann. Folglich kann die Belegung der Chronologie mit jährlich aufgelösten Proben, die ein EPS>0.85 (Expressed Population Signal; Briffa und Jones, 1992) zeigen, nicht gewährleistet werden.

Eine neue Methode nutzt versetzte Serien von 5-Jahres-Blöcken, sodass eine Isotopenchronologie entsteht, welche dem gleitenden 5-Jahres-Mittel der jährlich gemessenen Proben entspricht (Böttger und Friedrich, 2009). In Perioden, wo sowohl Datenreihen von in 5-Jahres-Blöcken als auch von jährlich geschnittenen Baumjahrringen vorliegen, ist der Verlauf der mittleren  $\delta^{13}$ C- und  $\delta^{18}$ O-Kurven, bei verringerter Varianz in 5-Jahres-Blöcken, sehr



Abb. 1. Die mittleren (A) δ<sup>13</sup>C- und (B) δ<sup>18</sup>O- Chronologien (*Pinus sylvestris*, Halbinsel Kola) für den Zeitraum 1755 bis 2005 gemessen in Jahrringzellulose von 13 Bäumen in jährlicher Auflösung (A1, B1) und von 11 Bäumen in 5-Jahres-Blöcken (A2, B2).

ähnlich (Abb.1). Die Berechnung der Korrelation zwischen zeitlich unterschiedlich aufgelösten Serien zur Ermittlung des EPS-Wertes stellt jedoch ein neues, spezielles Problem dar. Verschiedene Ansätze zur mathematisch-statistischen Behandlung inhomogener Isotopendatenreihen werden kritisch diskutiert.

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\* European climate of the last millennium (MILLEN-NIUM, 017008).

### Advances in automated multi-isotopic fingerprint analysis using Thermo Scientific Elemental Analyzers

D. Hatscher, O. Kracht, A. Hilkert, J. Schwieters

Thermo Fisher Scientific (Bremen) GmbH, Hanna-Kunath-Str. 11, 28199 Bremen, Germany

Corresponding author: deike.hatscher@thermofisher.com

The coupling of elemental analyzers with isotopic ratio mass spectrometers (IRMS) has proven to be the key for forensic applications, food analysis, or counterfeit identification due to its high significance by multi-isotope analysis of bulk samples. Continuous improvements on the ease of use and reliability of bulk stable isotope analysis (BSIA) are a substantial part in making this technique a routine application with high sample throughput.

The introduction of the ConFlo IV in 2007 was an initiating step towards a fully automated multi-isotope ratio analysis: all-time availability of five reference gases combined with multiple dilution steps for sample and reference gas account for high dynamic ranges of all CNHOS species. The automated fast switch between combustion ( $N_2$ ,CO<sub>2</sub>,SO<sub>2</sub>) and high tempera-

ture conversion ( $H_2$ ,CO) in Thermo Scientific elemental analyzers is another step forward in versatility, robustness, and ease of use. It allows isotopic fingerprinting of all five elements even during longer unsupervised periods and decreases down times, while ensuring safety.

We will discuss feasibilities as well as benefits of unattended, fully software controlled multiisotope analysis by switching from high temperature conversion to combustion and vice versa. The presentation will focus on the possible performance and precision for maximum sample throughput. Examples are given on reduction of analysis time and a significant increase of the capacity for high temperature conversion. Influences on source conditions, H<sub>3</sub><sup>+</sup>-factor and backgrounds by switching of the sample preparation systems will be addressed.

# Confirmation of the incorporation of dissolved molecular oxygen into sulphate during abiotic pyrite oxidation experiments

#### C.Heidel, M. Tichomirowa

TU Bergakademie Freiberg, Institute of Mineralogy, Brennhausgasse 14, 09599 Freiberg, Germany

Corresponding author: claudia.heidel@mineral.tu-freiberg.de

Pyrite (FeS<sub>2</sub>) oxidation produces acid waters with high sulphate, iron, and trace metal concentrations which pollute waters and soils (Acid Mine Drainage). Knowledge of oxidation mechanisms is a prerequisite to develop damage mitigation strategies and to interpret field data from AMD sites.

It is known that pyrite is oxidized by either dissolved molecular oxygen (O2) or ferric iron (Fe(III)) which act as electron acceptors in the cathodic reaction. Water ( $\delta^{18}OH_2O < 0\%$ ) or atmospheric-derived molecular oxygen ( $\delta^{18}O_{02}$ = 23.5‰) serve as oxygen sources during the anodic reaction of sulphide (S22-) to sulphate  $(SO_{A}^{2-})$  which proceeds stepwise via intermediate sulphur species with oxidation states between –I and +VI. Several pyrite oxidation experiments under acid, abiotic conditions have shown that oxygen in the produced sulphate largely derives from H<sub>2</sub>O. Furthermore, several laboratory studies have shown that  $\delta^{18}O_{SO4}$ values decrease in the course of time, i.e. the percentage of H<sub>2</sub>O-derived oxygen in sulphate increases while the percentage of O<sub>2</sub> in sulphate decreases. Final  $\delta^{18}O_{SO4}$  values indicated that oxygen in sulphate consists of 3-13% O<sub>2</sub>. However, the uncertainty of these estimations (at least ±10%) causes doubts about the incorporation of O<sub>2</sub> into sulphate. Therefore, abiotic aerobic pyrite oxidation experiments were performed at acid pH. <sup>18</sup>O-enriched O<sub>2</sub> was injected into the headspace of the reaction vessels to investigate if and how O<sub>2</sub> is incorporated into the produced sulphate.

The incorporation of dissolved O<sub>2</sub> into sulphate during pyrite oxidation was shown by  $\delta^{18}O_{SO4}$  values: the more <sup>18</sup>O-enriched O<sub>2</sub> was injected into the headspace, the higher the  $\delta^{18}O_{SO4}$  values were. Estimations indicated that the majority (ca. 92%) of oxygen in sulphate derived from H<sub>2</sub>O, but a significant amount (c. 8%) of oxygen

in sulphate originated from  $O_2$ . The incorporation of dissolved  $O_2$  presumably occurred during the last oxidation step from sulphite (S $O_3^{2^2}$ , +IV) to sulphate (S $O_4^{2^2}$ , +VI). However, some uncertainties about the oxidation mechanism still exist (e.g., oxidation on pyrite surface or in solution, potential oxygen isotope exchange between S $O_3^{2^2}$  and H<sub>2</sub>O).

Interestingly, decreasing  $O_2$  concentrations showed that the consumption of dissolved  $O_2$ was much larger than the amount of  $O_2$  incorporated into sulphate. A slight increase of  $\delta^{18}OH_2O$  values indicated that <sup>18</sup>O-enriched  $O_2$ was incorporated into  $H_2O$ . Hence, the major consumption of  $O_2$  is attributed to the cathodic reaction (0.5  $O_2 + 2 H^+ + 2 e^- --> H_2O$ ) where  $O_2$  serves as electron acceptor from pyrite iron sites. In addition,  $O_2$  might be also incorporated into  $H_2O$  during the oxidation of ferrous iron to ferric iron, albeit the reaction rate is slow at low pH.

Furthermore, an oxygen isotope enrichment factor between sulphate and O<sub>2</sub> was determined from a control experiment without injection of <sup>18</sup>O-enriched O<sub>2</sub> ( $\epsilon_{SO42-O2} = -8.4\%$ ).

 $\delta^{34}S_{so4}$  values agreed with the  $\delta^{34}S$  value of pyrite which indicated the short lifetime of intermediate sulphur species.

# Lake nutrient variability inferred from isotopic ( $\delta^{13}$ C, $\delta^{15}$ N) analyses of aquatic plant macrofossils

U.Herzschuh<sup>1,2</sup>, S. Mischke<sup>3</sup>, H. Meyer<sup>1</sup>, B. Plessen<sup>4</sup>, C. Zhang<sup>5</sup>

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Research Unit Potsdam, Germany
 <sup>2</sup>Department of Geosciences, University of Potsdam, Germany
 <sup>3</sup>Institute of Geological Sciences, Freie Universität Berlin, Germany
 <sup>4</sup>Helmholtz Centre Potsdam GFZ German Research Centre for Geosciences, Germany
 <sup>5</sup>Center of Arid Environment and Palaeoclimate Research, Lanzhou University, China

Corresponding author: Ulrike.Herzschuh@awi.de

This paper aims to highlight the potential of using stable isotopic analyses of aquatic macrophytes in palaeolimnological studies. Analyses of Potamogeton pectinatus material that were obtained from modern plants (n=68) and from late glacial and Holocene sediments from Koucha Lake (northeastern Tibetan Plateau; 34.0°N; 97.2°E; 4540 m asl), were analyzed for  $\delta^{\rm 13}C_{\rm Potamogeton}$  (modern:-23 - 0 , fossil: –19 - –4 %) and  $\tilde{\delta}^{15}N_{Potamogeton}$  (modern: -11.0 - +13.8%, fossil: -9.5 - +6.7%). Reliable fossil data were interpreted in terms of palaeo-nutrient availability and palaeo-productivity on the basis of the modern relationships between environmental data and proxies. Productivity of Potamogeton pectinatus mats as indicated by palaeo- $\epsilon_{Potamogeton-TIC}$  (i.e. the enrichment of  $\delta^{13}C_{Potamogeton}$ relative to the  $\delta^{13}C_{TIC}$ ) was reduced during periods of high conductivities especially during the early Holocene. The most tremendous shift in Lake Koucha aquatic productivity occurred ~7.4 cal kyr BP when the hydrological condition changed to an open lake system and water depth increased. By that time productivity increased strongly leading to a strong decrease in the water HCO<sub>3</sub><sup>-</sup> concentration as inferred from the application of  $\epsilon_{Potamogeton-TIC}$ -InHCO<sub>3</sub><sup>-</sup> transfer function. The correlation of the established proxies especially protamogeton-DIC/TIC with further environmental proxy data especially ostracod and pollen assemblages yielded that climate signals did not directly drove aquatic productivity in Koucha Lake but exerted a rather

indirect effect via changes of the hydrological system and related mineralization changes.

In palaeolimnological studies, organic matter sources were often inferred from isotopic analyses of bulk organic. Our results, however, indicate that even one species can cover almost the full proxy rang calling bulk studies aiming to source identification into question. Furthermore,  $\delta^{\rm 13}C_{\scriptscriptstyle bulk}$  and  $\delta^{\rm 15}N_{\scriptscriptstyle bulk}$  data are commonly used to track productivity change in lakes. Our results generally confirm the underlying assumptions of these proxies but we faced several complications to explain the variations of stable isotopic values of a single plant species. Interpretation of bulk proxies might be misleading when the organic matter is a mixture of different origin or the source changed within the record. For instance,  $\delta^{13}C_{hulk}$  values from Koucha Lake show a complete different data range and its variation are not correlated to  $\delta^{13}C_{Potagmogeton}$  partly even show the opposite signal. Interpretation is especially challenging when the original signal is blurred by decomposition processes which can hardly be evaluated in case of bulk proxy analyses.

### Multicollectors in isotope ratio MS

A. Hilkert<sup>1</sup>, C.B.Douthitt<sup>2</sup>

<sup>1</sup>Thermo Fisher Scientific (Bremen) GmbH, Germany <sup>2</sup>Thermo Fisher Scientific, United States of America

Corresponding author: andreas.hilkert@thermofisher.com

One of the basic features in Isotope Ratio MS is the simultaneous collection of all ion beams required in an isotope ratio application. The use of more than one collector enhances the precision of the measurement due to the constant acquisition of all ions over time. This also ensures the correlation of data points collected at the same time in both dual inlet and continuous flow applications.

IRMS and with it the multicollection started with the setup of two faraday cups for collection of masses 44 and 45 in  $CO_2$ . This was followed by the addition of a third collector for mass 46 to allow the correction of the interfering  ${}^{12}C^{17}O^{16}O$  ion on mass 45 via the  ${}^{18}O$  information plus the relation between  ${}^{18}O$  and  ${}^{17}O$ . With the extension to gases like N<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub> but also

triggered by the invention of the continuous flow application with its fast delivery of more than one gas universal collector arrangements were required.

A prerequisite for extended universal collectors was the development of new electronics for signal amplification and data collection. Today simultaneous detection of 10 ion beams on a wide focal plane, an enhanced dynamic range of 50 V on each preamplifier plus computer controlled switching of the amplifier gains allow tailored collector systems for many different applications and isotope ratio ranges.

The pros and cons of various collector configurations and their contribution to the development of new applications will be discussed.

# Identifizierung von Bicarbonat-Applikation bei Mensch und Pferd per IRMS

F. Hülsemann<sup>1,2</sup>, U. Flenker<sup>1</sup>, M. Machnik<sup>1</sup>, I. Schenk<sup>1</sup>, C. Zinner<sup>2</sup>, J. Mester<sup>2</sup>, W. Schänzer<sup>1</sup>

<sup>1</sup>Institut für Biochemie, Deutsche Sporthochschule Köln, Am Sportpark Müngersdorf 6, 50933 Köln <sup>2</sup>Das Deutsche Forschungszentrum für Leistungssport, Deutsche Sporthochschule Köln, Am Sportpark Müngersdorf 6, 50933 Köln

Corresponding author: f.huelsemann@biochem.dshs-koeln.de

Eine orale Gabe oder Infusion von Natriumhydrogencarbonat (Bicarbonat) vor körperlicher Belastung kann sowohl beim Menschen als auch beim Pferd leistungssteigernde Effekte haben. Die Gabe von Bicarbonat führt zu einer Erhöhung der Bicarbonatkonzentration und des pH-Wertes im Blut. Dies erleichtert bei intensiven Belastungen den Efflux von Laktat und H<sup>+</sup> aus der belasteten Muskulatur und verzögert dadurch den Abfall des intrazellulären pH-Wertes. Im Pferderennsport gilt eine Gabe von Bicarbonat vor dem Rennen als Verstoß gegen die Dopingregeln. Üblicherweise wird eine Bicarbonat-Applikation durch den Anstieg des Gesamtkohlendioxidgehaltes im Blut detektiert. Die Analyse von  $\delta^{13}$ C des Bicarbonats im Blut oder Urin könnte zur Bestätigung exogener Bicarbonat-Gaben herangezogen werden, da zwischen exogenem und endogenem Bicarbonat signifikante Unterschiede in  $\delta^{13}$ C bestehen.

Im Rahmen zweier Pilotstudien wurden beim Mensch und Pferd nach oraler Bicarbonat-Gabe in Blut (Pferd), Urin (Mensch und Pferd) und Atemgas (Pferd) die  $CO_2$  und  $HCO_3^-$  Fraktionen (im Folgenden bezeichnet als  $tCO_2$ ) isoliert und per IRMS gemessen. Aus flüssigen Matrices wurde  $tCO_2$  mit Hilfe von Ba(OH)<sub>2</sub> gefällt und isoliert,  $\delta^{13}C$  anschließend nach Säurefreisetzung bzw. aus Atemgas direkt per IRMS bestimmt.

Im Rahmen der Studien beim Mensch und Pferd konnte in allen Matrices der Effekt des applizierten Bicarbonates auf  $\delta^{13}$ C des isolierten tCO<sub>2</sub> bzw. exhalierten CO<sub>2</sub> festgestellt werden.

In der placebokontrollierten Studie beim Menschen war  $\delta^{13}$ C von tCO<sub>2</sub> im Urin nach Applikation von Bicarbonat signifikant erhöht und nach sechs Stunden noch nicht wieder auf die Basiswerte zurückgegangen. Bei Ausscheidungsversuchen mit Pferden konnte der Einfluss des exogenen Bicarbonates auf  $\delta^{13}$ C von Atemgas, urinärem Harnstoff sowie urinärem tCO<sub>2</sub> als auch BlutplasmatCO<sub>2</sub> festgestellt werden. In allen Matrices und Fraktionen stieg  $\delta^{13}$ C signifikant an, wobei sich allerdings das Ausmaß der Änderungen in  $\delta^{13}$ C zwischen den verschiedenen Matrices und Fraktionen unterschied.

Die Pilotstudien beim Mensch und Pferd zeigen, dass zusätzlich zum reinen Mischungseffekt von exogenem und endogenem Bicarbonat augenscheinlich auch veränderte Stoffwechsellagen zu signifikanten Isotopenfraktionierungen von Bicarbonat im Organismus führen. Für eine routinemäßige Anwendung der IRMS in der Pferdedopinganalytik sind daher weitere Studien sowohl zum Einfluss von Bicarbonat-Applikationen als auch physiologischen Prozessen auf die tCO<sub>2</sub>-Fraktionen in Urin und Blut bzw. CO<sub>2</sub> im Atemgas nötig.

# Zur Sauerstoff-Isotopen Biogeochemie von Phosphat in brackischen Nebenmeeren: I. Das Schwarze Meer

K. Isensee<sup>1</sup>, S. Hille<sup>1</sup>, O. Dellwig<sup>1</sup>, R. Blake<sup>2</sup>, M.E. Böttcher<sup>1</sup>

<sup>1</sup>Leibniz Institut für Ostseeforschung, Seestr.15, 18119 Warnemünde <sup>2</sup>Universität Yale, Geology and Geophysics Department, P.O. Box 208109, New Haven, CT 06520-8109 USA

Corresponding author: kirsten.isensee@io-warnemuende.de

Phosphor (P) ist von großer Bedeutung für die Funktionsfähigkeit und das Wachstum von allen Lebewesen und limitiert in Form von Phosphat (DIP) die Produktivität in vielen limnischen aber auch marinen aquatischen Systemen. Daher ist es von großer Bedeutung, die Biogeochemie der P-Transformationsprozesse in marinen Ökosystemen besser zu verstehen. In der Wassersäule, aber auch in Sedimenten finden biogeochemische Prozesse statt, die den P Kreislauf beeinflussen. Diese Prozesse beinhalten: Mikrobielle Umsätze (Aufnahme und Metabolismus) von anorganischen und organischen P Verbindungen, Cextrazelluläre enzymatisch katalysierte Regeneration von P aus organischem Material, <a>Tredox-gesteuerte</a> Bindung bzw. Freisetzung an Eisenoxiden,

Aufnahme und Freisetzung von Polyphosphaten und Bildung von Apatiten oder anderen P-haltigen Mineralen aus DIP. Es ist außerdem gezeigt worden, dass die durch Schwefelbakterien gesteuerte Bildung von Phosphoriten unter anoxischen Verhältnissen den P Kreislauf nachhaltig beeinflussen kann. Die genannten Prozesse überlagern sich in Sedimenten. Die Sauerstoffisotopensignatur von P in gelösten und partikulären P Verbindungen bietet die Möglichkeit, biologische und abiotische Prozesse des P Kreislaufs zu identifizieren. Wir präsentieren in der vorliegenden Studie die ersten O-lsotopendaten für das gelöste Phosphat in der Wassersäule des Schwarzen Meeres. Das Schwarze Meer ist das größte permanent euxinische System der Erde und das ,Typ-System' für Anoxia in der Erdvergangenheit. Die Proben wurden während Ausfahrten der FS Meteor (M51-4, M72-5) genommen.

Neben hydrographischen, und physikalischen Basis-Parametern wurden in wässerigen Lösungen partikuläre (z.B. P, Fe, Mn, Al) und gelöste Elemente (z.B. pH, DIP, Fe, Mn, O<sub>2</sub>, H<sub>2</sub>S, DIC) geochemisch untersucht. Die O-Isotopie im gelösten Phosphat wurden nach Überführung in Silberphosphat gemessen; die O-Isotopensignatur des Wassers wurde der Literatur entnommen. Im Schwarzen Meer wird in der euphotischen Zone DIP durch Primärproduzenten assimiliert und in organische Biomasse eingebaut. In der Wassersäule stattfindende mikrobielle Abbauprozesse von abgestorbener Biomasse führen zur Remineralisierung von P. Darüber hinaus wird sorptiv unter oxischen Bedingungen an Eisenoxide gebundenes DIP an der pelagischen Redoxkline aufgrund der reduktiven Auflösung der Fe-Oxy(hydroxi)de wieder freigesetzt und nimmt an einem kurzgeschlossenen Redoxklinen P Kreislauf teil. Im Vergleich zu den Wassersäulen-Signaturen wurden außerdem anorganisch-gebundenes P laminierter brackischer (MUC Probe) und biturbater (ehemals) limnischer Sedimenten (Schwerelot-Probe) analysiert.

Die Sauerstoff-Isotopenverhältnisse des gelösten Phosphats unterhalb der Redoxkline zeigen eine gegenüber dem umgebenden Wasser (-1 to -2‰ vs SMOW; Swart et al., 1991; DSR 38: S761) deutlich schwerere Isotopensignatur (+21.7 bis +24.3 ‰ vs. V-SMOW) und nehmen mit der Tiefe zu. Variationen der Isotopenwerte in und direkt unterhalb der Redoxkline sind wahrscheinlich auf redox-abhängige Änderungen in der Fe-P-Biogeochemie zurückzuführen.

Die Isotopendaten unterhalb der pelagischen Redoxkline nähern sich an das temperaturabhängige Isotopenaustauschgleichgewicht an; bei 500 und 2000 m bsf überschreiten sie diesen Wert sogar. Dieses Ergebnis ist möglicherweise darauf zurückzuführen, dass isotopisch schwereres Fe-gebundenes P in der Tiefe freigesetzt wird, oder dass isotopisch schweres P aus dem Marmara Meer/Mittelmeer in den Pool eingemischt wird.

In den brackischen und ehemals limnischen Sedimenten des Schwarzen Meeres ist die Isotopie des anorganisch gebundenen P deutlich leichter (+18.3 bzw. +17.7‰). Dieser Unterschied zum Pelagial ist wahrscheinlich auf den benthischen enzymatischer Abbau von organisch gebundenem P zurückzuführen, der zu einem starken kinetischen Isotopeneffekt zum anorganischen P führt (Liang & Blake, 2007). Darüber hinaus können Sorptions-Desorptions und diffusive Transport-Prozesse im Sediment die Isotopensignatur beeinflussen.

Die Untersuchungen wurden durch die DFG gefördert (JO 307/6-1 an MEB; HI1338/1-1 an SH), das Leibniz Institut für Ostseeforschung (MEB) sowie die Universität Yale (RB). C. Borowski (MPI Bremen) sei gedankt für die exzellente Koordination und Fahrtleitung von M72-5.

## Zur Sauerstoff-Isotopen Biogeochemie von Phosphat in brackischen Nebenmeeren: II. Die Ostsee

K. Isensee<sup>1</sup>, S. Hille<sup>1</sup>, M. Nausch<sup>1</sup>, O. Dellwig<sup>1</sup>, R. Blake<sup>2</sup>, M.E. Böttcher<sup>1</sup>

<sup>1</sup>Leibniz Institut für Ostseeforschung, Seestr. 15, 18119 Warnemünde

<sup>2</sup>Universität Yale, Geology and Geophysics Department, P.O. Box 208109, New Haven, CT 06520-8109 USA

Corresponding author: kirsten.isensee@io-warnemuende.de

Phosphor (P) ist von großer Bedeutung für die Funktionsfähigkeit und das Wachstum von allen Lebewesen und limitiert in Form von Phosphat (DIP) die Produktivität in vielen limnischen aber auch marinen aquatischen Systemen. Daher ist es von großer Bedeutung, die Biogeochemie der P-Transformationsprozesse in marinen Ökosystemen besser zu verstehen. In der Wassersäule, aber auch in Sedimenten finden biogeochemische Prozesse statt, die den P Kreislauf beeinflussen Diese Prozesse beinhalten: Dikrobielle Umsätze (Aufnahme und Metabolismus) von anorganischen und organischen P Verbindungen, **3** extrazelluläre enzymatisch katalysierte Regeneration von P aus organischem Material, 
 redox-gesteuerte Bindung bzw. Freisetzung an Eisenoxiden,

➔ Aufnahme und Freisetzung von Polyphosphaten und ➡Bildung von Apatiten oder anderen P-haltigen Mineralen aus DIP. Es ist außerdem gezeigt worden, dass die durch Bakterien geochemischer Gradienten gesteuerte Anreicherung von sedimentärem P in Phosphoriten der P Kreislauf nachhaltig beeinflusst werden kann. Die genannten Prozesse überlagern sich in Sedimenten. Die Sauerstoffisotopensignatur von P in gelösten und partikulären P Verbindungen bietet die Möglichkeit, biologische und abiotische Prozesse des P Kreislaufs zu identifizieren.

Wir präsentieren in der vorliegenden Studie die ersten Sauerstoff-Isotopendaten für das gelöste Phosphat in der Wassersäule der anoxischen Ostsee-Tiefs (Landsort Tief (LT) und Gotland Tief (GT)), sowie für anorganisch gebundenes Phosphat in Sedimenten des Finnischen Meerbusens und des Gotland-Beckens. Die Probennahme erfolgte unter anderem während Ausfahrten der FS Prof. A. Penck und M.S. Merian.

Neben der Erfassung von hydrographischen und -physikalischen Parametern wurden in wässrigen Lösungen auf partikuläre (z.B. P, Fe, Mn, Al) und gelöste Elemente (z.B. pH, DIP, Fe, Mn, O<sub>2</sub>, H<sub>2</sub>S, DIC) hin geochemisch untersucht. Die O-Isotopie des gelösten und festphasengebundenem anorganischen Phosphats wurde nach Überführung an Silberphosphat vermessen, die O-Isotopensignatur des Wassers wurde der Literatur entnommen. In der Ostsee wird in der euphotischen Zone DIP durch Primärproduzenten assimiliert und in organische Biomasse eingebaut. In der Wassersäule und im Sediment stattfindende mikrobielle Abbauprozesse von abgestorbener Biomasse führen zur Remineralisierung von P. Darüber hinaus wird in hohem Maße sorptiv an Eisenoxide gebundenes DIP aus oxischem Bodenwasser in die Sedimente eingetragen. An der (pelagialen oder benthischen) Redoxkline wird diese Fraktion aufgrund der reduktiven Auflösung der Fe-Oxide wieder freigesetzt und kann zurück in die oxischen Bereiche diffundieren, wo es erneut organisch oder anorganisch gebunden werden kann.

Die Sauerstoff-Isotopenverhältnisse des DIP in der Wassersäule von Landsort-Tief und Gotland-Tief zeigen eine gegenüber dem umgebenden Wasser deutlich schwerere Isotopensignatur (+19.3 und +22.7‰ (LT) bzw. +22.3‰ (GT) vs. V-SMOW). Variationen an der pelagischen Redoxkline des LT sind möglicherweise auf redox-abhängige Änderungen in der Fe-P Biogeochemie zurückzuführen. Die Isotopendaten unterhalb der pelagischen Redoxkline sind schwerer als das für das Isotopenaustauschgleichgewicht erwartet wurde. Dieses Ergebnis ist möglicherweise darauf zurückzuführen, dass am schweren Isotop angereichertes Fe-gebundenes Phosphat in der Tiefe freigesetzt und in einen komplexen Kreislauf an der Redoxkline eingebunden wird.

In den brackischen und limnischen Sedimenten des Gotland-Beckens und des Finnischen Meerbusens ist die Isotopie des anorganisch gebundenen P deutlich leichter (+13.9 bzw. +17.4‰) und generell um leichte Isotope angereichert gegenüber Werten, die unter Bedingungen des Isotopen-Austauschgleichgewichtes mit Porenwasser erwartet würden. Dieser Unterschied zum Pelagial und dem thermodynamischen Gleichgewicht ist wahrscheinlich auf den benthischen enzymatischen Abbau von organisch gebundenem P zurückzuführen, der zu einem starken kinetischen Isotopeneffekt zum anorganischen P führt (Liang & Blake, 2007). Darüber hinaus können sowohl Sorptions-Desorptions als auch diffusive Transport-Prozesse von DIP im Sediment die Isotopensignatur beeinflussen. Überraschenderweise sind die beobachteten Isotopenwerte der Sedimenten des Finnischen Meerbusens und des Gotland-Beckens recht ähnlich.

Die Untersuchungen wurden durch die DFG gefördert (HI1338/1-1 an SH), das Leibniz Institut für Ostseeforschung (MEB, MN) sowie durch die Universität Yale (RB).

# Steady-state and non steady-state of soil respired $\delta^{13}CO_2$ in a douglas fir forest, Oregon, USA

Z.E. Kayler<sup>1,4</sup>, E.W. Sulzman<sup>2</sup>, A.C. Mix<sup>3</sup>, B.J. Bond<sup>1</sup>

<sup>1</sup>Department of Forest Ecosystems and Society, Oregon State University, 321 Richardson Hall Corvallis, Corvallis, OR 97331, USA

<sup>2</sup>Department of Crop and Soil Science, 3017 Agricultural and Life Science Building, Oregon State University, Corvallis, OR 97331, USA

<sup>3</sup>College of Oceanic and Atmospheric Science, Oregon State University, COAS Admin, Bldg. 104, Corvallis, OR 97331, USA

<sup>4</sup>Institute of Landscape Matter Dynamics, Leibniz Center for Agricultural Landscape Research, Eberswalder Strasse 84, D-15374, Müncheberg, Germany

Corresponding author: z.kayler@gmail.com

The isotopic signature of soil respiration  $(\delta^{13}C_{R-s})$  is a potentially powerful tool to study the geochemical and biological pathways of carbon through an ecosystem over the long-term. However, Seasonal patterns are often difficult to interpret because of non steady-state conditions. Few studies have quantified the impact of non steady-state on the measurement of  $\delta^{13}CR$ -s in the field and as a result there is little empirical evidence about the mechanisms causing non steady-state. We address these issues by measuring  $\delta^{13}C_{R-s}$  over two growing seasons in a steeply sloped watershed. Our goals were to 1) detect and quantify deviations of  $\delta^{13}CO_2$  from steady-state, 2) determine whether processes

that occur in the day versus the night manifest in seasonal differences of  $\delta^{13}C_{R-s}$ , and 3) evaluate the potential impact of measured soil biophysical factors on non steady-state events. The average seasonal range of  $\delta^{13}CR$ -s at our site was 4.8‰. We found distinct seasonal patterns in the steady-state estimates of  $\delta^{13}C_{R-s}$ typified by depleted signals in the middle of summer and enriched peaks in spring and autumn. We were not able to detect a difference between steady-state estimates made during the day versus the evening. There were several measurements of  $\delta^{13}C_{R-s}$  where the difference between an isotopic mixing model and a soil bio-physical profile model were more enriched or depleted than the 4.4‰ correction for soil gas diffusion. In general, the deviation from the 4.4‰ correction was less than 1‰. The isotopic gradient, expressed as the ratio of  $\delta^{13}CO_2$  between two depths, was the variable most correlated with estimates of  $\delta^{13}C_{R-s}$  made during non steady-state. In turn, the isotopic gradient measured during non steady-state was a function of soil moisture and soil temperature. We found that thermal diffusion is one mechanism

behind non steady-state events, but potentially other fluxes, such as vapor, may also be important. We provide evidence that isotopic non steady-state in soil is a common phenomena and is variable in space and time. Future studies of seasonal patterns in  $\delta^{13}C_{\rm R-s}$  need to verify that the assumption of steady-state is met to ensure that interpretations of the variability in  $\delta^{13}C_{\rm R-s}$  are correct.

### Measurements of $\delta^{13}$ C values of methane from anaerobic digesters: Comparison of continuous-flow isotope ratio mass spectrometry and laser absorption spectroscopy

F. Keppler<sup>1</sup>, S.Laukenmann<sup>1</sup>, J. Rinne<sup>1</sup>, H. Heuwinkel<sup>1</sup>, M. Greule<sup>1</sup>, M. Whiticar<sup>3</sup>, J. Lelieveld<sup>1</sup>

<sup>1</sup>Max-Planck-Institute for Chemistry, Joh.-Joachim-Becher-Weg 27, D-55128 Mainz, Germany <sup>2</sup>Agri-food and Biosciences Institute for Northern Ireland, Newforge Lane, Belfast BT9 5PX, UK <sup>3</sup>School of Earth and Ocean Sciences, University of Victoria, P.O. Box 3050, Victoria, BC, V8W 2Y2, Canada

Corresponding author: frank.keppler@mpic.de

The analysis of stable carbon isotope ratios  $(^{13}C/^{12}C \text{ ratios or } \delta^{13}C \text{ values})$  of methane by Isotope Ratio Mass Spectrometry (IRMS) is an extremely useful tool for environmental research, such as atmospheric sciences (Johnson et al. 2002, Brenninkmeijer et al., 2003). The analytical precision of carbon stable isotope measurements of CH<sub>4</sub> using Continuous-Flow IRMS is often reported to be better than 0.3 %. As an alternative, 15 years ago, Bergamaschi et al. (1994) showed that a laser-based method (Long-Path Diode Laser Absorption Spectrometer) could be a valid approach to precisely measure <sup>13</sup>C/<sup>12</sup>C ratios of sources of atmospheric methane. Subsequently, several laboratory demonstrations of isotope ratio measurements have been reported for methane using different laser and spectroscopic techniques. Nevertheless, both CF-IRMS and Laser Absorption Spectroscopy techniques are generally limited to laboratory-based applications. Laser-based instruments are now available from several companies, which are portable enough to be used in field applications.

In this study we have analyzed several methane gas standards and a large number of biogas samples with two analytical techniques: Gas Chromatography Combustion Isotope Ratio Mass Spectrometry (GC-C-IRMS) and High-Resolution Direct Absorption Laser Spectroscopy. We used the same samples to establish and compare the precision of the two techniques independently and quantify any systematic bias or offset between the two analytical techniques.

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### Are meromictic lakes potential bioreactors for natural attenuation in mining landscapes?

K. Knöller<sup>1</sup>, A. Seebach<sup>1</sup>, I. Baneschi<sup>2</sup>

<sup>1</sup>UFZ – Helmholtz Centre for Environmental Research, Department of Isotope Hydrology, Theodor-Lieser-Str. 5, 06120 Halle, Germany,

<sup>2</sup>CNR – Geosciences and Earth Resources Institute, Via Moruzzi 1, 56124 Pisa, Italy

Corresponding author: kay.knoeller@ufz.de

According to recent models, climate change may enhance the development of a permanent stratification in many lakes in the mid latitudes. In contrast to lakes showing a complete seasonal turnover, those permanently stratified or meromictic lakes provide a constant anoxic reaction zone. For pit lakes in mining areas affected by high mineralization and acidification the presence of such a reaction zone could be a chance for a natural attenuation of the contaminant load. This is especially due to anoxic microbial processes such as iron reduction or sulfate reduction producing alkalinity and reducing the loads of solutes by the formation of insoluble precipitates.

A meromictic lake (Lake Moritzteich) in the Lusatian lignite mining district (Germany) was chosen to study the biochemical cycling with respect to natural attenuation processes.

Hydrochemical and isotope methods were used to investigate water samples from vertical lake profiles, from groundwater wells surrounding the lake, and from sediment cores taken from the deepest part of the lake. From the same cores sedimentary sulfur species were isotopically analyzed.

Preliminary hydrochemical investigations suggested that the permanent stratification in the lake is maintained by iron oxidation and precipitation in the well mixed surface layers (mixolimnion) and by iron reduction and iron redissolution in the deeper, anoxic layers (monimolimnion).

The stable isotope compositions as well as tritium values from lake and groundwater samples indicated an intense interaction of lake water and adjacent groundwater. This interaction includes groundwater inflow, lake water outflow, and –depending on seasonal variation- a backflow of groundwater originally ex-filtrated from the lake. The groundwater exchange significantly contributes to matter fluxes in the lake and is in part responsible for maintaining the permanent stratification.

Lake water sulfate is enriched in <sup>34</sup>S up to 30 ‰ (CDT). This enrichment and a positive correlation of  $\delta^{34}$ S and  $\delta^{18}$ O values of sulfate observed in lake water profiles are normally indicative for bacterial sulfate reduction. However, sulfate concentrations in the lake water suggest a vertical mixing of sulfate rather than sulfate reduction. The reaction zone where sulfate reduction is obviously taking place seems to be confined to the lake sediment. In the sediment an enrichment of <sup>34</sup>S up to 39 ‰ (CDT) in pore water sulfate and an accumulation of isotopically light FeS/FeS<sub>2</sub> are observed. The presence of elemental sulfur in the top layers of the lake sediment indicates a re-oxidation that is related to the deposition of iron hydroxides formed in the mixolimnion. Iron reduction as the dominating process in the lake water of the monimolimnion consumes a considerable part of the electron donors that would be needed to maintain bacterial sulfate reduction at a higher rate. Nevertheless, the alkalinity produced by iron reduction in the lake water as well as the precipitation of iron sulfides in the lake sediment as a result of bacterial sulfate reduction contribute considerably to naturally attenuate the impact of lignite mining on the aquatic system.

### Stabilisotopenuntersuchungen in der ungesättigten Zone zur Bestimmung der Grundwasserneubildung auf der Nordseeinsel Borkum

P. Königer<sup>1</sup>, S. Möhring<sup>2</sup>, A. Mulch<sup>2</sup>, H. Wiederhold<sup>1</sup>

<sup>1</sup>LIAG Leibniz Institut für Angewandte Geophysik, Geozentrum Hannover, Stilleweg 2, 30655 Hannover <sup>2</sup>Institut für Geologie, Leibniz Universität Hannover, Callinstraße 30, 30167 Hannover

Corresponding author: paul.koeniger@liag-hannover.de

Grundwasserneubildung ist ein wichtiger Schlüsselparameter für die nachhaltige Bewirtschaftung von Grundwasserressourcen und eine umfassende Darstellung von Wasserbilanzen bei hydrologischen Untersuchungen. Unter den direkten Methoden zur Bestimmung der Grundwasserneubildung gelten Isotopenmethoden als vielversprechendes Verfahren. Stabile Isotope des Wassers (Deuterium, <sup>2</sup>H und Sauerstoff-18, <sup>18</sup>O) können die Bestimmung von Wasserbewegung und Grundwasserneubildung ermöglichen, wenn saisonale



Abb. 1. Lage der Beprobungspunkte und DWD Wetterstation auf Borkum (schwarze Punkte). Farbabstufungen repräsentieren den spezifischen Widerstand 5 m unter NN. Blaue Farben zeigen relativ hochohmige Bereiche, die als Ausdehnung einer Süßwasserlinse in dieser Tiefe interpretiert werden können. Rote Farben repräsentieren niedrige Widerstände, bzw. Salzwasseranteile (Steuer et al. 2009).

Schwankungen der Isotopenzusammensetzung im Niederschlag (Jahreszeiteneffekt) über die ungesättigte Zone verfolgt werden können (Saxena 1984). Hierfür ist, bei der herkömmlichen analytischen Bestimmung des Isotopengehalts über Massenspektrometrie (IRMS), die guantitative Extraktion von Bodenwasser aus dem Bodensubstrat notwendig. Für Wasserbilanzuntersuchungen auf der Nordsee Insel Borkum (53°36' N, 06°42' O, Höhe 3 m NN) (Abb. 1) wurden im Rahmen des INTER-REG IVB Projektes CLIWAT (Climate & Water) Untersuchungen zur Grundwasserneubildung durchgeführt und Methoden zur Vakuumextraktion von Bodenwasser (West et al. 2006, Vendramini et al. 2007, Peters et al. 2008) weiter entwickelt.

Bodenprofile wurden im Januar 2009 im Bereich Borkum Waterdelle (bis 1 m Tiefe) und im März 2009 im Bereich Borkum Ostland (bis zu 6 m Tiefe) entnommen. Aus den Bodenproben wurde das Bodenwasser im Labor extrahiert. Hierfür wurde ein modifiziertes Vakuumextraktionsverfahren getestet, mit dem ein höherer Probendurchsatz möglich ist. In Abbildung 2 sind δ<sup>18</sup>O Werte von extrahiertem Bodenwasser im Vergleich zum ursprünglichen Isotopengehalt des Testwassers (bei unterschiedlichen Ausgangszusammensetzungen von -22.23‰, -8.06 ‰ und -1.20‰ für δ<sup>18</sup>O und -180.2‰, -58.9‰, und -7.7‰ für  $\delta^2$ H), bei variierender Extraktionsdauer (2.5, 5, 10, 15, 20 und 40 min) und bei unterschiedlichem Wassergehalt der Bodenproben (5, 7, 9 und 12%) dargestellt. Die Isotopenanalytik wurde mit einem Thermo Finnigan Delta Plus XP IRMS durchgeführt,

das für die  $\delta^{18}$ O Messung mit einer Gasbench II und für die  $\delta^{2}$ H Messung mit einem H/Device gekoppelt ist. Die Wasserproben zeigen nach der Laborextraktion Standardabweichungen im Größenbereich der instrumentellen Genauigkeit von +/- 0.2 und +/- 1.0‰ für  $\delta^{18}$ O und  $\delta^{2}$ H. Für Destillationszeiten unter 10 Minuten zeigen sich deutliche Abweichungen durch unvollständige Extraktion. Für das hier verwendete feinbis mittelsandige Substrat zeigen sich keine tendenziellen Abweichungen bei variierendem Wassergehalt.

Die  $\delta^{18}$ O Werte, die für die Profile im Gelände ermittelt wurden, sind in Abbildung 3 dargestellt. Im Januar 2009 (Borkum, Wassereinzugsgebiet Waterdelle, Grundwasserstand bei ca. 1.20 m u. GOK) steht nur ein geringmächtiges Profil für die Auswertung zur Verfügung, das jedoch deutliche Schwankungen im Isotopengehalt aufweist (vgl. Abb. 3). Für das Profil I im März 2009 können Wintersignale in ca. 80, 320 und 550 cm Tiefe interpretiert werden. Für das Profil II im März 2009 zeigt sich eine starke Abweichung hin zu erhöhten  $\delta^{18}$ O und  $\delta^{2}$ H Werten im tieferen Bereich des Profils, die auf Grund der Lage der Entnahmestelle (in der Nähe eines Überflutungsbereiches) eventuell auf Mischung mit Meerwasser zurückzuführen ist.

Die Grundwasserneubildung über saisonale Isotopensignale in der ungesättigten Zone lässt sich bei einem Wassergehalt des feinsandigen Bodenmaterials von ca. 5% auf ungefähr 113 mm für 2006 und 125 mm für 2007 abschätzen (Profil I März 2009). Ein Vergleich



Abb. 2. Bodenwasserextraktion zur Isotopenanalyse: A) bei unterschiedlichem  $\delta^{18}$ O Gehalt des Ausgangswassers, B) bei variierender Extraktionsdauer und C) bei unterschiedlichem Bodenwassergehalt. Der Isotopengehalt des Initialwassers und die Standardabweichung für Wasserproben sind als durchgezogene bzw. gestrichelte Linien dargestellt.

mit einer langjährigen Abschätzung der Grundwasserneubildung für Borkum, die bei 784 mm mittlerem Jahresniederschlag für den Beobachtungszeitraum 1961 bis 1990 im Bereich von Profil I zwischen 100 und 150 mm liegt (NIBIS 2008, Lemke et al. 2008), zeigt eine relativ gute Übereinstimmung.

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Abb. 3.  $\delta^{18}$ O Werte im Bodenwasser aus drei Profilen der ungesättigten Zone auf Borkum entnommen im Zeitraum Januar bis März 2009 (gestrichelte Linie entspricht den  $\delta^{18}$ O Werten im Grundwasser an den jeweils nächstgelegenen Beobachtungsstellen).

# Produktion und Konsumption der klimarelevanten Spurengase $N_2O$ und $CH_4$ in einem sauren Niedermoor

#### J. Köpp, G. Gebauer

BayCEER - Labor für Isotopen-Biogeochemie, Universität Bayreuth

Correspoding author: julia.koepp@uni-bayreuth.de

Zur Simulation extremer Witterungsereignisse wurden in einem sauren Niedermoor im Fichtelgebirge (NO-Bayern, Deutschland) drei Manipulationsflächen im Zeitraum von 11.06.2008 bis 07.08.2008 drainiert und durch ein Dach aus transparenter Folie vor Regen geschützt. Danach wurde einen Tag lang künstlich beregnet (100 mm pro Manipulationsfläche). Als Kontrollen standen drei entsprechende Flächen zur Verfügung, die nur den natürlichen Wetterereignissen ausgesetzt waren. Im Rahmen der Forschergruppe: "Bodenprozesse bei extremen meteorologischen Randbedingungen" der Deutschen Forschungsgemeinschaft (DFG) wurden Gasflussmessungen der klimarelevanten Spurengase Lachgas (N<sub>2</sub>O) und Methan (CH<sub>4</sub>) zwischen den Moorkörper und der Atmosphäre gemessen.

Zur Bestimmung der N<sub>2</sub>O-Flüsse diente die "closed chamber"-Methode in Kombination mit einem photoakustischen Infrarot-Analysator. Um die CH<sub>4</sub>-Flüsse zu errechnen, wurde aus den geschlossenen Kammern jeweils im Abstand von 12 Minuten insgesamt fünf Gasproben entnommen. Mittels eines Gaschromatographen wurde anschließen die CH<sub>4</sub>-Konzentration der Gasproben bestimmt und über den Anstieg der Fluss aus oder in den Moorkörper ermittelt.

Zu Beginn der Drainage konnte ein Anstieg der  $N_2O$ -Emissionen detektiert werden. Mit stärkerer Wasserspiegelabsenkung nahm die Intensität der  $N_2O$ -Flüsse ab, so dass der Moorkörper teilweise sogar zu einer leichten  $N_2O$ -Senke wurde. Diese Funktion des Moorkörpers hielt jedoch nur vorübergehend an, da nach der Beregnung ein kurzzeitig sehr starker Anstieg der  $N_2O$ -Flüsse detektiert wurde. Die Manipulation schien keinen signifikanten Einfluss auf die CH<sub>4</sub>-Flüsse zu haben, jedoch war tendenziell ein Absinken der CH<sub>4</sub>-Emission nach der Beregnung zu verzeichnen, mit teilweise negativen Flüssen.

Diese an der Oberfläche bestimmten Flüsse setzten sich jedoch aus verschiedenen Prozessen zusammen, die gleichzeitig in verschiedenen Bodentiefen ablaufen können. Um die kausalen Zusammenhänge hinter den Flussdaten besser nachzuvollziehen, wurden von jeder Versuchsfläche Bodenluftproben entlang eines Profils bestehend aus sechs Tiefen (-10 bis -60 cm) entnommen. Diese wurden anschließend verwendet, um mittels PreCon-GC-IRMS entweder ihre N<sub>2</sub>O Konzentrationen,  $\delta^{15}$ N- und  $\delta^{18}$ O-Werte oder ihre CH<sub>4</sub>-Konzentrationen und  $\delta^{13}$ C-Werte zu bestimmen. Aus den gewonnenen Daten können Rückschlüsse auf die Entstehungs- und Konsumptionszonen und auf die dafür zuständigen vorwiegend mikrobiellen Prozesse gezogen werden.

Die Daten der Bodenprofile zeigen, dass die Hauptproduktionszone für N<sub>2</sub>O (Bodenluftkonzentrationen bis zu 10 ppm bei Umgebungsluftkonzentrationen von ca. 0,35 ppm) sowie für CH<sub>4</sub> (Bodenluftkonzentrationen bis zu 500 ppm Umgebungsluftkonzentrationen von ca. 1,18 ppm) sich in ca. 40 bis 50 cm Tiefe befindet. Auch die negativen  $\delta^{15}$ N-Werte (bis zu -20‰ bei δ15N-Werten der Umgebungsluft von 4‰) sowie  $\delta^{13}$ C-Werte (bis zu -70‰ bei  $\delta^{13}$ C-Werten der Umgebungsluft von ca. -45‰) weisen darauf hin. Die Konzentrationsabnahme zu den oberen Bodenschichten hin, sowie die Anreicherung an <sup>15</sup>N bzw. <sup>13</sup>C in der Bodenluft deuten die Konsumption von N<sub>2</sub>O und CH<sub>4</sub> an. Insgesamt nahmen die N2O- und CH4-Konzentrationen in den Bodenschichten während des Experimentzeitraums ab.

Demnach kann das Moor bei abgesenktem Wasserspiegel durch mikrobielle Konsumption im oberen aeroben Moorkörper sowohl eine temporäre  $N_2O$ - als auch  $CH_4$ -Senke darstellen.

### Continuous on-line water vapor isotope measurements in Antarctica

J. Landsberg<sup>1</sup>, K. Holmen<sup>2</sup>, E. Isaksson<sup>2</sup>, D. Romanini<sup>3</sup>, H.A.J. Meijer<sup>1</sup> and E. Kerstel<sup>1,3</sup>

<sup>1</sup>Center for Isotope Research, University of Groningen, The Netherlands

<sup>2</sup>Norwegian Polar Institute. Tromso, Norway

<sup>3</sup>Laboratory for Molecular and Laser Physics, J. Fourier University of Grenoble, France

Corresponding author: e.r.t.kerstel@rug.nl

In the context of a globally warming climate it is crucial to study the climate variability in the past and to understand the underlying mechanisms (1).

Precipitation deposited on the polar ice caps provides a means to retrieve information on temperature changes (through the paleo-temperature dependence of the isotopic composition of the ice) and atmospheric composition (of gas stored in bubbles in the ice) on time scales from one to almost one million years, with subannual resolution in the most recent centuries. However, it is now widely recognized that the calibration of the paleo-thermometer is highly problematic. For this reason attempts to model the global water cycle, including the isotope signals, are ongoing with the aim of providing a more physical basis of the isotope - temperature relation. Currently, there is a large divergence in the results obtained by different modeling strategies. The missing link in these model studies is their forcing by experimental data on the predeposition isotopic composition of the vapor phase compartment of the hydrological cycle. We propose to measure the isotopic composition of moisture carried towards and deposited on Antarctica, in order to constrain the numerical models. In this context we will develop a modified, more sensitive and precise, version of a laser water vapor isotope spectrometer,

originally designed for stratospheric studies (2,3). This instrument will enable the continuous, online measurement of all three stable isotope ratios of atmospheric water vapor. So far, such data is non-existent. Our data should improve the validity of the models and improve the understanding of the physical mechanisms at the basis of the isotope thermometer. This in turn will lead to an increased confidence in the predictions of (general circulation) models concerning climate variability.

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### Methodische Aspekte bei der Messung von $\delta^{13}$ C in DOC am LC IsoLink

R. Langel<sup>1</sup>, L. Szwec<sup>1</sup>, L. Schwendenmann<sup>2</sup>, J. Dyckmans<sup>1</sup>

<sup>1</sup>Kompetenzzentrum Stabile Isotope, Büsgen-Institut, Universität Göttingen, Büsgenweg 2, 37077 Göttingen <sup>2</sup>Waldbau und Waldökologie der Tropen, Burckhardt-Institut, Universität Göttingen, Büsgenweg 1, 37077 Göttingen

Corresponding author: rlangel@gwdg.de

Die Messung von gelöstem organischem Kohlenstoff (DOC) am LC IsoLink über nasschemische Oxidation zu CO<sub>2</sub> bietet gegenüber der Gefriertrocknung und Messung am Elementaranalysator wesentliche Vorteile, da einerseits die zeitraubende Probenvorbereitung (Gefriertrocknung, Einwiegen des Trockenrückstands) entfällt und damit auch mögliche Artefakte durch Substanzverlust beim Trocknen und andererseits die erforderliche Probenmenge deutlich geringer ist. In einem Vergleich von DOC-Proben konnte gezeigt werden, dass die Messungen im Trockenrückstand und mittels LC IsoLink sich nicht unterscheiden. Allerdings ist bei der Messung über nasschemische Oxidation eine sorgfältige Kontrolle des pH-Wertes der DOC-Lösung notwendig, da bei pH-Werten über 5,5 möglicherweise Karbonat chemisch in der Probe gelöst sein kann. Das Austreiben des chemisch gelösten anorganischen Kohlenstoffs gelingt nicht durch reines Ansäuern, sondern erfordert das Entgasen im Heliumstrom.

# Are $\delta^{18}$ O values of plant sugars influenced by extraction and isolation proceedures?

A. Lenz<sup>1</sup>, R.A. Werner<sup>1</sup>, A. Kahmen<sup>2</sup>

<sup>1</sup>Institute of Plant Sciences, ETH Zurich, Switzerland <sup>2</sup>Center for Stable Isotope Biogeochemistry, University of California, Berkeley, USA

Corresponding author: rwerner@ipw.agrl.ethz.ch

The  $\delta^{18}O$  values of plant organic matter can be used to deduce environmental and ecophysiological information. Cellulose has been the target substance of paleo-climatological studies since the 1970s because of a more or less constant oxygen isotope enrichment of the carbohydrate relative to leaf water. Recently also mono- and disaccharides are receiving increasing attention. The <sup>18</sup>O/<sup>16</sup>O ratio of sugars transported in phloem sap can help to get information on the course and possibly also on the regulation of transport of the sugars from leaves to storage organs. The routine methods for extracting and isolating sugars from plant tissues for isotope ratio measurement (for δ<sup>13</sup>C determination) always include solution of the sugars in water - normally of different δ<sup>18</sup>O value relative to the original leaf or stem water. According

to our knowledge no standardized and tested method for the extraction and preparation for <sup>18</sup>O measurement of sugars is described in literature. One critical point in the extraction protocol is the drying process. The hygroscopicity of sugars might influence the  $\delta^{18}O$  value during storage. Additionally, water molecules might be bound to the sugar in form of thermostable water of crystallization. Monosaccarides like glucose and fructose which contain exchangeable C=O groups will exchange oxygen atoms with surrounding water molecules under drying conditions with heating the samples. First results of drying aqueous glucose, fructose and sucrose solutions using different equipment (lyophyllisation, speed vac, and drying oven) and their impact on  $\delta^{18}$ O values will be presented.

# Palaeoclimate reconstruction of the Piànico Interglacial (400ka old) by means of stable isotopes analyses on endogenic calcite

C. Mangili, A. Brauer, B. Plessen

Deutsches GeoForschungsZentrum, Sektion 5.2 – Climate dynamics and landscape evolution, Telegrafenberg, 14473 Potsdam, Germany

Corresponding author: mangili@gfz-potsdam.de

Stable isotope analyses on endogenic calcite are a good proxy for reconstructing palaeoclimate conditions and oscillations. The palaeolake sequence of Piànico (Southern Alps, Italy; 400 ka old) includes a succession of ca 15,500 varves that formed under interglacial conditions; each varve includes 1) a spring-summer light layer, composed of up to 96% of endogenic calcite, and 2) a darker and thinner winter layer, formed mainly by diatom frustules.

Detrital layers, mainly constituted by Triassic dolomite from the catchment, are sometimes included in the varves. As the stable isotope values of the dolomite would bias the stable isotope values of the endogenic calcite, we developed a sampling methodology based on the selection of detrital layer free intervals on thin sections prior to the sampling. For this study, each sample included precisely five varve years. The period of peak interglacial conditions is characterised by  $\delta^{18}$ O values of endogenic calcite between -8‰ and -10‰. During the upper half of the interglacial, four significant negative  $\delta^{18}$ O oscillations occurred. The most prominent of these oscillations has an amplitude of -1.1‰ and lasted 780 varve years. The three other oscillations are shorter (125–195 varve years) and of lower amplitude (0.4–0.9‰). These four  $\delta^{18}$ O oscillations are interpreted as cooling periods and reflect natural intra–interglacial climate dynamics. So far, a 780 year long cold phase has not been observed in the Holocene; this suggests unknown mechanisms controlling interglacial climate dynamics.

An additional major drop in  $\delta^{18}$ O occurs 315 varve years before the end of continuous calcite precipitation in the lake. This shift marks the end of long interglacial conditions, and the beginning of harsher climate conditions and glacier advances in the Southern Alps.

### Isotope und Eisbohrkerne

#### H. Miller

Alfred Wegener Institute for Polar and Marine Research, Am Alten Hafen 26, D-27568 Bremerhaven, Germany

Corresponding author: Heinrich.Miller@awi.de

Die großen und kalten polaren Eisschilde sind nicht nur wesentliche Faktoren im globalen Klimageschehen, sie stellen auch ein herausragendes Archiv des Paläoklimas und der generellen Bedingungen der Paläoumwelt dar. Dieses Archiv wird durch Bohrungen erschlossen und an den so gewonnenen Eisbohrkernen können mit Hilfe einer Reihe von analytischen Verfahren Proxies für die Umweltbedingungen der Vergangenheit bestimmt werden.

Ein wesentlicher Indikator für das Klima ist die Temperatur und das auf den stabilen Isotopen des Wasserstoffs und des Sauerstoffs basierende Paläothermometer wird seit Jahrzehnten sehr erfolgreich in der Analyse von Eisbohrkernen angewandt. Ebenso erlauben moderne Verfahren die Bestimmung des  $\delta^{13}$ C am Methan oder CO<sub>2</sub> der im Eis eingeschlossenen Luft. Damit lassen sich dann Aussagen treffen über mögliche Mechanismen der natürlichen Veränderlichkeit des Kohlenstoffkreislaufes.

Im Vortrag wird nach einer Einführung über die polaren Eisschilde und ihre Funktion die Arbeit des im Eis sehr speziellen Bohrens selbst erläutert und im zweiten Teil wird anhand von Ergebnissen verdeutlicht welch große und sichere Aussagekraft in der Ergebnissen der Isotopenanalytik steckt und wie diese zu unserer heutigen Kenntnis über das Klimasystem beitragen. Im allgemeinen stellen die aus Isotopenwerten des Eises abgeleiteten Temperatur- und Niederschlagsdaten für die Vergangenheit den primären Datensatz für Paläoklimarekonstruktionen dar, weil sie zeitlich hochaufgelöst und recht gut datierbar sind.



Abb. 1. oben: Bohren eines tiefen Eiskerns im Dronning Maud Land im Rahmen des EPICA Projektes unten: Eislabor zur Präparation von Eiskernen im Alfred Wegener Institut, Bremerhaven

### Permafrost ice – a Quaternary climate archive

H. Meyer<sup>1</sup>, A. Dereviagin<sup>2</sup>, T. Opel<sup>1</sup>, G. Schwamborn<sup>1</sup>, L. Schirrmeister<sup>1</sup>, H.-W. Hubberten<sup>1</sup>

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Research Unit Potsdam, D-14473 Potsdam, Germany <sup>2</sup>Lomonosov Moscow State University, Department of Geology, 119992, Moscow, Vorobyovy Gory, Russia.

Corresponding author: Hanno.Meyer@awi.de

Permafrost regions are known to be susceptible to recent climate warming particularly with regard to positive feedback mechanisms (e.g. by the potential release of stored carbon) from permafrost. However, little is known about the potential of permafrost ice - so called ground ice - to store climate and environmental changes. Stable water isotope methods can - under certain circumstances - reveal climate information from permafrost ice and trace the changes through time. Stable water isotopes (δD,  $\delta^{18}$ O) are well established as mostly relative paleotemperature proxies for climate studies related to ice caps and glaciers in Greenland, Antarctica and other parts of the world. For permafrost research, the water isotopes have yet been underutilized.

Ground ice is defined as all types of ice contained in frozen or freezing ground, including pore ice, segregated ice, as well as ice wedge ice. Ice wedges are most promising as paleoclimate archives. They are distinctive due to their vertically-oriented foliations and air bubbles. Ice wedges form as winter thermal contraction cracks are periodically filled by surface water (mainly from snow melt), which quickly (re) freezes at negative ground temperatures. The seasonality of thermal contraction cracking and of the infill of frost cracks are generally related to winter and spring, respectively. Ice wedges are, thus, assumed to be indicative of winter climate conditions. The processes involved are most likely free of any fractionation during freezing. Segregated ice forms by the process of ice segregation (motion of ground water in the sediment column towards a freezing front). Segregated ice is rather a mixture of winter and summer precipitation, which additionally has undergone fractionation during freezing. One must bear in mind that ground water in permafrost regions is mostly related to the active layer (a sub meter to meter thick layer, which melts in summer and freezes in winter). A third type of ground ice, so called pore ice also known as ice cement, is also intrasedimental ice occurring in the pores of soils, which was formed in situ (without water migration towards a freezing front). This type of ice is typical for relatively coarse-grained sediment. Here, also ground water is the main water source.

All these different types of ground ice have a different genetic background, which can be traced by stable isotope methods. This includes the type of water involved (e.g. summer vs. winter precipitation, with relevant isotopic composition) as well as the amount of fractionation occurring during phase transitions in the water cycle. Under favorable conditions (such as minimal fractionation during freezing) the stable isotope composition of these different types of ground ice can be used as paleo archive: (1) for the differentiation of stratigraphical units i.e. Holocene ground ice being generally 3 to 7‰ heavier in  $\delta^{18}$ O than Pleistocene ground ice, (2) as centennial-scale climate archives for paleotemperature reconstruction as well as indication of (3) changing atmospheric moisture sources from climate-relevant d excess (d excess =  $\delta D-8^*\delta^{18}O$ ) records. In this paper, we tackle the potential of the different types of ground ice from Siberian and North American permafrost to trace past climate changes from relative isotope variations in intrasedimental ice to a detailed high-resolution winter climate record from Alaskan ice wedges for the Late Glacial-Holocene transition.

# Analysis of carbohydrate concentrations and stable carbon-isotope ratios in natural and <sup>13</sup>C enriched samples using liquid chromatography coupled to isotope ratio mass spectrometry (LC-IRMS)

T.C.W. Moerdijk-Poortvliet, H.T.S. Boschker, P. van Breugel, M. Houtekamer, J.J. Middelburg

Netherlands Institute of Ecology (NIOO-KNAW), Centre for Estuarine and Marine Ecology, P.O. Box 140, 4400 AC Yerseke, the Netherlands

Corresponding author: t.moerdijk@nioo.knaw.nl

Liquid chromatography interfaced with isotope ratio mass spectrometry (LC-IRMS) is a relatively new methodology. The first commercial instrumentation (LC-IsoLinkTM) became available in 2004<sup>1</sup>. Since then a number of researcher have shown that this technique can provide high precision carbon-isotope ratios for a range of compounds.

We developed a method to analyze stable carbon isotope (<sup>13</sup>C/<sup>12</sup>C) ratios in a variety of carbohydrates using LC-IRMS<sup>2</sup>. Chromatography is based on strong anion-exchange columns with low strength NaOH eluents. An eluent concentration of 1 mM resulted in low background signals and good separation of most of the typical plant neutral carbohydrates.

We also show that more strongly bound carbohydrates such as acidic carbohydrates can be separated by inclusion of  $NO_3^-$  as an inorganic pusher ion in the eluent. Analysis of neutral carbohydrate concentrations and their stable carbon isotope ratios is shown for plant materials and marine sediment samples both at natural abundance and for <sup>13</sup>C-enriched samples.

The main advantage of LC-IRMS analysis over traditional gas-chromatography based methods (GC-IRMS) is that no derivatisation is needed. Derivatisation introduces an additional source of errors into the isotopic determination, especially at natural abundance. Therefore, LCIRMS is an ideal alternative to GC-IRMS since it allows simple sample treatment and an improved accuracy and reproducibility.



Fig. 1. Chromatogram of neutral carbohydrates, 1500 2M



Fig. 2. The natural variation of  $^{13}\text{C}$  Glucose in various species and materials: C\_3 plants, soils, roots, lichens, mosses, algae, C\_4 plants

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<sup>2</sup>Boschker, H.T.S. et al., Rapid Commun. Mass Spectrom. 2008; 22: 3902-3908

# The vertical distribution of $\delta^{13}$ C values to predict mineralized N in soil in a tropical montane rain forest in Ecuador

Y. Oelmann<sup>1</sup>, U. Hensler<sup>1</sup>, C. Valarezo<sup>2</sup>, W. Wilcke<sup>1</sup>

<sup>1</sup>Earth System Science Research Center, Geographic Institute, Professorship of Soil Geography/Soil Science, Johannes Gutenberg University, Johann Joachim Becher-Weg 21, 55128 Mainz, Germany
<sup>2</sup>Universidad Nacional de Loja, Dirección General de Investigaciones. Ciudadela Universitaria Guillermo Falconí, sector La Argelia, Loja, Ecuador

Corresponding author: yvonne.oelmann@uni-mainz.de

Slow nutrient turnover in soil is a possible reason for reduced growth of tropical montane forests. Our objectives was to evaluate selected proxies to predict potential net N mineralization in soil in a montane rainforest (1870-2190 m asl) in Ecuador. We determined release of N (potential net N mineralization) in a laboratory incubation of organic layers and of mineral soil for 92 days and initial pH, concentrations of C and N, and  $\delta^{13}$ C and  $\delta^{15}$ N values in Oi, Oe, Oa, and A horizons.

Altitude correlated positively with C and N storage and negatively with potential N mineralization of the complete soil profile which contributes to the explanation of reduced growth at higher altitudes. Nitrogen turnover times of the soil profiles ranged between 4 and 20 yrs and were significantly correlated with the vertical distribution of  $\delta^{13}$ C values from Oi to A horizons (either expressed as the slope of the regression between organic C concentrations in soil and  $\delta^{13}$ C values from Oi to A horizons [ $\beta_c$ ] or as the absolute difference in δ13C values between Oi and A horizons [ $\Delta \delta^{13}$ C Oi – A]). The  $\beta_{c}$  values of the tropical montane rain forest under study were greater than observed for temperate forests which coincided with faster organic matter recycling. Because minimum values of  $\beta_{c}$  or  $\Delta \delta^{13}$ C Oi – A were greater than 1 ‰, the Suess effect can be assumed negligible in our study. The  $\beta_c$  or  $\Delta \delta^{13}$ C Oi – A correlated closely with potential net N mineralization of the soils profiles (Figure 1; 0.60 < r < 0.87, p<0.01) providing a tool to upscale potential net N mineralization to larger areas without laborious incubations.



Fig. 1. Regression of potential net N mineralization of the soil profile on (A)  $\beta_c$ , (the slope of the regression of  $\delta^{13}$ C values on log C concentrations of the depth profile), and (B) on  $\Delta\delta^{13}$ C Oi – A( the difference in  $\delta^{13}$ C between the Oi and A horizon). Triangles and circles refer to ridge and valley positions respectively. The regression includes ridge and valley positions because there was no significant difference in  $\beta_c$  or  $\Delta\delta^{13}$ C Oi – A between topographic positions. \*\* p < 0.01, \*\*\* p < 0.001.

# Late Holocene climate change in the Eurasian Arctic – Evidence from Akademii Nauk Ice Core (Severnaya Zemlya)

#### T. Opel<sup>1</sup>, D. Fritzsche<sup>1</sup>, H. Meyer<sup>1</sup>

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Research Unit Potsdam, Telegrafenberg A 43, D-14473 Potsdam, Germany

#### Corresponding author: thomas.opel@awi.de

Ice cores are well known as one of the best archives for providing information on paleoclimatic and paleoenvironmental changes on different temporal and spatial scales. A 724 m deep ice core was drilled recently on the relatively low-altitude Akademii Nauk (AN) ice cap (Severnaya Zemlya) to gain high resolution paleoclimatic information from the Central Russian Arctic. The AN ice core provides significant proxy data for the reconstruction of regional climate and environmental changes; although the ice cap is affected by strong summertime melt water infiltration. We present data of stable water isotopes ( $\delta^{18}$ O, deuterium excess d), meltlayer content and major ions of the upper 535 m, covering about 1 700 years in an annual to multi-annual resolution. The core chronology is based on volcanic reference layers and stableisotope annual layer counting.

The AN  $\delta^{18}$ O data are highly correlated to instrumental temperature data from the Western Eurasian Arctic and can therefore be used as valuable near-surface temperature proxy for this region. The long-term decrease of AN  $\delta^{18}O$  and also sea salt ion concentrations reflects the growth of AN ice cap over large parts of the Late Holocene. AN δ18O data reveal major temperature changes in the last centuries, particularly rapid warming and cooling events in the 15th and 16th centuries, the absolute minimum around 1800 and the exceptional warming to the double-peaked early 20th century maximum, which represents the absolute temperature maximum in the Late Holocene. These changes indicate considerable shifts in atmospheric circulation patterns, accompanied by sea ice extent changes. However, no pronounced Medieval Warm Period or Little Ice Age is visible in our AN data. Generally, AN  $\delta^{18}$ O values coincide well with that of the Austfonna ice core (Svalbard), underlining the regional significance of AN ice core data.

In the 20th century, AN d excess variations are connected with regional sea ice extent changes. Low sea-ice extent allows a higher contribution of regional moisture, leading to lower d excess due to colder evaporation conditions. In turn, a high sea-ice extent prevents a considerable regional moisture contribution to the precipitation on Akademii Nauk ice cap, which is therefore characterized by higher d excess values. This pattern indicates that d excess can provide information on the proportion of regional moisture in the precipitation and therefore on regional sea ice extent changes.

The major ion concentrations in AN ice core reflect the atmospheric aerosol content. Warmer periods show evidence of higher sea-salt ion concentrations due to less sea-ice extent. Outstanding peaks in sulphate represent major volcanic eruptions. The 20th century ion records indicate major shifts in atmospheric circulation and significant anthropogenic pollution.

# Determination of <sup>13</sup>C/<sup>12</sup>C ratios of endogenous urinary steroids excreted as sulphates: Methods validation and reference population

T. Piper, U. Flenker, W. Schänzer

Institute of Biochemistry, German Sport University, Cologne, Germany

Corresponding author: t.piper@biochem.dshs-koeln.de

The application of a comprehensive gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS)-based method for stable carbon isotopes of endogenous urinary steroids excreted as sulphates is presented. The key element in sample preparation is the consecutive clean up with high performance liquid chromatography of underivatized and acetylated steroids, which allows the isolation of 7 sulphated analytes from a single urine specimen: dehydroepiandrosterone, androsterone, etiocholanolone, epiandrosterone, 5-pregenen-3b,17,20a-triol, 5-androsten-3b,17bdiol and 5-androsten-3b,17a-diol)

Depending on the biological background, the determination limit for all steroids ranges from 5 to 10 ng/mL for a 10 mL specimen. The method was validated by means of linear mixing models for each steroid, which covers the items repeatability and reproducibility. Specificity was further demonstrated by gas chromatography/mass spectrometry (GC/MS) for each analyte, and no influence of the sample preparation or the quantity of analyte on carbon isotope ratios was observed. In order to determine naturally occurring  ${}^{13}C/{}^{12}C$  ratios of all implemented steroids, a reference population of n = 67 subjects was measured to enable the calculation of reference limits for all relevant steroidal D values. With each batch of samples a blank urine was processed to test the method's repeatability over six month.

In comparison to GC/C/IRMS determinations of steroids excreted as glucuronides can in general be stated that sulphated steroids tend to be more enriched in <sup>13</sup>C. Especially dehydroepiandroster-one and 5-pregenen-3b,17,20a-triol differ by more than 1 ‰. The presumed precursor of epitestoster-one, 5-androsten-3b,17a-diol is enriched by 1.3 ‰ in contrast to epitestosterone-glucuronide. Differences between the genders are more pronounced in glucuronidated steroids but found in sulphated steroids, too. Contraceptives seemed to be responsible for the difference between genders.

### Small pelagic seabirds in polar waters - stable isotopes reveal migration and foraging patterns

Petra Quillfeldt, Rona McGill, Robert W. Furness, Christian C. Voigt, Juan F. Masello

Max-Planck-Institut für Ornithologie

Corresponding author: petra.quillfeldt@gmx.de

Small pelagic seabirds are difficult to observe in their vast marine ecosystems, and little is known about their distribution and behavior outside the breeding season. In the Southern Ocean, the carbon stable isotope ratio declines markedly with more southern latitude, providing a characteristic stable carbon isoscape. This can be used as a tracer for the movement of seabirds between breeding and wintering areas, by comparing stable isotope ratios of feathers grown at different times of the year. We studied movements of thin-billed prions (Aves, Procellariiformes), breeding at the Subantarctic Falkland/Malvinas Islands. We here present data on migration patterns, individual strategies and historical changes in migratory patterns. This study shows that pelagic seabirds can have highly flexible and rapidly evolving migration strategies within populations, including migration towards more poleward waters in winter. Flexibility in migration at the individual level enables Thin-billed prions to exploit a highly unpredictable environment.

# Variability in tree ring stable C and O isotopes as a response to increasing CO<sub>2</sub>

R. Siegwolf<sup>1</sup>, M. Saurer<sup>1</sup>, O. Sidorova<sup>1,2</sup>

<sup>1</sup>Paul Scherrer Institut, 5232 Villigen, Schweiz <sup>2</sup>V.N. Sukachev Institute of Forest SB RAS, Akademgorodok, Krasnoyarsk 660036, Russia

Corresponding author: rolf.siegwolf@psi.ch

With the increasing industrialization since the last 150 years, the atmospheric CO<sub>2</sub> concentration has increased as a result of the increased use of fossil fuels. This does not only affect the global climate but leaves also its fingerprints on the vegetation. Plants respond to increasing atmospheric CO<sub>2</sub> (c<sub>2</sub>) instantaneously with an increased photosynthetic rate, while stomatal conductance is reduced. This results in lower intercellular CO<sub>2</sub> concentration (c<sub>i</sub>) or a lower c/c<sub>a</sub> ratio, which is reflected in a reduced <sup>13</sup>C discrimination during photosynthesis. This has also implications on the water use efficiency. However, the longer plants are exposed to elevated CO<sub>2</sub> the more they acclimatize i.e. down regulate the photosynthetic capacity, along with an increase in stomatal conductance. The degree of this down regulation varies between the different plant species. There is still an uncertainty about the long-term effects of elevated CO<sub>2</sub> on plants, in particular on trees. Here the use of tree rings represents a valuable proxy to detect the response of trees over the last 150 years.

In this presentation stable C and O isotope data from tree rings for the last 150 years from Switzerland and Siberia (Russia) are shown. A detailed demonstration of the data analysis will be given. With the help of a conceptual approach we link gas exchange mechanisms with  $\delta^{13}$ C and  $\delta^{18}$ O data. With this conceptual approach (Saurer and Siegwolf, 2007) we can distinguish whether trees respond to elevating CO<sub>2</sub> with an increase in the photosynthetic rate or with changes in the stomatal conductance or both. The understanding of the physiological response patterns of trees to elevated CO<sub>2</sub> allows an improved interpretation of climate data for the last 150 years.

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### Myco-heterotrophy in a selection of Western Australian orchids

J. Sommer<sup>1</sup>, K.W. Dixon<sup>2</sup>, M.I. Bidartondo<sup>3</sup>, G. Gebauer<sup>1</sup>

<sup>1</sup>Laboratory of Isotope Biogeochemistry, BayCEER, University of Bayreuth, 95440 Bayreuth, Germany

<sup>2</sup>Botanic Gardens and Park Authority, Kings Park and Botanic Garden, West Perth, Western Australia 6005, Australia

<sup>3</sup>Imperial College London & Royal Botanic Gardens, Kew TW9 3DS, UK;

Corresponding author: summerlikewinter@yahoo.com

The Western Australian flora – is one of the renowned hotspots in plant diversity on Earth and the Orchidaceae is one of the largest and most diverse plant family. The orchids of Western Australia with over 400 recognized taxa of which 76 are Declared Rare or Priority Flora and their ecology are the topic of this project.

C and N stable isotope natural abundances in leaves of selected orchids and reference plants and a linear two-source mixing model were used to investigate different nutrition modes on a broad range of taxonomic orchid groups in Western Australia.Myco-heterotrophic plants are characterized by a strong enrichment in the heavy isotopes (<sup>15</sup>N ,<sup>13</sup>C) in comparison to the reference plants from the same habitat. This typical isotope signature results from the organic nutrient gain through their mycorrhizal association. Furthermore, mycorrhizal fungi from specific parts of the orchid roots were identified by molecular DNA analysis.

Data from this investigation provide evidence that at least four nutitional modes can be found among orchids from Western Australia: (1) green species fully autotrophic when adult (e.g. *Caladenia latifolia*), (2) achlorophyllous species fully mycoheterotrophic throughout their life cycle (e.g. *Gastrodia lacista*), (3) green species gaining organic N through the fungal source (e.g. *Prasophylum elatum*) and (4) green species transferring carbohydrates to their fungal partners (e.g. *Corybas recurvus*).

### Messung und Simulation der Entstehung der N-Gase durch Nitrifikation und Denitrifikation mittels eines <sup>15</sup>N-Markierungsversuches

C.F. Stange<sup>1</sup>, R. Russow<sup>1</sup>

1Helmholtz-Zentrum für Umweltforschung - UFZ, Theodor-Lieser-Str. 4, D-06120 Halle

Corresponding author: florian.stange@ufz.de

Schon lange ist bekannt, dass NO ein obligates Zwischenprodukt der  $N_2O$ - und  $N_2$ -Bildung durch Denitrifikation ist. Trotzdem wird bei Messungen im Freiland, bei denen mittels <sup>15</sup>N Tracertechnik zwischen den Quellen unterschieden wurde, immer wieder die Nitrifikation als Hauptquelle festgestellt. Und dies auch unter Umweltbedingungen, die eindeutig die Denitrifikation bevorzugen und unter denen die  $N_2O$ -Emission hauptsächlich denitrifikatorischen Ursprunges ist. Daher wurde schon seit längerem (Firestone & Davidson, 1989) die Hypothese aufgestellt, dass das denitrifikatorisch gebildete NO durch die Mikroorganismen sehr weiter zu N<sub>2</sub>O reduziert wird, bevor es an die Bodenoberfläche diffundieren und letztendlich emittieren kann. Dies sollte besonders bei hoher Wassersättigung des Bodens – also denitrifikationsfördernden Bedingungen zutreffen ("diffusion limitation" Hypothese).

Zum Testen dieser Hypothese wurde ein <sup>15</sup>N Markierungs-Experiment durchgeführt, bei dem die Bedingungen möglichst optimal für die Diffusion waren (also ohne hohe Wassersättigung). Um trotzdem hinreichende Denitrifikationbedingungen zu erhalten, wurde während des Versuches der Sauerstoffpartialdruck schrittweise von 20% über 2% und 0,3% auf 0,0% gesenkt. Zur Unterscheidung der Quellen der N-Spurengase und zur Aufklärung der Reaktionswege wurden drei Parallelversuche durchgeführt. In allen drei Varianten wurden Ammonium, Nitrat und Nitrit zu dem Boden gegeben, aber jeweils nur eine der N-Verbindung war <sup>15</sup>N markiert.

Die NO Emission stiegt mit sinkendem Partialdruck des Sauerstoffes von 0,9 auf 3,7 µg Kg<sup>-1</sup> h<sup>-1</sup> an. Auch die N<sub>2</sub>O Emission stiegt an, doch betrug nur ein zehntel der NO-Emission. Die <sup>15</sup>N-NO<sub>2</sub><sup>-</sup> Variante belegt, dass Nitrit der fast alleinige Vorgänger des emittierten NO ist. Dabei kann das Nitrit durch Nitrifikation bzw. durch Denitrifikation gebildet sein. Unter hohen Sauerstoffpartialdruck trägt die Nitrifikation ca. 90% zur Nitritbildung bei, wobei der Anteil mit sinkendem O<sub>2</sub>-Partialdruck schnell sinkt und bei Sauerstoffmangel 100% der Nitritbildung durch die Denitrifikation erfolgt. Die Versuche zeigen, dass durch die Denitrifikation in erheblichem Ausmaß freies NO gebildet wird und festigt damit die "diffusion limitation" Hypothese.

Entgegen den Ergebnissen der NO-Bildung konnte für die geringe N<sub>2</sub>O-Bildung kein eindeutiger Vorgänger ausfindig gemacht werden. Die Bildung des N<sub>2</sub>O durch Nitrifikation erfolgt anscheinend nicht oder zumindest nicht ausschließlich über Nitrit (Nitrifizierer Denitrifikation). Auch trägt ein (oder mehrere) in allen Versuchsvarianten unmarkierter Pool (z.B. org. Substanz) substanziell zur  $N_2O$ -Emission bei (z.B. heterotrophe Nitrifikation). Aufgrund der geringen Flussraten sind jedoch die Ergebnisse der  $N_2O$ -Messungen mit großen Unsicherheiten behaftet. Die Ergebnisse dieser Studie sind kürzlich in SBB erschienen (Russow et al., 2009).

Der Experimentalversuch wurde mit verschiedenen Modellansätzen simuliert Dabei konnte die beste Übereinstimmung zwischen Daten und Modell dann erreicht werden, wenn man im Modellansatz von drei verschiednen Nitritpools ausgeht. Diese drei Nitritpools besitzen unterschiedliche <sup>15</sup>N-Häufigkeiten, die sich aus den <sup>15</sup>N-Häufigkeiten ihres Ursprunges (nitrifikatorisch aus Ammonium oder denitrifikatorisch aus Nitrat) ergeben.

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### C and N isotope signatures of myco-heterotrophic plants associated with arbuscular mycorrhiza from a tropical rain forest - A new facet of nutrient exchange between fungi and plants

M. Stöckel<sup>1</sup>, V. Merckx<sup>2</sup>, G. Gebauer<sup>1</sup>

1Laboratory of Isotope Biogeochemistry, Bayreuth Center of Ecology and Environmental Research (Bay-CEER), University of Bayreuth, 95440 Bayreuth, Germany <sup>2</sup>Department of Plant and Microbial Biology, University of California, Berkeley, California 94720-3102, USA

Corresponding author: marcus.stoeckel@uni-bayreuth.de

In the mycorrhizal symbiosis, plants exchange carbohydrates from photosynthesis for mineral nutrients acquired by fungi from the soil. This mutualistic arrangement has world wide been subverted by a few hundreds of mycorrhizal plants that lack the ability to photosynthesize and thrive into the deepest shade of forests. These 'myco-heterotrophic' plants either associate with ectomycorrhizal (ECM) and arbuscular mycorrhizal (AM) fungi, which are simultaneously mycorrhizal with neighbouring photosynthetic trees, or with usually saprotrophic, wood-rotting (SAP) fungi. Results from recent investigations document that the C and N isotope signatures of various myco-heterotrophic Orchidaceae and Ericaceae associated with ECM fungi and of a myco-heterotrophic orchid associated with a SAP fungus are driven by the isotope signatures of their respective fungal hosts and therefore are significantly enriched in <sup>13</sup>C and <sup>15</sup>N in comparison to photosynthetic plants from the same habitats. For the fungal partners of these myco-heterotrophs carbohydrates from tree photosynthesis or from wood rotting and organic N compounds from soil or wood decay through fungal exoenzyme production serve as C and N sources, respectively.

Here we report for the first time on C and N isotope signatures of two myco-heterotrophic species associated with AM fungi and growing in a tropical rain forest in French Guiana: *Voyria aphylla* (Gentianaceae) and *Dictyostega orobanchoides* (Burmanniaceae). These two myco-heterotrophs are again significantly enriched in <sup>13</sup>C, however, are not distinguished in their N isotope signature from accompanying plants. Based on these findings we conclude that the AM hosts of these plants in contrast to ECM and SAP fungi utilize inorganic N compounds as preferred N source.

### Zwischen Grün und Weiss - Zusammenhang zwischen dem Chlorophyllgehalt der Blätter und dem Grad der Mykoheterotrophie bei der Orchidee Cephalatera Damasonium

M. Stöckel<sup>1</sup>, C. Meyer<sup>1</sup>, G. Gebauer<sup>1</sup>

<sup>1</sup>Labor für Isotopen-Biogeochemie, Bayreuther Zentrum für Ökologie und Umweltforschung (BayCEER), Universität Bayreuth, 95440 Bayreuth, Deutschland

Corresponding author: marcus.stoeckel@uni-bayreuth.de

Über 400 Gefäßpflanzenarten sind keine Parasiten auf autotrophen Pflanzen und besitzen dennoch kein Chlorophyll. Ihnen fehlt somit die Voraussetzung, die für Pflanzen essentielle Kohlenstoffquelle CO<sub>2</sub> erschließen zu können. Um ihren Kohlenstoff- und wahrscheinlich auch Teileihres Stickstoffbedarfs zu decken, bedienen sich diese Pflanzen ihrer Mykorrhizapilzpartner. Ihre Ernährungsweise wird als Mykoheterotrophie bezeichnet. Nicht nur chlorophylllose Arten können sich dieser Ernährungsvariante bedienen. Untersuchungen an grünen Vertretern der Orchidaceae und Ericaceae machten deutlich, dass auch sie teilweise große Anteile ihres Kohlenstoffs (C) und Stickstoffs (N) von assoziierten Pilzpartnern beziehen können. Diese so genannte partielle Mykoheterotrophie wird durch Analyse der natürlichen Häufigkeit der stabilen C und N Isotope identifiziert. Der Anteil des vom Pilzpartner stammenden C bzw. N kann sogar mit Hilfe eines linearen Mischungsmodells abgeschätzt werden.

In den gemäßigten Breiten handelt es sich bei diesen assoziierten Pilzen um mit Bäumen Ektomykorrhiza formende Arten, welche im Vergleich zur umgebenden autotrophen Vegetation sowohl an <sup>13</sup>C als auch an <sup>15</sup>N angereichert sind. Da sie den partiell mykoheterotrophen Pflanzen als Nährstoffquelle dienen, werden deren δ13Cund  $\delta^{15}$ N-Werte ebenfalls umso positiver, je mehr sie vom Pilz Gebrauch machen. Ein einheimischer Vertreter der partiell mykoheterotrophen Orchideen ist das weiße Waldvögelein, Cephalanthera damasonium. Von dieser Orchideenart treten vereinzelt chlorophyllfreien Mutanten (Albinos) auf, die durch den Zugang zu einer alternativen Kohlenstoffquelle, im Gegensatz zu nicht mykoheterotrophen Arten, lebensfähig sind und ihren grünen Artgenossen in punkto Vitalität in nichts nachstehen.

Wir berichten nun erstmalig über das Ernährungsverhalten, von *C. damasonium* Individuen, die einen kontinuierlichen Übergang zwischen grünem Wildtyp und chlorophyllfreier Mutante darstellen. An 28 *C. damasonium* Individuen aus einem Laubmischwald, sowie einem Buchenwald im Nordosten Bayerns wurden der Chlorophyllgehalt der Blätter und die C-Isotopensignatur bestimmt. Dadurch konnten Aussagen zum Grad der Mykoheterotrophie bei den verschiedenen Phänotypen getroffen werden. Zwischen den gemessenen Größen tritt eine positive Korrelation auf: je weißer die Blätter der einzelnen Individuen sind, desto mehr C erhalten sie vom Pilz. Des Weiteren wurde eine positive Korrelation zwischen dem Chlorophyllgehalt und der C-Konzentration in den einzelnen Blättern festgestellt.

# Identifying water sources and the impact of decreasing $\delta^{18}$ O values of sulfate from precipitation in the region of Freiberg, Southeastern Germany

M. Tichomirowa<sup>1</sup>, C. Heidel<sup>1</sup>, M. Junghans<sup>2</sup>, F. Haubrich<sup>3</sup>

<sup>1</sup>TU Bergakademie Freiberg, Institut für Mineralogie, Brennhausgasse 14, 09596 Freiberg

<sup>2</sup>TU Bergakademie Freiberg, IUZ, 09596 Freiberg

<sup>3</sup>TU Dresden, Institut für Bodenkunde und Standortlehre, Pienner Str. 19, 01737 Tharandt

Corresponding auhor: tichomir@mineral.tu-freiberg.de

Three main sources were determined by chemical and isotope investigations of various water types (bulk atmospheric precipitation, groundwater, river water, flowing mine water, mine drainage galleries, flooding mine water) in the Freiberg region, an area with a long mining history and formerly very high pollution levels of SO<sub>2</sub> ("Black Triangle"). Endmember I is sulfate from groundwater which finally derives from atmospheric precipitation. Endmember II is sulfate formed due to oxidation processes of ore sulfides remained after mining ended in the unflooded und flooded part. Endmember III is sulfate washed out from abundant waste and slag deposits left behind after a long mining and industrial history of this region.

A lower input of "industrial" derived sulfate from waste and slag deposits was found for the time period 1997 to 2002 in some drainage galleries and flooding water, discharging their water into local rivers. On the other hand, groundwater shows decreasing sulfate concentrations mainly after 2002. We attribute this to a time delayed response of the major decrease of industrial SO<sub>2</sub> emissions (starting from 1990) and a corresponding decrease in air SO<sub>2</sub> concentration. Dissolved sulfates from atmospheric precipitation and groundwater record a large shift in their oxygen isotope composition at least from 2006, whereas their sulfur isotope composition remained constant. This caused a varying decrease of the oxygen isotope composition of sulfate in other water types (river water, mine water). One possible explanation for this oxygen isotope decrease is that less "primary" sulfates contributed to atmospheric sulfate. However, this has to be confirmed by further data from a broader regional or even global scale.

# Application of compound-specific carbon and hydrogen isotope ratios to evaluate alteration processes in petroleum reservoirs

A. Vieth<sup>1</sup>, M. Gabriel<sup>1</sup>, H. Wilkes<sup>1</sup>

<sup>1</sup>German Research Centre for Geosciences GFZ, Section Organic Geochemistry, Telegrafenberg, D-14473 Potsdam

Corresponding author: vieth@gfz-potsdam.de

The natural biodegradation of hydrocarbons in geological reservoirs is one of the main global controls on the occurrence, composition and quality of crude oils. Biodegradation in petroleum reservoirs will take place near the oil-water interface and was described to be of interest in reservoirs that were not exposed to temperatures > 80°C (Wilhelms et al., 2001). The oilwater contact provides conditions that are the most conducive to microbial activity. Diffusive transport of hydrocarbons through the oil column to the oil-water contact will provide electron donors, whereas inorganic nutrients required for microbial growth can be transported by water flow or diffusion in the water column to the oil-water contact (Head et al., 2003). Biodegradation processes in crude oils were described to lead to the quasi-sequential removal of compound groups as follows: n-alkanes > branched alkanes > alkylbenzenes > alkylnaphthalenes > alkylcyclohexanes, alkylphenanthrenes and alkyldibenzothiophenes > isoprenoids ( $C_{15+}$ ) > regular steranes > hopanes > aromatic steranes (Peters & Moldowan, 1993; Wenger et al., 2002). However, recent work on molecular changes in biodegraded oils indicates that the degradation patterns of light hydrocarbons and n-alkanes differ in different petroleum systems. This suggests that microbial communities are different and therefore generate different molecular degradation patterns which have to be evaluated individually for each system (Elias et al., 2007).

Biodegradation processes typically lead to enrichment of the molecules with the heavier isotope in the residual fraction of a substrate due to kinetic isotope effects of the first irreversible reaction in a degradation pathway. The relation between decrease in concentration and change in isotopic composition of the residual substrate can be described by the Rayleigh Equation (equation 1) where F is the fraction of the hydrocarbon remaining (C/Ci), R is the isotopic composition of the hydrocarbon at a particular F and Ri is the initial isotopic composition.

$$\frac{R}{R_i} = F^{(a-1)} \qquad \text{(equation 1)}$$

The isotope fractionation factor ( $\alpha$ ) relates the changes in the isotopic composition to changes in the concentration of the residual fraction during the transformation. It is quite common to use the enrichment factor  $\epsilon$  (equation 2) instead of  $\alpha$ . The Rayleigh Equation provides the opportunity to quantify the amount of biodegradation based on carbon or hydrogen isotope ratios and the appropriate isotope fractionation factor independent from concentration measurements.

$$\varepsilon = (\alpha - 1) \cdot 100$$
 (equation 2)

In petroleum reservoirs the enrichment in <sup>13</sup>C of selected petroleum hydrocarbons has been used as a qualitative indicator of biodegradation but can also be used to quantify biodegradation of selected light hydrocarbons (Vieth & Wilkes, 2006). The complex situation within petroleum reservoirs will limit the application of stable isotopes as indicators of biodegradation processes if oil samples with origin from different source rocks, thermal maturities as well as charging and mixing histories are evaluated.

It is known that the application of stable isotopes for the assessment of biodegradation of individual hydrocarbons becomes increasingly insensitive with increasing chain length of the target compounds as a result of the dilution of the isotope effect occurring at the reactive site over the whole molecule. Assuming that for field studies at least a change in  $\delta^{13}$ C of 2 ‰ for an individual compound would be required for a reliable assessment of biodegradation the isotope method will be limited to compounds with a maximum number of approximately 10 carbon atoms (Wilkes et al., 2008). Comparable limitations are expected to occur for the effects of biodegradation on the hydrogen isotopic compositions of individual hydrocarbons. In petroleum reservoirs, therefore, the isotope ratios of larger *n*-alkanes, as well as pristane and phytane will remain unchanged during biodegradation and will reveal information about charging and migration.

Based on these conceptual assumptions the stable carbon and hydrogen isotopic compositions of light hydrocarbons, *n*-alkanes, pristane and phytane of oil samples from different petroleum reservoirs have been evaluated and several new isotope parameters have been developed to assess and differentiate alteration processes that occurred and influenced the molecular and isotopic composition of the oils on the reservoir scale.

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### Nitrogen retention in the Oder Lagoon, Baltic Sea

M. Voss<sup>1</sup>, B. Deutsch<sup>1</sup>, I. Liskow<sup>1</sup>, M. Pastuszak<sup>2</sup>, U. Schulte<sup>3</sup>, S. Sitek<sup>4</sup>

<sup>1</sup>Leibniz Institute for Baltic Sea Research, Seestr. 15, 18119 Rostock, Germany <sup>2</sup>Sea Fisheries Institute, Kołłątaja 1, PL-81-332 Gdynia, Poland

Corresponding aurhor: maren.voss@io-warnemuende.de

The Baltic Sea receives nutrients from a drainage area populated by 85 million people. Moreover the Baltic Sea receives 15,000 m<sup>3</sup>s<sup>-1</sup> of river water mainly in its eastern parts and inflows of North Sea waters from the west. The nitrogen load from all rivers draining into the Baltic Sea is 702 kt y<sup>-1</sup> and app. twice as high as the ones from atmospheric deposition and nitrogen fixation. Most of the rivers draining densely populated catchments with high shares of arable land are located in the south and southeast of the Baltic Sea. Among theses

are the five biggest rivers in terms of N loads; the Neva, the Vistula, the Daugava, the Nemunas and the Oder Rivers. These rivers – except the Neva River which mainly receives the urban waste waters of the city of St. Petersburg - carry nitrogen from diffuse nitrogen sources mainly from arable land and husbandry. These loads are very difficult to control and until now not much success on the reduction has been reported.

Natural nitrogen removal can be significant when the residence time in an estuary is long
enough and when the site offers zone of natural denitrification. This may be the case in lagoons, bays, eelgrass stands, and swamps. Budget calculations of nutrients and particles in the Oder lagoon and the Pomeranian Bay had been done by but concentrated on conceptual models and the annual losses. They described high deposition rates of N over the past decades which have reached a saturation level above which no further deposition seems to occur.

Here the evaluation of the processes acting as sources and sinks of nutrients during the passage of the Oder River waters by means of isotopic signatures in dissolved and particulate material has been done. We had two sites selected one located upstream in he Oder River (station Widuchowa) before the water entered the Oder Lagoon, the other at the major outflow (Swina Canal) to the Baltic Sea. The differences between both sampling spots were taken as indication of processes happening within the lagoon.

Over two years nitrate  $\delta^{15}N$  and  $\delta^{18}O$  and ammonium  $\delta^{15}N$  was measured along with the nutrient concentrations and particulate organic matter and its isotope signatures. Runoff from the Oder River is usually highest in late winter and spring after the snow melt. Although both years sampled for this study were very different in their flow pattern, the mean nitrate loads for the climatic winter (December, January, February) and spring (March, April, May) periods were always highest. Phosphate and particulate matter however had their highest annual loads in the summer and  $PO_4^{3-}$  is known to be limiting for primary production in spring.

The concentrations of particulate matter and nutrients were much lower in the outlet to the Baltic than at the station upstream. Furthermore all the variables seemed to vary less after some residence time in the lagoon. We evaluated the data by season and found several relationships indicating different microbial fractionation processes. Strong relationships between the nitrate and  $\delta^{15}N$  over the whole year suggested nitrate uptake as important process. Nitrification of ammonium was a significant process in March/ April/May. The data from the Swina Canal had only few significant relationships and seemed to be controlled by the processes in the lagoon and some minor inflow from the Baltic into the lagoon. Overall the Oder Lagoon acts an important reactor for inorganic and organic material depending on the residence time of the water in the lagoon.

# Incorporation of diazotrophic fixed N<sub>2</sub> by mesozooplankton speciescase studies in the southern Baltic Sea using <sup>15</sup>N-stable isotope tracer addition.

#### N.Wannicke, F. Korth, M. Voss

Leibniz Baltic Sea Research Institute, Seestr.15, D-18119 Warnemünde

Corresponding author: nicola.wannicke@io-warnemuende.de

During two simultaneous cruises in the Central Baltic Sea in July 2007 we applied a <sup>15</sup>N tracer addition approach to constrain the impact of N<sub>2</sub> fixation on mesozooplankton (> 200  $\mu$ m) production in the Central Baltic Sea. We determined rates of diazotroph <sup>15</sup>N<sub>2</sub> fixation as well as uptake of diazotrophic derived <sup>15</sup>N by mesozooplankton species. Diazotrophic <sup>15</sup>N<sub>2</sub> fixation rates were low representing prebloom situations. First order estimates using a

two source mixing model of natural  $\delta^{15}$ N- PON abundance revealed that diazotrophic nitrogen contributed to 27 ± 8% to mesozooplankton biomass. Additionally, the application of the tracer showed that fixed <sup>15</sup>N was detectable in the mesozooplankton fraction within one hour after the onset of the incubation. On a daily basis 100% of newly fixed <sup>15</sup>N and 14% of cyanobacteria standing stock were incorporated by mesozooplankton species in our experimental set-ups. By applying size fractionation experiments, we determined that the majority of <sup>15</sup>N transfer (67%) was mediated by released nitrogenous compounds and their channelling trough the microbial loop towards the mesozoo-plankton community. Moreover, it was also possible to show that direct grazing on filamentous

cyanobacteria accounted for 33% of gross  ${}^{15}N$  incorporation. Thus, N<sub>2</sub> fixing cyanobacteria are ecologically more important as instantaneous sources of nitrogen for higher trophic level of the Baltic Sea food web than previously assumed.

# Can isotopic signatures of soil-emitted $N_2O$ be used as indicators of $N_2$ -fluxes?

R. Well<sup>1</sup>, H. Flessa<sup>1</sup>

<sup>1</sup>Institut für Agrarrelevante Klimaforschung, Johann Heinrich von Thünen-Institut, Bundesforschungsinstitut für Ländliche Räume, Wald und Fischerei, Bundesallee 50, D-38116 Braunschweig

Corrsponding author: reinhard.well@vti.bund.de

There is few information on N<sub>2</sub> fluxes from denitrification in the field, because this process is difficult to measure in situ. Isotopologue signatures of N<sub>2</sub>O such as  $\delta^{18}$ O, average  $\delta^{15}$ N  $(\delta^{15}N_{hulk})$  and  ${}^{15}N$  site preference (SP = difference in  $\delta^{15}N$  between the central and peripheral N positions of the asymmetric N<sub>2</sub>O molecule) can be used to constrain the atmospheric N<sub>2</sub>O budget and to characterize N<sub>2</sub>O turnover processes including N<sub>2</sub>O reduction to N<sub>2</sub>. However, the use of this approach to study N<sub>2</sub>O dynamics in soils requires knowledge of isotopologue fractionation factors ( $\epsilon$ ) for the various partial processes involved, e.g. N<sub>2</sub>O production by nitrification or denitrification, N<sub>2</sub>O reduction by denitrification and diffusive transport. The aim of our study was to investigate whether isotopologue signatures of soil-emitted N<sub>2</sub>O can be used to estimate N<sub>2</sub>O reduction, and accordingly N<sub>2</sub> formation.

Two arable soils were incubated in the laboratory under varying conditions in order to manipulate the partial processes of N<sub>2</sub>O turnover.  $\varepsilon$  of  $\delta^{18}$ O,  $\delta^{15}$ Nbulk and SP was determined in experiments, where only one of the partial processes was governing the isotopic signature of N<sub>2</sub>O in the incubation system of the respective treatment.  $\varepsilon$  of N<sub>2</sub>O reduction to N<sub>2</sub> was derived by (i) comparing treatments with and without inhibition of N<sub>2</sub>O reduction (indirect approach) or (ii) by monitoring the time course of isotopic signatures of N<sub>2</sub>O applied to the headspace of  $NO_3^{-}$ -depleted anaerobic soil (direct approach). Moreover, we incubated the soils under conditions favoring denitrification (high moisture, low  $O^2$  level,  $NO_3^{-}$  fertilization) and monitored isotopic signatures of emitted  $N_2O$ . In parallel experiments with <sup>15</sup>N-labeled  $NO_3^{-}$  pool we measured  $N_2$  fluxes directly. Isotopologue signatures were compared with <sup>15</sup>N<sub>2</sub> flux data in order to check their relationship with  $N_2$  production.

# Stable isotopes in (sub-)arctic freshwaters and ostracod calcite

S. Wetterich<sup>1</sup>, H. Meyer<sup>1</sup>, B. Plessen<sup>2</sup>, L. Schirrmeister<sup>1</sup>

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Department of Periglacial Research, Telegrafenberg A43, 14473 Potsdam, Germany

<sup>2</sup>Deutsches GeoForschungsZentrum Potsdam, Section 5.2, Telegrafenberg, 14473 Potsdam, Germany

Corresponding author: sebastian.wetterich@awi.de

Ostracods (crustaceans) are small aquatic organisms mostly about 1 mm long (different species range in size from 0.3 to 30 mm; Athersuch et al. 1989). The term 'ostracod' derives from the Greek word 'όστρακον' (ostrakon) which means 'shell' or 'mussel' and describes the outer structure of the animal. The bi-valved shell of ostracods consists of low-magnesium calcite (Kesling 1951); these valves are often preserved as fossils in lacustrine sediments.

Here we present stable isotope records from (sub-)Arctic freshwaters and ostracod calcite in periglacial landscapes of Northeast and Central Yakutia (Northeast Siberia; Wetterich et al. 2008).

In (palaeo-)limnological studies, the stable oxygen ( $\delta^{18}$ O) and carbon ( $\delta^{13}$ C) isotope records of ostracod calcite are considered to provide a restricted reflection of the isotopic composition of host water and total dissolved inorganic carbon (TDIC) at the time of shell secretion (e.g. Griffiths and Holmes 2000). The  $\delta^{18}$ O of ostracod calcite is commonly used as a proxy for precipitation/evaporation ratios and for the temperature of the lake water, and the



Fig.1. Plot of oxygen and hydrogen isotopes ( $\delta^{18}$ O and  $\delta$ D) in lake water and precipitation in Central and Northeast Yakutia. Regional evaporation effects on the waters are expressed as Local Evaporation Lines (LELs)

 $\delta^{13}$ C may reflect changes in carbon quality and sources and bioproductivity (e.g. von Grafenstein et al. 1999).

The  $\delta^{18}$ O -  $\delta$ D plots of host waters reveal evaporation effects at both study sites (Figure 1).



Fig. 2. Stable oxygen isotopes in host waters and ostracod calcite of: (a) C. candida (squares) and C. muelleri jakutica (circles); (b) F. inaequivalvis (triangles) and C. weltneri (diamonds). Data from Central Yakutia are shown by grey symbols and those from NE Yakutia by white symbols

The periglacial waters are mainly affected by the general climatic setting, the water source (precipitation or river water), and the influence of meltwater from the frozen ground, and the  $\delta^{18}$ O in host waters and ostracod valves are correlated if the species studied were found in high frequencies and over large gradients in the host water proxies (Figure 2).

The relationship between salinity (expressed as electrical conductivity, EC) and  $\delta^{18}$ O of lake waters as a likely evaporation-controlled expression of ionic concentrations was studied in Central and Northeast Yakutian sites where the data showed the existence of an EC gradient from about 0 to 6 mS/cm. A logarithmic correlation between  $\delta^{18}$ O of lake water and water EC has been found (Figure 3) which is controlled by Rayleigh distillation processes, wherein light

isotopes evaporate faster than heavy ones leading to nonequilibrium enrichment of the residual water (Clark and Fritz 1997).

Depending upon relative humidity, this process leads to an asymptotic increase in  $\delta^{18}$ O values under high evaporation conditions; a steady-state value is reached which is strongly influenced by the salinity of the residual water (e.g. Gat 1979, 1981). However, because this interpretation is based on few data, it must be considered a provisional explanation for the observed scatter. The correlation between EC and  $\delta^{18}$ O of ostracod calcite is weak (Figure 3) due to the sparse database and the numerous controls on ostracod isotope uptake. More data and sampling of time-series during the ice-free



Fig. 3. Plot of electrical conductivity and oxygen stable isotopes in (a) host waters and (b) ostracod calcite. Data from Central Yakutia are shown by grey symbols and those from NE Yakutia by white symbols



Fig. 4. Stable carbon isotopes in host waters and ostracod calcite of (a) C. candida (squares) and C. muelleri jakutica (circles), and (b) F. inaequivalvis (triangles) and C. weltneri (diamonds). Data from Central Yakutia are shown by grey symbols and those from NE Yakutia by white symbols

season are required to elucidate this relationship.

The  $\delta^{13}$ C in TDIC of freshwaters is controlled by fractionation during several carbon cycles; the most important influences are the isotopic composition of inflows, organic decay, bacterial processes, CO<sub>2</sub> exchange between air and lake water, and photosynthesis/respiration of aquatic plants. (e.g. Leng and Marshall 2004). The last two controls are characterised by high seasonal and even daily variability; thus it is more difficult to interpret these data, since periodic sampling during the open-water season is required to register carbon cycle dynamics. Therefore, reliable correlations between the  $\delta^{13}$ C data from host waters and from ostracod calcite have not been found. The  $\delta^{13}$ C records from all study sites scatter over great ranges (Figure 4) and any interpretation of such relationships is complicated.

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# Α

Iris Adam BayCEER-Labor für Isotopen-Biogeochemie Universität Bayreuth Universitätsstraße 30, 95447 Bayreuth Tel: +49-(0)172-7914619 iris.adam@uni-bayreuth.de

#### Bernhard Aichner

Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-2882194 Bernhard.Aichner@awi.de



#### Athanasia Barka

IGÖ Josef Wirth Weg 19, App.0120 80939 München Tel: +49-(0)176-70138853 athanasia.barka@helmholtz-muenchen.de

#### Dr. Giovanna Battipaglia

Swiss Federal Research Institute-WSL Zuercherstrasse 111, 8903 Birmensdorf Switzerland Tel: +31-205257439 giovanna.battipaglia@wsl.ch

#### Melanie Behrens

Alfred-Wegener-Institute for Polar and Marine Research Am Alten Hafen 26, 27568 Bremerhaven Tel: +49-(0)471-48311396 melanie.behrens@awi.de

#### Boris Biskaborn

Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-288-217 boris.biskaborn@awi.de

#### Dr. Markus Boner

TÜV-Rheinland-Agroisolab GmbH Karl-Heinz-Beckurts-Str. 13, 52428 Jülich Tel: +49-(0)2461-690 290 m.boner@de.tuv.com

#### Prof. Michael E. Böttcher

Leibniz Institute for Baltic Sea Research Seestr.15, D-18119 Warnemünde Tel: +49-(0)381-5197-402 michael.boettcher@io-warnemuende.de

#### Dr. Willi A. Brand

MPI Biogeochemie Jena PO Box 100164, 07701 Jena Tel: +49-(0)3641-576400 wbrand@bgc-jena.mpg.de

Isabel Brauner IVA Analysentechnik e.K. Meerbuscher Strasse 64-78 Alte Seilerei, Haus 5 40670 Meerbusch Tel: +49-(0)2159-69420 ib@iva-analysentechnik.de C

# С

#### Bernhard Chapligin

Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Germany Tel: +49-(0)331-288-2152 bernhard.chapligin@awi.de

#### Hans Heinrich Cordt

IRMS-ctrl Hans Heinrich Cordt Loher Weg 18, 24787 Fockbek Tel: +49-(0)151-15772383 hans.cordt@irms-ctrl.de

#### Markus Czymzik

GFZ-Potsdam Telegrafenberg, 14473 Potsdam Tel: +49-(0)331-288-1379 czymzik@gfz-potsdam.de

# F

#### **Ulrich Flenker**

Manfred-Donike-Institut / Inst f. Biochemie Deutsche Sporthochschule Köln Am Sportpark, Müngersdorf 6, 50933 Köln Tel: +49(0)221-4984-5060, -7154 u.flenker@biochem.dshs-koeln.de

#### Prof. Hilmar Förstel

TÜV Rheinland Agroisolab GmbH Kalr-Heinz-Beckurts Str. 13, 52428 Jülich Tel: +49-(0)2461-690293 h.foerstel@agroisolab.de

Claudia Frey Leibniz-Institut für Ostseeforschung Seestraße 15, 18119 Rostock Tel: +49-(0)176-24250292 claudia.frey@io-warnemuende.de

#### Prof. Hans Friedrichsen FU Berlin Assmannshauser Str 12, 14197 Berlin

Tel: +49-(0)30-8223700 hansfriedrichsen@aol.com

#### Dr. Diedrich Fritzsche

Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-288-2117 diedrich.fritzsche@awi.de

#### Dr. Gerhard Fusch

Universität Greifswald Soldmannstraße 15, 17475 Greifswald Tel: +49-(0)3834-866393 gerhard.fusch@uni-greifswald.de

# G

Michael Gabriel GFZ Potsdam Telegrafenberg, 14473 Potsdam Tel: +49-(0)331-288-1433 gabriel@gfz-potsdam.de

Prof. Gerhard Gebauer BayCEER - Labor für Isotopen-Biogeochemie Universität Bayreuth, GEO I 95440 Bayreuth Tel: +49-(0)921/-552060 gerhard.gebauer@uni-bayreuth.de

#### Dr. Matthias Gehre

Helmholtz Zentrum für Umweltforschung UFZ Department Isotopenbiogechemie Permoserstraße 15, 04318 Leipzig Tel: +49-(0)341-235-1361 matthias.gehre@ufz.de

#### Heike Geilmann

MPI-Biogeochemie Max-Planck-Institut für Biogeochemie Hans-Knöll-Straße 10, 07745 Jena Tel: +49-(0)3641-576407 geilmann@bgc-jena.mpg.de

#### Dr. Robert van Geldern

Geozentrum Nordbayern University of Erlangen-Nuremberg Schlossgarten 5, 91054 Erlangen Tel: +49-(0)9131-85-24780 robert.van.geldern@geol.uni-erlangen.de

Dr. Anette Giesemann Institut für Agrarrelevante Klimaforschung Johann Heinrich von Thünen Institut (vTI) Bundesallee 50, D-38116 Braunschweig Tel: +49-(0)531-596-2538 anette.giesemann@vti.bund.de

#### Dr. Stefanie Goldberg

BayCEER - Labor für Isotopen-Biogeochemie Geo 2, Universitätsstraße, 95440 Bayreuth Tel: +49-(0)176-24776283 stefanie.goldberg@uni-bayreuth.de

Dr. Markus Greule Max-Planck-Institut für Chemie Joh.-Joachim-Becher-Weg 27, 55128 Mainz Tel: +49-(0)6131-305381 m.greule@mpic.de

#### Ursula Günther

Helmholtz Zentrum für Umweltforschung UFZ Department Isotopenbiogechemie Permoserstraße 15, 04318 Leipzig Tel: +49-(0)341-235-1362 ursula.guenther@ufz.de



#### Deike Hatscher

Thermo Fisher Scientific (Bremen) GmbH Hanna-Kunath-Str. 11, 28199 Bremen Tel: +49-(0)421-5493552 deike.hatscher@thermofisher.com

#### Marika Haupt

Helmholtzzentrum für Umweltforschung-UFZ Department Isotopenhydrologie Theodor-Lieser-Str. 4, 06120 Halle (Saale) Tel: +49-(0)345-5585225 marika.haupt@ufz.de

#### Klaus Hecker

HEKAtech GmbH Friedrich List Allee 26, 41844 Wegberg Tel: +49-(0)2432-493649 info@hekatech.com

#### Claudia Heidel

TU Bergakademie Freiberg Institut für Mineralogie Tel: +49-(0)3731-394310 claudia.heidel@mineral.tu-freiberg.de

#### Dr. Wolf-Dieter Hermichen

Alfred-Wegener-Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-288-2185 wolf-dieter.hermichen@awi.de

#### Dr. Andreas Hilkert

Thermo Fisher Scientific (Bremen) GmbH Hannah-Kunath-Strasse 11 28199 Bremen Tel: +49-(0)421-5493-434 andreas.hilkert@thermofisher.com

#### Ulrike Hoff

Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-288-2194 Ulrike.Hoff@awi.de

# Prof. Hans-Wolfgang Hubberten Alfred Wegener Institute

for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-288-2100 hans-wolfgang.hubberten@awi.de

#### Thomas Huber

Chem. und Veterinäruntersuchungsamt Freiburg Bissierstr. 5, 79114 Freiburg Tel: +49-(0)761-8855-3145 Thomas.Huber@cvuafr.bwl.de

#### Dr. Frank Hülsemann

Institut für Biochemie Deutsche Sporthochschule Köln Am Sportpark Müngersdorf 6, 50933 Köln Tel: +49-(0)221-4982-5060 f.huelsemann@biochem.dshs-koeln.de

Kirsten Isensee Leibniz-Institut für Ostseeforschung Warnemünde Seestrasse 15, 18119 Rostock Tel: +49-(0)381-5197163 kirsten.isensee@io-warnemuende.de

# Κ

Dr. Zachary Kayler Institute for Landscape Matter Dynamics Leibniz Center for Agricultural Landscape Haus 21, Eberswalder Strasse 84 15374 Müncheberg, Germany Tel: +49(0)-33432-82485 zkayler@gmail.com

#### Dr. Frank Keppler

Max-Planck-Institut für Chemie J.-J.-Becherweg 27, 55128 Mainz Tel: +49-(0)6131305316 frank.keppler@mpic.de

#### Dr. Kay Knöller

Helmholtz-Zentrum für Umweltforschung Department Isotopenhydrologie Theodor-Lieser-Str. 4, 06120 Halle/Saale Tel: +49-(0)345-5585433 kay.knoeller@ufz.de

#### Dr. Paul Königer

LIAG Leibniz Institut für Angewandte Geophysik Geozentrum Hannover Stilleweg 2, 30655 Hannover Tel: +49-(0)511-643-3072 paul.koeniger@liag-hannover.de

Julia Köpp BayCEER - Labor für Isotopen-Biogeochemie Universität Bayreuth Universitätsstr. 30, 95447 Bayreuth Tel: +49-(0)921-552324 juila.koepp@uni-bayreuth.de

#### Conrad Kopsch

Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-288-2126 conrad.kopsch@awi.de

#### Dr. Oliver Kracht

Thermo Fisher Scientific (Bremen) GmbH Hanna-Kunath-Str. 11, 28199 Bremen Tel: +49-(0)421-5493-0 oliver.kracht@thermofisher.com

# L

#### Janek Landsberg

Center for Isotope Research, University of Groningen, The Netherlands 3 Allee de la Sylphide, 38100 Grenoble, France Tel: 0175 621 3890 janek.landsberg@gmail.com

#### **Reinhard Langel**

Kompetenzzentrum Stabile Isotope Büsgenweg 2, 37077 Göttingen Tel: +49-(0)551-39-8104 rlangel@gwdg.de

#### Volker Leinweber

HEKAtech GmbH Friedrich List Allee 26, 41844 Wegberg Tel: +49-(0)2432-493649 info@hekatech.com

#### Annika Lenz

ETH Zurich Institute of Plant Science Grasland Group Universitaetsstrasse 2, CH-8092 Zurich Switzerland Tel: +41(0)-446323689 annika.lenz@ipw.agrl.ethz.ch

#### Petra Linke

Max-Planck-Institut für Biogeochemie Hans-Knöll-Strasse 10, 07745 Jena Tel: +49-(0)3641576406 plinke@bgc-jena.mpg.de

# Μ

Dr. Clara Mangili

Deutsches GeoForschungsZentrum. Sektion 5.2 -Klimadynamik und Landschaftsentwicklung Telegrafenberg, 14473 POTSDAM Tel: +49-(0)3312881355 mangili@gfz-potsdam.de

#### Dr. Hanno Meyer

Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-288-2115 Hanno.Meyer@awi.de

#### Tanja Moerdijk

Netherlands Institute of Ecology (NIOO-KNAW) Korringaweg 7, 4401NT Yerseke the Netherlands Tel: +31-(0)113 577300 t.moerdijk@nioo.knaw.nl

# $\mathbf{O}$

Dr. Yvonne Oelmann Professur für Bodenkunde/Bodengeographie, Geographisches Institut Johannes Gutenberg-Universität Mainz Johann Joachim Becher-Weg 21, 55128 Mainz Tel: +49-(0)61313922137 yvonne.oelmann@uni-mainz.de

#### Thomas Opel

Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331-288-2142 thomas.opel@awi.de

# Ρ

#### Thomas Piper

Birgit, Plessen

Institute of Biochemistry German Sport University Cologne Am Sportpark Müngersdorf 6, 50933 Cologne Tel: +49-(0)221-4982 7154 t.piper@biochem.dshs-koeln.de

Dr. Birait Plessen Deutsches GeoForschungsZentrum Telegrafenberg, Sektion 5.2, 14473 Potsdam Tel: +49-(0)331-288-1482

#### Kerstin Pralle IVA Analysentechnik e.K. Meerbuscher Strasse 64-78 Alte Seilerei, Haus 5 40670 Meerbusch Tel: +49-(0)2159-69420 kp@iva-analysentechnik.de

# (J

Dr. Petra Quillfeldt Max-Planck-Institut für Ornithologie Vogelwarte Radolfzell Schlossallee 2, 78315 Radolfzell Tel: +49-(0)7732-150114 quillfeldt@gmx.de

# R

Juergen Richter Max-Planck-Institut for Biogeochemistry Jena Adolf-Reichwein-Str. 16, 07745 Jena Tel: +49-(0)3641-576402 jrichter@bgc-jena.mpg.de

Dr. Michael Rothe Max Plank Institut für Biogeochemie Jena BGC-Jena Hans Knöll Str. 10, 07747 Jena Tel: +49-(0)3641576405 mrothe@bgc-jena.mpg.de

#### Deborah Rupprecht Institut für Nutzpflanzenwissenschaften und Ressourcenschutz (INRES) Rhein. Friedrich-Wilhelms-Universität, INRES Abtg. Pflanzenernährung Karlrobert-Kreiten-Str. 13, 53115 Bonn Tel: +49-(0)228-73-2155, -1631 d.rupprecht@uni-bonn.de

# S

#### Henk Schierbeek

Erasmus University Pob 2040 3000 CA, Rotterdam The Netherlands Tel: +31-(0)624756196 h.schierbeek@erasmusmc.nl

Dr. Johannes Schwieters Thermo Fisher Scientific (Bremen) GmbH Hanna-Kunath-Str. 11, 28199 Bremen, Germany Tel: +49-(0)421-5495287 johannes.schwieters@thermofisher.com

#### Rolf Siegwolf

Paul Scherrer Institut 5232 Villigen-PSI, Schweiz Tel: +41-(0)56310-2786 rolf.siegwolf@psi.ch

#### Janine Sommer

BayCEER - Labor für Isotopen-Biogeochemie Universitaetsstr. 30, 95447 Bayreuth Tel: +49-(0)174-4586801 summerlikewinter@yahoo.com

#### Karin Sörgel

Leibniz-Institut für Zoo- und Wildtierforschung Alfred-Kowalke-Str. 17, 10315 Berlin Tel: +49-(0)30-5168519 soergel@izw-berlin.de

#### Florian Stange

Helmholtz Zentrum für Umweltforschung UFZ Department of Soil Physics Helmholtz Centre for Environmental Research Theodor-Lieser-Str. 4, 06120 Halle Tel: +49-(0)345-558-5418 florian.stange@ufz.de

#### Marcus Stöckel

BayCEER - Labor für Isotopen-Biogeochemie Universität Bayreuth Universitätsstr. 30, 95440 Bayreuth Tel: +49-(0)921-552171 marcus.stoeckel@uni-bayreuth.de

#### Dr. Gerhard Strauch

Helmholtz Zentrum für Umweltforschung UFZ Department Hydrogeology Permoserstr. 15, 04318 Leipzig Tel: +49-(0)341-2351985 gerhard.strauch@ufz.de

#### Lars Szwec

Kompetenzzentrum Stabile Isotope Büsgenweg 2, 37077 Göttingen Tel: +49-(0)551-39-8104 lszwec@awda.de

# LIST OF PARTICIPANTS

## LIST OF PARTICIPANTS

# T

#### Dr. Marion Tichomirowa

Institut für Mineralogie TU Bergakademie Freiberg Brennhausgasse 14, 09596 Freiberg Tel: +49-(0)3731-393528 tichomir@mineral.tu-freiberg.de

# U

**Dr. Gerd von Unruh** Friedländer Weg 49, 37085 Göttingen Tel: +49-(0)551-4997447

# V

Dr. Andrea Vieth

Deutsches GeoForschungsZentrum GFZ Telegrafenberg D-14473 Potsdam Tel: +49-(0)331-288-1431 vieth@gfz-potsdam.de

#### Susann Vogler

Leibniz Institute for Baltic Sea Research Warnemünde IOW - Sektion Marine Geologie Seestraße 15, 18119 Rostock Tel: +49-(0)381-5197-3430 susann.vogler@io-warnemuende.de

Anzeige

#### Dr. Christian C. Voigt

Leibniz-Institut für Zoo- und Wildtierforschung Alfred-Kowalke-Str. 17 10315 Berlin Tel: +49-(0)30-5168517 voigt@izw-berlin.de

Filip Volders Elementar Donaustr. 7, 63452 Hanau Tel: +49-(0)6181-9100507 volders@elementar.de

Dr. Maren Voß Leibniz Institut Für Ostseeforschung Seestr. 15, 18119 Rostock Tel: +49-(0)381-5197209 maren.voss@io-warnemuende.de

# W

Nicola Wannicke Leibniz-Institut für Ostseeforschung Seestrasse 15, 18119 Rostock Tel: +49-(0)381-5197-474 Nicola. Wannicke@jo-warnemuende.de

Dr. Stephan Weise Helmholtz Zentrum für Umweltforschung UFZ Department Isotopenhydrologie Theodor-Lieser-Str. 4, 06120 Halle Tel: +49-(0)345-558-5435 stephan.weise@ufz.de Dr. Reinhard Well

Institut für Agrarrelevante Klimaforschung Johann Heinrich von Thünen-Institut Bundesallee 50, 38116 Braunschweig Tel: +49-(0)531 596 2535 reinhard.well@vti.bund.de

Dr. Roland A. Werner Institute of Plant Sciences Universitätsstrasse 2, CH - 8092 Zurich Switzerland Tel: +41/44/63-26754 rwerner@ipw.agrl.ethz.ch

Dr. Sebastian Wetterich Alfred Wegener Institute for Polar and Marine Research Telegrafenberg A43, 14473-Potsdam Tel: +49-(0)331 288 2207 sebastian.wetterich@awi.de

#### Vera Winde

Institut für Ostseeforschung Warnemünde Seestr. 15, 18119 Rostock-Warnemünde Tel: +49-(0)381-5197-395 vera.winde@io-warnemuende.de



#### Andreas Ziegler Elementar Donaustr. 7, 63452 Hanau Tel: +49-(0)6181-910041 ziegler@elementar.de

DER IRMS-ctrl WEG

function doDecideWhatToDo\_AndWhereToGo myMachine, myBudget, \ mySatisfaction, myExpertise, myDayByDayJob, myNewIdeas, myWishes if myMachine = old and myBudget < 100k€ \

- or mySatisfaction = bad \
- or myExpertise > whatICanDo\_Now \
- or myDayByDayJob ≠ routine \
- or myNewIdeas > whatICanDo\_Now \
- or myWishes > whatICanDo\_Now then
- put "let IRMS-ctrl into myLab" into myDecision
- else

if myMachine = new and mySatisfaction = bad then put "let IRMS-ctrl into myLab" into myDecision

else

put "stay there" into myDecision

end if

return myDecision

end doDecideWhatToDo\_AndWhereToGo

http://www.irms-ctrl.de

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- 2001/2 nicht erschienen
- 2001/3 High-Resolution Lake Sediment Records in Climate and Environment Variability Studies. 6<sup>th</sup> Workshop of the European Lake Drilling Programme ELDP. Progamme, List of Participants, Abstracts, Excursion Guide. May 11-16, 2001, GFZ Potsdam, Germany. – 162 S. – Verkaufspreis: € 17,-
- 2001/4 Evolution des Systems Erde während des jüngeren Paläozoikums im Spiegel der Sediment–Geochemie. 3. Kolloquium im DFG-Schwerpunktprogramm "SPP 1054". Zusammenfassung der Tagungsbeiträge. 28.–30. März 2001, Neustadt a. d. Weinstraße. – 84 S. – Verkaufspreis: € 11,50
- **2001/5 5. Geochemie-Tagung.** Zusammenfassungen der Tagungsbeiträge. 21.-23. Juni 2001, Tübingen. 90 S. *Verkaufspreis:* € *11,50*
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- 2002/2 nicht erschienen
- 2002/3 IAMG 2002. 8<sup>th</sup> Annual Conference of the International Association for Mathematical Geology. Program and Abstracts. Volume 1. Sept. 15-20, 2002, Berlin. 524 S. Verkaufspreis: € 25,-
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- **2003/3** Sediment 2003. Programme, Abstracts and Field Trips. June 10-14, 2003, Wilhelmshaven, Germany. 200 S. *Verkaufspreis:* € 16,50
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- 2003/5a 9<sup>th</sup> International Symposium on Antarctic Earth Sciences. Antarctic Contributions to Global Earth Sciences. Exkursionsführer / Field Guide. September 8-12, 2003, Potsdam, Germany. 133 S. Verkaufspreis: € 13,-
- 2003/5b Biodiversität. 73. Jahrestagung der Paläontologischen Gesellschaft. Kurzfassungen der Vorträge und Poster. 29. September - 3. Oktober 2003, Mainz, Germany. – 289 S. – *Verkaufspreis:* € 21,- vergriffen
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- 2004/2 18<sup>th</sup> International Senckenberg Conference. VI International Palaeontological Colloquium in Weimar. Late Neogene and Quaternary Biodiversity and Evolution: Regional Developments and Interregional Correlations. Conference Volume. April 25-30, 2004, Weimar, Germany. – 289 S. – Verkaufspreis: € 21,-
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- 2004/4 XXVIII SCAR & COMNAP XVI. SCAR Open Science Conference. "Antarctica and the Southern Ocean in the Global System". XI SCARLOP Symposium. "Towards the International Polar Year and Beyond". Abstract Volume. July 25-31, 2004, Bremen, Germany. 480 S. Verkaufspreis: € 26,-
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- 2009/1 KALMAR First Bilateral Workshop on Russian-German Cooperation on Kurile-Kamchatka and the Aleutean Marginal Sea-Island Arc Systems. Programme and Abstracts. Petropavlovsk-Kamchatka, Russia, April 27 - May 1, 2009. – 73 S. – Verkaufspreis: € 10,-
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