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

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I Introduction

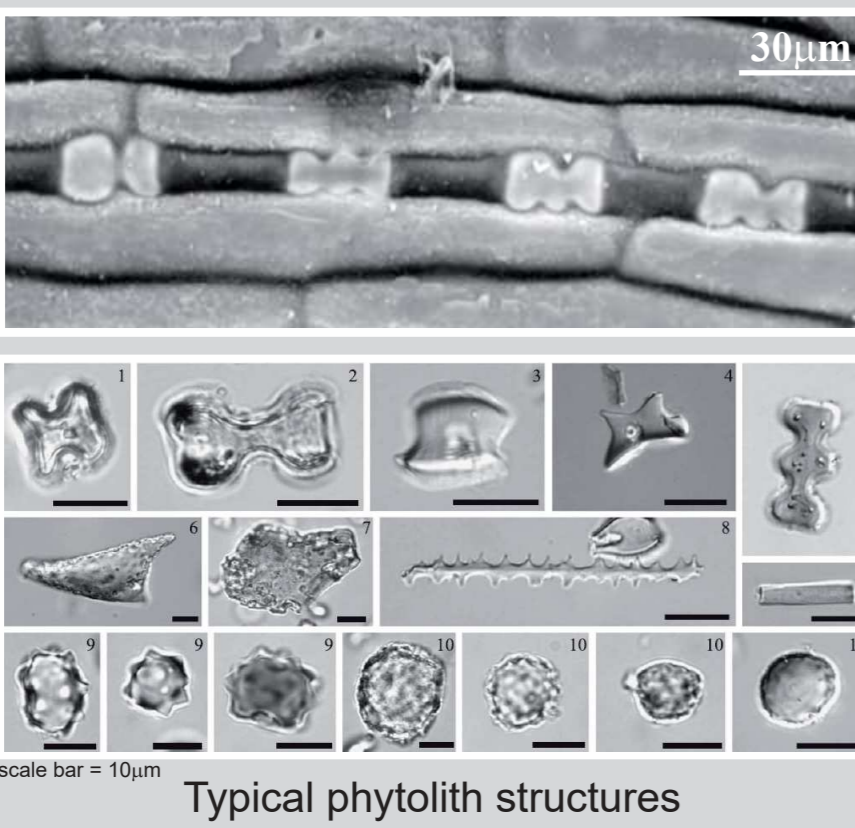
Phytoliths are micrometric amorphous silica particles that form in living plant cells.

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

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

Raman spectroscopy

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

Protein stains + PCR

- glycoproteins but no DNA

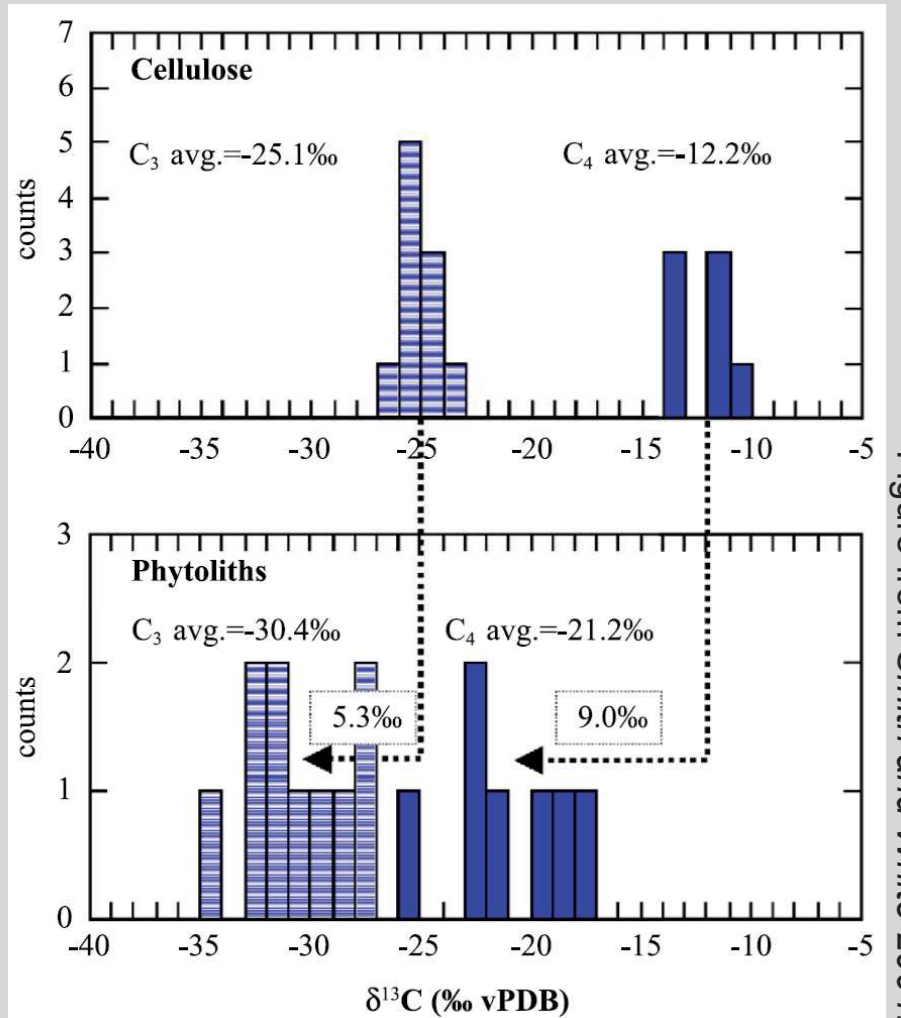
GC-MS
Perry et al. 1987, Pironon et al. 2001, Smith and Anderson 2001.

Raman spectroscopy
Pironon et al. 2001.

Protein stains + PCR
Elbaum et al. 2009.

¹⁴C signature

Attempts were made to use phytC ¹⁴C 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

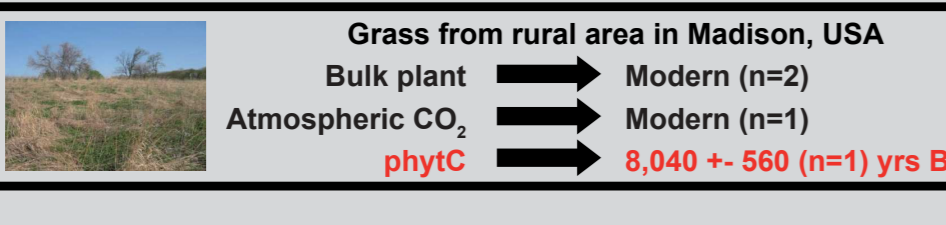
- Attempts to obtain **absolute chronologies** (e.g. comparison ¹⁴C-AMS phytC/TL on tephra) (Kelly et al. 1991, Mulholland and Prior 1993, McLaren and Umlauf 2000, Piperno and Stohert 2003, Prior et al. 2005, Rieser et al. 2007).
- Measurements of PhytC from modern plants (Santos et al. 2010).

Inexplicably old values/Inverted chronologies.

For the first time :

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

Bulk plant tissues are modern.



Phytolith ¹⁴C values are more negative than grass cellulose ¹⁴C values.

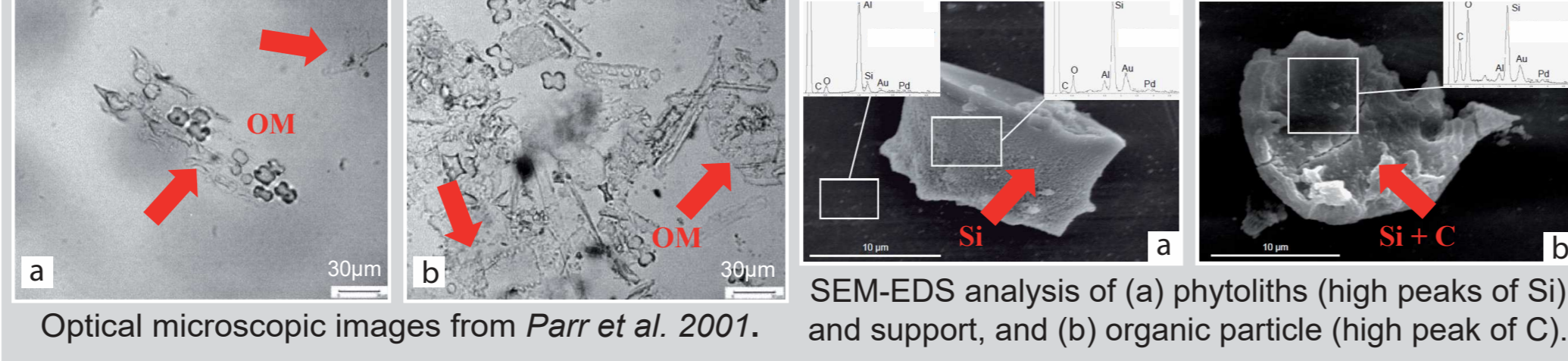
PhytC always yields ages of several thousand years (from 2,280 BP to 8,040 BP).

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) Parr et al. 2001
- Microwave digestion (b) Kelly et al. 1999
- Wet oxidation using H₂SO₄+H₂O₂ Kelly et al. 1999



Optical microscopic images from Parr et al. 2001. SEM-EDS analysis of (a) phytoliths (high peaks of Si) and support, and (b) organic particle (high peak of C).

Organic matter (OM) still remains.

Set up of new phytolith extraction protocols

- Combination of published extraction protocols. (Geiss 1978, Kelly et al. 1999, Parr et al. 2001, Prior 2005, Piperno 2006)
- 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.
- 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 ¹³C 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).

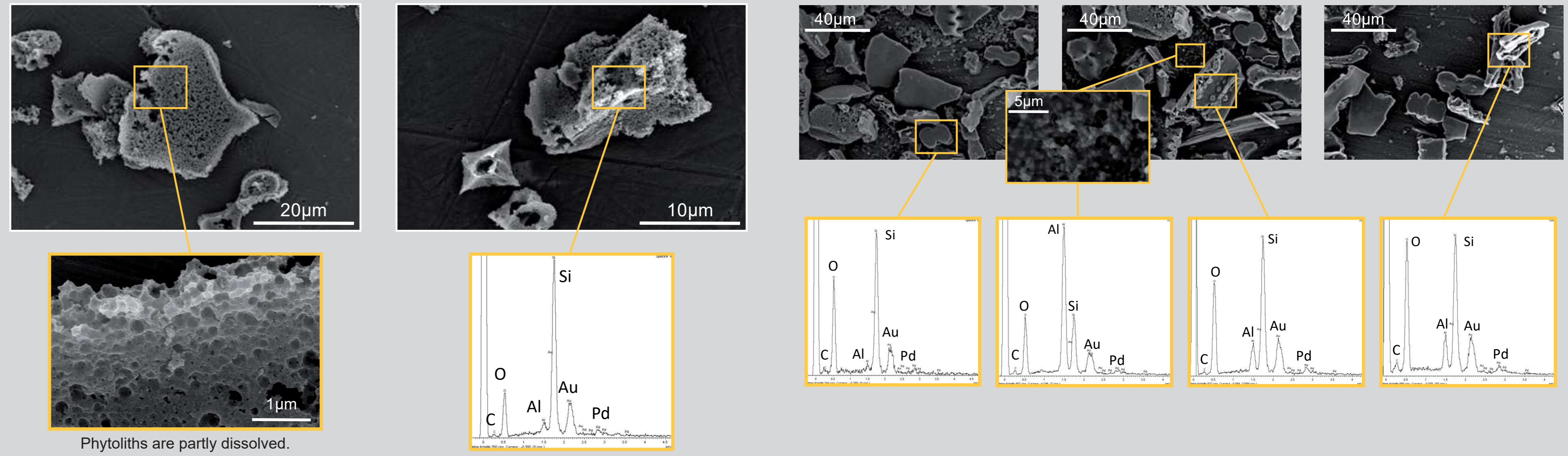
Targets were measured in the AMS (NEC 0.5MV 1.5SDH-2) compact system (Southon et al. 2004).

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).



SEM images and EDS analysis of phytoliths (high peak of Si).

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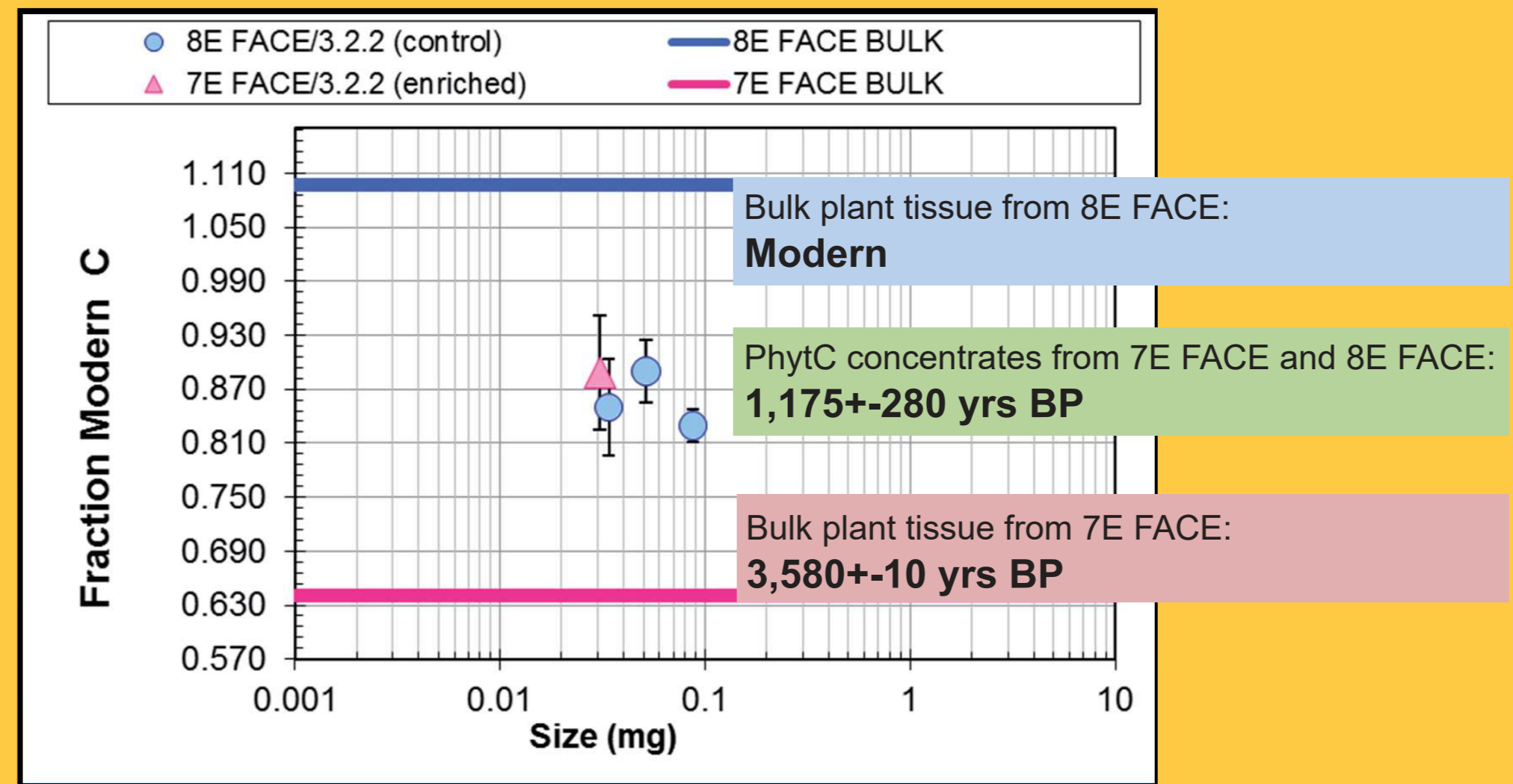
SEM images and EDS analysis of phytoliths (high peak of Si).

Phytoliths are partly dissolved.

1. All particles analysed by EDS are siliceous.

2. No Ca was analyzed.

¹⁴C values obtained for the FACE samples



14C-AMS measurements of 7E FACE and 8E FACE (bulk plant tissue and phytC for each sample).

- 8E FACE/3.2.2 (control)
- 7E FACE/3.2.2 (enriched)
- 8E FACE BULK
- 7E FACE BULK

Bulk plant tissue from 8E FACE: **Modern**

PhytC concentrates from 7E FACE and 8E FACE: **1,175±280 yrs BP**

Bulk plant tissue from 7E FACE: **3,580±10 yrs BP**

1. Photosynthesized bulk plant tissues from 7E FACE sample shows distinct ¹⁴C value due to fossil CO₂ "tag" relative to 8E FACE control plot (subjected to modern-air CO₂).

2. PhytC from both samples shows similar ¹⁴C signatures, different from those of atmospheric and tagged CO₂.

¹³C measurements: ¹³C values obtained for bulk plant tissue FACE 7E and 8E are respectively -9.7 ‰ (n=2) and -11.2 ‰ (n=2) while ¹³C value of phytC from FACE 8E is -21.6 ‰ (n=2).

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 ¹³C 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.