Compendium

of

Dating Methods in Environmental Sciences

TECHNISCHE
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1st Scientific Symposium of the CFEA
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CFEA
Core Facility
Environmental Analytics

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Compendium of
Dating Methods in Environmental Sciences

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Dating Rocks, Soils and Sediments

Introduction (Michael Zech)

Environmental scientists often ask the question “When and where happens or happened what, and why does or did it happen?”

Amongst geoscientists, the research topic referring to “what” thereby for instance deals with the formation of rocks and minerals including zircons and speleothems, the formation of landscape surfaces, the eolian, glacial or fluvial transportation and -location of minerogenic particles as well as organic matter, and the sedimentation and accumulation of these particles and organic substances in geoarchives such as loess paleosol sequences, lake sediments, etc. At the same time, a wide range of different proxies in various kinds of geoarchives is applied in order to infer environmental and climatic conditions under which those geoarchives form or formed.

Anyway, without additionally addressing the “when” of the above-formulated question, our knowledge about our environment and the processes forming it will always remain incomplete. This makes geochronology and geochronologists applying different dating methods crucial for environmental research. At the same time, the crucial need of geochronological applications as well as development and further improvement of respective methods fosters interdisciplinary exchange and brings together (geo-)scientists from different fields. This is nicely reflected by all the experts contributing to this 1st Scientific Symposium of the Core Facility of Environmental Analytics at TU Dresden and having contributed to this “Compendium of Dating Methods in Environmental Sciences”. We are very grateful to all of them, and in this first chapter entitled “Dating Rocks, Soils and Sediments”, we enjoy reading the contributions and dating method fact sheets of geologists, chemists, physical geographers, sedimentologists, soils scientists, etc. … and a forensic researcher.

This last aspect highlights that sometimes it’s not only thrilling to know when something happened, but also who did it :-).

U-Pb dating of zircon by LA ICP MS: Method and application

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Zircon ($ZrSiO_4$) is a very common mineral in igneous, sedimentary, and metamorphic rocks. Further, it occurs in loose sediments and volcanic ashes. Zircon is common in felsic to intermediate rocks and rare in mafic to ultramafic rocks, where it can be replaced by the mineral Baddeleyite (ZrO_2). Zircon crystals in rocks are very tiny and show normally a size of 80 to 120 µm, but a spread between 5 and 400 µm is normal. The mineral zircon is extremely weathering-resistant and shows a hardness of 7.5 (Mohs). It has a density of 4.7 g/cm^3 and is under normal pressure stable until 1676 °C. During growth of the crystal in a melt, zircon incorporates U, Th, Hf, Y, and Rare Earth Elements in its lattice. Further, zircon shows an extremely high closing temperature of c. 800-900 °C (depending on author) for the U-Th-Pb isotopic system. All these features make the mineral zircon to one of the most important minerals for the age dating of rocks, loose sediments, and tuffs. Even extra-terrestrial materials such as moon rock and meteorites can be dated by the analysis of U-Th-Pb isotopes from zircon and other U-bearing minerals like apatite, rutile, and monazite. During growth, the mineral zircon incorporate U- and Th-isotopes into the lattice and no significant Pb. When the zircon underwent the closing temperature of c. 900 °C, the system is closed and the production of radiogenic lead inside the crystal starts:

$$^{238}U \rightarrow {}^{206}Pb + 8\alpha + 6\beta + 47\ MeV$$

$$^{235}U \rightarrow {}^{207}Pb + 7\alpha + 4\beta + 45\ MeV$$

$$^{232}Th \rightarrow {}^{208}Pb + 6\alpha + 4\beta + 40\ MeV$$

With $\lambda_{238} = 1.55125 \times 10^{-10}$a-1 ($t_{1/2}$ = 4.468 Ga), $\lambda_{235} = 9.8485 \times 10^{-10}$a-1 ($t_{1/2}$ = 703.8 Ma), and $\lambda_{232} = 0.495\ 10^{-10}$a-1 ($t_{1/2}$ = 14.05 Ga) the equations for the age calculation are:

$$Age_{206/238} = 1/\ \lambda_{238} \times \ln\ (^{206}Pb/^{238}U + 1)$$

$$Age_{207/235} = 1/\ \lambda_{235} \times \ln\ (^{207}Pb/^{23}5U + 1)$$

$$Age_{208/232} = 1/\ \lambda_{232} \times \ln\ (^{208}Pb/^{232}Th + 1)$$

If the zircon crystal underwent during its geological history ultra-high temperature and ultra-high pressure conditions, the closing temperature can be overstepped and the U-Th-Pb isotope system will be reset in this case. Lead loss can be caused by a number of geological processes. Aggressive fluids, mostly in combination with higher metamorphic conditions or metamictization processes are often the cause for the infiltration of “common lead” into the zircon crystal. Common lead is a mixture of the lead isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb, which intrudes the zircon crystal from outside. Common lead can be detected by the analysis of ^{204}Pb. If common lead is present in the zircon crystal, for age calculation via the U-Th-Pb system a common lead correction can be done to estimate the true age (Stacy and Kramers 1975, Anderson et al. 2019, Vermeesch 2021).

Several ways are possible for the analysis of U-Th-Pb isotopes in zircon. The most import applications are TIMS (Thermal Ionization Mass Spectrometry), SHRIMP (Sensitive High Resolution Ion Microprobe), and LA ICP-MS (Laser Ablation and Inductively Coupled Plasma – Mass Spectrometry). Here, we concentrate on LA ICP-MS (Jeffries 1989, Gerdes and Zeh 2009). In our lab we use an excimer laser RESOlution SE (Applied Spectra, ESI) coupled to an ICP-MS ELEMENT XR (Thermo Fisher). Zircon crystals are isolated from rocks, loose sediments, or volcanic ash by heavy mineral separation and mounted on a double sided adhesive tape. After fixing in an epoxy resin block, zircon crystals are polished to half of the thickness. By scanning electron microscopy (SEM) and cathodoluminescence imaging (CL) internal structures, such as zoning, old inherited cores, or metamorphic and metamict domains are visualized. Zircon mounts are placed in a laser chamber and ablated by a laser beam with a wave length of 193nm with a diameter normally ranging from 20 to 35 µm, depending on size and the U-concentration of the zircon (Fig. 1). During laser ablation, ions are spilled by a carrier gas (He) into the ICP-MS, were U-Pb-Th and Hg isotopes were analysed by the double focussing sectorfield ICP-MS (ELEMENT XR). As reference materials we use the native zircon crystals GJ1, Plesovice, and Temora. In addition, there is the artificial NIST 612 glass in use. There are software applications such as ISOPLOT, IOLITE, and GLITTER for data reduction and age calculation available. In addition, there are in-door spread sheets from several labs in use.

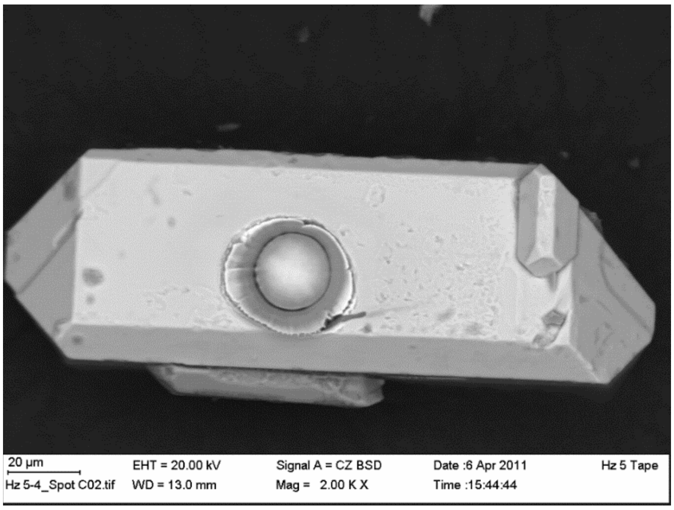

Fig. 1:
SEM image (BSE) of a zircon crystal from the Brocken granite (Harz Mountains). Laser spot diameter is 30 µm and forms a crater with a depth of c. 30 µm (image by Mandy Zieger-Hofmann).

The U-Pb age dating method relies on two separate decay chains, the uranium series from ^{238}U to ^{206}Pb, and from ^{235}U to ^{207}Pb. If both ages overlap, the age is concordant. If this is not the case, the result is discordant and a single spot analysis may not display the true age. Results can be plotted on diverse diagrams. Commonly the concordia diagrams of Wetherill (1956, ^{206}Pb/^{238}U and $^{207/235}$U) and Tera-Wasserburg (1972, ^{206}Pb/^{207}Pb and ^{238}U/^{206}Pb) are often used.

Geochronology is a key discipline in geosciences. Without age determination, geological processes and their dynamics are only reconstuctable in a relative way. “No dates – no rates” (citation from Sam Bowring, MIT) means, to fully understand the past events preserved in the rock record you have to understand their timing. The ages, which can determined by the U-Pb method ranges from about 160 ka (Guillong et al. 2014) to the origin of the solar system at 4.56 Ga (Patterson et al. 1955). Mostly, U-Pb age dating serve to determine the age of intrusion or extrusion ages of igneous rocks (Zieger et al. 2020). U-Pb ages of volcanic ashes are the ultimate tool for stratigraphic ages shown in the International Chronostratigraphic Chart of the IUGS (https://stratigraphy.org/chart). Important system boundaries such as the Precambrian-Cambrian boundary are dated by the U-Pb method (Linnemann et al. 2019). Siliciclastic sedimentary rocks often yield high numbers of detrital zircon. U-Pb LA ICP MS ages of the latter (n=120 or more per sample) allow to establish zircon populations, which can be used for provenance studies from local up to global scales for plate tectonic and palaogeographic reconstructions (Gärtner et al. 2017) and major events in Earth history (Zieger-Hofmann et al. 2022). The youngest zircon population deliver the Maximum Depositional Age (MDA) for the sediment. The age of a metamorphic event or a metamorphic overprint, respectively, can be determined by U-Pb in-situ age dating of a metamorphic rim from a zircon or from an inherited metamorphic core trapped in a complex zircon crystal (Linnemann et al. 2011, Fig. 2).

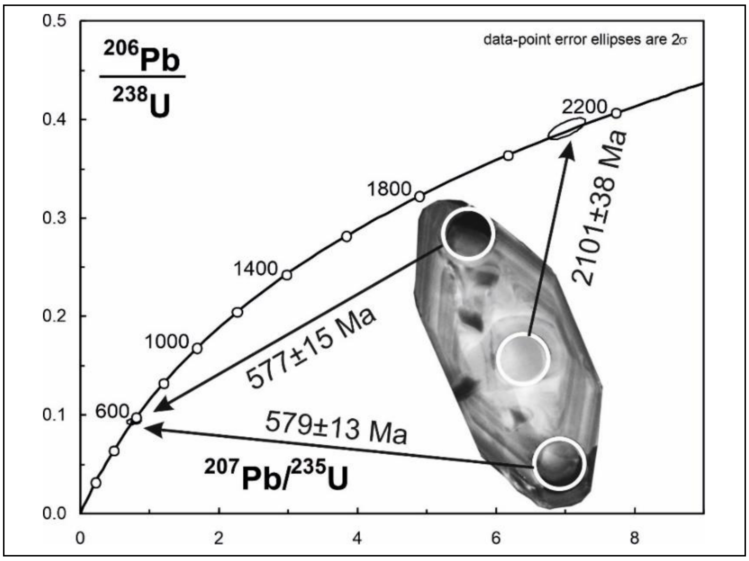

Fig. 2:
Concordia plot of three spots of a complex zircon grain taken from an Ordovician sandstone of the Tassili Ouan Ahaggar (Algerian Sahara). Spot sizes are 35 µm. (from Linnemann et al. 2011).

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U-Pb dating of Zircon (Ulf Linnemann)

application	Zircon ($ZrSiO_4$) is a very common mineral **in igneous, sedimentary, and metamorphic rocks**. It occurs also in loose **sediments** and **volcanic ashes**. During growth of the crystal in a melt, zircon incorporates U, Th, Hf, Y, and Rare Earth Elements in its lattice. Further, zircon is extremely weathering-resistant and shows an high closing temperature of c. 900 °C for the U-Th-Pb isotopic system.
dating range	▪ from about 160 ka (Guillong et al. 2014) to the origin of the solar system at 4.56 Ga (Patterson et al. 1955). ▪ mostly, U-Pb age dating serve to determine the age of intrusion or extrusion ages of igneous rocks (Zieger et al. 2020) and ▪ U-Pb ages of volcanic ashes are the ultimate tool for stratigraphic ages shown in the International Chronostratigraphic Chart of the IUGS ▪ important system boundaries such as the Precambrian-Cambrian boundary are dated by the U-Pb method (Linnemann et al. 2019).
sample processing	At first, zircon crystals have to be isolated from the samples by heavy mineral separation and mounted on a double sided adhesive tape. After fixing in an epoxy resin block, zircon crystals are polished to half of the thickness. By scanning electron microscopy (SEM) and cathodoluminescence imaging (CL) internal structures, such as zoning, old inherited cores, or metamorphic and metamict domains are visualized. Zircon mounts are placed in a laser chamber and ablated by a laser beam with a wave length of 193nm with a diameter normally ranging from 20 to 35 µm, depending on size and the U-concentration of the zircon During laser ablation, ions are spilled by a carrier gas (He) into the ICP-MS, were U-Pb-Th and Hg isotopes were analysed by the ICP-MS. As reference materials the native zircon crystals GJ1, Plesovice, and Temora are recommended.
analytical instrument	**LA ICP-MS** (Laser Ablation and Inductively Coupled Plasma Mass Spectrometry
data analysis / processing	▪ software applications such as ISOPLOT, IOLITE, and GLITTER for data reduction and age calculation available ▪ Commonly the concordia diagrams of Wetherill (1956, ^{206}Pb/^{238}U and ^{207}/^{235}U) and Tera-Wasserburg (1972, ^{206}Pb/^{207}Pb and ^{238}U/^{206}Pb)
available labs	**FIERCE:** Institut für Geowissenschaften, Goethe-Universität, Altenhöferallee 1, D-60438 Frankfurt am Main, gerdes@em.uni-frankfurt.de **GeoPlasmaLab:** Senckenberg Naturhist.Sammlungen Dresden, Museum für Mineralogie und Geologie, GeoPlasmaLab, Königsbrücker Landstraße 159, D-01109 Dresden, ulf.linnemann@senckenberg.de, mandy.hofmann@senckenberg.de
useful links	IUGs: https://stratigraphy.org/chart

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Dating landscape surfaces and processes using cosmogenic nuclides

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Earth is continuously bombarded by high-energy cosmic rays, which produce cosmogenic nuclides through nuclear reactions in the atmosphere and in the rocks on the Earth' surface. The long-lived radionuclides ^{10}Be ($T_{1/2}$ = 1.4 Myr), ^{26}Al ($T_{1/2}$ = 0.7 Myr) and ^{36}Cl ($T_{1/2}$ = 0.3 Myr) accumulate in exposed rocks and can be used to study a variety of geological processes. Exposure age dating of stable surfaces is used, for example, for palaeoglacial reconstructions (dating of moraine boulders or glacially polished rocks), natural hazard assessment (landslides, rock falls, fault surfaces) or landscape evolution studies. Nuclide concentrations in eroding surfaces correlate with the rate of erosion and can be used to investigate current or past erosion rates (e.g. from river sand samples or fluvial terraces). Measurements of nuclides with different half lives can be combined to calculate burial ages, a tool in Quaternary geochronology but also for dating archaeological sites. Because cosmogenic radionuclides are extremely rare their measurement is performed by Accelerator Mass Spectrometry (AMS). This contribution gives an overview of cosmogenic nuclide applications with examples from Earth and Environmental Sciences and provides a brief insight into sampling, sample preparation and AMS measurement.

Fig 1: 6 MV tandetron DREAMS at Helmholtz-Zentrum Desden-Rossendorf used for AMS analysis of ^{10}Be, ^{26}Al, ^{36}Cl, and other radioisotopes (©HZDR / O. Killig).

Fig 2: Sampling of a glacial boulder for 10Be exposure age dating (© Dr. E. Grin).

Analysis of cosmogenic radionuclides (Konstanze Stübner)

application	Determination of cosmogenic radionuclide concentrations, e.g. ^{10}Be and ^{26}Al in quartz or ^{36}Cl in whole rock samples. Calculation of exposure ages and erosion rates with applications in quaternary geochronology, palaeoglacial reconstructions, landscape evolution studies and archaeology
dating range	Holocene to Pleistocene.
sample processing	Quartz purification from bedrock or sand samples; the processing of quartz requires hydrofluoric acid. Purification of target elements through wet chemical methods (ion exchange chromatography). A typical target consists of 1-2 mg BeO or Al_2O_3 extracted from ~20 g quartz (see www.hzdr.de/db/Cms?pNid=1426).
analytical instruments	Ratios of radionuclide to stable isotope ($^{10}Be/^{9}Be$, $^{26}Al/^{27}Al$, $^{36}Cl/^{35}Cl$) on the order of 1E-11 to 1E-14 are measured by Accelerator Mass Spectrometry (AMS). Stable isotope concentrations are determined from the amount of spike added or analysed by ICP-MS or ICP-OES (e.g. natural Al in quartz samples)
precision	analytical uncertainty typical 3 to 8%
data analysis/ processing	The interpretation of cosmogenic nuclide concentrations requires knowledge of the site-specific nuclide production rates. Point based exposure ages or erosion rates can be computed with online calculators (e.g. stoneage.hzdr.de/). Specific algorithms have been developed for the computation of burial ages or catchmentwide erosion rates.
limitations/ perspectives	▪ Accuracy of interpreted dates is limited by our current knowledge of cosmogenic nuclide production rates (^{10}Be better than ^{26}Al and ^{36}Cl). ▪ Saturation (secular eq.) occurs after 1-4 Myr of exposure. ▪ Technical developments improve the detection limits for low nuclide concentrations (e.g. young samples, rapidly eroding settings; see www.hzdr.de/db/Cms?pOid=65291&pNid=1437).
available labs	▪ DREAMS and HAMSTER at Helmholtz-Zentrum Dresden-Rossendorf (www.hzdr.de/ams) ▪ CologneAMS, Univ. Cologne (cologneams.uni-koeln.de/) ▪ VERA at Univ. Vienna (isotopenphysik.univie.ac.at/en/vera/) ▪ ASTER at Cerege, Aix-en-Provence (www.cerege.fr/en/) ▪ SUERC at Univ. Glasgow (www.gla.ac.uk/research/az/suerc/ams/) ▪ Aarhus AMS Centre (c14websub.au.dk/)

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Luminescence dating – potentials and limits for illuminating past sedimentation processes

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Luminescence dosimetry provides a powerful tool for geochronological research by determining the last exposure of selected minerals (quartz, feldspar) to light. The method is used to date sedimentation events associated to a wide range of surface processes and spans over up to several hundreds of thousand years. The resulting ages and corresponding rates allow insights into the timing of past paleo-environmental conditions and the rates of changes. The talk will cover the basic physical and analytical principles of luminescence dating techniques and showcases its strength and limitations using selected examples of application studies from high mountain, arctic and fluvial sediments.

Photo: M. Fuchs 2014, fieldwork as part of the CarboPerm project (BMBF funded), Bol'shoy Lyakhovski, New Siberian Islands

Luminescence dating (Margret Fuchs)

application	Luminescence dosimetry for sediment dating used to determine timing and process rates during the last few hundreds of thousand years
sample processing	Sample recovery and treatments require protection against light exposure, only subdued red/orange lab light Specific sample preparation procedures apply for the ▪ extraction of the target mineral (quartz, feldspar or poly-mineral) ▪ extraction of the target grain size fraction (fine, medium, coarse grains) ▪ preparation of the selected aliquot type (single grain, multi-grain of given monolayer diameter)
analytical instruments	Luminescence measurement systems combine excitation sources (diodes, lasers), a dose rate source and a photon-detector (PMT, CCD camera) integrated with technical solutions to allow for automated sequences of measurement steps such as sample transport, heating, bleaching etc. Common available systems are TL/OSL readers from Risø and Lexyg readers from Freiberg Instruments.
data analysis	The age (A) equation is $A = D_e / D_r$ D_e is determined based on the relation of detected luminescence to absorbed dose as an equivalent to the accumulated dose since last light exposure until sampling. D_r is determined based on gammaspectrometric analysis of radionuclides in the sediment (sedimentary dose rate) and sediment location related exposure to cosmogenic radiation (cosmic dose rate) and corrected using estimates of the sediments water content, sediment density and depth below surface.
limitations/ perspectives	Suitability relies strongly on the mineral's luminescence properties such as weak signals, missing fast and/or dominance of later signal components, anomalous fading, strong sensitivity changes.
available labs	**HZDR** Dresden-Rossdorf, Freiberg, Group Near-field Sensing) (www.hzdr.de/db/!ContMan.Visi.Card?pUser=15926&pNid=3055) **Leibniz Institute for Applied Geophysics** (Manfred.Frechen@LIAG-Hannover.de) **University Heidelberg** (www.geog.uni-heidelberg.de/geomorph/lumineszenz.html) **University of Giessen** (www.uni-giessen.de/de/fbz/fb07/fachgebiete/geographie/arbeitsgruppen/physisch/forschung) **University of Cologne** (www.geographie.uni-koeln.de/forschung/arbeitsgruppen/geomorphologie-und-geochronologie/lumineszenzlabor-cll)

^{14}C dating – principles, recent methodological innovations and exemplary applications

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Radiocarbon (^{14}C) dating is an important tool in archaeology and paleo-environmental sciences to determine the age of various carbon-containing materials. Based on the continuous production of ^{14}C in the stratosphere, its radioactive decay of and its uptake in all living organisms, the age of preserved carbonaceous material can be determined via this cycle: When an organism dies, it no longer incorporates new ^{14}C, but the number of atoms decreases due to radioactive decay instead. The radioactive clock "starts ticking" with the half-life of 5730 years, which allows dating of organic or carbonaceous material up to 50'000 years.

In early years of radiocarbon research (i.e., from the 1950s to the 1980s), gas proportional counters (and later liquid scintillator counters) were employed for measurement of the radioactivity of ^{14}C. Since 1977, accelerator mass spectrometry (AMS) has been increasingly used and has become the main technique for ^{14}C dating today. In AMS, ^{14}C is measured together with the stable carbon isotopes ^{12}C and ^{13}C quasi simultaneously in order to achieve high precision and accuracy of measurement reaching values of typically <3‰. This work presents the principles of ^{14}C dating as well as some recent technical developments and provides an overview of applications.

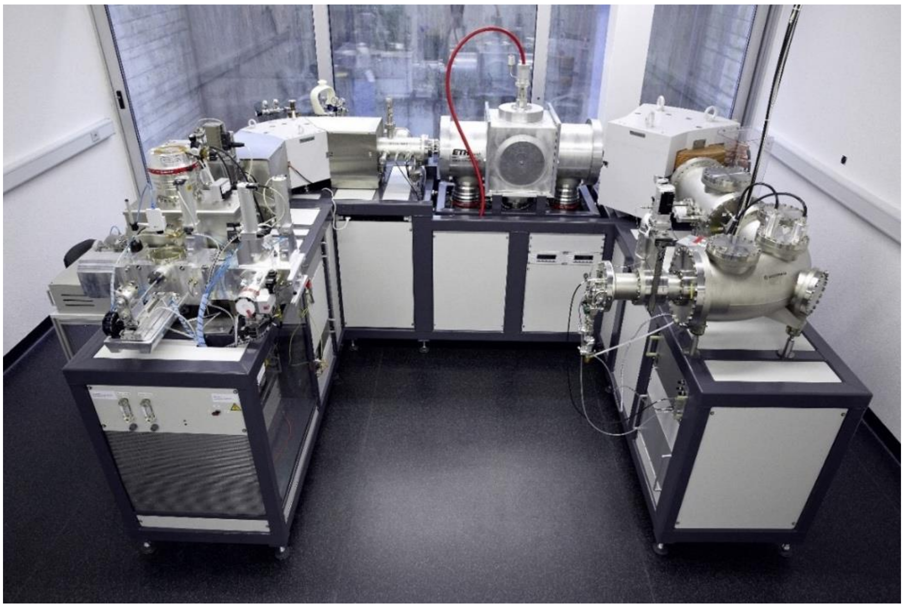

Fig. 1: The AMS system MICADAS at the University of Bern

Radiocarbon Dating (Sönke Szidat)

application	Dating of environmental archives, dating of archaeologic finds, source apportionment of atmospheric CO_2 and particulate matter, investigation of the carbon cycle
sample processing	Isolation of the fraction of interest (incl. decontamination), e.g. by acid-base-acid pretreatment Measurement of graphitized targets of as CO_2 (gas ion source)
analytical insruments	Accelerator mass spectrometry (AMS)
data analysis	Data correction and normalization using standards and blank materials calibration via calibration curves
limitations/ perspectives	Age limit ~50 ka Dating may be impossible for samples treated with conservation agents
available labs	**LARA**, University of Bern (www.14c.unibe.ch/) **LIP,** ETH Zurich, https://ams.ethz.ch/ **CEZA,** Curt-Engelhorn Zentr. Archäometrie Mannheim (www.ceza.de/) **MPG-Jena** (www.bgc-jena.mpg.de/servicegruppen/14c-analytik) **Hydroisotop GmbH** Schweitenkirchen (www.hydroisotop.de/) **SUERC**, University of Glasgow (www.gla.ac.uk/research/az/suerc/radiocarbondating/) **University of Groningen** (www.rug.nl/research/centre-for-isotope-research/) **Kiel University** (www.leibniz.uni-kiel.de/de/ams-14c-labor) **Lund University** (www.geology.lu.se/research/laboratories-equipment/radiocarbon-dating-laboratory) **University of Oxford** (www.c14.arch.ox.ac.uk) **Aarhus University** (www.c14.dk/) **VERA**, University of Vienne (www.isotopenphysik.univie.ac.at/vera/)
references	I. Hajdas, P. Ascough, M. H. Garnett, et al., Radiocarbon dating. Nat Rev Methods Primers 1, 62 (2021). S. Szidat, R. Stapfer, Radiokohlenstoffdatierungen heute, Mitteilungen der Naturforschenden Gesellschaft in Bern, 75, 20-39 (2018).

Corroborating chronologies using paleomagnetic secular variations

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Paleomagnetic reversals have often been used to date sedimentary sequences in the past. In a similar way paleomagnetic excursions like for example the Laschamp event, which in some cases can be correlated with ^{10}Be records, have been used. Unfortunately, these variations only provide one point in time and are only applicable to older sediment sequences. In the more recent past Paleomagnetic Secular Variations (PSV) have been used to corroborate chronologies or even date younger sedimentary sequences. Best results are obtained during the past 10 ka using existing records and geomagnetic field models for comparison but boundaries are pushed towards older records.

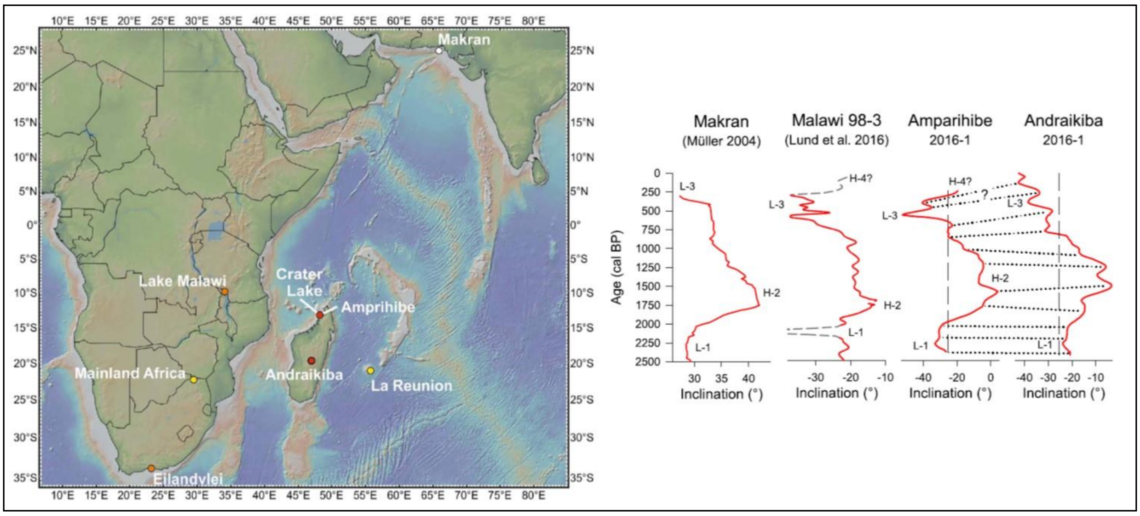

Fig:1: Comparison of inclination records from southern Africa and beyond (source: Haberzettl et al. 2021)

Paleomagnetic secular variations (Torsten Haberzettl)

application	Paleomagnetic secular variation stratigraphy, checking initial chronologies of sediment sequences, dating sediment sequences
dating range	works best in Holocene boundaries are pushed towards older sequences covering the past 100 ka
sample processing	U-channels taken from sediment cores; measuring the Natural Remanent Magnetization (NRM) during stepwise AF demagnetization, calculation of paleomagnetic secular variations
analytical instruments	Superconducting Rock Magnetometer (SRM)
data analysis/ processing	Comparing declination, inclination and intensity to existing records and geomagnetic field models
limitations/ perspectives	Undisturbed sediments, certain grain sizes, certain mineralogy
available labs	University of Greifswald, University of Quebec at Rimouski, Oregon State University, GFZ Potsdam, University of Bremen, University of Lund
references	HABERZETTL, T. (2015): Advances in Limnogeology and Paleolimnology with a special focus on corroborated chronologies using paleomagnetic secular variations. Habilitation Thesis Friedrich-Schiller-University Jena, http://nbn-resolving.de/urn:nbn:de:gbv:27-20160107-133023-6. HABERZETTL, T., K. HENKEL, T. KASPER, M. AHLBORN, Y. SU, J. Wang, E. Appel, G. ST-ONGE, J. STONER, G. DAUT, L. ZHU, R. MÄUSBACHER (2015): Independently dated paleomagnetic secular variation records from the Tibetan Plateau. Earth and Planetary Science Letters 416, 98-108. HABERZETTL, T., K.L. KIRSTEN, T. KASPER, S. FRANZ, B. REINWARTH, J. BAADE, G. DAUT, M.E. MEADOWS, Y. SU, R. MÄUSBACHER (2019): Using 210Pb-data and paleomagnetic secular variations to date anthropogenic impact on a lake system in the Western Cape, South Africa. Quaternary Geochronology 51, 53-63. HABERZETTL, T., T. KASPER, J.S. STONER, J.J. RAHOBISOA, G. DAUT (2021): Extending and refining the paleomagnetic secular variation database for south-eastern Africa (Madagascar) to 2500 cal BP. Earth and Planetary Science Letters 565, 116931.

A dual chronological approach for more robust paleoclimate reconstructions in semi-arid regions – a case study from Mongolian lakes

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Semi-arid Mongolia is a highly sensitive region to paleoclimate changes, but the region’s paleoclimatic evolution and its underlying forcing mechanisms have been controversially discussed. In this context, chronological control of the region’s existing paleoenvironmental reconstructions is often imprecise because chronologies are mostly derived from few ^{14}C-dates on bulk organic material. Bulk organic carbon often has to be used in semi-arid regions due to the absence of terrestrial macrofossils. Compared to terrestrial macrofossils, which are assumed to be rapidly deposited in lakes, bulk organic carbon can be “pre-aged” because organic material accumulates in the catchment over hundreds to thousands of years and possibly overestimates the “true” deposition age when ending up in the lake.

This study presents a dual chronological approach from two high-altitude lakes in the Mongolian Khangai and Altai Mountains (Fig.1) to establish the best possible chronologies. We extensively ^{14}C-dated different organic compounds from the lake sediments of both lakes and evaluated the ^{14}C-based chronologies by paleomagnetic secular variations (PSV). ^{14}C-dating of bulk organic carbon and terrestrial macrofossils from the sediments of Shireet Naiman Nuur (Nuur = lake) in the Mongolian Khangai Mountains provide a robust and precise chronology for the past 7.4 ± 0.3 cal. ka BP. PSV confirmed this ^{14}C-based chronology because it resembles the predictions of global geomagnetic field models for the site.

Fig. 1. Shireet Naiman Nuur in the Mongolian Khangai Mountains (© P. Strobel)

For the Khar Nuur sediments in the Mongolian Altai Mountains, bulk organic carbon and aquatic macrofossils were ^{14}C-dated, providing a chronology for the past 4.2 +0.4/-0.3 cal. ka BP. PSV pattern from this lake resembles those from Shireet Naiman Nuur and global geomagnetic field models for the site, but with a constant offset of 730 ± 30 yr. While we can exclude possible reservoir effects from terrestrial pre-aging and hardwater effects, the ~730 yr offset in PSV is likely the result of a constant lock-in depth of magnetic particles 26 ± 2 cm below the sediment-water interface. We therefore emphasize the importance of the potential lock-in depth and reservoir effects that can challenge the establishment of chronologies in lake sediments from semi-arid regions, but the combination of ^{14}C-dating and PSV give two independent chronological indicators for establishing and improving chronologies in such regions. Based on our good chronological control, we finally reconstructed variations in paleotemperature and paleohydrology based on established sedimentological proxies and innovative compound-specific δ^2H analyzes of specific biomarker compounds.

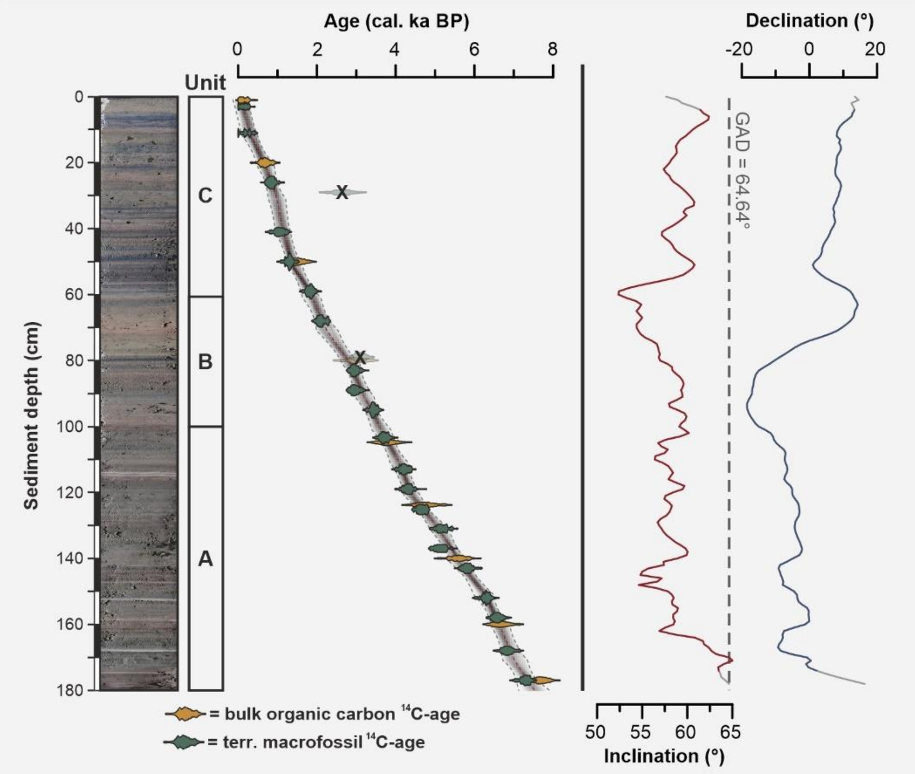

Fig.2. Chronostratigraphy of the Shireet Naiman Nuur sediments (modified after Bliedtner et al., 2022, Frontiers in Earth Science).

Speleothems: Insights and approaches of a key continental archive

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Speleothems, such as stalagmites, are currently among the most important and sought-after archives of past climate and environmental change on the continent. This is partly because their physical and chemical characteristics, including stable isotopes and trace elements, serve as proxies for past climate parameters. However, the greatest strength of speleothems is that these freshwater carbonates can be dated using U-series techniques, provided that the samples are sufficiently clean, i.e., poor in non-carbonate detritus. Thanks to major advances in U-series dating, chronologies of proxy parameters (especially the oxygen isotopic composition) based on speleothems are considered the most accurate and precise ones for the past about 600-700 ka.

In this talk, the usefulness of speleothem data in modern paleoclimate research will be demonstrated using case studies, focusing on recent work in caves of the European Alps.

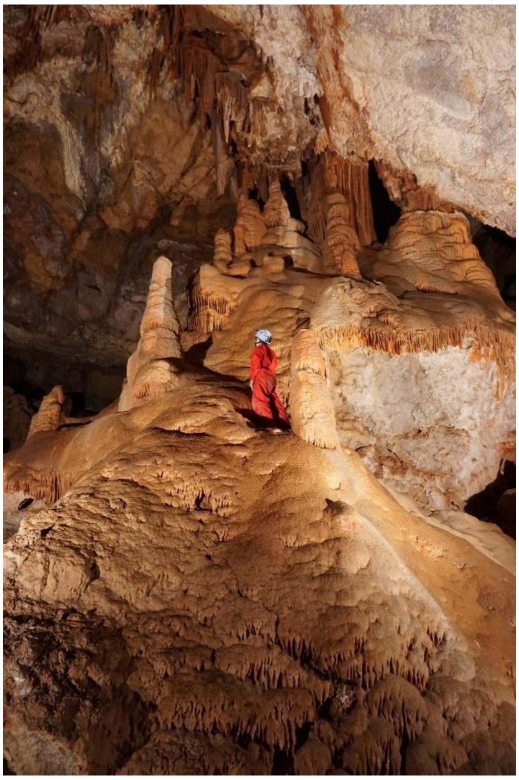

Fig. 1 Large and currently inactive stalagmite and flowstone formations in a cave in Iran bear witness to a wetter climate in the recent geological past

Fig. 2: Cross section of a pair of stalagmites from a mountain cave in Northern Italy, showing internal stratigraphy and growth discontinuities marked by color changes

U-Th dating (^{230}Th method) (Christoph Spötl)

application	▪ applicable to carbonates (calcite, aragonite) ▪ ideal candidates are speleothems and reef corals ▪ less ideal candidates are travertine and spring tufa ▪ challenging are marine carbonate sediments, teeth, bones and lignite
sample processing	wet chemical dissolution, ion exchange and spiking
analytical instruments	Multi collector-ICP-MS (previously single collector-ICP-MS, TIMS – or alpha counting in the old days)
data analysis	correction for detrital Th (if needed)
limitations/ perspectives	dating range 0 to about 600-700 ka. Several labs are now achieving epsilon precision (i.e., better than i.e. better than per-mil-level) on the final ages
available labs	e.g., Minneapolis, MIT, Albuquerque (USA), Xian (China), Melbourne (Australia), Göttingen, Heidelberg and Mainz (Germany), Taipei (Taiwain), Singapur
references	CHENG, H., EDWARDS, R.L., SHEN, C.-C., POLYAK, V.J., ASMEROM, Y., WOODHEAD, J., HELLSTROM, J., WANG, Y., KONG, X., SPÖTL, C., WANG, X., ALEXANDER, E.C. (2013): Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. – Earth and Planetary Science Letters, 371-372, 82-91. SPÖTL, C. & BOCH, R. (2019): Uranium series dating of speleothems. – In: White, W. B., Culver, D.C., Pipan, T. (eds.): Encyclopedia of Caves. 3rd ed., 1096-1102, London, Academic Press. WENDT, K.A., LI, X., EDWARDS, R.L. (2021): Uranium–Thorium dating of speleothems. – Elements, 17, 87-92.

Sherlock Stones – Insights into forensic soil science with a focus on dating

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Determining the mineral composition of (top) soils is crucial in forensic investigations, either for sample comparison, or, even more for samples' provenance. Maintaining these demands in a timely manner, high-throughput chemical characterization (SEM-EDX) of single mineral grains and U-Th-Pb age determination (LA-ICP-MS) of specific mineral phases, e.g., zircon or apatite, are applied. Compiling these data from case work and the available literature allows the set-up of extensive, searchable databases with a high spatio-temporal resolution. The latter are mandatory for quick delimitation of search areas but also to estimate the individuality of a sample. Furthermore, working with such a database is particularly useful for cold cases, but can also show potential connections of cases hitherto independent from each other, which lead to new investigative approaches.

Using these (semi-)automated approaches limits the influence of the human factor or individual variability to a minimum. Further advantages are time-independent use of analytical facilities and increased statistical significance in individual sample characterization due to very high numbers of single grain SEM-EDX (n >> 1 000 … 200 000) and U-Th-Pb mineral measurements. Nevertheless, these methods do not completely replace the classical optical microscope-based studies, but reduce them in terms of mineral characterization to a level of plausibility control. Since about five years, this approach is applied at the Kriminalwissenschaftliches und -technisches Institut (KTI) at the Landeskriminalamt (LKA, Saxon State Office of Criminal Investigations, Dresden) of Saxony and yields very promising results concerning the gained information for case work at coevally highly increased case and sample numbers.

Main challenges for almost all investigations are extremely limited amounts of trace material, time pressure, unexpected changes in the legal proceedings, etc.

Although provenance or sample comparison of soils is the main task, there are also other cases that demand for innovative method application. For example the dating and provenance of personal belongings or artwork and the rough age estimation of organic material like bones (e.g. pre or post a specific date/event) or wood. Finally, experiments on the age estimation on sunken material using growth rates, ^{14}C and stable isotope patterns of sessile molluscs are currently in an early experimental state.

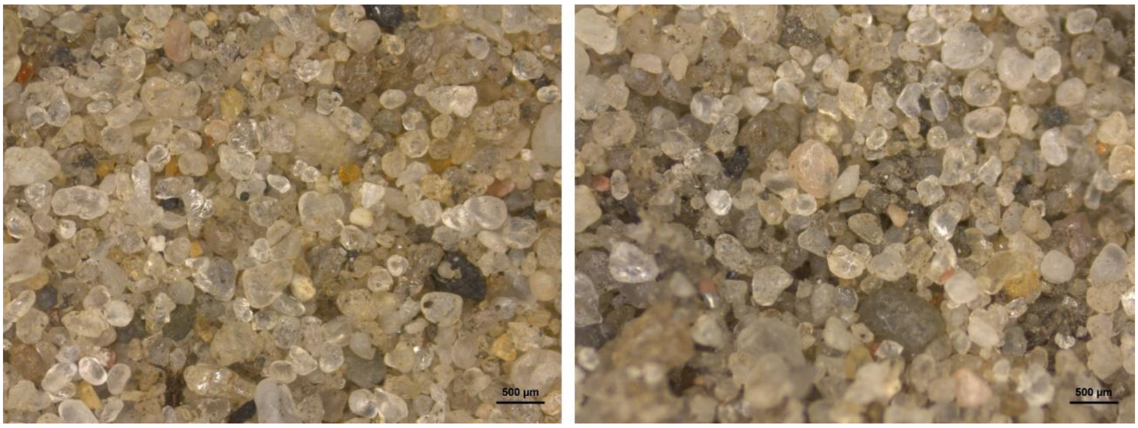

Fig. 1: Two nearly identical soil samples from different places illustrating some the challenges of forensic soil investigation.

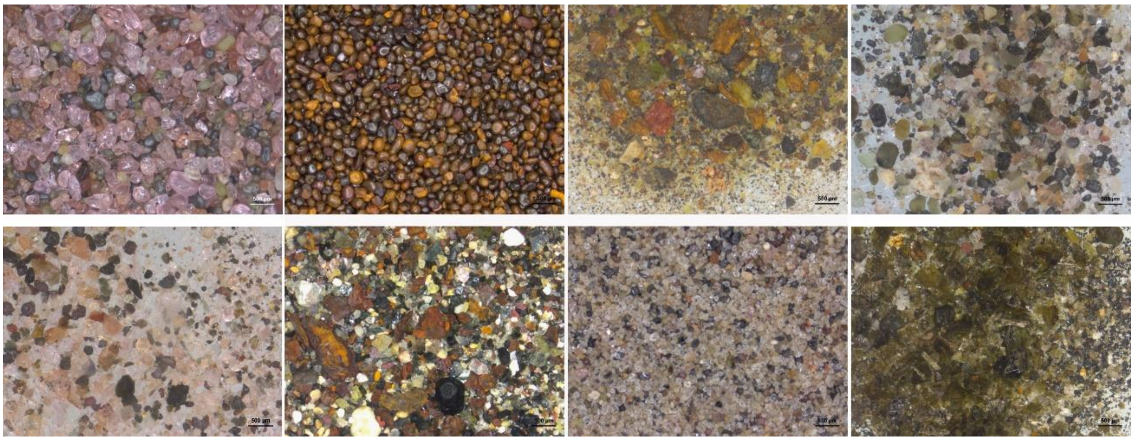

Fig. 2: Selection of heavy mineral concentrates from casework and reference samples showing the huge potential of this method for rapid data acquisition for forensic purposes.

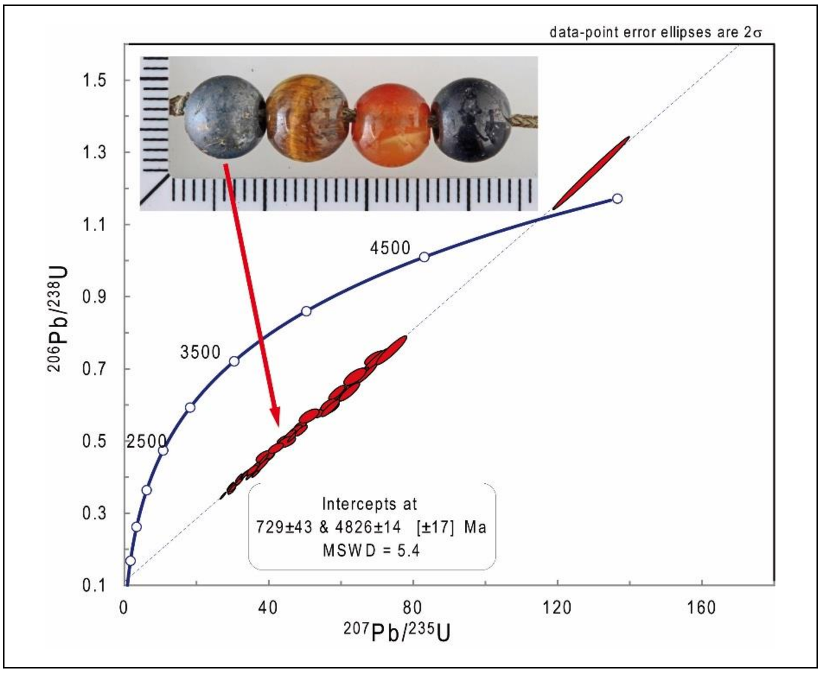

Fig.: 3 Results of U-Pb age determination on a hand-made hematite bead.

Forensic Investigations Methods (Andreas Gärtner)

application	Analyses of soils for forensic purposes span a broad variety of methods and typically aim to evaluate if the trace soil coms from a specific place or object, and if not, where else it might have been taken from. Additional questions that regularly appear are about material characterisation and identification, whereas the bandwidth of objects and materials is extremely diverse. ▪ SEM-EDX on minerals and inorganic material (no dating method…, applied daily, in-house), ▪ U-Th-Pb (applied regularly, in-house), ▪ ^{14}C, dendrochronology, stable isotopes, growth rates of sessile molluscs (applied rarely / experimental, in-house and with co-operating institutes) Questions linked to soil analyses (selection): ▪ provenance/comparison of soil samples and rock fragments (typical), ▪ age estimation on organic material (rarely), ▪ age estimation on sunken material (experimental)
samples	▪ samples from crime scenes (often only some mg of material) and from around the suspect place supplemented by a large collection of reference soil samples, ▪ soil material (minerals, biogenic compounds, anthropogenic material), but also metal alloys (e.g. fake precious metals), jewellery, wood, building material, etc., ▪ SEM-EDX of (heavy) minerals: ca. 300-500 samples per year, >> 10 Million single grain analyses in less than five years, ▪ LA-ICP-MS (dating, chemical composition, etc.): regularly, but less than SEM-EDX
sample processing	▪ (heavy) mineral characterisation: (heavy) mineral separation, mounting on carbon tape, coating, SEM-EDX analysis / Raman spectroscopy / microscopy, (near) real-time data processing and evaluation, databases, ▪ U-Th-Pb dating of minerals: (heavy) mineral separation, selection of mineral phase, SEM imaging, (optional: mounting → polishing → CL imaging), LA-ICP-MS analysis, data processing and evaluation, databases, ▪ other (dating) methods → according to the requirements
analytical instruments	LA-ICP-MS, SEM-EDX, RFA, X-ray Diffraction, Raman Spectroscopy, FTIR, microscopy, …

data analysis/ processing	▪ (heavy) mineral characterisation: AZTEC templates (OXFORD instruments), Crystal Sleuth, RRUFF database, ▪ large collection of reference minerals / materials for direct comparison, ▪ U-Th-Pb dating of minerals: AGeRAp (EXCEL-based program, developed by Axel Gerdes and Richard Albert, Goethe University Frankfurt am Main), R templates, - other (dating) methods → according to the requirements or external analyses
limitations	beside limitations of each method (see this volume): ▪ extremely limited amounts of sample material (often only some mg), ▪ provenance studies rely to a good spatio-temporal resolution of databases, ▪ time pressure (e.g., juristic deadlines → management of external analyses), …
perspectives	high demand and huge potential for the age estimation on sunken material using growth rates, ^{14}C and stable isotope patterns of sessile molluscs (currently in an experimental state)

Map of some Labs for Dating Rocks, Soils and Sediments in Europe

List of Labs & Links: (of which the European ones are shown in the map)

Method	Labs & Links
U-Pb-Dating of Zircon	**[Z1] GeoPlasmaLab:** Senckenberg Naturhistorische Sammlungen Dresden, (www.senckenberg.de/de/institute/senckenberg-naturhistorische-sammlungen-dresden/) **[Z2] FIERCE** at Universität Frankfurt a. Main (www.fierce.uni-frankfurt.de/)
Cosmogenic radionuclides (^{10}Be, ^{26}Al in quartz, ^{36}Cl in rock)	**[CR1] DREAMS** & **HAMSTER** at HZDR Dresden-Rossendorf (www.hzdr.de/ams) **[CR2] CologneAMS**, Univ. Cologne (www.cologneams.uni-koeln.de/) **[CR3] VERA** at Univ. Vienna (www.isotopenphysik.univie.ac.at/vera/) **[CR4] ASTER** at Cerege, Aix-en-Provence (www.cerege.fr/en/) **[CR5] SUERC** at Univ. Glasgow (www.gla.ac.uk/research/az/suerc/ams/) **[CR6] Aarhus** AMS Centre (www.c14websub.au.dk/)
Luminescence dosimetry of sediment	**[LD1] HZDR** Dresden-Rossdorf, Freiberg, Group Near-field Sensing) (www.hzdr.de/db/!ContMan.Visi.Card?pUser=15926&pNid=3055) **[LD2] Leibniz Institute for Applied Geophysics** (Manfred.Frechen@LIAG-Hannover.de) **[LD3] University Heidelberg** (www.geog.uni-heidelberg.de/geomorph/lumineszenz.html) **[LD4] University of Giessen** (www.uni-giessen.de/de/fbz/fb07/fachgebiete/geographie/arbeitsgruppen/physisch/forschung) **[LD5] University of Cologne** (www.geographie.uni-koeln.de/forschung/arbeitsgruppen/geomorphologie-und-geochronologie/lumineszenzlabor-cll)
Radiocarbon (^{14}C)	**[RC1] LARA**, University of Bern (www.14c.unibe.ch/) **[RC2] Hydroisotop GmbH** Schweitenkirchen (www.hydroisotop.de/) **[RC3] LIP**, ETH Zurich (www.ams.ethz.ch/) **[RC4] CEZA**, Curt-Engelhorn Zentr. Archäometrie Mannheim (www.ceza.de/) **[RC5] MPG-Jena** (www.bgc-jena.mpg.de/servicegruppen/14c-analytik) **[RC6] SUERC**, University of Glasgow (www.gla.ac.uk/research/az/suerc/radiocarbondating/) **[RC7] University of Groningen** (www.rug.nl/research/centre-for-isotope-research/) **[RC8] Kiel University** (www.leibniz.uni-kiel.de/de/ams-14c-labor) **[RC9] Lund University** (www.geology.lu.se/research/laboratories-equipment/radiocarbon-dating-laboratory) **[RC10] University of Oxford** (www.c14.arch.ox.ac.uk) **[R1C1] Aarhus University** (www.c14.dk/) **[RC12] VERA**, University of Vienne (www.isotopenphysik.univie.ac.at/vera/)
Paleomagnetic reversals for sediment sequences	**[PM1] University of Greifswald** (www.geo.uni-greifswald.de/lehrstuehle/geo-graphie/physische-geographie/labore-laboratories/sedimentlabor-sediment-lab/) **[PM2] Leibniz Institute for Applied Geophysics** (www.leibniz-liag.de/forschung/methoden/gesteinsmagnetik.html) **[PM3] GFZ Potsdam** (www.gfz-potsdam.de/sektion/geomagnetismus/) **[PM4] University of Bremen** (www.geophysik.uni-bremen.de/page.php?pageid=14) **[PM5] University of Lund** www.geology.lu.se/research/laboratories-equipment/palaeomagnetic-laboratory) **Quebec at Rimouski** (www.paleomag.uqar.ca/?lang=fr) **Oregon State University** (www.paleomag.ceoas.oregonstate.edu/paleo-geomagnetism/)

Dating Wood

Introduction (Ernst van der Maaten)

Studying tree rings can tell a lot about a tree, its' history as well as about the environmental conditions it was exposed to. A central principle of dendrochronology, which is the scientific discipline dealing with the dating of tree rings, is the principle of crossdating. It refers to the matching of ring-width patterns and suggests that tree growth is determined by common limiting factors (Fig. 1). Crossdating provides the quality control needed to assign rings to exact calendar years.

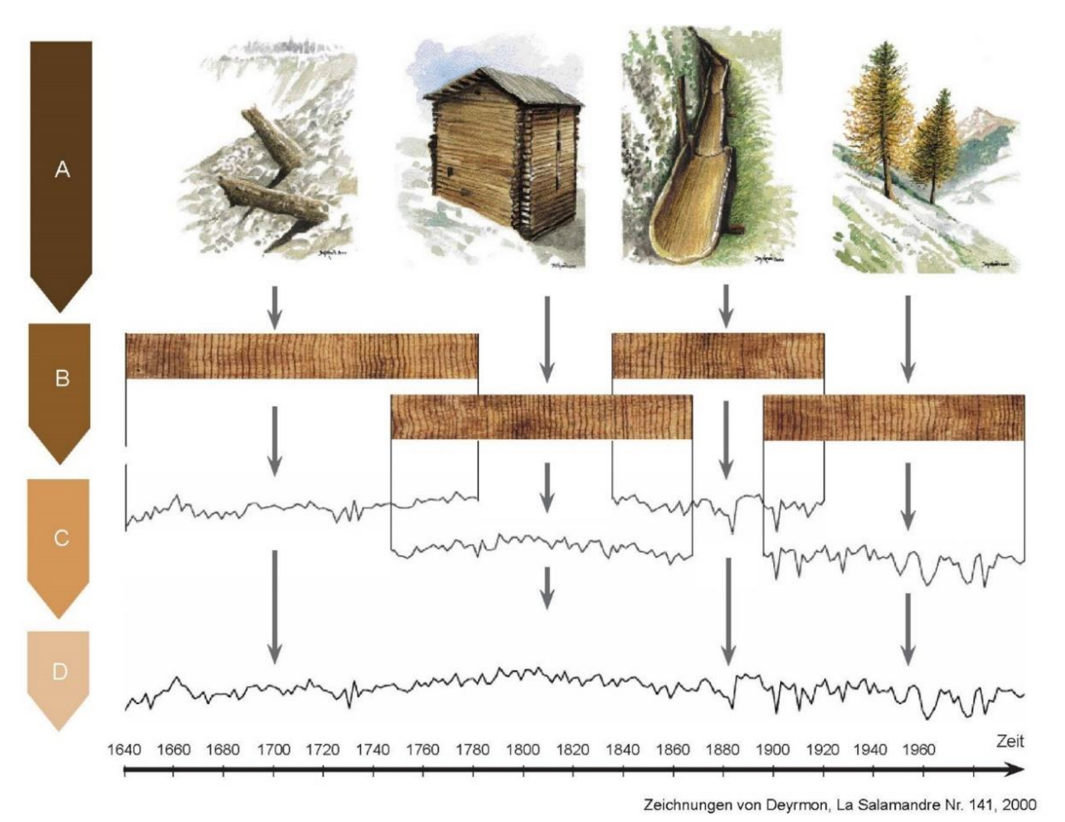

Fig.1: Principle of cross-dating. (A) Timbers from, for example, glacial moraines, old buildings, water pipes, or living trees are searched for; (B) samples are taken; (C) tree-ring widths are measured and dated; and (D) compiled into a chronology.

Many subfields within dendrochronology have been developed over time, highlighting the diverse insights that tree rings may offer. The most important ones are:

- **Dendroarchaeology:** mainly deals with dating, e.g., of beams and posts from old buildings or dwellings. Besides construction dates, the specific context of the wooden objects may be used to increase the understanding of human behavior in the cultures under study.
- **Dendroclimatology:** deals with past climatic variability. Based on tree-ring chronologies and instrumental climate data, climate conditions are reconstructed. Millennium-long tree ring-based reconstructions, e.g., of temperature in northern Scandinavia, help to put our current climate into perspective.

- **Dendroecology:** refers to a subfield that uses tree-ring based methods to answer ecological questions, i.e. that deal with interactions of organisms (in this case: trees) with their environment. For example, for enhancing the resilience of forests to climate change, dendroecological studies focusing on the climate sensitivity of tree growth, provide important information.
- **Dendrogeomorphology:** uses tree rings to date or reconstruct geological processes. One main characteristic of trees that is made use of, is that trees gather the most light while standing up straight. When a tree is tilted, e.g., due to rockfall, it will try to straighten the stem as quickly as possible through the formation of reaction wood. Such wood can then be used to date the geological event.
- **Dendrochemistry:** uses the characteristic of trees that they absorb chemical elements along with the intake of water and gasses. Since these elements are stored in the perennial parts of trees, tree rings can be chemically analyzed to serve as a record of contamination, nutrient availability, and pollution.

Although these subfields rely on the same basic method, concepts and principles, differences exist in sampling approaches, sample preparation and analytical techniques, both depending upon the nature of the woody material under study as well as on the specific research questions.

Tree rings and the stories they tell

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Dendrochronology, i.e. the scientific method of dating tree rings, is useful for answering many different questions: About the age of a tree or building, about the growth of a tree or forest stand over time, or about growth responses to external factors like climate, insect calamities or fires. In the talk, the main principles and concepts upon which dendrochronology relies will be addressed. Examples of the application of tree-ring based methods in archaeological, landscape evolutionary, ecological, climatological and geomorphological contexts will be provided, while highlighting its' perspectives and limitations.

Photo: Marieke van der Maaten-Theunissen

Photo: Marieke van der Maaten-Theunissen

Tree-rings Analysis (Ernst van der Maaten)

application	Dendrochronology, i.e. the scientific method of dating tree rings. Tree-ring analyses can be used to answer diverse archaeological, climatological, ecological and geomorphological questions. One may, for example, date historic or subfossil woods, study the climate sensitivity of tree growth, or reconstruct environmental conditions and geomorphological processes. Besides classical tree-ring width (TRW), various other tree-ring parameters can be analyzed, namely: wood density (WD), blue intensity (BI), wood anatomy (WA), wood chemistry (WC) and stable isotopes (SI).
samples	According to the specific research question and study material, either increment cores, stem discs / cookies or smaller wooden parts are collected. Given the variety of questions that may be addressed with tree rings, no general rule of thumb regarding **sample size** exists. However, to minimize the probability of being in error, reliable dates must be supported by sufficient samples (Principle of replication). In climate sensitivity studies, usually two cores per tree are extracted from 10-15 individuals per site to obtain reliable site chronologies. Samples from living trees are usually air-dried before their surface is cut with a core microtome / razor blade and (or) sanded with fine-grit sand paper to highlight annual rings. For dry historic wood air-drying is superfluous, whereas for subfossil woods that were preserved under wet conditions, it is counterproductive, as the sample would be destroyed through shrinking when the water evaporates. Hence, subfossil woods are usually kept wet. The exact **sample preparation** depends upon the tree-ring parameter to be analyzed. Whereas for TRW measurements a surface preparation generally suffices, other parameters require more sophisticated sample preparation. For WA measurements, for example, samples are often embedded whereafter thin sections are cut with a microtome.
sample processing	After preparation, samples are often **digitized**. For measuring TRW, devoted systems, such as the Advanced Tree-Ring and Image Capturing System ‘ATRICS’, for WD, X-ray based scanners, for BI, flatbed scanners, and for WA, slide scanners are used. For determining the chemical composition of wood both direct (i.e. inductively coupled plasma atomic emission spectroscopy ‘ICP-AES’ and inductively coupled plasma mass spectroscopy ‘ICP-MS’) and indirect systems are used (X-ray fluorescence / reflectometry ‘XRF’). Mass spectrometers are further used to measure SI. The actual **measurements**, e.g., of TRW or WA properties, are done in software such as CooRecorder or ROXAS.
analytical instruments	Depending upon tree-ring parameter to be analyzed (see above).

precision	Crossdating, i.e. the matching of ring-width patterns, is the central principle in tree-ring research. It provides the quality control needed to assign rings to exact calendar years. The temporal resolution of ring-width measurements from wood from seasonal climates is annual.
data analysis/ processing	R is commonly used to analyze tree-ring data. Add-on packages such as dplR, treeclim and pointRes allow, amongst others, to build chronologies, to analyze climate–growth relationships as well as to study extraordinary growth responses, respectively.
limitations	Dating of wood at an annual resolution is only possible when suitable **reference chronologies** are available. Such chronologies are created by extending chronologies from living trees back in time by overlaying tree-ring series from successively older woods. Further, tree-ring analyses are spatially limited to regions with seasonal climates. Given that tree-ring parameters are relevant to answer questions in scientific fields ranging from archaeology to ecology, future applications are manifold. Methodological advances in the various sub-fields are made to increase the applicability as well as to improve tree-ring based methods, e.g., by using X-ray computed tomography for non-destructive dendrochronology with archaeological woods or paraffin embedding of tree-ring samples to obtain high-quality thin sections for WA analyses.
perspectives	Given that tree-ring parameters are relevant to answer questions in scientific fields ranging from archaeology to ecology, future applications are manifold. Methodological advances in the various sub-fields are made to increase the applicability as well as to improve tree-ring based methods, e.g., by using X-ray computed tomography for non-destructive dendrochronology with archaeological woods or paraffin embedding of tree-ring samples to obtain high-quality thin sections for WA analyses.
available labs	Many **tree-ring labs** exist in Germany, Europe and beyond, all having their own specific expertise and focus. The interactive tree-ring lab map of the Association for Tree-Ring Research, a Europe-based association of tree-ring researchers, is providing an overview as well as the possibility to filter labs according to their expertise and (or) research equipment: https://tree-ring.shinyapps.io/ATRmap/

Alternative methods for timber dating and provenancing

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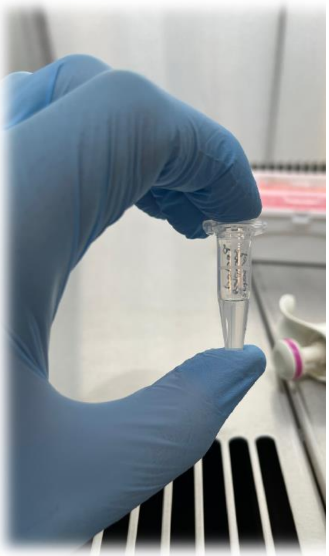
Dendroprovenancing, the identification of the origin of archaeological timber, involves comparing tree-ring width series from an object of investigation to reference chronologies spatially distributed in the potential source area. However, challenges such as a lack of rings in historical objects and limited reference data hinder its effectiveness. Furthermore, the extensive logging history and, as a result, absence of forest in relevant (low)elevations restricts the creation of long ring-width chronologies. To address these limitations, alternative approaches are necessary.

Enhancing timber origin identification can be achieved by considering additional wood-anatomical variables. Notably, oak earlywood vessel chronologies have proven effective in capturing distance from the shore, surpassing ring widths in quality assessment. In contrast, coniferous trees present elevation challenges. Overcoming this, image colour intensity analysis, specifically utilizing blue intensity, shows promise. This technique overcomes elevation-related issues and allows to identify elevational groups of material from in Central Spain, providing valuable insights.

However, these techniques still rely on the presence of long-lived trees in potential source areas. To overcome this, alternative methods capturing unique site-specific characteristics have been explored. Molecular analysis of timber is a promising yet challenging approach. Obtaining sufficient DNA from archaeological timber is complex but opens up extensive possibilities for dendroprovenancing, which was successfully demonstrated for oak timber from Baltic states. Nonetheless, precise timber origin identification using molecular methods often requires high genetic diversity in the study area, which can be a limiting factor. An alternative approach involves utilizing site geology, as non-essential microelements and nutrients in wood reflect site conditions. For example, strontium (Sr) reflects site geology, while the Ca/Sr ratio, encompassing both physiological and geological signals, accurately identifies timber in previously undated materials from Southern Spain.

Recent technological advancements have led to the development of alternative approaches in dendroprovenancing for archaeological studies. These approaches show great promise, but the creation of detailed reference data is still in the early stages.


Itrax Multiscanner



Some Labs and Links for Dating Wood

Method	**Labs & Links**
Preparation of wood samples for measuring **tree-ring width, wood density, blue intensity, wood anatomical features, wood chemistry** and **stable isotopes**	**DendroLab** TU Dresden, Chair of Forest Growth and Woody Biomass Production (www.tu-dresden.de/bu/umwelt/forst/ww/waldwachstum/dendrolab) **Association for Tree-Ring Research (ATR)**: provides an interactive map of tree-ring labs (www.tree-ring.shinyapps.io/ATRmap/)

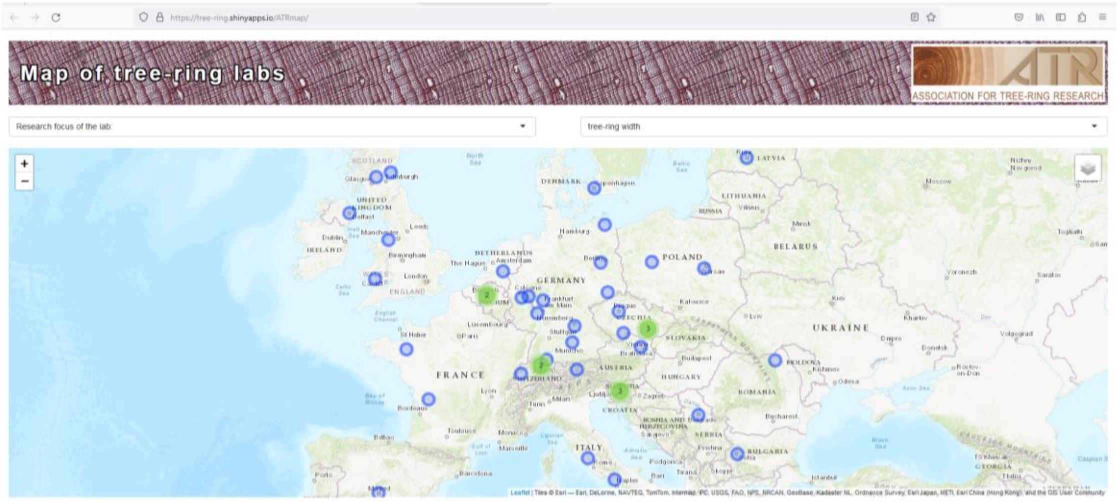


Fig.: Screenshot of the interactive map on tree-ring with analysing labs (www.tree-ring.shinyapps.io/ATRmap/

Dating Aquatic Systems

Introduction (Diana Burghardt)

Origin and flow paths of surface water and groundwater are of great interest in many hydrological and hydrogeological studies. Therefore, measurement of different tracer substances at different locations, deeps and times are useful, also in order to calibrate numerical models. In this context, the following articles and fact sheets address the application of noble gas tracers and isotope tracers in aquatic systems. The figure below shows time ranges, where these tracer can only be applied in groundwater systems. However, their investigations are challenging due to processses like dispersion, mixing and sorption in porous media, why multiple tracer measurements will help to decrease uncertainties.

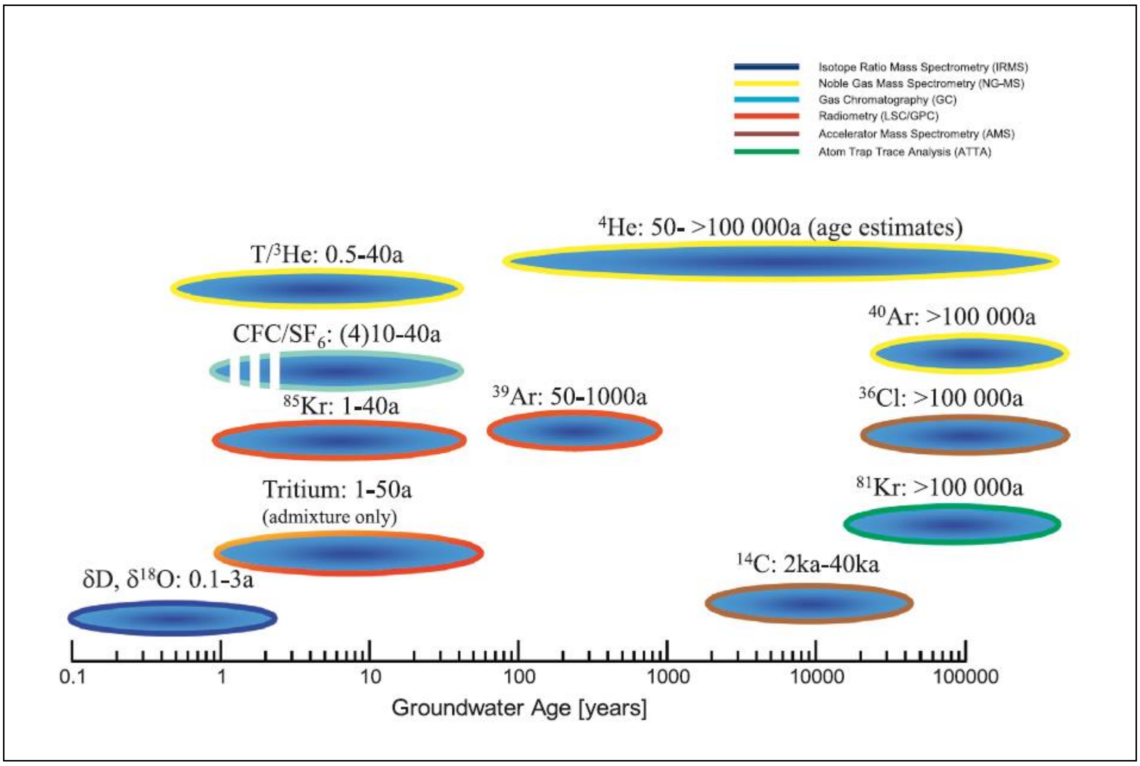


Figure: Time ranges, were different noble gas tracers and isotope tracers can be applied to investigate origin and flow paths in groundwater systems.(Suckow, A., 2014)

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Dating of groundwater, ocean water and glacier ice with ^{81}Kr, ^{85}Kr, and ^{39}Ar

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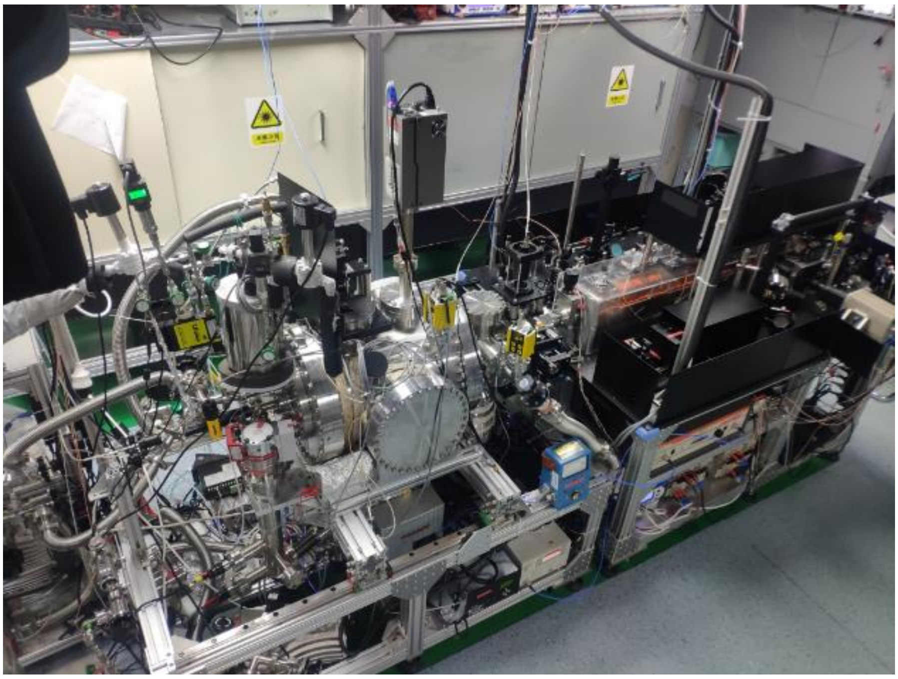
The noble gas radioisotopes ^{81}Kr ($t_{1/2}$=229 ka), ^{85}Kr ($t_{1/2}$=12 a) and ^{39}Ar ($t_{1/2}$=268 a) are valuable dating tools for groundwater, ocean water and glacier ice, serving applications such as drinking water management, ocean current tracing and climate reconstruction. Together with ^{14}C, these radioisotopes cover an age range from present back to 1.3 million years. Due to their extremely low environmental abundances (10^{-17}…10^{-11}) corresponding to only a few thousand atoms perkilogram of water or ice, their detection is very challenging and in the case of ^{81}Kr, has practically not been possible in the past.

In the recent two decades, the laser-based method Atom Trap Trace Analysis (ATTA), which detects single atoms via their fluorescence in a magneto-optical trap, has succeeded in measuring these radioisotopes on natural levels. Initially, tons of water or ice were necessary for ATTA, which severely hampered its use for dating of environmental samples. Due to progress in the ATTA instruments, the sample size could be lowered to ~10 kg of water or ice, allowing for applications such as dating of deep water from the Pacific Ocean and ice cores from Antarctica and Tibet. Here, we will present an overview of the ATTA method, recent dating results on groundwater, ocean water and glacier ice as well as our latest advances towards ^{81}Kr and ^{39}Ar dating with 1 kg of water or ice.



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Dating of groundwater, ocean water and glacier ice with ^{81}Kr, ^{85}Kr and ^{39}Ar (Florian Ritterbusch)

application	^{85}Kr, ^{39}Ar and ^{81}Kr dating Dating of Ocean water, Groundwater and Glacier ice
samples	1-10 kg of water or ice, depending on the required precision
sample processing	Groundwater: degassing in the field with membrane contactor Ocean water: transfer of water from standard Niskin bottles to steel containers Ice: extraction of air from bubbles in the ice by melting
analytical Instruments	Atom Trap Trace Analysis
data analysis	Single atom counting stratistics
limitations/ perspectives	limitations: sample size, precision perspective: ^{81}Kr and ^{39}Ar dating with 1 kg of ice
available labs	Heidelberg University (www.kip.uni-heidelberg.de/oberthaler/research/atta www.iup.uni-heidelberg.de/de/research/hydrotrap#Methoden) University of Science and Technology of China (USTC), Hefei, China (https://atta.ustc.edu.cn/en-us/events/attaprimer.html) Argonne National Laboratories (www.anl.gov/phy/tracer) University of Adelaide / CSIRO (www.csiro.au/en/research/natural-environment/water/groundwater- resources/noble-gas-facilities)

Real time on-site gas analysis - a ballad of (noble) gases, Arsenic, seismicity and trees

Rolf Kipfer

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Atmospheric noble gases enter aquatic systems by gas/ water partitioning. Therefore, aquatic noble gas concentrations in waters reflect the physical conditions prevailing during gas exchange. Consequently, applications of dissolved atmospheric noble gases are constrained to the analysis of gas partitioning processes between phases, but also allow the reconstruction of past environmental/ climate conditions [1]. These concepts in concert with the mechanistic understanding of the gas/ water partitioning in porous media allow e.g. to reconstruct ground water recharge in Northern America in response to the last glaciation [2, 3]. Most recently novel experimental methods enable to analyze the noble gas concentrations in minute amounts of water (< 1 mg, 4) and to determine (noble) gas concentrations in various terrestrial fluids online under field conditions [5, 6]. These methods allow to retrieve past environmental information from noble gases in fluid inclusions in speleothems [7] and yield information on the fluid transport around Black Smokers and ocean sediments [8, 9], on submarine ground water discharge [10] and on the possible effect of CH_4 formation on the mobilization on As in ground waters [11].

The presentation aims to summarize and to comment our recent developments on the application of atmospheric noble gases to study aquatic environments, trees [12] and the possible relation between fluid dynamics and seismic activity [13].

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Real time on-site gas analysis (Rolf Kipfer)

application	Studying the dynamics of conventional (lake, ocean, groundwater) and unconventional (pore water of sediments, trees) water bodies and analysing the evolution of gases and fluids (e.g., relation of fluid dynamics and seismicity, relation of (geogenic) Arsenic and gases).
samples	Individual samples in copper tubes or other adequate gas-tight metal containers. Online gas and Rn measurements.
analytical instruments	Transient trace gas analytics (noble gases, tritium, ^{3}H-^{3}He, Rn, CFCs, SF_6, Gas Equilibrium Inlet Mass Spectrometry for (noble) gas measurements in the field) Static mass spectrometers, GCs, alpha and gamma spectrometry, mobile and self-contained MS for being used in the field
data analysis	Self-tailored data reduction and analysis.
perspectives	Gas measurements in the context of seismicity, trees, CO_2 sequestration, geothermal applications and nuclear waste disposal.
available labs	www.eawag.ch/en/department/wut/main-focus/environmental-isotopes/

Groundwater Age: how multi-tracer studies and noble gas (isotope) data shed new light on an old concept

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Dating methods like radiocarbon, ^{40}K/^{40}Ar or the U/Th series nuclides are well established in the geosciences, allowing to determine the “age” of fossils, anthropogenic development, sediment layers etc. However, for water bodies (ocean, groundwater, lakes) the anthropocentric concept of “age” is highly misleading (Suckow, 2014). Water inherently mixes during flow and therefore any sample does not represent an individual entity, like e.g. a piece of charcoal would in the sediment record. A consequence is that the application of a single “dating” method cannot give a unique answer to the hydrologically relevant questions of flow velocity, amount of recharge, exchange between aquifers, or spread (advection & dispersion) of a contaminant. This is true even for the chemically most ideal noble gas tracers (Torgersen and Stute, 2013) or their radioactive isotopes such as ^{85}Kr, ^{39}Ar, ^{81}Kr (Purtschert et al., 2013), and even more so for tracers that inherently show more complications during application, such as the chemical alterations known and observed for the CFCs (IAEA, 2006), radiocarbon (Plummer and Glynn, 2013) , and ^{36}Cl/Cl(Phillips, 2013). Instead, the problem of characterizing a groundwater body must be addressed with multiple tracers covering more than one of the available time scales – and the longer the time scale in question is, the more tracers are needed.

Here we first present a very short case study in the Precipice Sandstone in Queensland (part of the Great Artesian Basin flow system, one of the largest aquifer systems in the world) in which the application of radiocarbon gave a comparably straightforward result (Suckow et al., 2020a; Suckow et al., 2018). Then a more complex system is presented with the overlying Hutton Sandstone, demonstrating how the application of ^{14}C and ^{36}Cl gave contradictory results and how this was reconciled (Suckow et al., 2020b). Results from the final case study of the Cambrian Limestone Aquifer (CLA) in the Northern Territories of Australia show a counter-intuitive development (increase) of measured ^{14}C values in flow direction and unreliable values for CFCs and SF_6. This last case study is situated in a large karst system with precipitation gradients from savanna to tropical landscapes and focused recharge through sinkholes. In such complex aquifers, only multi-tracer studies allow process conceptualisations detailed enough to integrate the contradicting results into a useful understanding of the groundwater system.

Fig. 1:
Adelaide Noble Gas Machine HelixMS (Thermo Fisher Sci.)

Fig.2:
Copper tubes for gas-free storage of 40 mL water samples for subsequent helium extraction

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Multi-tracer studies and noble gas (isotope) analysis (Axel Suckow)

application	^{18}O, ^{2}H, ^{3}H, CFCs, SF6, H1301, ^{85}Kr, ^{39}Ar, ^{14}C, ^{36}Cl, ^{81}Kr, ^{4}He Multi-tracer applications in Groundwater
samples	Water bottles, copper tubes, field degassing systems for RNGI, field filtration, field titration, field acidification
sample processing	Gas extraction, electrolytic enrichment, cryo and getter separation techniques
analytical instruments	IRMS, Gas chromatography, AMS, ATTA, Noble gas mass spectrometry
data analysis/ processing	Self-written measurement control, post-processing, LIMS & lumped parameter models
limitations/ perspectives	Environmental physics (that is: carrier dilution for ^{14}C & ^{36}Cl, mixing, dispersion)
available labs	around the planet: 4 ATTA labs, a dozen noble gas labs, several dozen AMS labs, hundreds of stable isotope labs, thousands of chemistry labs

The importance of groundwater age for the search for a repository for nuclear waste in Germany (and some insights into the distribution of groundwater ages)

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After the decommissioning of the last nuclear power plants in Germany in spring 2023, the question of a safe disposal of the nuclear waste becomes more urgent. The general concept prescribes that the waste is to be safely stored underground and within the borders of Germany. Low-level waste, which generates no or only low heat, will be disposed of in a former iron ore mine. In 2017, the German parliament passed a new law, the site selection act (Standortauswahlgesetz), which describes the necessary steps that have to be taken for the selection of a site for the subsurface disposal of high-level, heat-generating nuclear waste. §23 of said law describes the minimum requirements of such a site, e.g. the depth and thickness of the host formation and its hydraulic conductivity. §22 on the other hand defines six exclusion criteria, which – even when only one is violated – would result in the exclusion of the studied site. They include geological features (isostatic rise, tectonic, seismic and volcanic activity), mining and finally the absence of young groundwater in the selected site and its surrounding host formation. The site to be selected should be able contain the nuclear waste for at least one million years to prevent the transport of significant concentrations of radionuclides into the environment.

The site selection act prescribes that salt (in the form of diapirs and stratiform deposits), clay and crystalline rocks should be considered as host rocks. Especially the first two usually have very little to no free-flowing groundwater and taking a sample for regular age dating is thus often not feasible. In this case, natural tracer profiles provide an alternative pathway to regular age dating, especially in argillaceous rocks. Therefore, core samples are taken and their porewater is analyzed for the concentrations of conservative tracers such as chloride, bromide, stable isotopes and helium-4. If the resulting distribution of concentrations over the depth of the formation can be explained by purely diffusive transport, this can be counted as proof of the integrity of the formation, since no advection has taken place.

However, the deep host formation is often surrounded by permeable formations or elements, which could provide a contact to the shallow subsurface and its aquifers, which are commonly used in Germany for drinking water supply. Several potential pathways connecting the deeper and the shallow geosphere are possible, including fault zones. In Northern Germany, deep erosional features in the form of sub-glacial meltwater valleys (buried valleys) are common. They can penetrate into depths of several hundreds of meters and their backfill material often hosts important freshwater aquifers. On the other hand, they can sometimes violate the integrity of clay formations, leading to the local ascent of saline water from deeper formations, which can reach the surface in the form of brackish springs. Groundwater ages can be useful to investigate the interactions between shallow and deep formations. In a first step, all groundwater ages from Germany were collected and stored in a database. The hydrogeologically relatively homogeneous Quaternary and Tertiary unconsolidated rock cover of the North German Basin was selected to study the distribution of tritium-helium ages, e.g. to investigate the maximum depth of "young" groundwater.

Other options to investigate the ages of deeper groundwater include stable isotope signatures and dissolved noble ages, which can hint at the paleo-climate at the time of recharge as well as long-lived radioactive isotopes such as chlorine-36 and krypton-81.

Low-level radioactivity measurements as a tool for sensitive and precise dating

Detlev Degering

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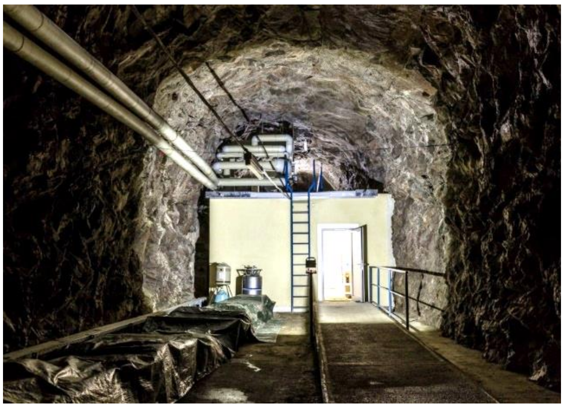
Dating of environmental samples often requires low decision limits of natural radionuclides. On one hand, the investigated nuclide itself is used for dating; here low-level analyses extend the datable time range. On the other hand, radioactive disequilibria in the decay series are necessary for or may influence the determination of the dating result; here a high sensitivity enables the determination of the largest possible number of decay series members and enhances the precision of the age result.

The Felsenkeller underground laboratory in Dresden provides very favourable conditions for the determination of low amounts of radioactivity. It is situated under an overburden of 45 m of rock in cellars of a former brewery. Its radiation background is well characterised with respect to the contribution of ambient radiation, the cosmic ray component and the neutron flux. Two measuring chambers act as accessible shielding and contain nine low-level gamma spectrometers and two low-level liquid scintillation counters. The Felsenkeller laboratory is specialised in the analysis of naturally occurring gamma emitters and of Tritium at environmental levels. The annual throughput amounts to about 2500 samples for gamma spectrometry and 300 … 400 for low-level Tritium analysis.

The application of low-level radioactivity measurements in dating methods will be illustrated by several examples. This includes identification of radioactive disequilibria for dosimetric dating methods, dating of sulfate precipitates in geothermal plants and experiences in the determination of Tritium in precipitation. Last, but not least determination of short living radionuclides serves for the identification of recent meteorite falls, as shown by the last two events (Flensburg 2019, Elmshorn 2023)



Low-level Tritium analysis by liquid scintillation counting

(Detlev Degering)

application	Hydrogeology, estimation of mean groundwater residence times,
dating range	Percentage of resent groundwater up to about 70 yeas
samples	volume several 100 ml, water
sample **processing**	distillation, electrolytical enrichment, liquid scintillation counting
analytical **instruments**	low-level tritium analysis by liquid scintillation counting
data analysis / processing	recovery and background control
precisions	detection limit: 1 TU (0.1 Bq/L)
limitations	heavily polluted water, mixture with other components (e.g. oil) detection limit: 1 TU (0.1 Bq/L), thus not applicable for old waters
perspectives	use of higher scintillator volumes (> 100 ml)
useful links	https://www.vkta.de/en/analytics/

Low-level gamma spectrometry (Detlev Degering)

application	▪ geology, archaeology, paleoclimatology, environmental sciences, hydrogeology, (analytical services for) dosimetric dating (OSL, TL), ^{210}Pb dating,
samples	▪ mass 10 - 1000 g, in special cases down to 0.1 g, solid as well as liquid materials
sample processing	▪ drying, crushing, grinding (if necessary), non-destructive possible
analytical instruments	▪ low-level gamma spectrometry ▪ low-level Tritium analysis by liquid scintillation counting
data analysis/ processing	▪ calibration with certified reference materials/ standard materials, gamma spectrum processing
limitations	▪ aggressive substances, large sample volumes (> 1 L), detection limits: 0.1 … 1 Bq/kg (solids) or Bq/L (liquids) (direct measurement, depending on radionuclide and total activity of the sample)
perspectives	▪ further background reduction by application of an active shielding

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^{3}H-^{3}He-Dating summarized by MSc candidate Johannes Lieder (TU Dresden, Institute of Groundwater Management) after hospitation of the helis-lab at University Bremen kindly supervised by Jürgen Sültenfuß

application	• dating young groundwaters (months to decades) • investigation of temporal and spatial dynamics of aquifers → flow velocity, dispersion rate, recharge rate etc. • differentiation between young and fossil waters → origin and protection status of thermal waters, mineral waters and groundwaters in general • differentiation between recharge components • tracing water motions within the ocean
samples	• **^{3}H:** typically, dry 1 litre glass bottles used • **^{3}He:** typically 1m long soft copper tubes (approx. 40 ml) used, some laboratories use diffusion collectors as an alternative • **^{3}H & ^{3}He** samples do not need to be stabilised
sample **processing**	• **^{3}H-sample processing for helium in growth method: (1)** water samples are degassed in special vacuum extraction unit, removing helium from the water, among other gasses, (2) samples are stored in hermetically sealed glass flasks, (3) after a few weeks or months (depending on the estimated tritium concentration), the accumulated ^{3}He gets detected in the mass spectrometer • **^{3}He-sample processing: (1)** transfer of samples into a high vacuum system (approx. 10^{-7} mbar), (2) samples get degassed quantitatively by a cryogenic system, (3) at liquid nitrogen temperatures all gases except He and Ne are removed from the samples, (4) some laboratories also use activated carbon on which helium and neon adsorbate
analytical instrument	• **^{3}H:** sector field mass spectrometer for measurement of decay product ^{3}He (helium in-growth method), alternatively, some laboratories use a liquid scintillation counter (LSC) for counting β~ decay events • **^{3}He:** sector field mass spectrometer
precision	**^{3}H:** 0,02 -0,03 TU, **^{3}He**: 0,5%
data analysis / processing	• separation of tritiogenic He ($^3He_{trit}$) from other He components (excess air, proportion corresponding to solution equilibrium, decay of U and Th, mantle He) necessary → e.g. by measuring ^{20}Ne, ^{22}Ne and ^{4}He and determining the ^{3}He/^{4}He ratio • with the separated $^3He_{trit}$ concentrations and the ^{3}H concentrations, the ^{3}H-^{3}He ages (t) can then be calculated, whereas t corresponds to the time difference between sampling and the last contact of the water with the atmosphere

limitations	• the half-life of tritium (12.32 years) limits dating with ^{3}H-^{3}He to groundwaters formed within the last decades • dispersive transport must be negligible compared to advective transport • all other helium sources must be well quantified • after ^{3}H input, no further exchange between ^{3}He of the aquifer with the atmosphere should happen, so that the method is not applicable to spring water.
perspectives/ further applications	• method will become much more important in the future, as ^{3}H concentrations in groundwaters are steadily decreasing due to the radioactive decay of tritium → dating with ^{3}H-^{3}He will thus replace ^{3}H-dating as soon as the ^{3}H values fall below the analytical detection limit • further advantages are, that ^{3}He and ^{3}H are not subject to chemical reactions, contamination potential is negligible and sampling is easy
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^{14}C-DOC$_{PPL}$ Dating

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The radioactive isotope ^{14}C has a half-live time of 5’730 years and is formed in the atmosphere, the exposure of cosmic radiation hitting nitrogen atoms. Through the biosphere (microbial CO_2 and DOC production in the soil), ^{14}C reaches the groundwater and is used to determine the mean residence time or “age” of the groundwater. To determine the initial carbon content of waters hydrochemical analyses are interpreted with regard to the δ^{13}C values. The age of the groundwater is calculated by the radioactive decay of ^{14}C after entering the soil zone. This method can be used to determine the age of groundwater, which is between 1’000 years and several 10’000 years old.

The isotopic composition (^{13}C/^{14}C) of dissolved inorganic carbon (DIC) in water is controlled by its origin and water-rock-interaction. Not only the solution of atmospheric CO_2, but also CO_2 from the unsaturated zone in the soil and the rising CO_2 from the deep underground as well as the dissolution of carbonate rocks contribute to the DIC composition of groundwater.

Since various processes in the subsurface can influence the inorganic carbon content, especially the dissolution of ^{14}C-free carbonate rock material and the associated hardening of the water, the ^{14}C-DIC method may not be suitable for some groundwaters. As an alternative, ^{14}C can also be measured in a biological relatively inert fraction of the dissolved organic carbon (DOC). In this case, no complex correction procedures are usually needed to determine the ^{14}C-DOC$_{PPL}$ groundwater age.

DOC$_{PPL}$ fractions are supposed to be very suitable for dating old groundwater. The solid phase extraction of organic substances using PPL resins is a very reliable and sufficient method for extracting the DOC from natural water. The SPE-PPL method (Dittmar et al. 2008) is particularly capable of extracting hydrophobic and highly to non-polar organic substances and the extracted DOC fraction shows a comparable composition to the intrinsic dissolved organic matter of the groundwater.

The ^{14}C activity of organic matter in the soil zone is generally equivalent to the atmospheric ^{14}C-CO_2 activity. As there are usually no other factors influencing the ^{14}C-DOC$_{PPL}$ activity during infiltration of the percolating groundwater, the accurate determination of the groundwater age is based on the atmospheric ^{14}C input signal, which has not been constant during the last 50’000 years (Figure 1). Therefore, the calculated ^{14}C-DOC$_{PPL}$ ages are calibrated with the IntCal13 curve from Reimer et al. (2013). However, the dissolution of potentially ^{14}C-DOC-free sedimentary organic carbon (SOC) in organic-rich sediments can influence the dating result. This influence can be recognised on the basis of the δ^{13}C-DOC$_{PPL}$ value. To account for possible variations and changes in the initial atmospheric activity due to exchange processes with ^{14}C-free or in ^{14}C-reduced organic matter (e.g. organic rich argillaceous soil) in the soil zone, the atmospheric ^{14}C input may be attenuated to 0.85 ± 10 pmC (Geyer et al., 1993). Therefore, the ^{14}C-DOC$_{PPL}$ age is calculated with the upper limit of no or almost negligible attenuation (0.95 fraction of atmospheric ^{14}C input) and the lower limit with noticeable attenuation in the soil zone (0.75 fraction of atmospheric ^{14}C input).

The results of the measurement of δ^{13}C values are related to the international standard VPDB (Vienna fossil Belemnite of Pee-Dee-Formation), and are given as the relative deviation in the so-called δ-notation. The ^{14}C value is expressed in pmC (percent modern Carbon), whereas 100 pmC equates the specific ^{14}C activity of atmospheric CO_2 of the year 1950 (before present (BP)).

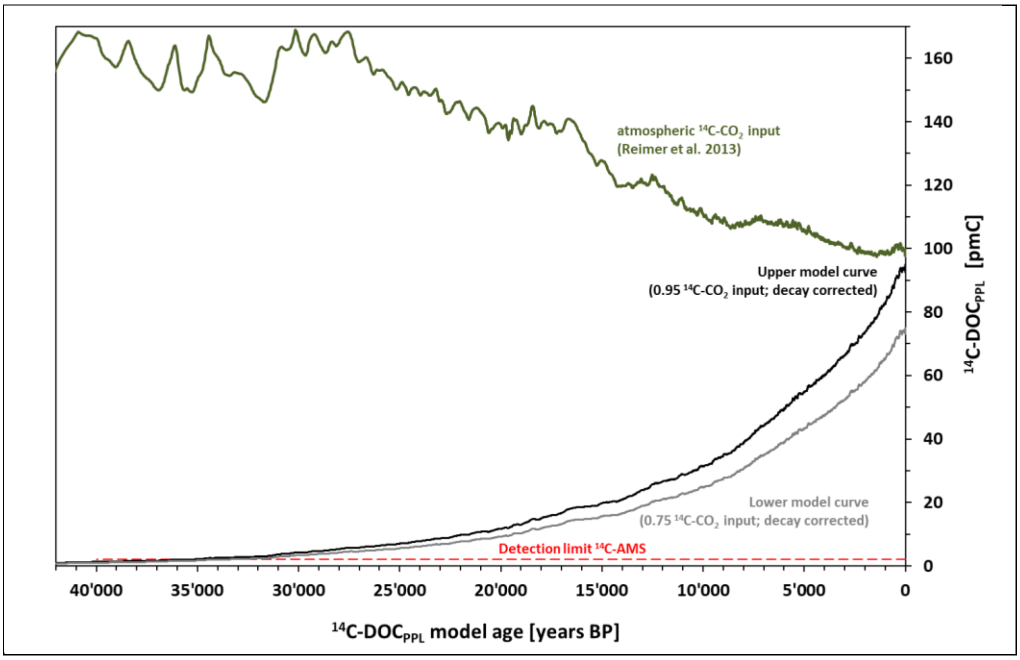

Figure 1: Variations of ^{14}C activity of atmospheric CO_2 over the past 50'000 years (prior to 1950 (BP)) based on InCal13 and Marine13 ^{14}C calibration curves of Reimer et al. (2013) and calculated decay curves for the boundary 0.95 and 0.75 model cases.

References

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^{14}C-DOC$_{PPL}$ (including δ^{13}C-DOC$_{PPL}$)

(Michael Heidinger, Gesine Lorenz, Hydroisotop GmbH)

application/ dating range	groundwater dating, age period about 1’500 to several 10’000 years
samples	sampling 5 to 10 L PE bottle; stabilised with HCl to pH<2 at sampling;
sample processing	solid phase extraction of organic substances using PPL resins; dissolution in methanol, transformation to graphite for AMS measurement of
Analytical instrument	AMS for ^{14}C (IRMS for δ^{13}C)
data analysis	see description below; unit of measured result ^{14}C-DOC$_{PPL}$: “pmC” (=percent modern carbon) unit of measured result ^{13}C-DOCPPL: “‰$_{VPDB}$”
limitations	▪ concentration of DOC$_{PPL}$ fraction in sample too low ▪ contamination of groundwater sample by drilling fluid etc. ▪ high concentration of other DOC substances, e.g. oil
perspectives	Possibility for groundwater dating of samples which can not be used for ^{14}C-DIC methods as ▪ CO_2 rich waters ▪ groundwater with very low DIC contents, e.g. from granite ▪ high saline groundwaters with very low DIC contents

CFC/ SF_6 Dating

Summary from Plummer L.N., Busenberg, E. (2006). Use of chlorofluorocarbons in hydrology—a guidebook. International atomic energy agency, Vienna, prepared by MSc candidate Johannes Lieder (TU Dresden, Institute of Groundwater Management), kindly reviewed by Axel Suckow

Chlorofluorocarbons (CFCs) are volatile, synthetic compounds of carbon, chlorine and fluorine. They were used at the beginning of 1930s for aerosol propellants and refrigerants. Assuming that the water sample was in solubility equilibrium with the unsaturated zone at the time of recharge, the dating of groundwater with CFCs is done by estimating the time when the water package was discharged into a groundwater system. Since the solubility of gases depends on temperature, pressure and dissolved solute content, the temperature and pressure that occurred during recharge must be estimated. Groundwater dating with CFCs also assumes that the local historical CFC composition of the air is known and that the composition of the air in the unsaturated zone largely corresponds to that of the atmosphere. By comparing the calculated partial pressures of CFCs in solubility equilibrium with the water sample with the historical CFC concentrations in the local air, the recharge date is finally determined. However, only CFC concentrations that are smaller than those that would be possible for water in solubility equilibrium with air at the time of the peak atmospheric concentration are realistic. In addition, for CFC concentrations near or below the detection limit, only a minimum age can be specified.

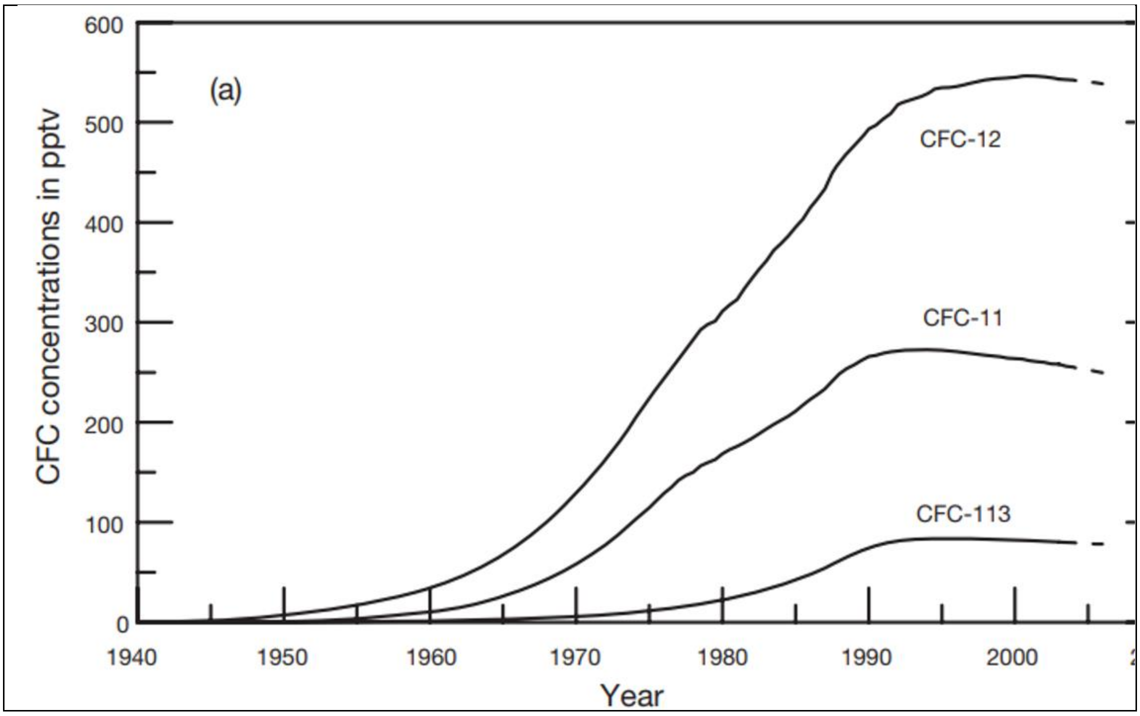

Fig1.: Concentrations of CFCs in the North American atmosphere (Plummer & Busenberg, 2006)

Dating with Chlorofluorocarbons (CFCs: CFC11, CFC12, CFC113), SF6 & H1301 (Summary from Plummer & Busenberg (2006), reviewed by A.Suckow)

application	▪ tracing and dating water post-1960 (by CFC11 & CFC12), 1970 (by CFC113), 1980 (by SF6) and 1985 (by H1301) rsp. ▪ estimating groundwater mixing properties ▪ calibrating lumped parameter models ▪ assessing susceptibility of drinking water sources to anthrop.contamination ▪ tracing of oceanic circulation, ventilation and mixing processes ▪ study deep circulation in lakes
samples	• wells should be purged before sampling • samples can be collected either using a special purpose ultra-clean pump, using existing pumps in bores that have these equipped, or using N_2 bailer methods • three field sampling variants have been established for CFCs: (1) water gets filled into 62ml glass ampoules, which are then sealed by melting of the neck, (2) samples get collected in 500 mL narrow neck glass bottles with glass stoppers, taken submerged in metal containers (sausage tins) also filled with water, (3) water samples get collected in 50 mL glass bottles with metal foil caps • SF6 & H1301 either collected in 500mL glass bottles as for CFCs or in 1L brown glass bottles • no stabilisation is required for any method
sample processing	▪ for air and water samples CFCs get pre-concentrated using purge and trap procedures and separated using gas chromatographic techniques
analytical instruments	▪ as gases, CFCs get measured with an electron capture detector (GC-ECD) ▪ results of CFC-Analysises expressed as concentrations in picogram per kg of water (pg/kg) → concentrations in water typically 0.3-1 pg/kg
data analysis	▪ groundwater containing CFCs must have a component of modern water
limitations	▪ numerous processes in the groundwater environment can significantly influence the CFC age of a water sample: contaminated sites (e.g. refrigerators in the soil), higher CFC mixing ratios in urban and industrialized areas, degradation of CFCs under anaerobic conditions ▪ adsorption of CFCs in clayey sediments, under-/overestimation of temperature during recharge, knowledge of historical local atmospheric CFC concentrations required, excess air (especially for SF6) ▪ high recharge altitude, thickness of unsaturated zone (delay during gas transport), Groundwater mixtures (true for all tracers), Drilling with air as drilling fluid contaminates the aquifer (common in arid areas)

perspectives	▪ mixing ratios of CFC-11, CFC-12 and CFC-113 peaked in the Northern Hemisphere in 1994, 2001 and 1996, respectively, and have remained nearly constant throughout the 1990s and early 2000s ' CFC measurements do not allow a unique age determination ▪ due to the many uncertainties and influencing parameters, use is always questionable, but the potential application is possible for the next 30 years.
references	Kendall, C., McDonnes, J.J. (1998). Isotope Tracers in Catchment Hydrology, Elsevier, Amsterdam (1998). ISBN 0-444-81546 Plummer, L.N., Busenberg, E. (2000). Chlorofluorocarbons. In: Environmental tracers in subsurface hydrology. Kluwer, Boston, pp 441–478 Plummer L.N., Busenberg, E. (2006). Chlorofluorocarbons in aquatic environments. In: Use of chlorofluorocarbons in hydrology—a guidebook. IAEA Plummer L.N., Busenberg, E., Cook, P.G., Solomon, D.K., Han, L.F., Gröning, M., Oster, H. (2006). Sampling and analytical methods. In: Use of chlorofluorocarbons in hydrology—a guidebook. IAEA, Vienna, pp 199-220 (Chapter 12)

Investigations on Well Water Composition at the Bank Filtration Site Görlitz by δ^{18}O and δ^{2}H Analysis

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The drinking water supply of the city of Görlitz (Saxony, Germany) is realized by a groundwater extraction, which is enriched by bank filtration from the river Neisse and artificial groundwater recharge via infiltration ponds. The first well-founded site concept model for the drinking water catchment area was developed in the 1970s (Dittrich, 1977). At that time, the groundwater regime in the southern part of catchment area was mainly characterized by the groundwater drainage for operating the Berzdorf open-cast lignite mine (see Fig. 1a). The flooding of the open-cast mine lake Berzdorf was completed in 2013.

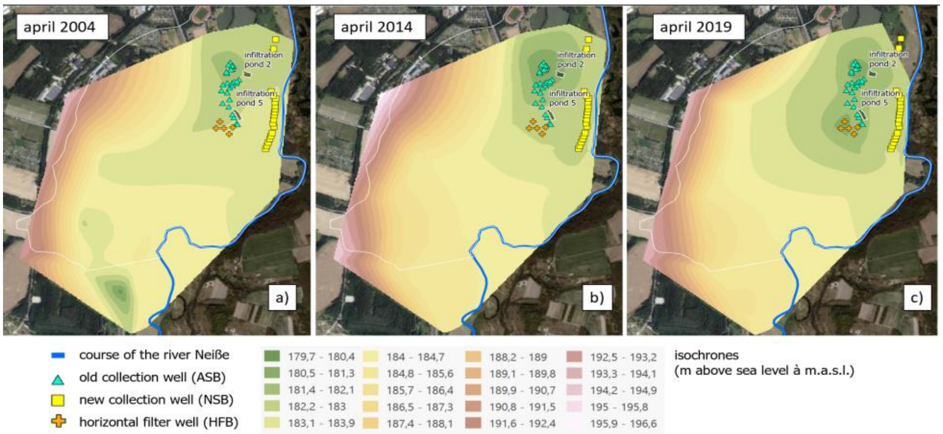

Fig. 1: development of groundwater levels for the studied drinking water catchment area from
a) April 2004 before flooding of the open-cast mine lake Berzdorf via b) April 2014 at the end of the flooding to c) April 2019 after the commissioning of a new horizontal filter well

Fig. 1 shows, that flooding of the open-cast mine lake has changed the groundwater regime in the southern part of the drinking water catchment area significantly. Additionally, the local groundwater supply is changing continuously due to more frequent summer droughts in the region and the reduced water demand of the city of Görlitz since the ending of the textile industry. Due to strongly varying water quality of the Neiße by trace substances from agriculture and wastewater treatment, the use of river water for managed groundwater recharge via filling infiltration ponds s. In 2016, the existing collection wells (ASB and NSB, rsp.), which combine the raw water extraction from 3 dug wells (Fig. 1, green triangles) and 19 vertical filter wells (Fig. 1, yellow squares), respectively, were reinforced with the commissioning of a horizontal filter well (HFB). Currently, HFB provides a daily pumping rate of approx. 4,500 m^3/d and ASB as well as NSB approx. 2,250 m^3/d each. (Fig. 1c).

Due to the significantly changed boundary conditions of the investigated drinking water catchment area, the existing site concept model is currently being upgraded. In order to contribute to this with information on the current groundwater composition, an isotopic hydrological investigation was carried out in September 2022, during which water samples were taken from the HFB horizontal filter well, two land-based groundwater monitoring wells, the Neisse River and two infiltration ponds.The analyzed δ^{18}O and δ^{2}H ratios were evaluated in comparison to a local meteoric water line (LMWL) established for Görlitz from 2014 to 2016 (Fig. 2). Subsequently, a mixing calculation was performed for the three possible sources infiltration ponds (a), bank filtrate of the river Neiße (b) and land-based groundwater (c) (Fig.3):

$$\delta_m^1 = f_a \cdot \delta_a^1 + f_b \cdot \delta_b^1 + f_c \cdot \delta_c^1 \quad (1)$$

$$\delta_m^2 = f_a \cdot \delta_a^2 + f_b \cdot \delta_b^2 + f_c \cdot \delta_c^2 \quad (2)$$

$$1 = f_a + f_b + f_c \quad (3)$$

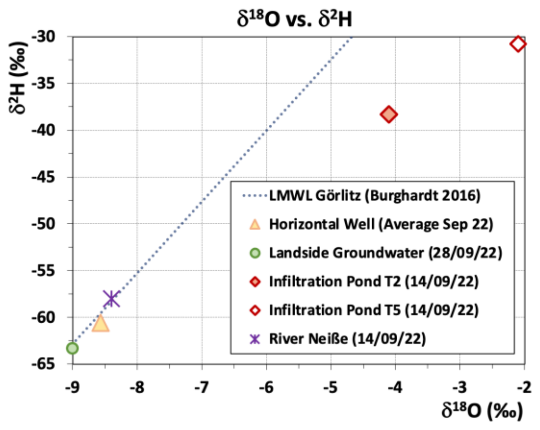

Fig. 2: Comparison of δ^{18}O/δ^{2}H of groundwater and surface water samples with the LMWL of Görlitz

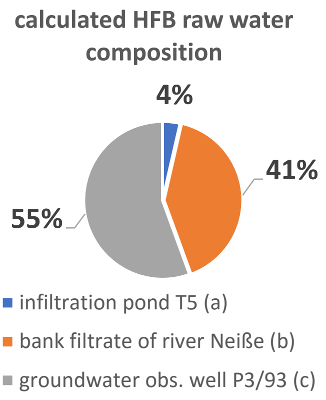

Fig. 3. Mixing calculation results for raw water composition of HFB

As shown in Fig. 2, δ^{18}O and δ^{2}H ratios of infiltration ponds samples deviate strongly from the LMWL. It indicates a strong evaporative influence (typical summer situation) and hardly no similarity with the raw water of HFB. In contrast, δ^{18}O and δ^{2}H ratios of HFB water sample plott about in the middle of Neiße river water and landside groundwater. The mixing calculation resulted in a percentage of about 55% landside groundwater, about 41 % bank filtrate and only about 4% water from the infiltration ponds in the raw water sample of HFB.

References

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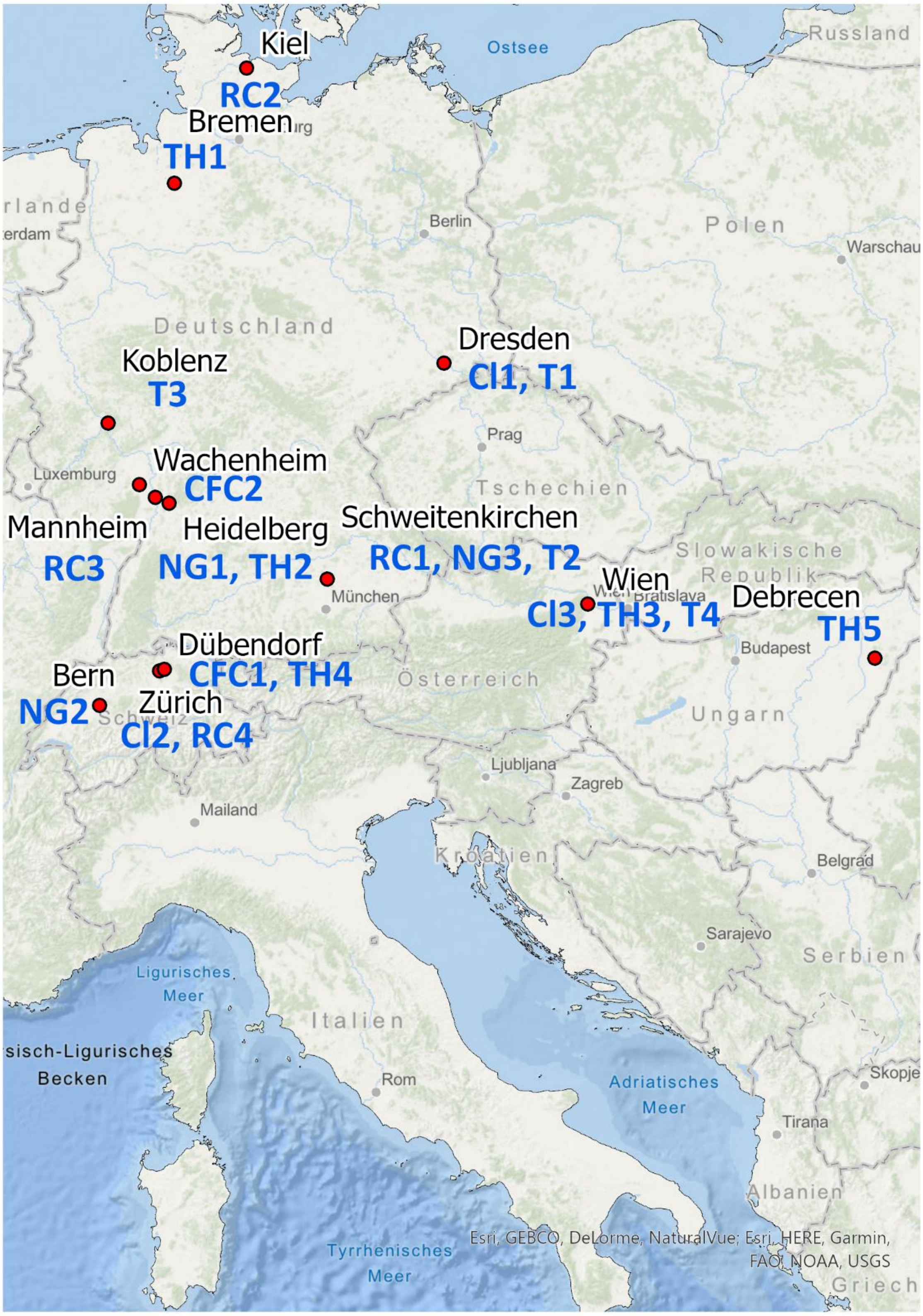
δ^{18}O- and δ^{2}H-Analysis of Surface water and Groundwater

(Diana Burghardt)

application	▪ origin and composition of groundwater ▪ investigation in surface water – groundwater interactions ▪ estimation of groundwater recharge percentages ▪ estimation of water fluxes in the critical zone ▪ role of pore water d18O on nitrification in agricultural studies ▪ measurements of matrix-bound water stable isotopes
samples/ sample processing	Only a small water sample volume is necessary for the analysis, usually a 2 mL vials with septum cap, ideally an additional reset 2 mL sample. For isotope analysis of pore water after vacuum distillation of a 20 g soil sample, a sample volume of 100 µL is necessary and filled in the 2 mL glas vials by the use of special inserts. In order to measure isotope ratios of matrix-bound soil water, special diffusion-tight, inflatable bags will be necessary for collection and storage of the soil samples. Water vapour in equilibrium with the soil will be analysed after a storage time of 24 hours by CRDS. There is no chemical stabilisation or filtration of the water samples necessary. Vials should filled nearly complete (without significant gas phase).
analytical instrument	▪ Cavity Ring Down Spectrometers (**CRDS** instruments) are state of the science. ▪ Conventional stable isotope analysis were performed by Stable Isotope Mass Spectrometers, coupled with a High Temperature Pyrolysis Unit (**HT-IRMS**)
precisions	**δ^{18}O:** 0.1‰ (CRDS), 0.2 ‰ (HT-IRMS); **δ^{2}H:** 1.0‰
data analysis / processing	▪ every analytical sequence of water samples will be prepared by quality assurance measures (scan of background gases, stability test and linearity test of the reference gases) ▪ for the calibration of δ^{18}O and δ^{2}H ratios measured, primary reference standards (international standards, available from the IAEA) and secondary standards (laboratory standards, initially calibrated to the international standards) have to be analyzed, the latter at the beginning, in the middle and at the end of each analytical sequence of water samples
limitations	Storage of samples in equilibrium with the atmosphere (e.g. in bottles with a significant gas phase or in open vessels) leads to an isotope fractionaction, that means a change of the original isotope ratios, due to evaporation.
references and useful links	HERBSTRITT, B., GRALHER, B., SEEGER, S., RINDERER, M., AND WEILER, M.(2022): Technical note: Mobile, discrete in situ vapor sampling for measurements of matrix-bound water stable isotopes, Hydrol. Earth Syst. Sci. Discuss. [preprint], https://doi.org/10.5194/hess-2022-393, in review, Ordering of international standards from IAEA: https://nucleus.iaea.org/sites/ReferenceMaterials GNIP Global Network of Isotopes in Precipitation (WISER database): www.iaea.org/services/networks/gnip

Map of some Labs for Dating Aquatic Systems



Some labs who are doing Dating analysis of Aquatic Systems:

(of which the European ones are shown in the map)

Method	Labs & Links
^{85}Kr, ^{39}Ar and ^{81}Kr via Atom Trap Trace Analysis (ATTA)	**[NG1] Heidelberg University** https://www.kip.uni-heidelberg.de/oberthaler/research/artta https://www.iup.uni-heidelberg.de/de/research/hydrotrap#Methoden **[NG2] University of Bern**, CEP (www.climate.unibe.ch/) **[NG3] Hydroisotop GmbH:** sampling, sample preparation, data evaluation (www.hydroisotop.de) **Argonne National Laboratories** (www.anl.gov/phy/tracer) **University of Sciences and Technology of China, Hefei** (https://atta.ustc.edu.cn/en-us/events/attaprimer.html) **CSIRO & The University of Adelaide** (only 85Kr & 81Kr): (www.researchers.adelaide.edu.au/profile/rohan.glover)
^{14}C (Radiocarbon) ^{14}C-DIC via LSC or AMS, ^{14}C-DOC-PPL) via AMS	**[RC1] Hydroisotop GmbH Schweitenkirchen** (www.hydroisotop.de/) **[RC2] AMS 14C Lab University of Kiel** (www.leibniz.uni-kiel.de/en/ams-14c-lab) **[RC3] CEZA**, Curt-Engelhorn Zentrum Archäometrie Mannheim (www.ceza.de/) **[RC4] LIP**, ETH Zurich (www.ams.ethz.ch/) **ANU,** Australian National University (www.earthsciences.anu.edu.au/people/academics/professor-stewart-fallon) **ANSTO**, Australian Nuclear Science and Technology Organisation (www.ansto. gov.au/our-facilities/centre-for-accelerator-science/radiocarbon-dating) **GNS** New Zealand (www.gns.cri.nz/partner-with-us/labs-and-facilities/rafter-radiocarbon-lab/)
^{3}H after electrolytical enrichment via LSC	**[T1] VKTA** low-level underground laboratory Felsenkeller (www.vkta.de/en/analytics/) **[T2] Hydroisotop GmbH Schweitenkirchen** (www.hydroisotop.de/) **[T3] BAFG** Koblenz Environmental Isotope Laboratory (www.bafg.de/DE/08_Ref/G4/Labor/labor_node.html) **[T4] IAEA** Vienna Isotope Hydrology Section (www.iaea.org/) **GNS** Wellingthon, New Zealand (www.gns.cri.nz)
^{36}Cl via AMS	**[Cl1] Helmholtz Zentrum Dresden Rossendorf,** (www.hzdr.de/db/Cms?pOid=27781&pNid=1061&pLang=en) **[Cl2] LIP**, ETH Zurich (www.ams.ethz.ch/) **[Cl3] VERA,** Vienna Environmental Radiocarbon Accelerator (www.tandfonline.com/doi/pdf/10.1080/10619127.2017.1351183) **ANU,** Australian National University (www.physics.anu.edu.au/research/npaa/ams/ **ANSTO**, Australian Nuclear Science and Technology Organisation (www.ansto.gov.au/people/dr-klaus-wilcken)

Method	**Labs & Links**
^{3}H-^{3}He & ^{4}He & ^{40}Ar/^{36}Ar after vaccum extraction via Noble Gas MS	**[TH1] helis Laboratory** University Bremen (www.noblegas.uni-bremen.de/index.html) **[TH2] Noble Gas Laboratory** University Heidelberg (www.hce.uni-heidelberg.de/analytics/lab_edelgas.html) **[TH3] IAEA** Vienna Isotope Hydrology Section (www.iaea.org/) **[TH4] EAWAG,** Department Water Resources & Drinking Water, CH-Dübendorf: (www.eawag.ch/en/department/wut/main-focus/environmental-isotopes/) **[TH5] HEKAL** Debrecen (Hungary) (www.hekal.eu/en/infrastructure/) **CSIRO, Commonwealth Scientific and Industrial Research Organisation** (www.csiro.au/en/research/natural-environment/water/groundwater-resources/noble-gas-facilities) **Dissolved and Noble Gas Lab**, US, University of Utah (www.noblegaslab.utah.edu) **WHOI** Woods Hole, US, also high precision ^{40}Ar/^{36}Ar : (www2.whoi.edu/site/igffacility/) **Scripps Institution of Oceanography, US (** also high prec.^{40}Ar/^{36}Ar) (www.sciencedirect.com/science/article/pii/S0009254121004010) **NOAA** Newport, Oregon, US (www.pmel.noaa.gov/eoi/chemistry/helium.html) **Lamont Doherty Earth Observatory, US**: (www.ldeo.columbia.edu/environmental-tracer-group/noble-gas-mass-spectrometer) **Lawrence Livermore National Laboratory** (https://people.llnl.gov/visser3)
CFCs/ SF$_6$ via GC-EDC	**[CFC1] EAWAG,** Dep. Water Res. & Drinking Water, CH-Dübendorf: (www.eawag.ch/en/department/wut/main-focus/environmental-isotopes/) **[CFC2] Spurenstofflabor Dr. Harald Oster**, D-Wachenheim **British Geological Survey** (Prof. Darren Gooddy (www.bgs.ac.uk/geological-research/science-facilities/environmental-geochemistry/dissolved-gases-facility/) **USGS** Reston Groundwater Dating Lab. (www.water.usgs.gov/lab/) **GNS** Wellingthon, New Zealand, Tritium and Water Dating Laboratory (www. gns. cri.nz/partner-with-us/labs-and-facilities/tritium-and-water-dating-lab/) **Tritium Laboratory, Rosenstiel School of Marine** (https://tritium.earth.miami.edu/) **Dissolved and Noble Gas Lab**, University of Utah (www.noblegaslab.utah.edu)
^{2}H & ^{18}O via CRDS or IRMS	many labs, associated in the **GIN German Isotope Network**: BFG Koblenz, BGR Spandau, Uni Erlangen, TU Dresden, UFZ Halle, Uni Darmstadt, IGB / Humboldt Uni Berlin, IOW Warnemünde, Hydroisotop Schweitenkirchen, Isodetect Leipzig, Uni Freiburg, Uni Gießen, Uni Braunschweig, Uni Kassel, ZALF Müncheberg.....

Associated Methods

^{18}O Analysis of Sugar Biomarkers and their potential to serve as Climate Indicator

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Heisenberg Chair of Physical Geography/ Paleoenvironmental Research, TU Dresden

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Similar to speleothems, well-dated sediments, mire archives and paleosols are valuable terrestrial geoarchives for establishing ^{18}O paleoclimate records. From a methodological point of view, respective ^{18}O analyses can be realised using gas chromatography – ^{18}O pyrolysis – isotope ratio mass spectrometry of plant-/algae-derived sugar biomarkers. While analytically quite challenging, e.g. because of possible oxygen contamination resulting from the hitherto used ^{18}O reactors, ^{18}O records from lacustrine sediment archives are well suited to infer lake evaporation histories. This is based on the ^{18}O enrichment of lake water associated with fractionation processes during evaporation. Fucose thereby turned out to be the most reliable aquatic sugar biomarker. Similarly, the coupling of terrestrial ^{18}O records established for leaf-derived sugar biomarkers such as arabinose and xylose with leaf wax-derived ^{2}H records offers the potential to reconstruct relative humidity. This is based on the finding, that the ^{18}O and ^{2}H enrichment of leaf water is primarily dependent on relative air humidity. Ongoing research focusses amongst others on developing a new ^{18}O pyrolysis reactor design in order to overcome the analytical challenges and thus to boost a wider applicability of compound-specific ^{18}O analyses.

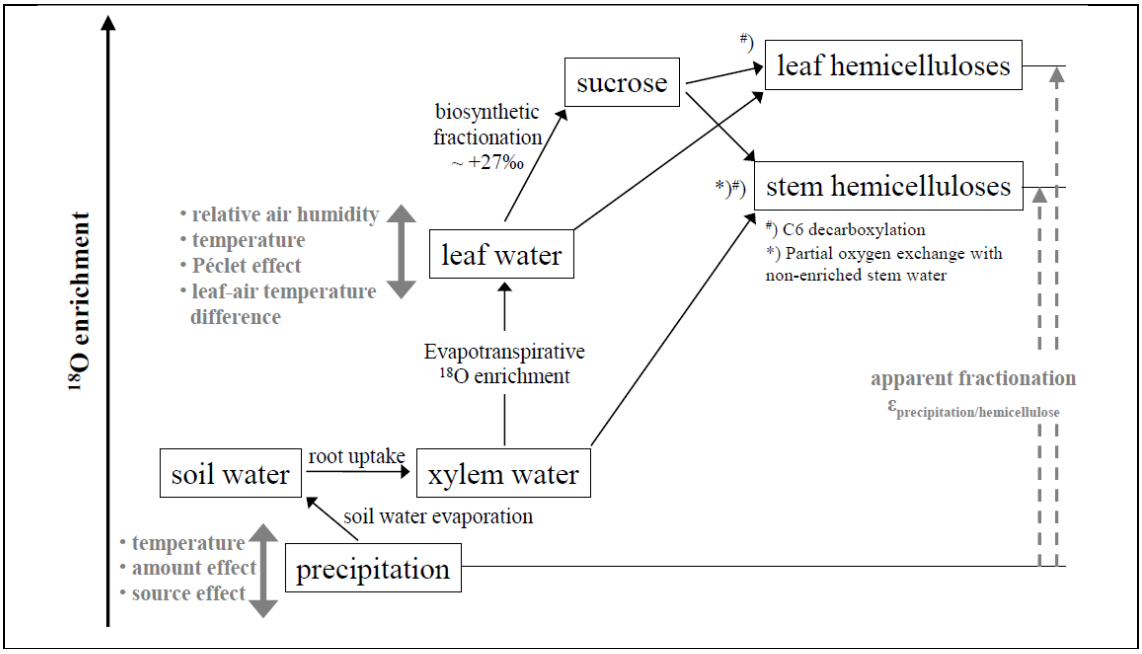

Fig. 1: Conceptual diagram illustrating the the major factors influencing the oxygen isotopic composition of hemicellulose-derived sugar biomarkers (from Zech et al., 2014)

Fig. 2: Left: afro-alpine Lake Garba Guracha at 4000 m asl in the Bale Mountains of Ethiopia. Middle: scary-looking self-constructed raft. Right: Retrieval of sediment cores from the coring platform.

References

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^{18}O Analysis of Sugar Biomarkers (Michael Zech)

application	▪ compound-specific ^{18}O analyses of plant-/algae-derived sugar biomarkers ▪ application to organic matter containing sediments, mire archives and paleosols (TOC >~1%) in order to establish paleoclimate ^{18}O records
samples	▪ air-dried and finely grinded plant ▪ soil and sediment samples ▪ sample aliquots containing ~15 mg TOC
sample **processing**	(1) acid hydrolyses of hemi-/polysaccharide-derived monosaccharides using 4M trifluoroacetic acid (TFA) at 105 °C for 4 hours (2) Purification over XAD and Dowex columns (3) Derivatisation of the pentose and 6-deoxy-sugar biomarkers arabinose, xylose, fucose and rhamnose, respectively, using methylboronic acid (MBA)
analytical instruments	Gas chromatography – online ^{18}O pyrolysis – isotope ratio mass spectrometry (GC-^{18}Opy-IRMS)
data analysis / processing	co-analysis of external sugar standards with known ^{18}O values at different concentrations in order to ensure the principle of identical treatment of samples and standards during GC-^{18}Opy-IRMS drift-correction and amount-correction
limitations	▪ not yet applicable/adopted to classical loess-paleosol sequences containing low amounts of TOC and high amounts of $CaCO_3$ ▪ not yet applicable to hexoses (including cellulose-derived glucose) ▪ analytically very challenging with regard to oxygen contamination during GC-^{18}Opy-IRMS
perspectives/ further applications	▪ high potential for reconstructing lake evaporation history ▪ high potential to serve as “paleohygrometer” when applied in a coupled approach together with leaf wax-derived ^{2}H results ▪ few applications beyond sugar biomarkers
available labs	chair of Physical Geography/ **Paleoenvironmental Research**, TU Dresden (www.tu-dresden.de/bu/umwelt/cfea/analytik/) working group of Youping ZHOU, Department of Ocean Science and Engineering, Southern University of Science and Technology, Shenzhen, China.

Dating Carbonates with $\delta^{18}O$- and $\delta^{13}C$-Analysis

(summarized by candidate MSc Johannes Lieder, TU Dresden Institute of Groundwater Management, kindly reviewed by Christoph Spötl)

application	▪ Marine carbonate organisms (e.g., foraminifera), speleothems, tufa, ostracods, mollusc shells, caliche, etc. ▪ Paleoceanographic studies (global ice volume effect, paleotemperature, etc) ▪ Paleoclimate records using $\delta^{18}O$ of speleothem or tufa samples ▪ Paleo-CO_2 reconstructions from soil carbonates via $\delta^{13}C$
samples	▪ only small sample quantities are needed (0.5 to 2 mg) ▪ low-magnesium calcite preferred ▪ diagenetic carbonates (sparite, calcite veins, void filling) should be avoided
sample processing	▪ micro-drilling or micro-milling ▪ reaction with orthophosphoric acid at constant temperature (release of carbon dioxide)
analytical instruments	▪ continuous-flow (e.g., Gasbench) or dual inlet IRMS
data analysis	▪ $\delta^{13}C$: per mil notation (‰) with respect to VPDB standard ▪ $\delta^{18}O$: per mil notation (‰) with respect to VPDB or VSMOW2 standard
limitations	▪ diagenesis may change the stable isotope composition, but inform about the diagenetic environment ▪ many organisms show “vital effects” that may shift the stable isotope composition → correction required
perspectives	▪ $\delta^{18}O$ is a key parameter of the hydrological cycle and can be used to compare e.g. ice-core records to marine records or speleothem records
available labs	▪ GeoZentrum Nordbayern (Friedrich-Alexander-Universität Erlangen-Nürnberg) ▪ University of Innsbruck (Quaternary Research Group) ▪ Beta Analytic Inc. ▪ Lamont-Doherty Earth Observatory (LDEO) ▪ Stable Isotope Ratio Facility for Environmental Research (SIRFER) ▪ Reston Stable Isotope Laboratory (RSIL)
references	Du, Y., Song, H. (2020). Refined protocol forδ13C analysis of calcite and dolomite in carbonate mixture samples. Rapid Commun Mass Spectrom. https://doi.org/10.1002/rcm.8743 Breitenbach, S.F.M, Bernasconi, S.M. (2011). Carbon and oxygen isotope analysis of small carbonate samples (20 to 100µg) with a Basbench II preparation device. Rapid Commun Mass Spectrom., 25(13):1910-1914. https://doi.org/10.1002/rcm.5052 Spötl, C. & Vennemann, T.W. (2003). Continuous-flow IRMS analysis of carbonate minerals. Rapid Communications in Mass Spectrometry, 17: 1004-1006.

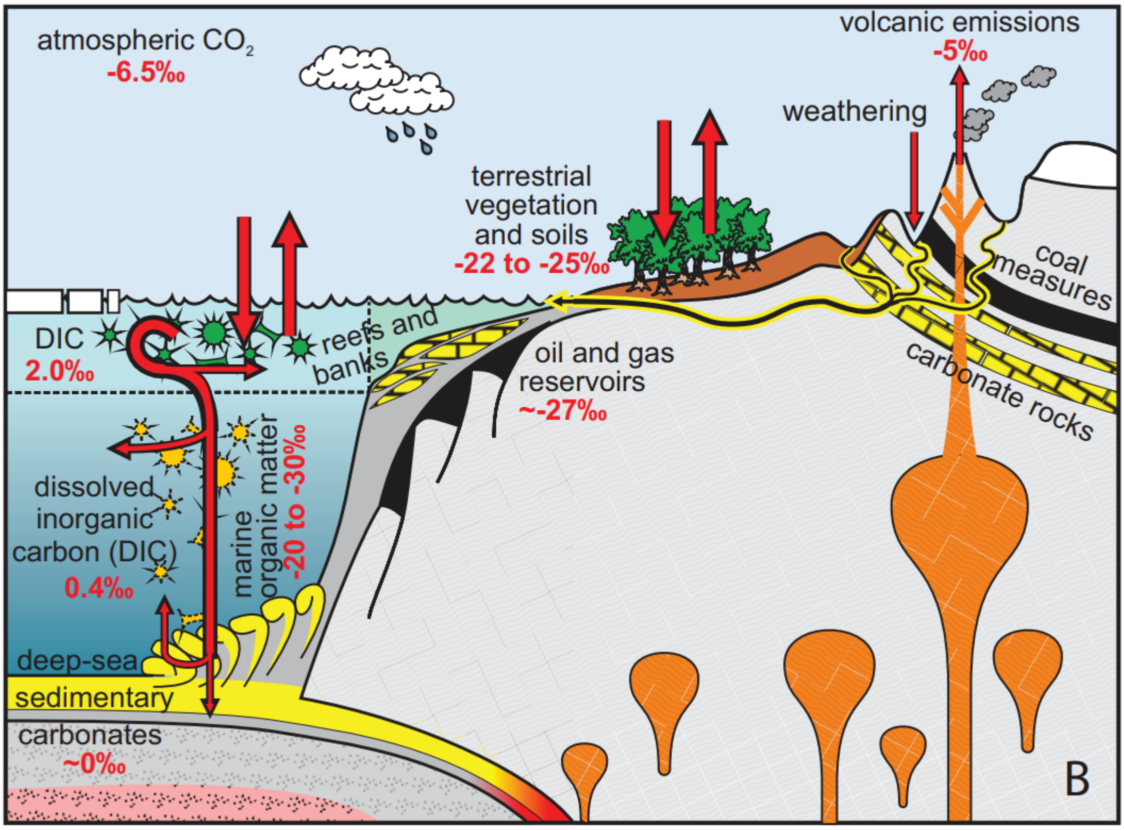

Fig:1: Global carbon cycle (Gradstein et al., 2020)

Poster Abstracts

P1 The deep Ohangwena aquifer in Angola and Namibia: Hydrochemical and tracer studies to explore a fresh paleo-groundwater resource in an arid and saline environment

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At the end of the last millennium, a freshwater aquifer (KOH 2) of considerable thickness and extent was discovered in the Ohangwena Region of northern Namibia in a stacked paleo-megafan system within the sedimentary succession of the Kalahari Group, at depths of about 180 m to over 300 m. The discovery of this new resource has attracted great public attention and raised high expectations. However, the recharge processes and hence sustainability of any future development of the aquifer remain largely uncertain.

In this study, we applied hydrochemical and comprehensive tracer studies of the KOH 2 aquifer. Stable isotopes, dissolved noble gas and N_2 contents were determined in order to draw conclusions about the (paleo)climatic conditions, in particular the temperature, during groundwater recharge. Radioisotopes ^{14}C, ^{36}Cl and ^{81}Kr were used to estimate the age distribution of groundwater in the KOH 2. Furthermore, ^{4}He concentrations and selected noble gas isotope ratios were measured and interpreted with respect to the age of groundwater.

The main objectives of the study was to gain insight into the origin, recharge and flow of groundwater in the KOH 2 aquifer, to determine the different ages and to draw conclusions about the renewability of water. Furthermore, the suitability and limitations of the applied methods were evaluated and compared. The poster will present our preliminary findings.

P2 Isotopes as tool for the evaluation of aquitard – aquifer interactions

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The assessment of geological sites as potential hosts for radioactive waste repositories requires a fundamental understanding of the hydrogeological and hydrogeochemical conditions. In geological environments, water occurs as advective flowing groundwater and as porewater in the inter- and intragranular pore space of the rock matrix. Both compartments interact with each other, mainly by diffusion. Due to the slow interaction, porewater is a valuable climatic and palaeohydrological archive, which delivers valuable information from the past, which can be extrapolated to future forecasts. Thereby isotopes play a significant role. Stable water isotopes can be used to evaluate the influence of meteoric water from different climatic epochs. Noble gas isotopes dissolved in porewater serve as an indirect dating method of porewater and chloride stable isotopes keep information about the origin of saline components in there. In low transmissive layered or fractured groundwater aquifers, the diffusion from and in the rock matrix plays a major role for the isotopic and chemical conditions of such groundwaters, leading to challenges in dating. Nevertheless, for a thorough evaluation of hydrogeological conditions and the palaeohydrological history of a potential investigation site, integrative porewater - groundwater studies are essential.

P3 Groundwater response to historic climate variability and change in Australia

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Climate change is projected to impact groundwater availability but the projections are highly uncertain. Quantifying the historic impact potentially allows for an improved understanding of the climate change impact on water resources due to the long memory of groundwater towards the past climate variability and trends. Analysing groundwater hydrographs over multiple decades allows for the quantification of the response of groundwater head to climatic changes. However, it is highly challenging to separate the impact of climate change on groundwater from other influential drivers, such as pumping for agricultural irrigation and land use changes. Adding to this is the often short and incomplete groundwater records. In this study, we establish and test methods to quantify the response of groundwater to climate variability and change at climate-dominated sites identified across Australia by using statistical and deterministic modelling approach. Results show that the national median sensitivity of groundwater level is 42 mm head change per 1 mm precipitation change. The intrinsic properties of the sites, such as climate type and hydrogeology, play a crucial role in controlling the response of groundwater to climate variations. With this improved understanding of groundwater response, we can work towards effective adaptive water management strategies for both human and natural systems.

P4 High-resolution reconstruction of land-use change in a central Kenya catchment using Pb-210 dating of dam sediments

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Globally, land-use change is a major driver of land-degradation. In tropical East African highlands, conversion of forested land to settlement and agriculture is a main driver of soil erosion. Studies have quantified the amount of sediment loss at different spatial scales but there is still a need to have a consolidative approach incorporating erosion processes within the catchment with the sediment deposited in the water-body. A source-to-sink approach allows us to test the impact of different land-use by linking the sediment in the water-body with its source in the catchment. Ruiru catchment in Central Kenya lies in an area with population growth accompanying land-use change from a forest to settlement and intensive agriculture. Ruiru dam, completed in 1950, has experienced a high level of sedimentation with the dam losing 11-14% of its original storage capacity. Ten sediment cores collected from the dam floor in 2017, 2022 and 2023 are to be dated using Pb-210 and Cs-137 and analysed combining µ-XRF core scanning, grain size, and biomarker analyses. Comparison with physicochemical signals of catchment samples from different land-uses will enable reconstruction of catchment sediment dynamics over the last 73 years. We hypothesize that erosion has increased with increased rate of land-use change and that different land-use types have different erosion impacts.

P5 The blind men and the elephant or how high-resolution mass spectrometry will revolutionize soil biogeochemical analysis

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Modern soil biogeochemical research requires sensitive and accurate methods of identification and quantification of organic molecules (biomarkers, molecular markers). The mass spectrometers available at our institute are outdated and represent the state of the art from more than 20 years ago. In order to conduct competitive high-quality research, we propose using High-Resolution Mass Spectrometry (HRMS) with Gas Chromatography (GC), Ultra High-Performance Liquid Chromatography (UHPLC), and Direct Analysis in Real Time (DART) interfaces. With such an instrument, masses of molecular ions can be determined with an accuracy of up to 240,000 at m/z 200, which enables cutting-edge analysis of elemental and isotope compositions several orders of magnitude more accurate than with our current instruments. A HRMS with GC, UHPLC, and DART interfaces offers the opportunity, as well as the need, to evaluate GC-MS methods used on existing equipment to eliminate potential erroneous results caused by isobaric and co-elution artefacts. In addition, deduction of the molecular formulae of macromolecules becomes possible, which is essential for advanced environmental analyses. Last but not least, multi-omics approaches in soil biogeochemical research can be performed, e.g., by combining several molecular markers classes such as phenols, terpenoids, and lipids.

P6 Analysis of trace isotopes with Accelerator Mass Spectrometry using HAMSTER and DREAMS

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The Helmholtz-Zentrum Dresden-Rossendorf (HZDR) is engaged in measuring long-lived radioisotopes via Accelerator Mass Spectrometry (AMS). Presently, the DREAMS facility, which is based on a 6-MV tandem accelerator, provides state-of-the-art capabilities for measurements of ^{10}Be, ^{26}Al, and a number of other AMS isotopes. This system is applied e.g. for dating marine archives with ^{10}Be over the past million years.

In addition, we are setting up a new compact AMS facility, HAMSTER (Helmholtz Accelerator Mass Spectrometer Tracing Environmental Radionuclides), which will be installed at HZDR in 2023. This system is specifically designed for the sensitive analysis of actinides (e.g. Pu isotopes) and will include a laser-based isobar suppressor that will allow for measurements of fission nuclides such as ^{90}Sr or ^{135,137}Cs. With the new system more projects will be feasible that aim at dating during the so-called Anthropocene.

The AMS measurements are available to external users via several funding instruments, e.g. in the form of proposals via the HZDR GATE system (https://gate.hzdr.de/user/).

P7 Dating methods for groundwater - Multi-tracer combination for the discretization of groundwater components of different ages

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Mixed water from deep groundwater and near-surface groundwater (rapidly regenerating groundwater) is very common in wells which are used for drinking water supply in Germany. Those groundwaters constitute a two (or more) component system with each component having different residence times.

For the evaluation of the protection against surface influences by anthropogenic activities (agriculture, industry, urbanisation, deposits and waste water) as well as for the sustainable use of deep resources, knowledge of the distribution and quality of each water component is essential. Multi-tracer combinations of isotopes (^{3}H, ^{85}Kr, ^{3}Htrit., ^{18}O/^{2}H, ^{13}C/^{14}C-DIC, ^{13}C/^{14}C-DOC-PPL, etc.) and trace gases (SF_6, F11, F12, F113) and supplemental hydrochemical data are used to quantify young and old components and to model the residence times of each component.

New approaches of water authorities in Germany are being developed, using quantifications of “deep groundwater” to limit and eliminate the use of such resources for irrigation, industrial use, production of lower quality soft drinks or alcoholic beverages and even for drinking water supply. Special modelling approaches are presented to identify groundwaters with percentages of “deep” or “old and valuable” groundwater of at least 50 %.

P8 Evaluating the quality of pure mineral extraction during luminescence sample preparation

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Through the last 50 years, Optically Stimulated Luminescence (OSL) dating has been applied to get absolute age estimates for the last exposure of minerals like quartz or feldspar to light or heat. The method provides manifold applications for unravelling the geochronological scale of surface processes and related sediment archives. Over time, technology and techniques improved creating new ways to get a more accurate age, to extend the dateable time span or to address mineral specific challenges. However, ensuring the quality of dating results commences with sample preparation and accurate extraction of the dosimeter of choice, commonly quartz or feldspar. Feldspars contaminating quartz extracts strongly impacts dating results. Standard separation procedures for quartz-based OSL dating involve a series of steps to enrich the quartz. The removal of feldspars focusses on the different densities of both minerals. But the range of feldspar group densities overlaps with the density of quartz. We determine the quality of quartz separation with respect to pure mono-mineral extracts using feldspar flotation. The froth-type method showed in past experiments quartz concentrations of 95-100 %. Using X-ray diffraction analysis, we trace the mineral compositions of each step of the process to illustrate the advantage of this froth method in getting high-purity quartz extracts.

P9 To reconstruct the historical forest in the Ore Mountains

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This poster presents the results of an anthracological investigation of historical charcoal kiln sites, which was carried out for the first time in the Westerzgebirge. Charcoal kiln sites are archives of landscape history, which can still be found today as relicts of charcoal burning in forest-rich regions dominated by mining. The charcoal remains preserved in the charcoal kiln sites provide data on the local forest history and allow a small-scale reconstruction of the historical forest stand. A dating of the pile sites is only possible by scientific methods, since historical sources do not provide any information. It will be shown the possibilities and limits of dendrochronology and Radiocarbon dating of charcoal remains from charcoal kiln sites.

P10 COST Action 'WATer isotopeS in the critical zONe: from groundwater recharge to plant transpiration - WATSON'

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The WATSON COST Action (CA19120; https://watson-cost.eu/) started in September 2020. It aims to integrate and synthesize current interdisciplinary scientific knowledge on the use of the stable isotopes of water to understand the mixing and partitioning of water in the Earth's Critical Zone. The network is organised into working groups that focus on a major scientific challenge: 1) groundwater recharge and soil water mixing processes; 2) vegetation water uptake and transpiration; and 3) catchment-scale residence time and travel times. A fourth working group organises the network and dissemination activities. WATSON aims at better connecting academia and stakeholders from industry, non-profit organizations, and government agencies. WATSON fosters the exchange of information and expertise among scientists and stakeholders, builds capacity in the use of the latest isotope, approaches and translates scientific cutting-edge knowledge into tangible outputs and recommendations on how to use stable water isotopes to effectively address water management needs.

P11 A Novel Approach to Estimate Radiocarbon Ages of Deep Groundwater in the Mekong Delta, Vietnam

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The steep growth in economy, agricultural production, and population since the 1990’s resulted in substantially increased stress on the water resources of the Mekong Delta in Vietnam. The overall goal of this study was to develop a conceptual model of the hydrogeochemical evolution along groundwater flow paths in the multilayered aquifer system. As an important step, this includes a reliable quantification of groundwater ages and their uncertainties using carbon isotopes. For estimation of the initial radiocarbon concentrations prior to radioactive decay and their associated uncertainties, we modified the mass balance modeling approach of PHREEQC by adding a stochastic initial concentration generated by forward reactions of the potential geochemical processes in the unsaturated zone during groundwater recharge.

P12 Using Environmental Tracer Data to Better Constrain Numerical Groundwater Model Parameters During Inversion

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The application of spatially distributed numerical groundwater models is ubiquitous in the environmental sciences and engineering, in decision-making contexts, water supply, and agriculture. It is known that using hydraulic head observations alone during parameter estimation results in non-uniqueness and equifinality. Environmental tracer data (such as radioactive isotope concentrations) can be a valuable data type to better constrain model parameters. Our project aims at reducing groundwater model uncertainty by using environmental tracer data in addition to head observations and to quantify the corresponding reduction of uncertainty with recently developed state-of-the-art Bayesian and frequentist statistical approaches. Corresponding parameter posterior distributions are obtained by using different data sets during inversion, allowing for the analysis of data worth and uncertainties in simulation and prediction. Furthermore, the results of statistical inversion are used in an optimal design framework to find locations in the model domain where future observations can reduce model uncertainty most effectively. Therefore, the worth of available observational data can be exploited as well as possible and new valuable measurement locations can be identified efficiently, ultimately increasing groundwater model performance.

P13 ESR Dating of Fluvial Sediments of the Northern France River Systems

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The glacial and interglacial climatic cycles of river systems in northern France have played a prominent role in the Quaternary geological and prehistoric development of the region. The north-ern latitudinal dispersion of hominin groups with Acheulian technology and associated bifacial tools is a continuous debate about the timing of Europe's earliest human occupation [1,2,3,4]. ESR dating of quartz grains is commonly applied to fluvial sediments can accurately describe early human settlements also capable of providing an accurate chronological framework.

Twenty sediment samples from different locations of the northern France River system for in-stance Cagny 'la Garene', St. Acheul, St. Valery, Wissant and Wimereux has been studied in this work. Each site was dated using the ESR multi-centre method applied on quartz grain, which combines the analysis of the responses of the three commonly used paramagnetic centres, i.e., Al, Ti-Li and Ti-H.

The results obtained allow a better definition of the different settlement stages of northern France and the interactions between the Lower and Middle Pleistocene climatic phases and the different Paleolithic settlements.

P14 An isotopic look at river bank filtration and its use for for sustainable management of groundwater resources near rivers

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River bank filtration is a natural and cost-effective method for sustainable management of groundwater resources near rivers. The question of supply with drinking water as well as raw water (agriculture, geothermal use) poses a continuously growing challenge for the water resources management in the future. Within the scope of the BMBF-Lurch IsoGW project, best practice sub-projects are being conducted at various pilot sites. The final best practice guide, derived from these studies, aims to demonstrate the application of established isotope hydrological methods for water suppliers and consulting firms. Stable and radiogenic water isotopes are used to characterise and quantify the groundwater recharge components, flow velocities, and mixing balances. In order to investigate the variability of hydrological processes in river bank filtration, the contribution of land-based groundwater and the Iller River to groundwater recharge is isotopically determined at the Ofterschwang site in the Upper Allgäu region over a period of more than 2 years. The site specification and initial results of these investigations are presented.

P15 ITCZ precipitation and cloud cover excursions control Cedrela nebulosa tree-ring oxygen and carbon isotopes in the northwestern Amazon

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The latest IPCC's Report indicates that North-Western South America (NWSA) precipitation is projected to increase. The region is of particular interest because it contains one of the three near-equatorial centers of intense convection that act as hubs of tropical circulation. Sadly, meteorological stations and long-term paleoclimate records are scarce. Therefore, our research focused on studying the past hydrology at low latitudes using dendrochronological methods to clarify ambiguous terminology regarding precipitation systems in South America, i.e., South American Monsoon System (SAMS) and Intertropical Convergence Zone (ITCZ) useful for calibrating future paleoarchives and validation of models. We used an Andean endemic tropical cedar tree (Cedrela nebulosa) to construct for the first time close to the equator tree-ring width, oxygen ($\delta^{18}O$), and carbon ($\delta^{13}C$) chronologies spanning 154 years (1864–2018). We found that ITCZ is the primary controller of hydrology, and a monsoonal pattern is not observed at this latitude. The $\delta^{18}O$ registers spring (Mar–Jun) rainfall due to the strong convection after the equinox following the cross-equatorial flow dynamics. Similarly, the cloud reduction due to ITCZ migration to Central America during summer (JAS) increases sunshine duration, enhancing the photosynthetic rate, ultimately controlling the $\delta^{13}C$ tree-rings variability. Overall, these results reveal that Cedrela nebulosa is well-adapted to wet environments and forms annual rings.

P16 ISOSIM – a Tool for the Simulation of Groundwater Residence Times with Lumped Parameter Models

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For the estimation of groundwater residence times, isotope analyses and conceptual lumped parameter models (LPMs) can provide valuable contributions. While making many simplifications, assumptions, and approximations, LPMs offer a starting point for further investigations as only stable or radioactive isotope concentrations are needed for the assessment. Compared to complex numerical groundwater flow and transport models, the effort needed to get initial estimates of groundwater residence time or age distributions with LPMs is miniscule.

First implementations of such LPMs for the use on a personal computer date back to the end of the last century. Most of these implementations, however, are no longer maintained, the code is no longer available, or the use with modern operating systems requires additional effort. Those first implementations were furthermore limited in options for graphical representations, uncertainty analysis, and the consideration of recharge inflow from the unsaturated zone. In recent decades, LPMs have been implemented more accessibly in Microsoft Excel, Microsoft Access, or as standalone programs (e.g. 'Boxmodel', Aeschbach-Hertig et al., 2006, 'TracerLPM', Jurgens et al., 2012) standalone / Visual Basic (e.g. 'Lumped', Ozyurt and Bayari, 2003) and MS Access (e.g. 'Lumpy', Suckow, 2012). While those implementations circumvent several drawbacks of the previous software generation, they are still not particularly user-friendly and cannot be adapted in a modular manner.

As part of the ISOSIM project funded by the Sächsische Aufbaubank (2020-2022, SAP grant number 100378518), the core functionality of the programs MULTIS and FlowPC (Richter et al., 1993, Maloszewski and Zuber, 1996) were implemented in the modular ISOSIM toolbox using the MATLAB programming environment. ISOSIM contains several options for treating the vadose zone passage and for parameter calibration and uncertainty analysis. The core routines from the MATLAB toolbox were then transferred into a package for the Python programming language, ISOSIMpy.

These implementations now allow for the estimation of residence time based on isotope concentration observations with single-species or two-species model concepts. Multiple LPMs, based on the convolution integral, are available to estimate residence times for the case of a single isotope species. Harp diagrams are used to assess residence times based on multiple isotope species. With that, gathered data can be quickly analysed with multiple LPMs in a single, user-friendly, and scalable framework. The script-based implementation is easily adaptable and multiple extensions are planned for the future. Already at this point, ISOSIMpy has been used for teaching students as well as practitioners to analyse isotope data in groundwater systems, while the MATLAB Toolbox is mainly targeted for advanced users and developers.

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P17 U-Pb dating of Neoproterozoic cap carbonates in southern Namibia

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Neoproterozoic sections in southern Namibia did lacked proper age dating and, based on this, correlation. Extensive field work, combined with detrital zircon studies and geochemical whole-rock analyses failed to conclusively solve this problem.

New LA-ICP-MS U-Pb dating attempts done on Cryogenian and Ediacaran limestones and dolomites acting as cap carbonates overlying Snowball Earth deposits in southern Namibia finally confirmed the assumed ages for the studied intervals and provided a reliable basis for correlations (Zieger-Hofmann et al., 2022).

Nevertheless, U-Pb age dating of Neoproterozoic carbonate samples is difficult and may lead to erroneous conclusions if analyses are performed in recrystallised or overprinted areas. This poster discusses the suitability of Neoproterozoic cap carbonates for U-Pb dating and the “pitfalls” that need to be avoided during analysis.

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ZIEGER-HOFMANN, M., ZIEGER, J., GÄRTNER, A., MENDE, K., SAGAWE, A., MOCKE, H., MHOJENI, K., MARKO, L., ALBERT, R., GERDES, A. AND LINNEMANN, U., 2022. Correlation of Neoproterozoic diamictites in southern Namibia. Earth Science Reviews 233, 104159.