Supporting Information to the manuscript:

Optimizing the Analyte Introduction for ^{14}C Laser Ablation-AMS

Caroline Welte[1,2], Lukas Wacker[1], Bodo Hattendorf[2], Marcus Christl[1], Joachim Koch[2], Christiane Yeman[1], Sebastian F.M. Breitenbach[3], Hans-Arno Synal[1], Detlef Günther[2]

[1] Laboratory of Ion Beam Physics, ETHZ, Otto-Stern Weg 5, HPK, 8093 Zurich, Switzerland

[2] Laboratory of Inorganic Chemistry, D-CHAB, ETHZ, Vladimir-Prelog Weg 1, 8093 Zurich, Switzerland

[3] Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum, Bochum, Germany

1. Introduction

All settings for the experiments using LA-ICPMS are summarized in Table 1. The exchange rate of the LA-AMS-cell is studied by modelling the signal of a stalagmite sample with a growth interruption between ^{14}C-free and ^{14}C-bearing layers. The minimum width of the hiatus has been estimated using LA-ICP-MS. All calculations of the model are given.

2. Measurement settings LA-ICP-MS:

Table 1 Instrument and gas flow settings of the ICP-MS and of the three different laser systems.

ICP-MS

	GED disabled	GED enabled
Carrier gas flow	1 L/min He	1 L/min He replaced by 0.32 L/min Ar
Make-up gas flow	0.8 L/min Ar	0.48 L/min Ar
Additional gas flow		1 L/min He

RF power (W)		1400	
Detector mode		Dual	
Dwell time		10 ms	
LA			
Wavelength (nm)	266	213	193
Pulse length (ns)	≈5	≈5	≈16
Repetition rate (Hz)	10	10	10
Spot size (μm^2)	150	100	90; 120
Fluence (J/cm^2)	4.2	3.3 – 19.1	7 – 22.5
Lateral velocity (μm/s)	20	20	20
CALIBRATION GAS			
Gas type		5% CO_2 in He 5.0, Messer Schweiz AG	
Gas flow rate (mL/min)		0.6	

3. Determination of the hiatus width using LA-ICP-MS

The minimum width of the hiatus in stalagmite sample SOP-20 has been determined using LA-ICP-MS. The instrument settings are listed in Table 2. A standard „high dispersion“ ablation cell was employed for LA under He atmosphere. For quantification pressed pellet from USGS MACS-3 was used as an external standard and 440000 mg/kg Ca as an internal standard for the stalagmite.

Table 2 Parameters used for LA-ICP-MS analyses of stalagmite SOP-20.

LA	GeoLas C (193 nm)
ICPMS	Perkin Elmer 6100 DRC+
Laser frequency	20 Hz
Spot size	44 µm diameter
Line speed	80 µm/s
Laser energy output	106 mJ
Laser fluence	11.5 J/cm^2

The stalagmite sample was ablated parallel to the LA-AMS laser tracks. Isotopes analyzed were ^{23}Na, ^{24}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{42}Ca, ^{88}Sr, ^{208}Pb, ^{232}Th and ^{238}U. The results for U are depicted in Figure 1. The region of the growth stop has been identified from optical analysis of the stalagmite to be approximately at a distance of 7.5 mm. The elevated U concentration marked by the red box is an indicator for dust deposits, which most likely represents the weathering crust on top of the old section. The gradient observed between 7.5 and 8 mm is probably caused by diffusion of U from the deposits into the old section. This allows to estimate an upper limit of the hiatus width on the order of 0.8 mm. The same signal but less pronounced was also found for ^{31}P and ^{88}Sr.

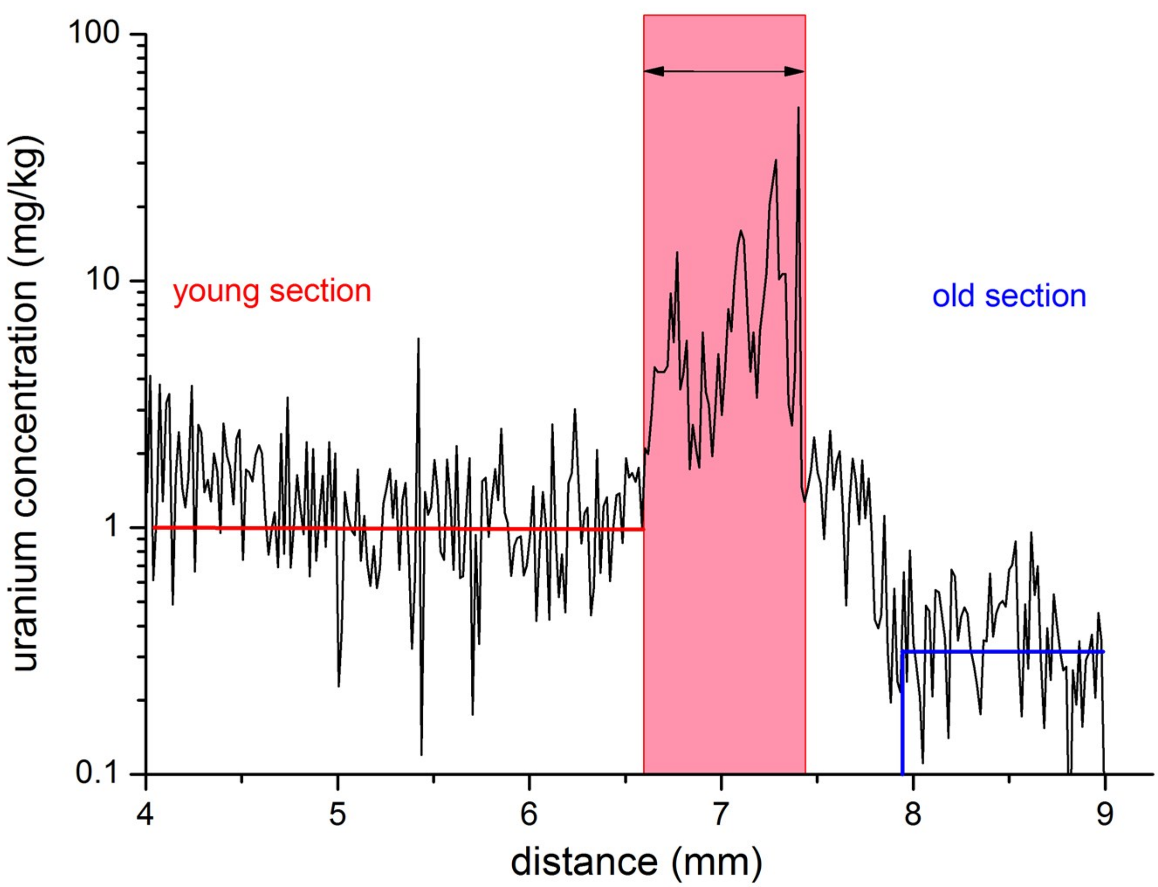

Figure 1 Uranium concentration as a function of the scanned distance of stalagmite SOP-20 for estimation of the hiatus width. The old section is marked in blue, the young section in red. Optical analyses allowed to determine the onset of the hiatus at 7.5 mm and the Peak in U-concentration (red box) most likely represents dust deposits that settled on top of the old section. The black arrow indicates the maximum step width to be 0.8 mm.

4. Model calculations:

^{12}C budget

The ^{12}C and ^{14}C production are treated separately. The number of ^{12}C atoms present in the LA-cell (referred to as C_{12}) is calculated as a function of time. It is assumed to be constant after a certain time span in which the amount is building up. A differential equation can be formulated to describe the constant production and exchange of the ^{12}C:

$$\frac{dC_{12}}{dt} = -a \cdot C_{12} + P_{12C} \qquad (1)$$

where P_{12C} represents the ^{12}C formation rate. The analytical solution of this equation is

$$C_{12}(t) = \frac{P_{12C}}{a} \cdot (1 - e^{-at}) \qquad (2)$$

The steady state value $C_{12,equ}(t>t_{equ})=P_{12C}/a$, where t_{equ} represents the time after which equilibrium is reached, is used for the subsequent calculations.

^{14}C budget

The number of ^{14}C atoms present in the LA-cell (referred to as C_{14}) is not constant over time, but depends on the ^{14}C concentration in the sample, and thus constitutes the sought parameter to be analyzed at maximum resolution. The ^{14}C concentration is described by an iterative calculation:

$$\Delta C_{14} = (P_{14C}(t) - a \cdot C_{14})\Delta t \qquad (3)$$

$$C_{14}(t + dt) = C_{14} + \Delta C_{14} \qquad (4)$$

where dC_{14} corresponds to the change in ^{14}C atoms per time interval $\Delta t = 1$ sec, $P_{14C}(t)$ to the time dependent formation rate of ^{14}C atoms and C_{14} to the amount of ^{14}C atoms present in the LA-cell.

A step function is superimposed on the ^{14}C production, accounting for the change in ^{14}C concentration at the hiatus in the stalagmite. Since the laser spot has a finite width the ^{14}C production is not a perfect step at the hiatus, but shows a slope, which is depicted in Figure 2 for three different scanning velocities. The calculation is performed for both, the scan from 'bottom to top' and for the reversed one.

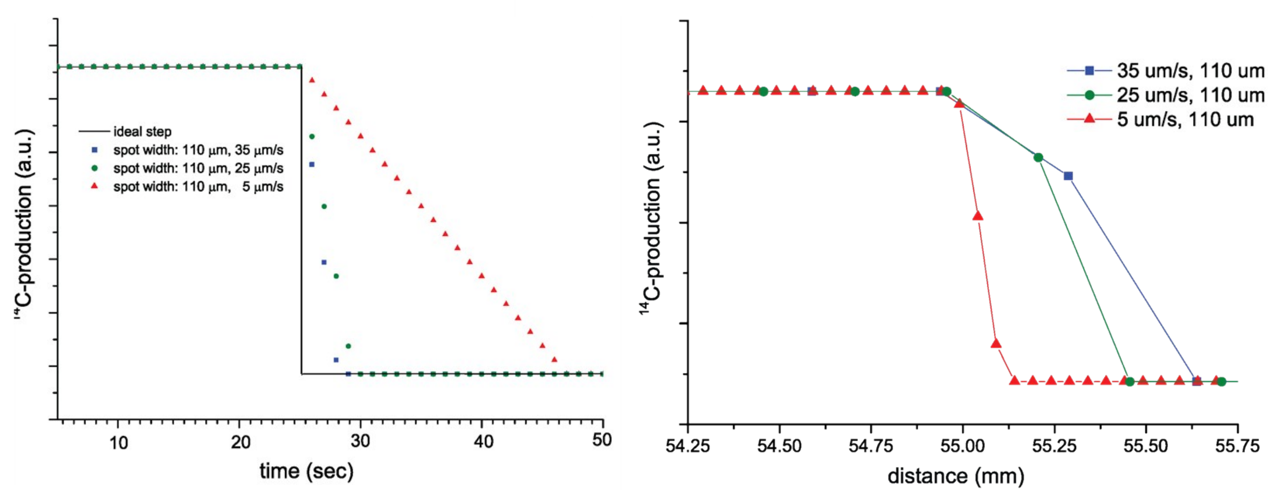

Figure 2 Modeled ^{14}C-production as a function of time (left) and of distance (right) for three scanning velocities and a constant laser spot size. The blurring of an "ideal" step due to the finite laser spot width and scanning velocity is shown. When using lower scanning velocities more time is needed to scan across the hiatus (left) and hence the spatial resolution is increased, while the blurring is reduced (right).

Combining ^{12}C with ^{14}C and assessment of the washout time

The mixed $^{14}C/^{12}C$ ratio R(t) is formed by dividing $C_{14}(t)$ by $C_{12,equ}(t>t_{equ}) = P_{12C}/a$ and the results are integrated using the same time intervals that were applied to the measured data. The reduced χ^2 comparing the modeled and measured data for both sub-scans is calculated and optimized (i.e. set as close as possible to 1) by adjusting the flow rate F_{out}. The corresponding exchange coefficient can then be used to calculate the time constant of the system $\tau = 1/a$.