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On new developments in accelerator mass spectrometry

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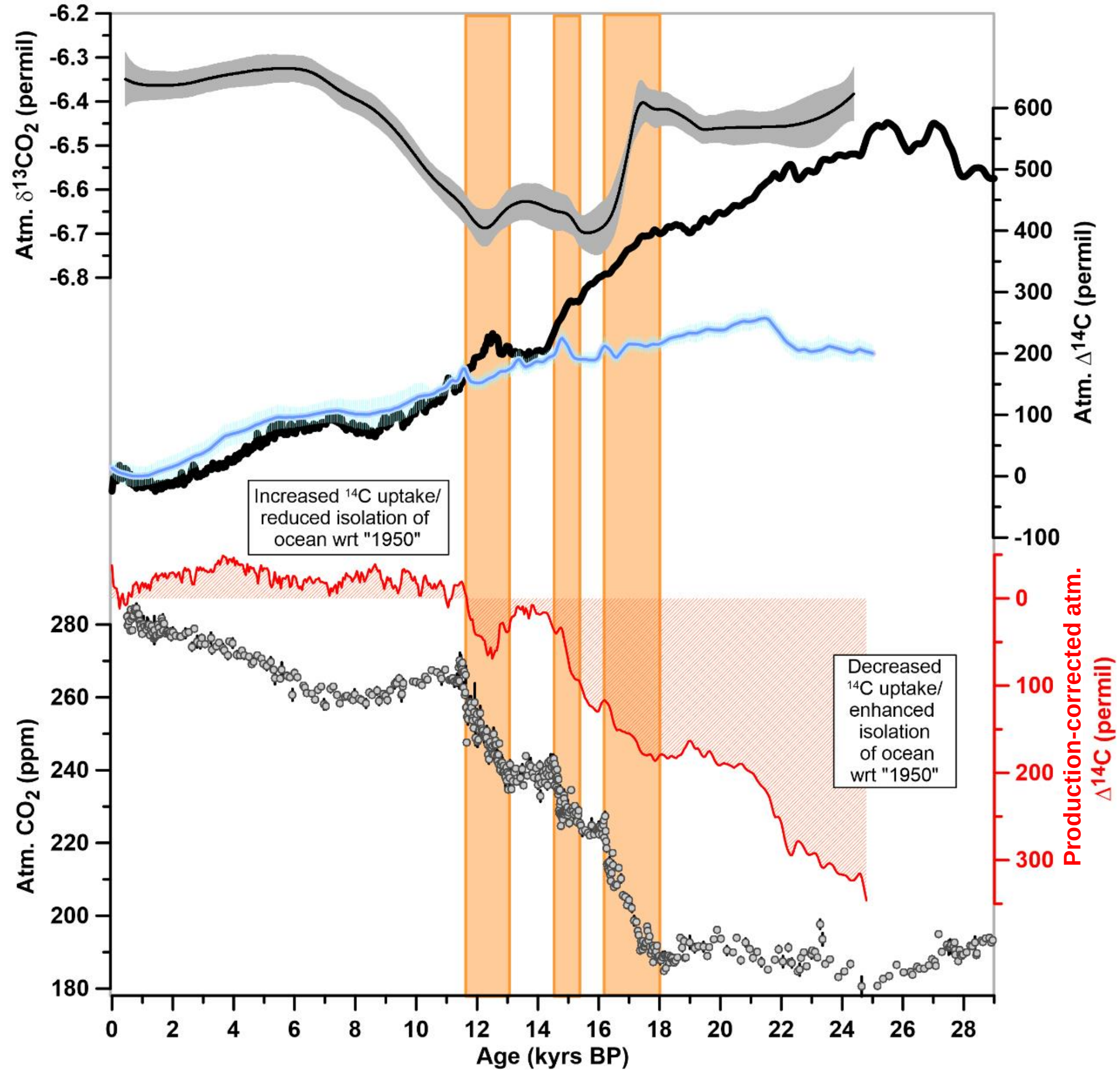


Marcott et al., 2014; Bereiter et al., 2015; Schmitt et al., 2012; Reimer et al., 2013; Hain et al., 2014

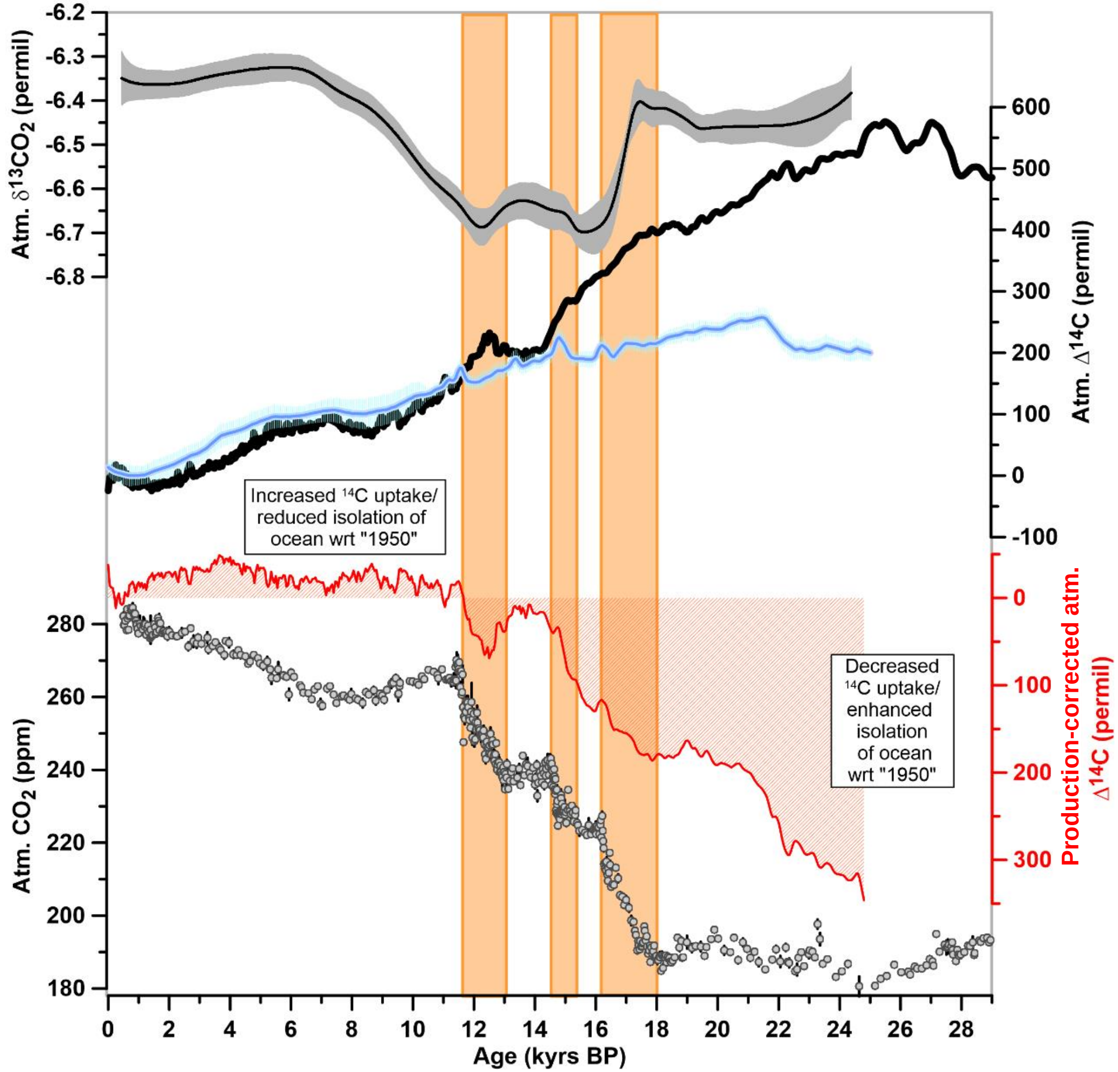
Problem: The drivers of past atmospheric CO_2 variations remain one of the strongly debated and researched topics in paleoclimatology. Helpful clues can be gained from assessing the mechanisms changing the carbon isotopic composition of $CO_{2,atm}$.

$\delta^{13}C$ composition of atmospheric CO_2:
Schmitt, et al., 2012. Carbon isotope constraints on the deglacial CO_2 rise from ice cores. Science 336 (6082), 711–714.
https://doi.org/10.1126/science.1217161

$\Delta^{14}C$ composition of atmospheric CO_2 (black)
Reimer, et al., 2013. IntCal13 and Marine13 radiocarbon age calibration curves 0-50,000 years cal BP. Radiocarbon 55 (4), 1869–1887.
https://doi.org/10.2458/azu_js_rc.55.16947

Production-driven $\Delta^{14}C$ changes (light blue):
Hain, et al., 2014. Distinct roles of the Southern Ocean and North Atlantic in the deglacial atmospheric radiocarbon decline. Earth Planet. Sci. Lett. 394, 198–208.
https://doi.org/10.1016/j.epsl.2014.03.020

Atmospheric CO_2:
Marcott, et al., 2014. Nature 514 (7524), 616–619. https://doi.org/10.1038/nature13799;
Bereiter, et al., 2015. Revision of the EPICA Dome C CO_2 record from 800 to 600 kyr bp. Geophys. Res. Lett. 42 (2), 542–549.
https://doi.org/10.1002/2014GL061957



New insights can be gained through ^{14}C dating of various climate archives with MICADAS.

MICADAS AMS: Mini Carbon Dating System

Since the early 2000s, ETH Zurich expedited the development of an AMS system that is fitted with a gas ion source and that allows online analysis of small-size samples in gaseous form: Synal, et al., 2007. MICADAS: A new compact radiocarbon AMS system. Nucl. Instruments Methods Phys. Res. B 259, 7–13. https://doi.org/10.1016/j.nimb.2007.01.138 Synal, 2013. Developments in accelerator mass spectrometry. Int. J. Mass Spectrom. 349–350, 192–202. https://doi.org/10.1016/j.ijms.2013.05.008

Pioneering work to improve non-graphitization analyses of diverse samples with MICADAS has shown promising outcomes, demonstrating the feasibility of analyses of samples as small as 1µg C (~8 µg $CaCO_3$) and single benthic foraminifera: e.g., Wacker, et al., 2013. Towards radiocarbon dating of single foraminifera with a gas ion source. Nucl. Instruments Methods Phys. Res. B 294, 307–310. https://doi.org/10.1016/j.nimb.2012.08.038

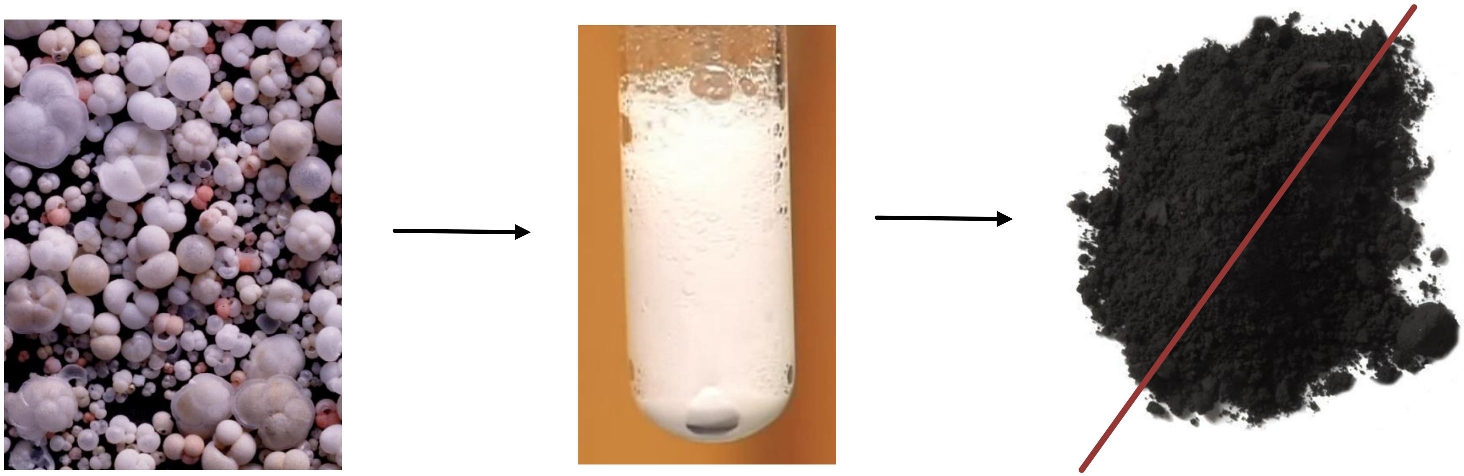
A number of labs have optimized ^{14}C dating with MICADAS, for instance of carbonates:

- BernMICADAS: Gottschalk, et al., 2018. Radiocarbon measurements of small-size foraminiferal samples with the Mini Carbon Dating System (MICADAS) at the University of Bern: Implications for paleoclimate reconstructions. Radiocarbon 60 (2), 469–491. https://doi.org/10.1017/RDC.2018.3
- AixMICADAS: Fagault, et al., 2019. Radiocarbon dating small carbonate samples with the gas ion source of AixMICADAS. Nucl. Inst. Methods Phys. Res. B 455, 276-283. https://doi.org/10.1016/j.nimb.2018.11.018
- ETH MICADAS: e.g., Fahrni, S., Wacker, L., Synal, H.-A., Szidat, S., 2013. Improving a gas ion source for ^{14}C AMS. Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 294, 320–327. https://doi.org/10.1016/j.nimb.2012.03.037 Ruff, et al., 2010. Gaseous radiocarbon measurements of small samples. Nucl. Instruments Methods Phys. Res. B 268 (7–8), 790–794. https://doi.org/10.1016/j.nimb.2009.10.032

The MICADAS allows to skip sample graphitization (required for most AMS systems), if desired.

$$3\,CaCO_3 + 2\,H_3PO_4 \rightarrow 3\,CO_2 + 3\,H_2O + 2\,PO_4^{3-} + 3\,Ca^{2+}$$

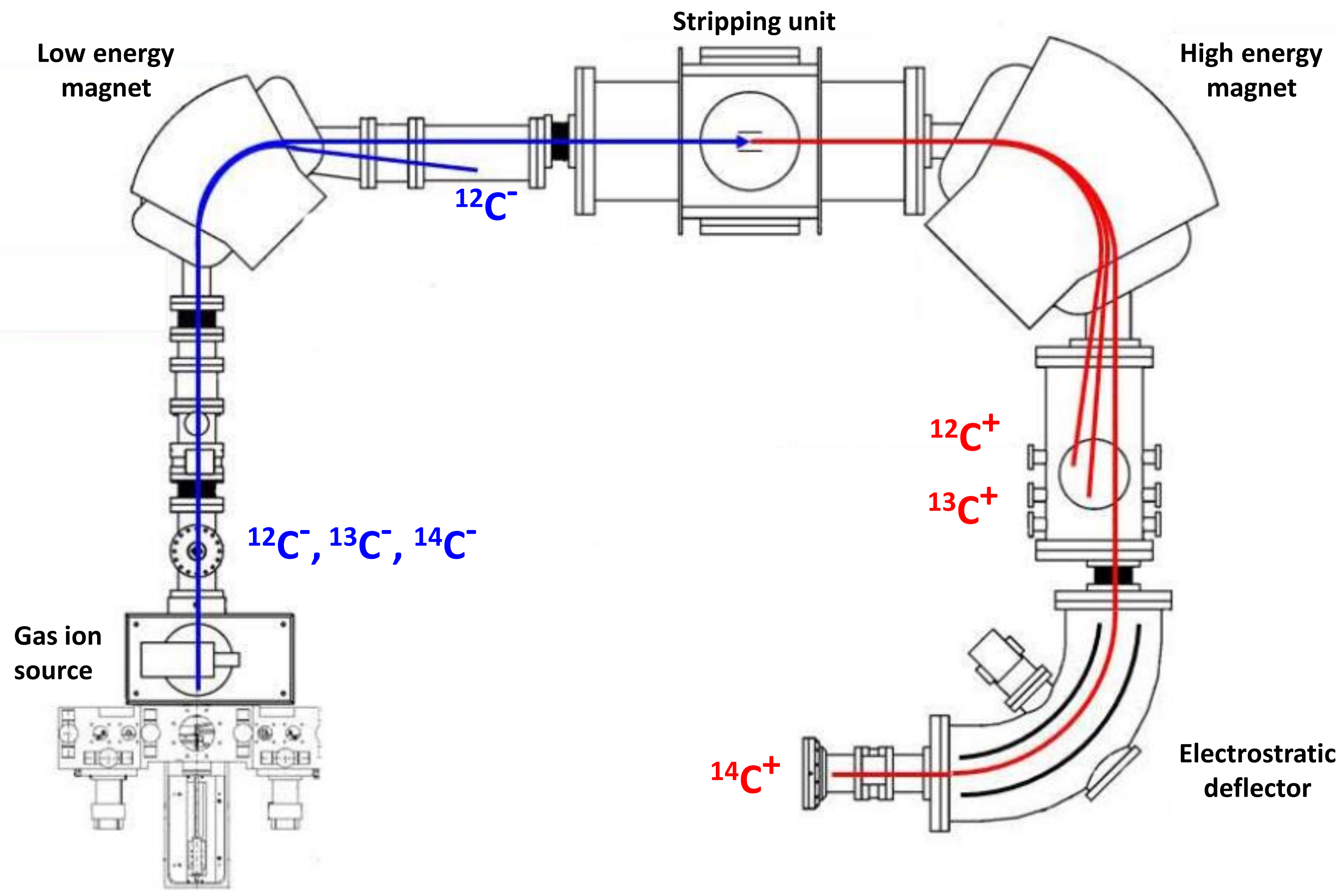
~~$CO_2 + 2\,H_2 \rightarrow C + 2\,H_2O$~~



The MICADAS AMS provides multiple ways for injecting the sample CO_2: e.g. Wacker, et al., 2013. A versatile gas interface for routine radiocarbon analysis with a gas ion source. Nucl. Instruments Methods Phys. Res. B 294, 315–319. https://doi.org/10.1016/j.nimb.2012.02.009

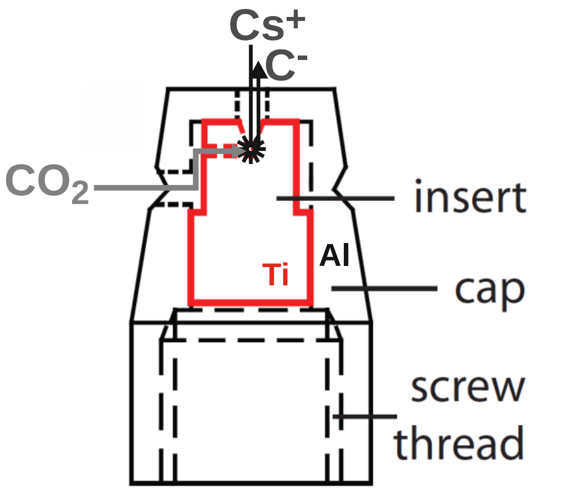
- sealed glass ampoules
- dissolution of carbonate samples
- combustion of organic matter in an elemental analyzer
- gas bottles (e.g. commercially purchased)

Elimination of equal-mass molecules and molecular ambiguities is prerequisite to detect long-lived radionuclides at natural concentration. The MICADAS achieves to sufficient level through two major adjustments.

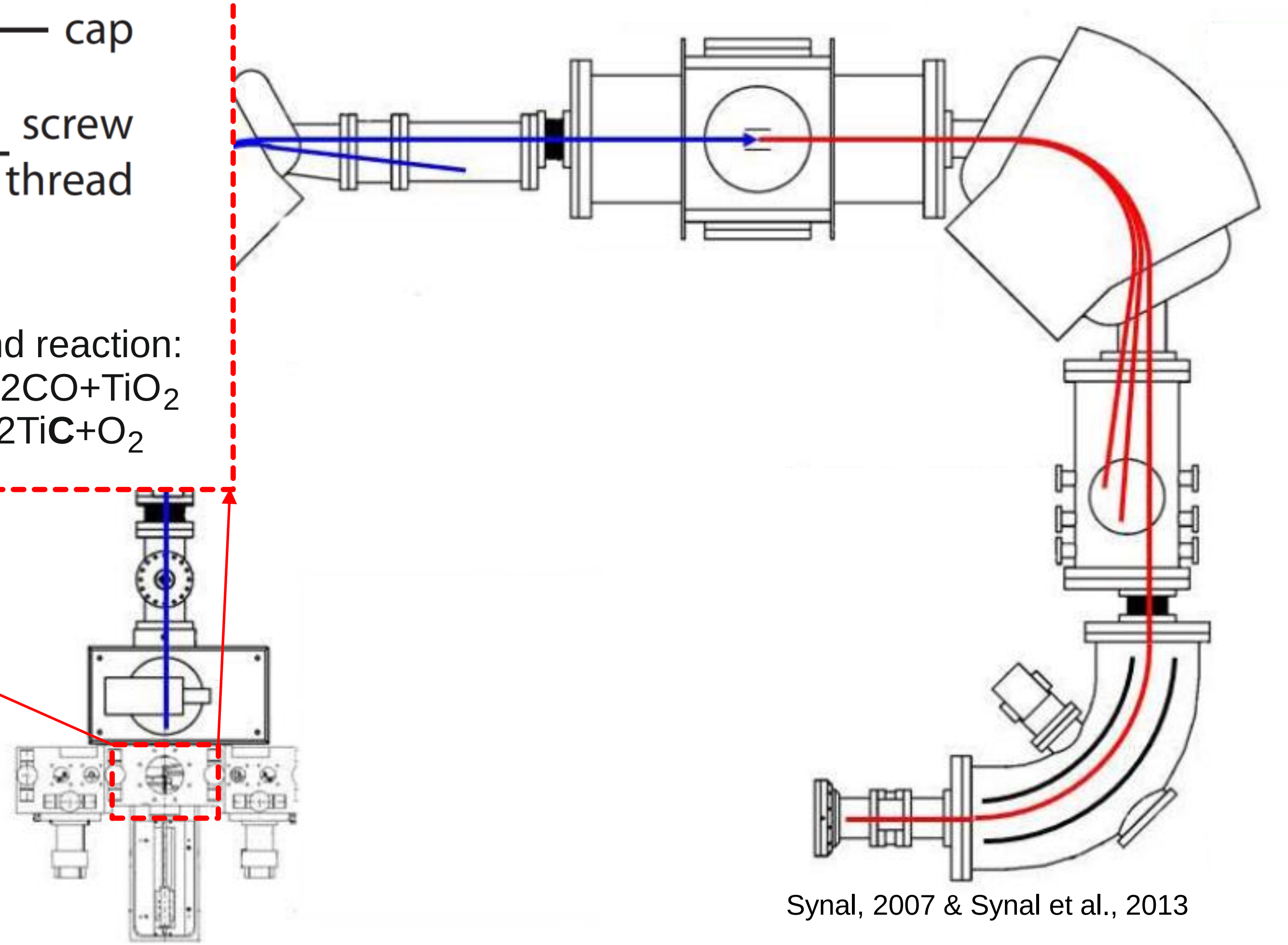


Synal, et al., 2007. MICADAS: A new compact radiocarbon AMS system. Nucl. Instruments Methods Phys. Res. B 259, 7–13. https://doi.org/10.1016/j.nimb.2007.01.138 Synal, 2013. Developments in accelerator mass spectrometry. Int. J. Mass Spectrom. 349–350, 192–202. https://doi.org/10.1016/j.ijms.2013.05.008

First, the sample can be injected as gas into the AMS, which upon interaction with sputtered Cs^+ on a Ti target surface forms C^- (see reactions left).



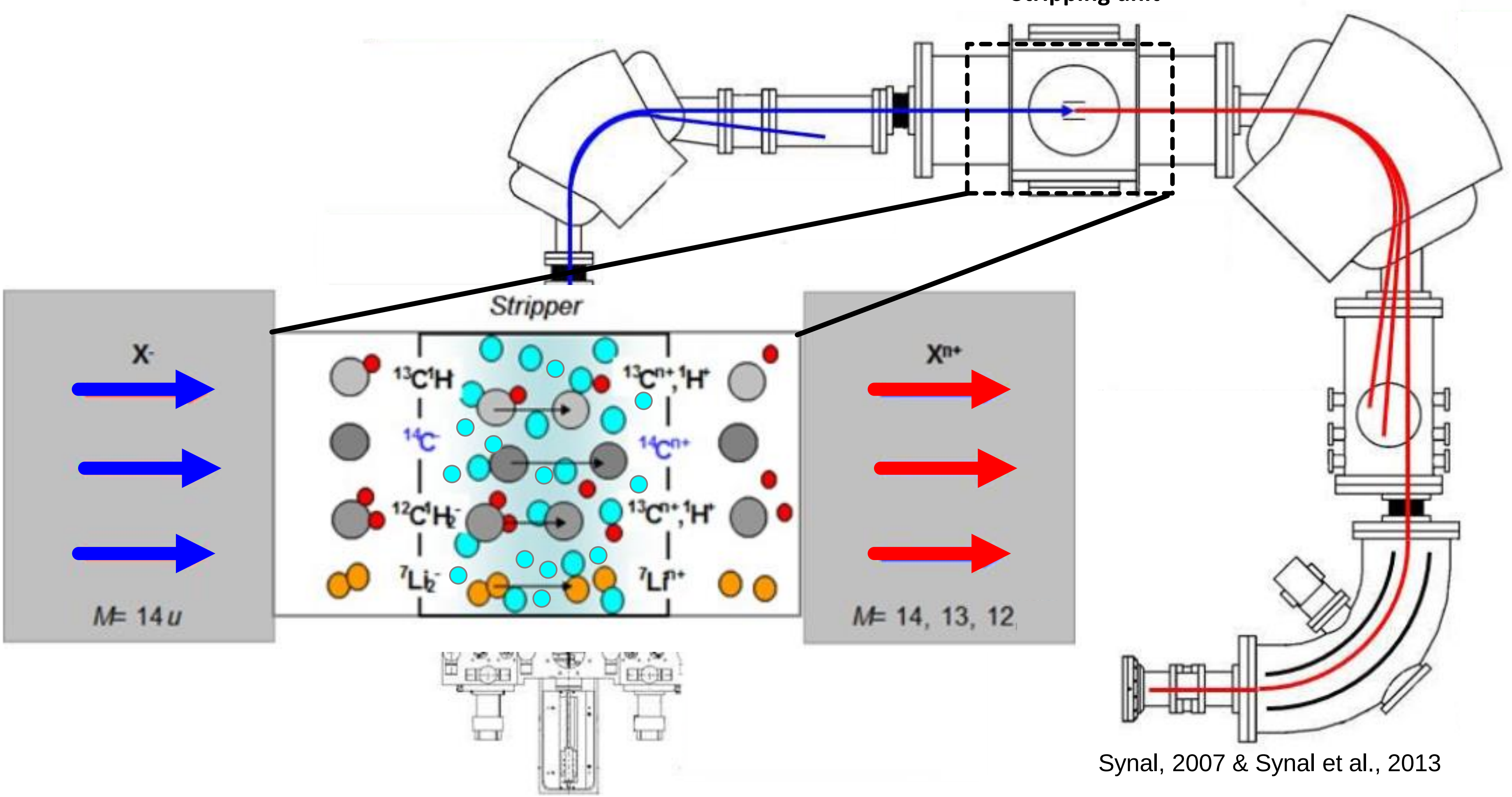
Gettering of CO_2 by Ti and reaction:
600-1000°C: $2CO_2+Ti \quad 2CO+TiO_2$
800-1000°C: $2CO+2Ti \quad 2Ti\mathbf{C}+O_2$



Synal, 2007 & Synal et al., 2013

Ruff, M., Wacker, L., Gäggeler, H.W., Suter, M., Synal, H.-A., Szidat, S., 2007. A Gas Ion Source for Radiocarbon Measurements at 200 kV. Radiocarbon 49 (2), 307–314. doi: 10.1017/S0033822200042235

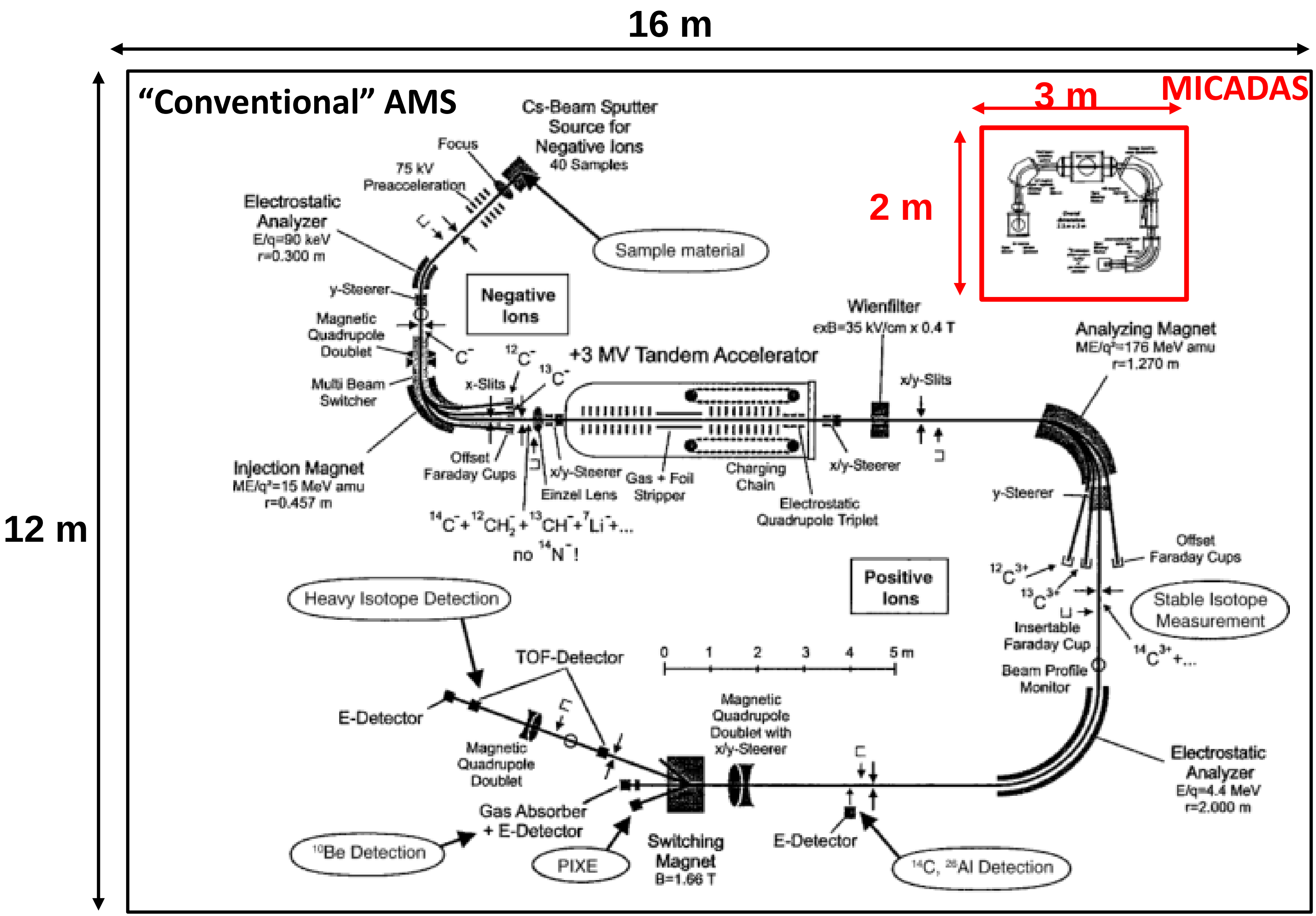
Second, the MICADAS has a higher density of stripping gas (He, N_2) in the stripping unit.
Charge states of >=3+ are required to dissociate equal-mass molecules. Sufficient elimination of equal-mass molecules can be achieved with charge state change of 1+ (collisional dissociation), which requires that the stripping gas density is higher than in conventional AMS.



Synal, 2007 & Synal et al., 2013

Synal, et al., 2007. MICADAS: A new compact radiocarbon AMS system. Nucl. Instruments Methods Phys. Res. B 259, 7–13. https://doi.org/10.1016/j.nimb.2007.01.138 Synal, 2013. Developments in accelerator mass spectrometry. Int. J. Mass Spectrom. 349–350, 192–202. https://doi.org/10.1016/j.ijms.2013.05.008

These changes have led to a much more compact AMS system operating at much lower terminal voltages <500kV.



Kutschera, W., 2005. Progress in isotope analysis at ultra-trace level by AMS. Int. J. Mass Spectrom. 242 (2–3), 145–160. https://doi.org/10.1016/j.ijms.2004.10.029

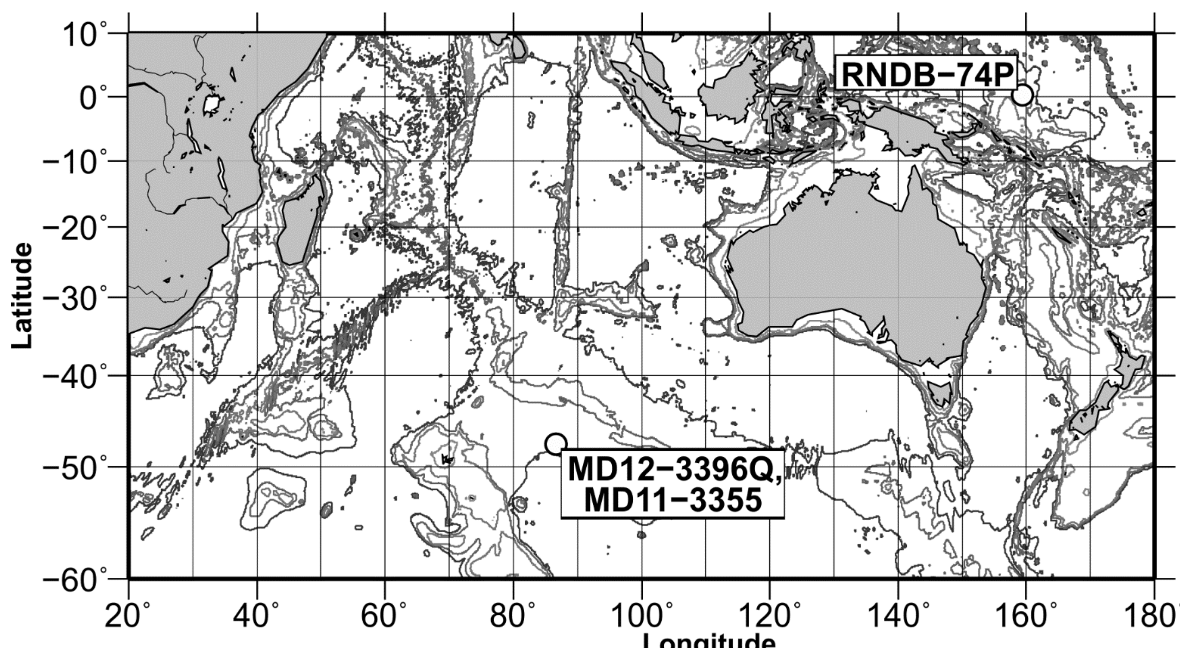
Here I want to focus on ^{14}C dating of foraminifera with MICADAS compared to traditional AMS systems (to assess its potential for ocean circulation and carbon cycle reconstructions).
I will discuss:

i) the reproducibility and precision of gas ^{14}C measurements of small carbonate samples (i.e., foraminifera),

ii) their consistency with conventional measurements of larger (graphitized) samples

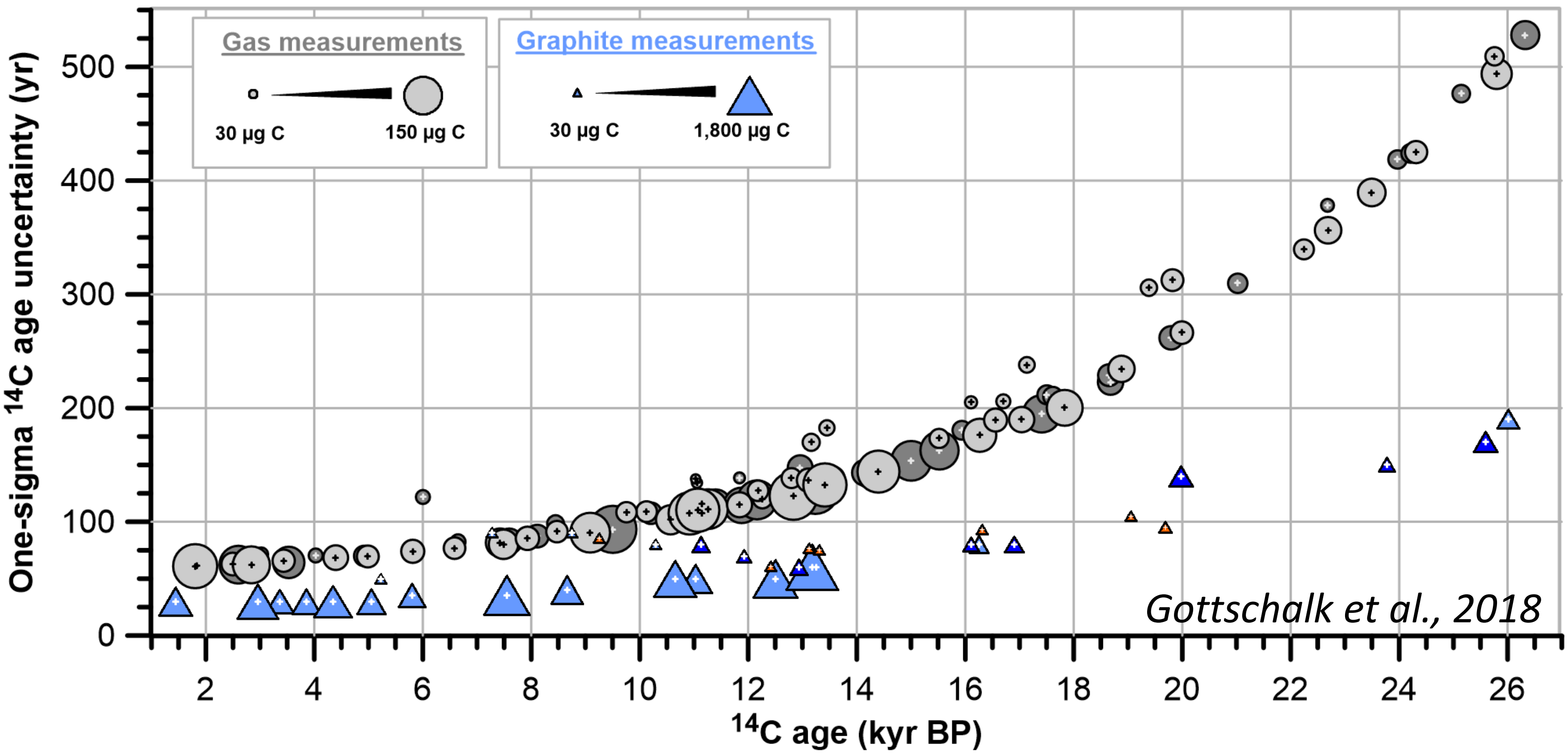
iii) the impact of contamination during sample preparation and analysis

Analyses are preformed in South Indian sediment core MD12-3396Q
that was obtained from a drift deposit with sediment rates >10 cm kyr^{-1}.



Gottschalk et al., 2018

Comparison between ^{14}C age uncertainties of "conventional" AMS (graphite) vs. MICADAS (gas analyses)



*Significantly larger uncertainties of ^{14}C ages for gas than for graphite measurements

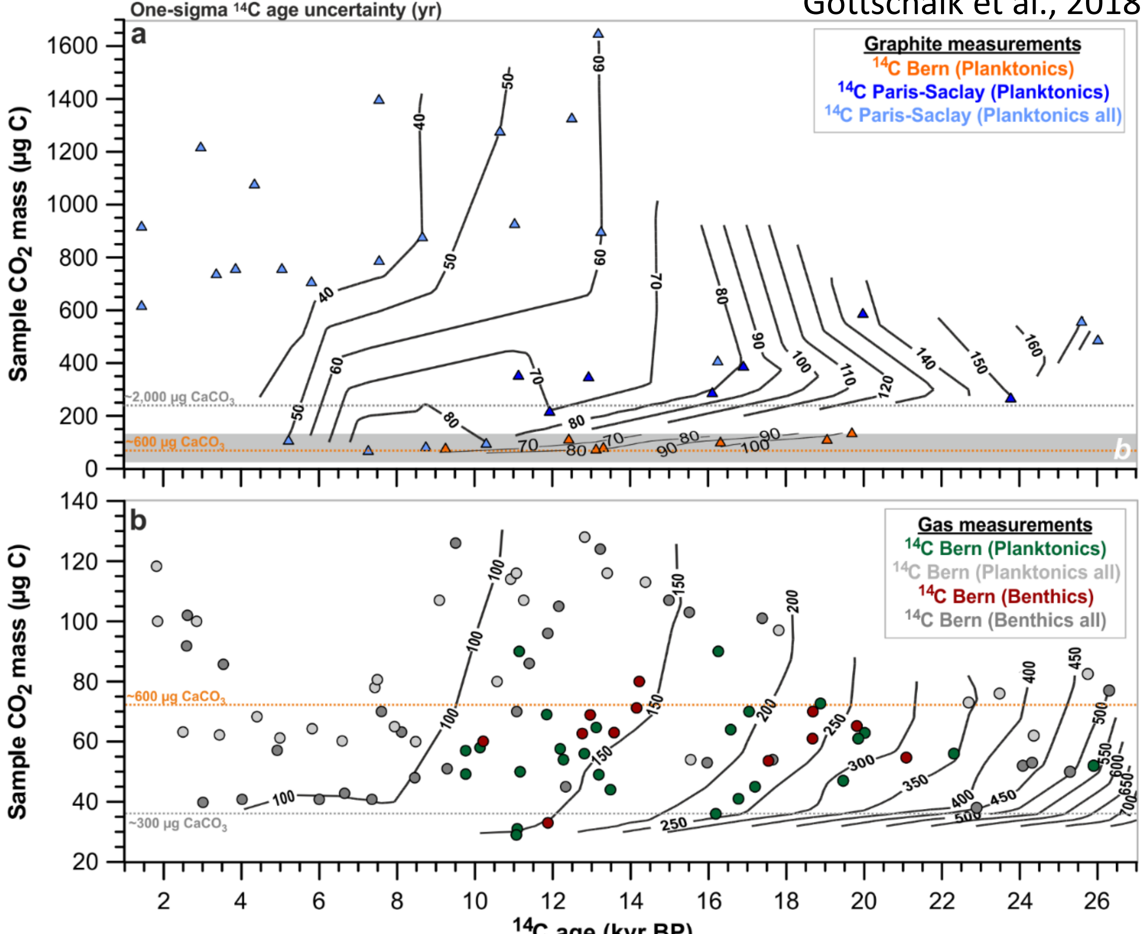
*The average difference ranges from a factor of approx. two during the Holocene to a factor of approx. three during the last ice age

Comparison between ^{14}C age uncertainties of "conventional" AMS (graphite) vs. MICADAS (gas analyses)

Gottschalk et al., 2018

Graphite

Gas



*Age uncertainties of graphite samples larger than ~250 µg C and of gas samples larger than ~40 µg C rapidly increase with ^{14}C age

*Below those sample sizes, age uncertainties increase both as a function of increasing ^{14}C age *and* decreasing sample size

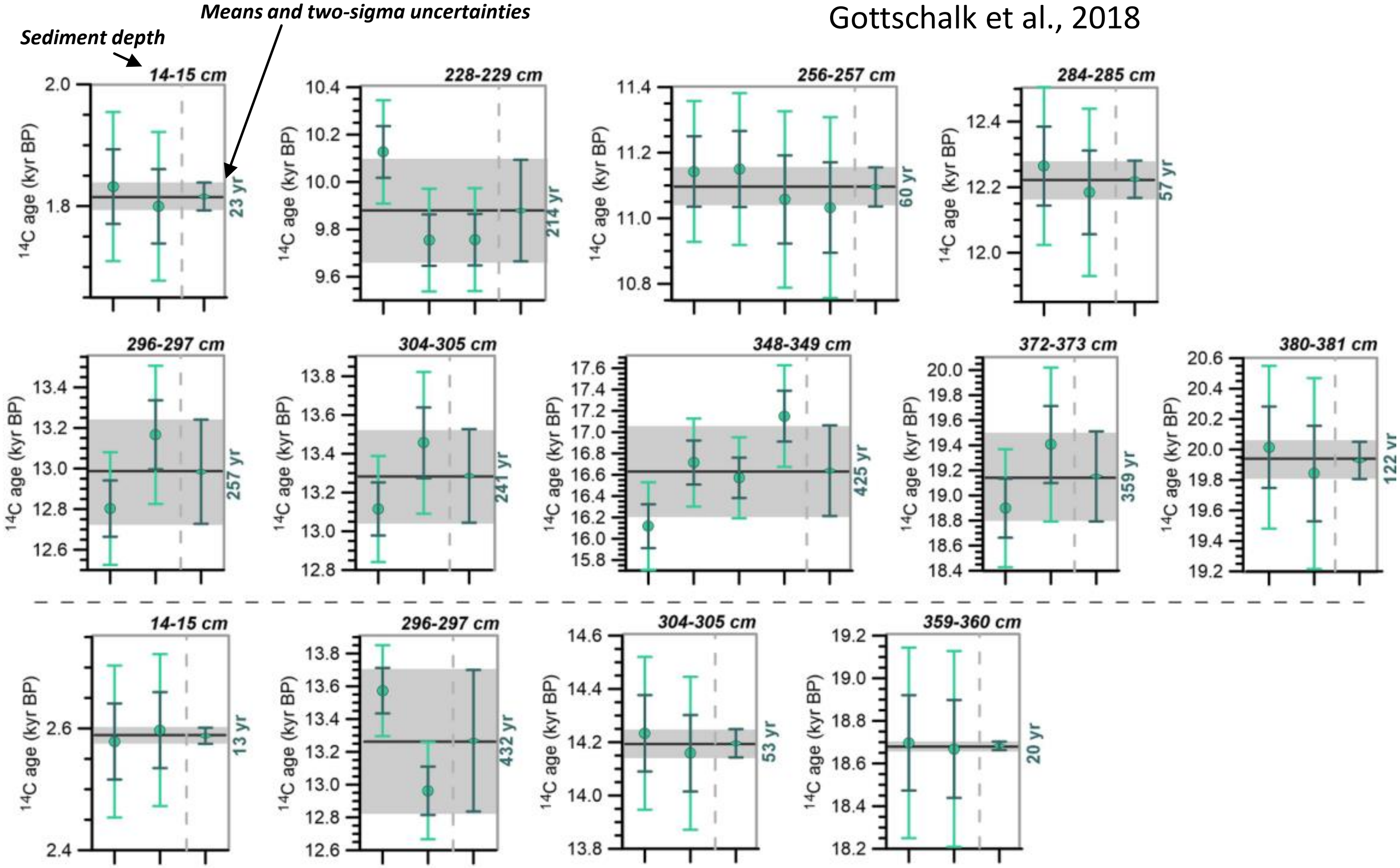
*This mainly comes down to ^{14}C counting statistics during AMS measurement

Reproducibility of replicate ^{14}C gas measurements of *N. pachyderma* with MICADAS

Gottschalk et al., 2018

Planktonic foraminifera

Benthic foraminifera

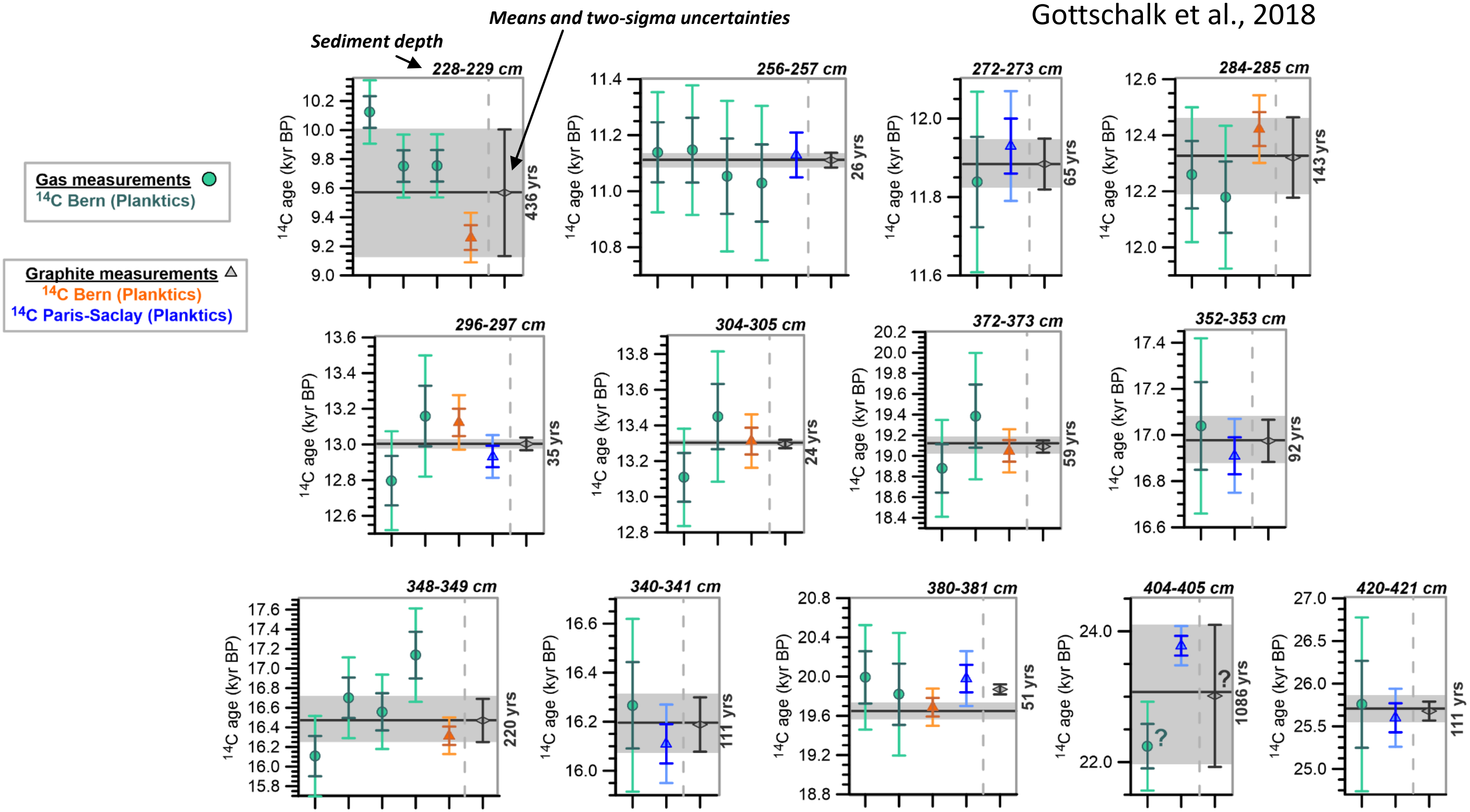


*Reproducibility of gas ^{14}C analyses: 170 ^{14}C years 1σ, *n*=13

*Slightly better for benthic foraminifera (130 ^{14}C years 1σ, *n*=4) vs. planktonic foraminifera (200 ^{14}C years 1σ, *n*=9)

Comparison of Graphite and Gas ^{14}C measurements on planktonic foraminifera

Gottschalk et al., 2018

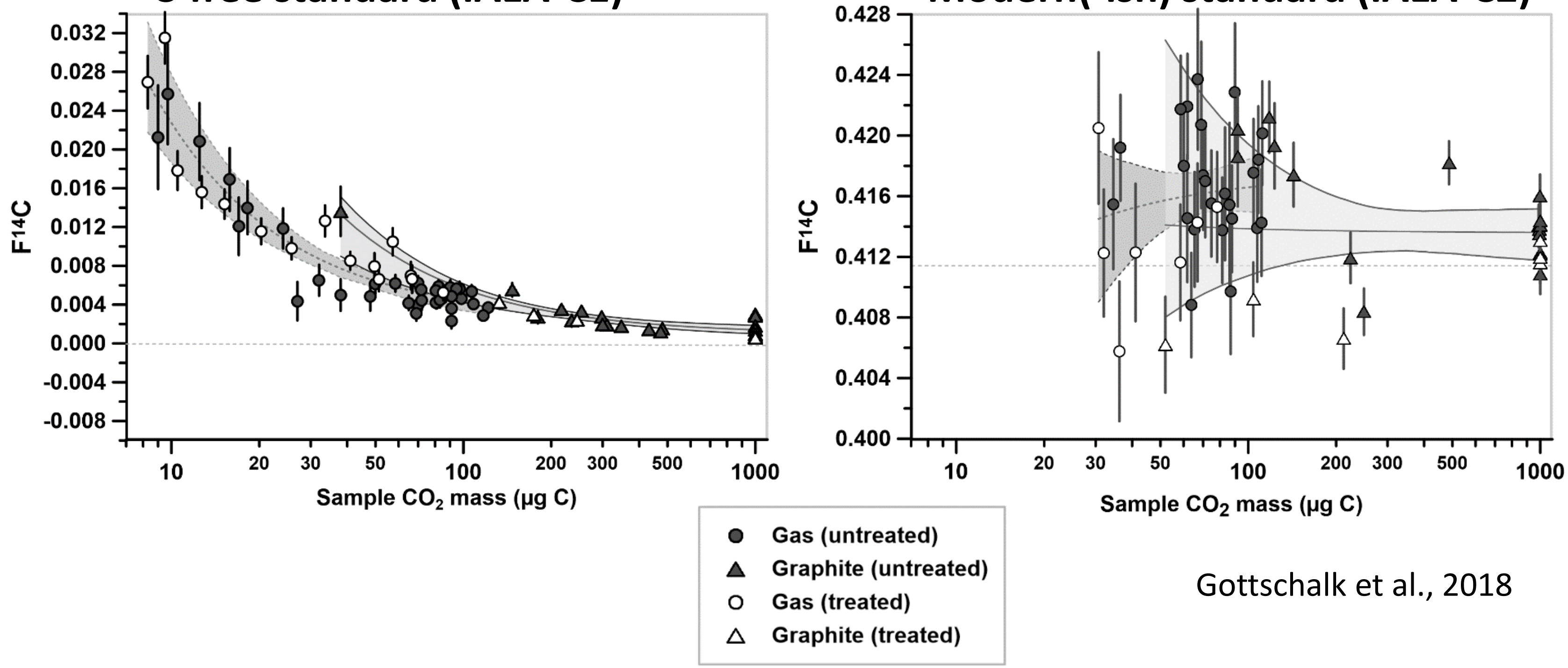


* Mean standard deviation between gas and graphite ^{14}C measurements is 170±140 yr (n=7), which is similar to their mean 1σ ^{14}C age (140±70 yr, n=14).

* Small-size Gas and large-size graphite ^{14}C analyses agree within 40±30 ^{14}C yrs (*n*=5), despite a sample size difference of a factor of ~10.

Impact of contamination on MICADAS ^{14}C dates

^{14}C-free standard (IAEA-C1) | Modern(-ish) standard (IAEA-C2)



Gottschalk et al., 2018

*It is crucial to accurately determine the mass and F-modern of contamination of the MICADAS that has a strong effect on small and/or old samples

*This can be done by determining the changes in a modern(-ish) and ^{14}C-free standard with sample size: Hua, et al., 2004. Small-mass AMS radiocarbon analysis at ANTARES. Nucl. Instruments Methods Phys. Res. B 223–224, 284–292. https://doi.org/10.1016/j.nimb.2004.04.057

*A modern certified carbonate standard that can be measured with the gas interface and used by the community should be implemented (see example in Fagault et al., 2019)

MICADAS ^{14}C analyses can be a game changer for ocean circulation and carbon cycle reconstructions in sample-limited archives.

But the sedimentation rate and foraminiferal abundances should be carefully assessed and measurements should be optimized to minimize potential biases (both of analytical and sedimentary origin).

Recommendations for MICADAS ^{14}C analyses:

*Obtain foraminiferal abundance changes in sediment core prior to dating/picking

*Measure foraminifera from abundance maxima (to circumvent biases from bioturbation)

*Benthic and planktic foraminiferal samples (for ventilation age reconstructions) should be size-matched, especially when they are very small (<250 µg $CaCO_3$)

*Perform replicate analyses, where possible

*Determine background and contamination levels for your local MICADAS

*Community-wide efforts to develop a modern-$F^{14}C$ standard to do so?

MICADAS ^{14}C analyses can be a game changer in sample-limited archives. But the sedimentation rate and foraminiferal abundances should be carefully assessed and measurements should be optimized to minimize potential biases (both of analytical or sedimentary origin).

Recent literature on additional controls on ^{14}C dates (e.g., bioturbation):

Missiaen, et al., 2020. Radiocarbon Dating of Small-Sized Foraminifer Samples: Insights Into Marine Sediment Mixing. Radiocarbon 62 (2), 313-333. https://doi.org/10.1017/RDC.2020.13

Ausín, et al., 2019. Radiocarbon Age Offsets Between Two Surface Dwelling Planktonic Foraminifera Species During Abrupt Climate Events in the SW Iberian Margin Paleoceanography and Paleoclimatology. Paleoceanogr. Paleoclimatology 34, 63–78. https://doi.org/10.1029/2018PA003490

Lougheed, et al., 2018. Moving beyond the age-depth model paradigm in deep sea palaeoclimate archives: dual radiocarbon and stable isotope analysis on single foraminifera. Clim. Past 14, 515–526. https://doi.org/10.5194/cp-14-515-2018

Thanks for reading!

I am looking forward to comments/questions/concerns. **@Jul_Gottschalk**