



Is 14C-AMS analysis of phytoliths a suitable tool ?

Rémi Corbineau, Guaciara M. Santos, Anne Alexandre, Paul E. Reyerson

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I Introduction

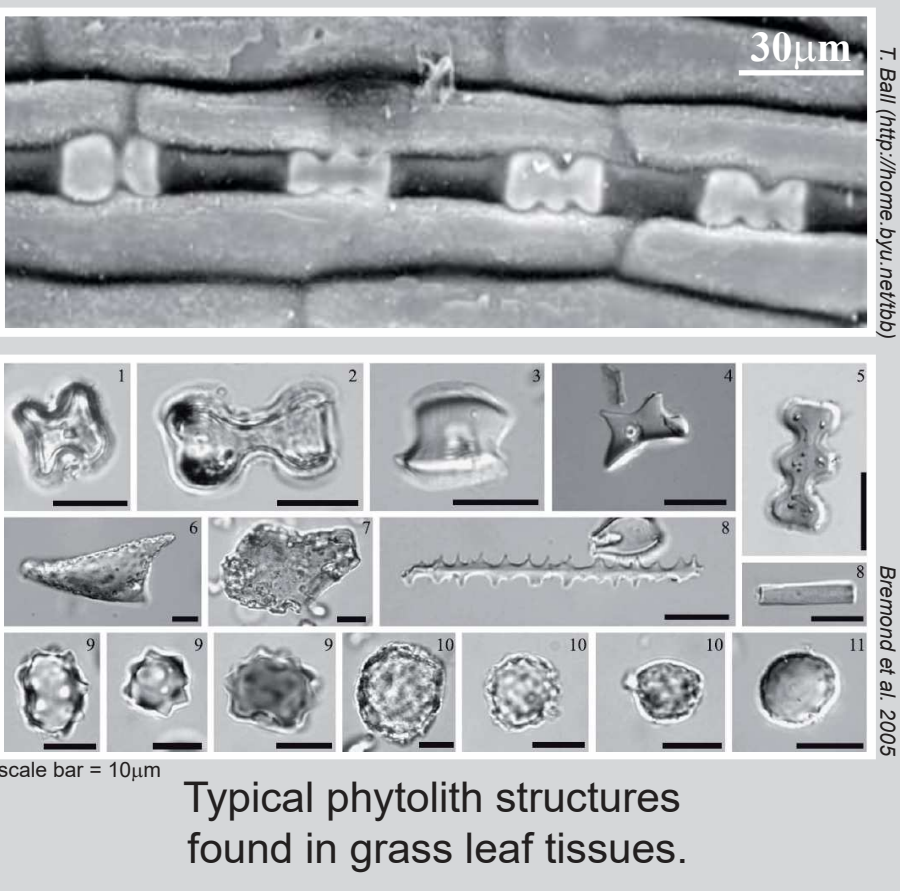
Phytoliths are micrometric amorphous silica particles that form in living plant cells.

Fossil phytolith assemblages are used as vegetation, climate, and archaeobotanical indicators.

Quantification of phytoliths helps to assess the global biogeochemical cycle of silicon.

Carbon (**phytC**) can be trapped during phytolith formation and represents less than 2% by dry weight.

Radiocarbon dating of phytC is immediately attractive because phytC is fully protected from oxidizing environments (Wilding 1967). Therefore, it would contribute to obtaining new absolute chronologies and would bring new insights on the global silicon cycle.



II State of the art: phytC investigations

Chemical composition

GC-MS
Perry et al. 1987, Pironon et al. 2001, Smith and Anderson 2001.

- sugars
- uronic acid
- lignin
- proteins
- lipids
- aromatic hydrocarbons (if heated at 400°C)

Raman spectroscopy
Pironon et al. 2001.

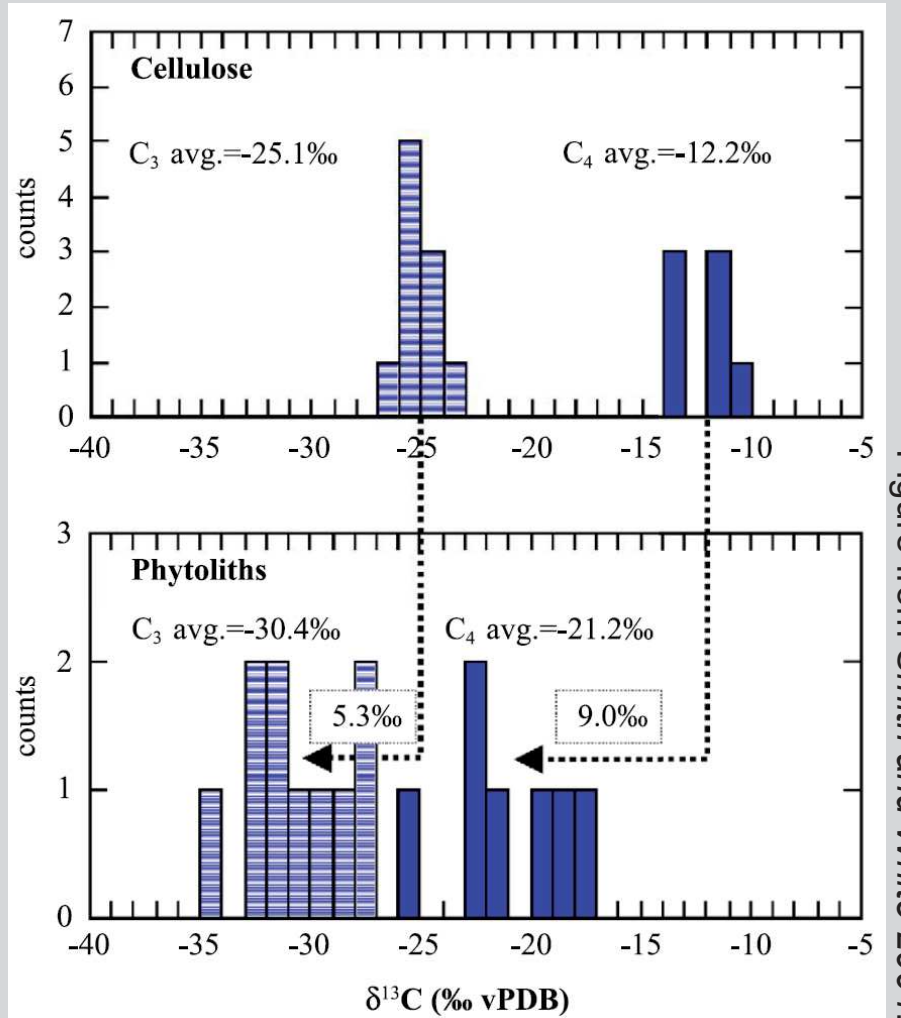
- aliphatic compounds
- graphite or coal (if heated at 400°C)

Protein stains + PCR
Elbaum et al. 2009.

- glycoproteins but no DNA

^{δ13}C signature

Attempts were made to use phytC ^{δ13}C signatures as **C3/C4 plant proxies** using IR-MS (*Kelly et al. 1991, McLaren and Umlauf 2000, Smith and White 2004, Webb and Longstaffe 2010*).



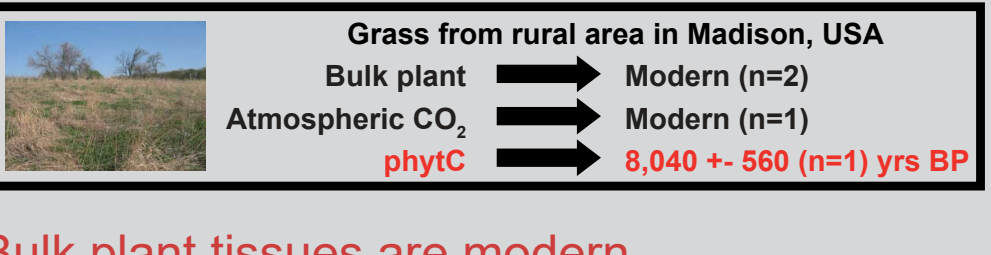
Direct ¹⁴C-AMS dating

1. Attempts to obtain **absolute chronologies** (e.g. comparison ¹⁴C-AMS phytC/TL on tephra) (*Kelly et al. 1991, Mulholland and Prior 1993, McLaren and Umlauf 2000, Piperno and Stothert 2003, Prior et al. 2005, Rieser et al. 2007*).

2. Measurements of PhytC from modern plants (*Santos et al. 2010*).

For the first time :

- Background assessments (BLANK)
- Accuracy tests (<1%)
- Replication tests



Phytolith ^{δ13}C values are more negative than grass cellulose ^{δ13}C values.

PhytC always yields ages of several thousand years (from 2,280 BP to 8,040 BP).

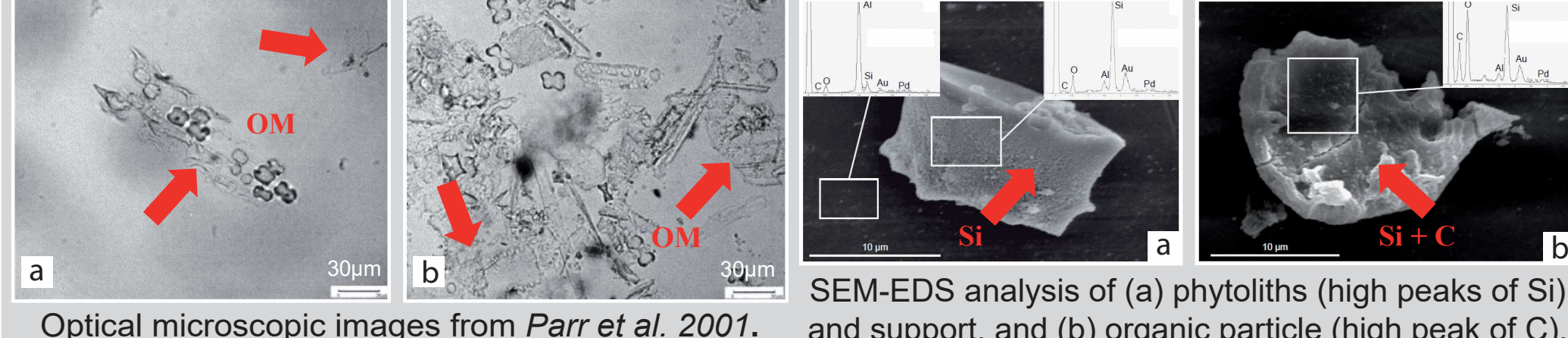
Were the phytolith extraction protocols efficient to remove all exterior carbon from phytoliths ?

III Material and Methods

Evaluation of phytolith extraction protocols commonly used

■ Dry ashing at 500°C (a)
■ Microwave digestion (b)
Parr et al. 2001

■ Wet oxidation using H₂SO₄+H₂O₂
Kelly et al. 1999



Set up of new phytolith extraction protocols

1. Combination of published extraction protocols.
(Geiss 1978, Kelly et al. 1999, Parr et al. 2001, Prior 2005, Piperno 2006)
2. Checking for potential sources of old C contaminant:
 - Phytoliths samples extracted in **two different laboratories**. (UW-Madison and CEREGE).
 - ¹⁴C-AMS analysis of a sample of ¹⁴C free SiO₂ powder subjected to the phytolith extraction procedure as a **BLANK**.
 - ¹⁴C-AMS analysis of laboratories ambient air.
3. Checking for samples purity: SEM-EDS.

Application to FACE grass samples

Phytolith samples were obtained from harvested *Sorghum bicolor* (a C4 silicon accumulator) grown within a **FACE** (Free-Air CO₂ Enrichment) experiment at Maricopa, Arizona, during 1998. In these experiments, controlled plots are exposed to enriched CO₂ concentrations with known ¹⁴C and ^{δ13}C values.

Sorghum was exposed to fossil CO₂ (dead or ¹⁴C-free) during a full growing season in one hand (**7E FACE**), and to modern CO₂ (modern-air) in the other hand (**8E FACE**). Soils are the same.

¹⁴C-AMS target preparation and measurement

50-300mg of phytoliths and SiO₂ were:

- baked at 160°C before evacuation,
- combusted at 900°C in quartz tube with CuO and silver wire.

(Santos et al. 2010)

Graphitization: Hydrogen reduction with Fe powder as catalyst (*Santos et al. 2004*).

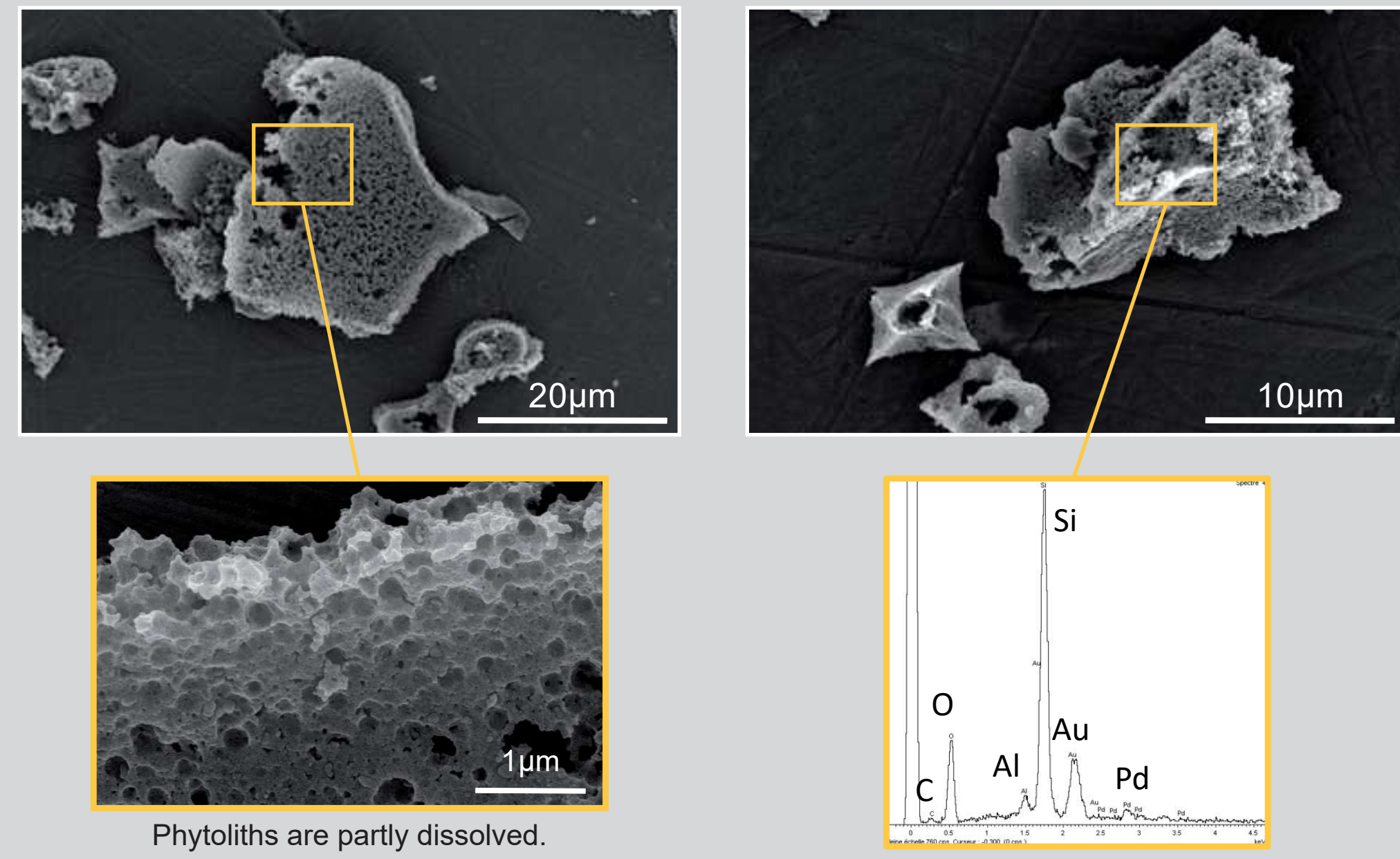
Targets were measured in the AMS (NEC 0.5MV 1.5SDH-2) compact system (*Southon et al. 2004*).

IV Results

Two phytolith extraction protocols leading to purity 100%

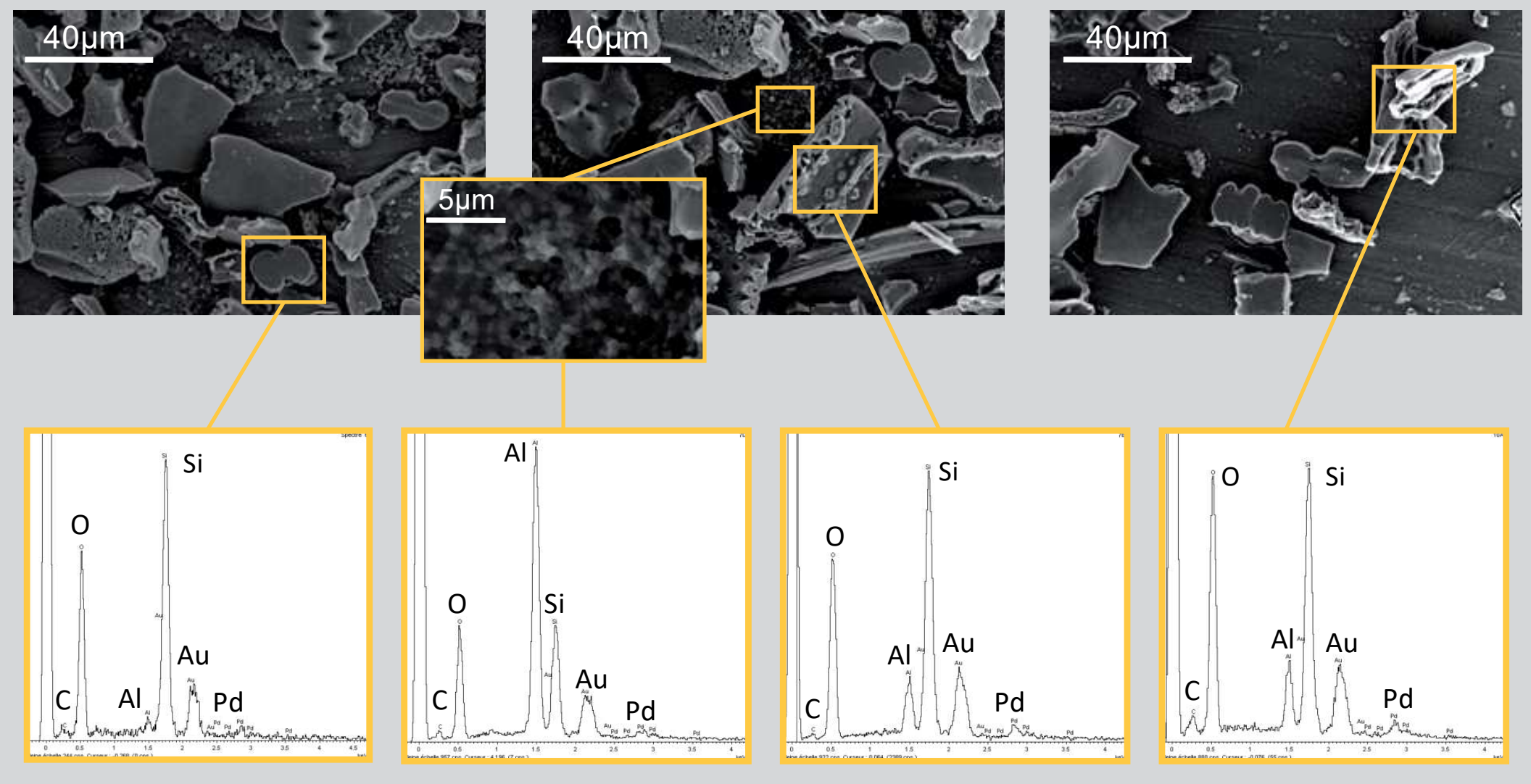
Protocol 1

Acid digestion (H₂SO₄, H₂O₂, HNO₃, KClO₃, KOH).
(Combined from Kelly 1999, Piperno 2006, Prior 2005).



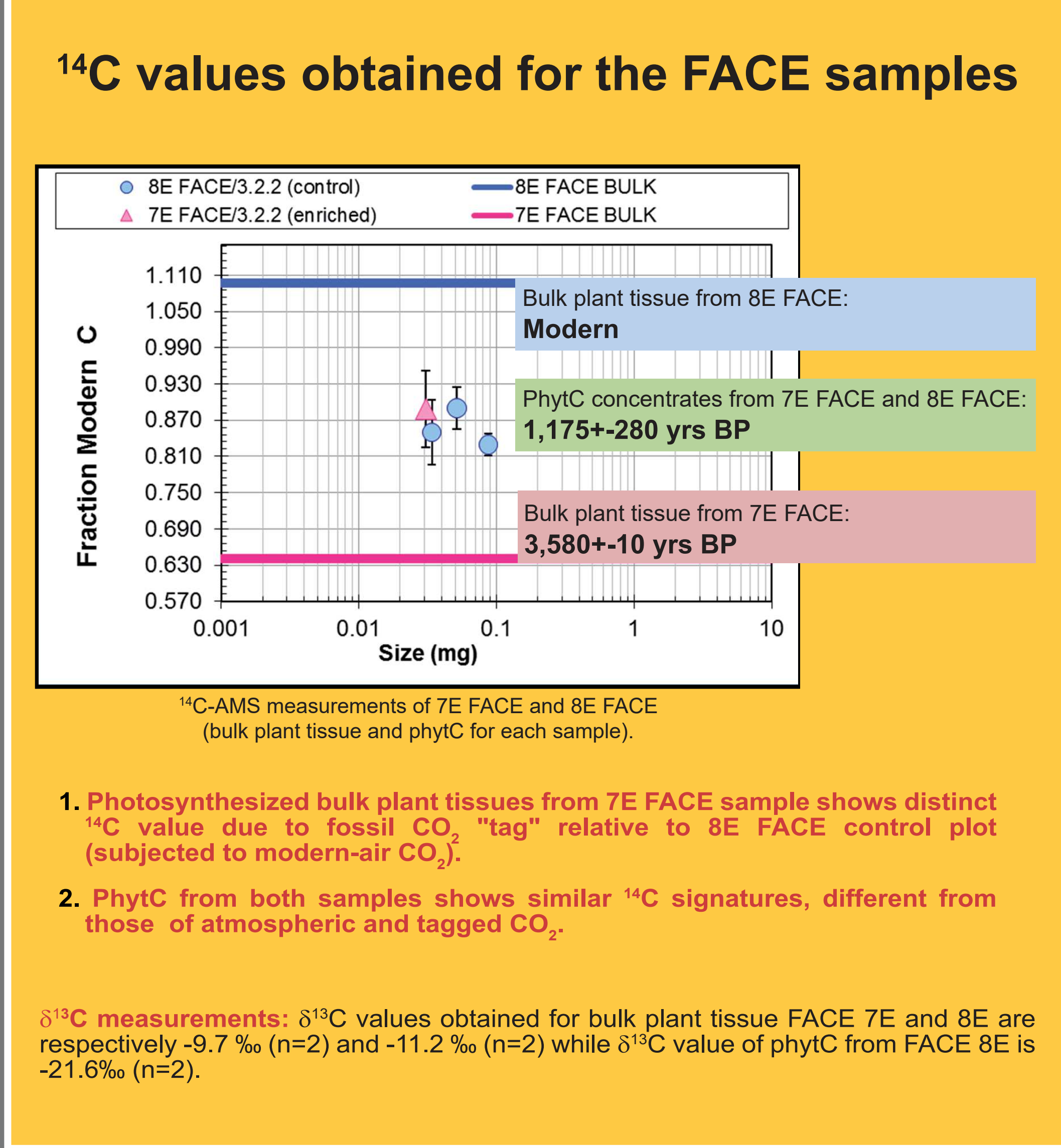
Protocol 2

Dry ashing (500°C) + acid digestion (HNO₃, HClO₄, H₂O₂).
(Combined from Kelly 1999, Parr et al. 2001, Piperno 2006).



1. **All particles analysed by EDS are siliceous.**

2. **No Ca was analyzed.**



V Discussion - Conclusions - Perspectives

While phytC is commonly assumed to originate from plant tissues and/or photosynthesis, these preliminary results suggest that **phytC from the FACE grasses may come from a similar soil source.**

These results will soon be confirmed or infirmed by :

- ➔ ¹⁴C analysis of FACE samples extracted using the same extraction protocols in a different lab (lab 2: UW).
- ➔ ¹⁴C analysis of phytC from archaeological samples of known ages.
- ➔ ¹⁴C analysis of phytC from grass planters fed by nutrients with different ^{δ13}C and ¹⁴C values.

The unexpected radiocarbon values of phytC highlight that **¹⁴C-AMS of phytoliths may not be a suitable dating tool** but brings new thrilling questions on plants nutrition and the related soil carbon cycle.

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contacts: corbineau@cerege.fr / gdossant@uci.edu / alexandre@cerege.fr / reyerson@wisc.edu