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## Is $^{14}\text{C}$ -AMS analysis of phytoliths a suitable tool?

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

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### I Introduction

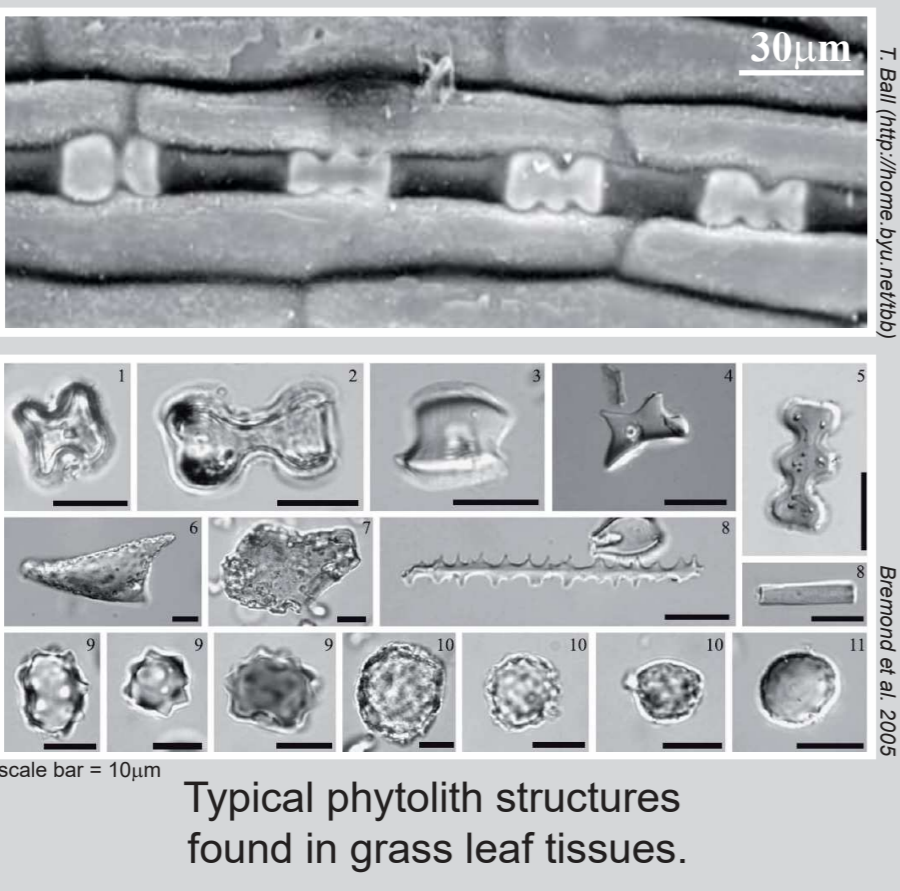
Phytoliths are micrometric amorphous silica particles that form in living plant cells.

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**

- 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

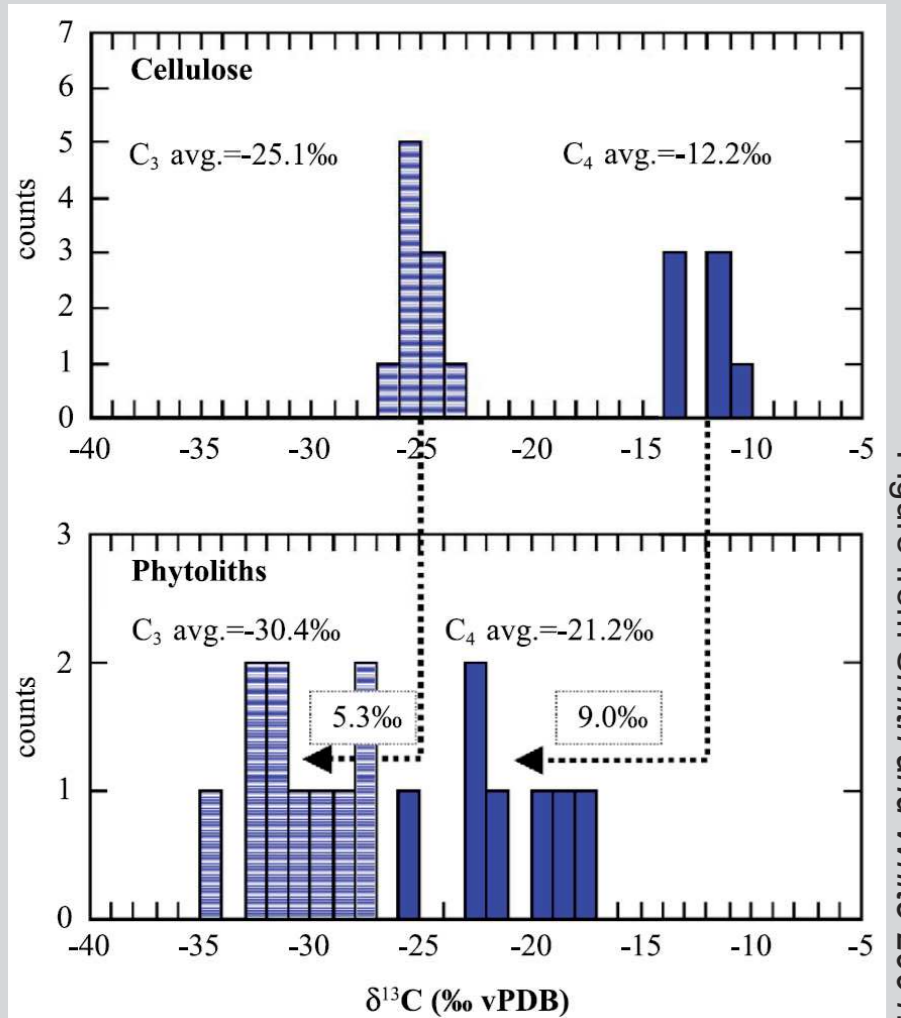
**GC-MS**  
Perry et al. 1987, Pironon et al. 2001, Smith and Anderson 2001.

**Raman spectroscopy**  
Pironon et al. 2001.

**Protein stains + PCR**  
Elbaum et al. 2009.

**<sup>14</sup>C signature**

Attempts were made to use phytC <sup>14</sup>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 <sup>14</sup>C-AMS dating**

- Attempts to obtain **absolute chronologies** (e.g. comparison <sup>14</sup>C-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

**Grass from rural area in Madison, USA**

Bulk plant	Modern (n=2)
Atmospheric CO <sub>2</sub>	Modern (n=1)
phytC	8,040 ± 500 (n=1) yrs BP

**Bulk plant tissues are modern.**

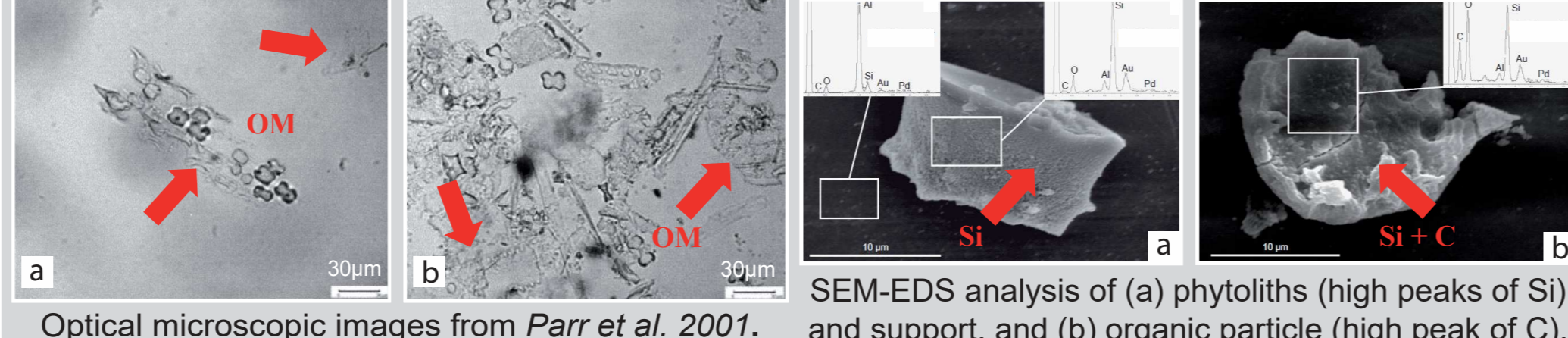
**PhytC always yields ages of several thousand years (from 2,280 BP to 8,040 BP).**

**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 H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O<sub>2</sub> 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).
  - <sup>14</sup>C-AMS analysis of a sample of <sup>14</sup>C free SiO<sub>2</sub> powder subjected to the phytolith extraction procedure as a **BLANK**.
  - <sup>14</sup>C-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 CO<sub>2</sub> Enrichment) experiment at Maricopa, Arizona, during 1998. In these experiments, controlled plots are exposed to enriched CO<sub>2</sub> concentrations with known <sup>14</sup>C and <sup>13</sup>C values.

Sorghum was exposed to fossil CO<sub>2</sub> (dead or <sup>14</sup>C-free) during a full growing season in one hand (**7E FACE**), and to modern CO<sub>2</sub> (modern-air) in the other hand (**8E FACE**). Soils are the same.

**<sup>14</sup>C-AMS target preparation and measurement**

50-300mg of phytoliths and SiO<sub>2</sub> 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).

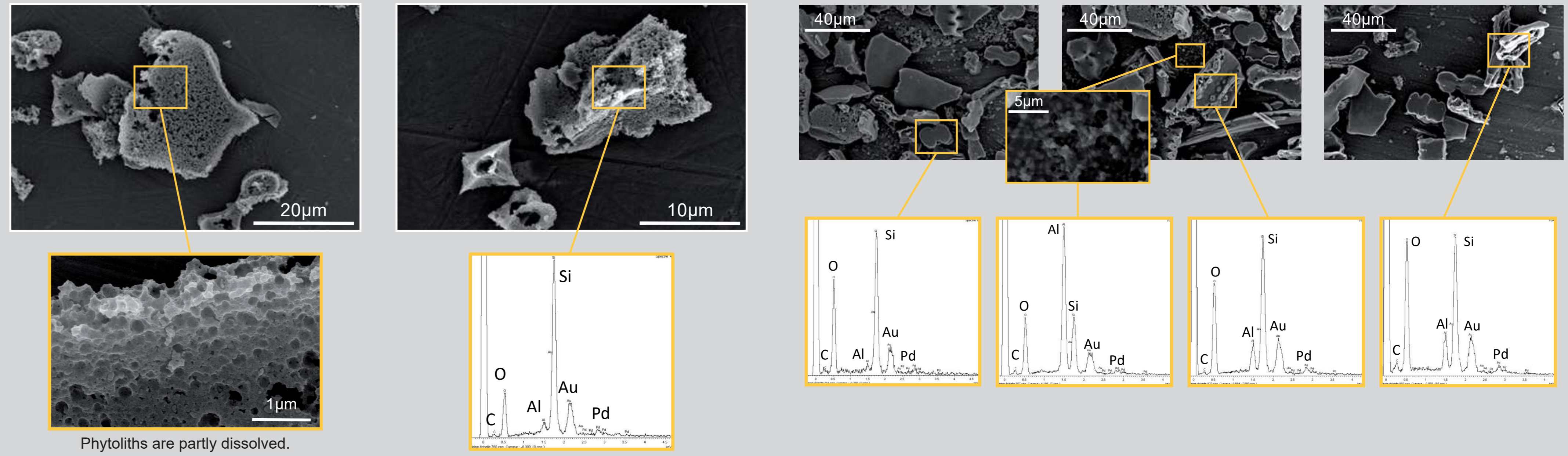
### IV Results

**Two phytolith extraction protocols leading to purity 100%**

**Protocol 1**  
Acid digestion (H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, KClO<sub>3</sub>, KOH). (Combined from Kelly 1999, Piperno 2006, Prior 2005).

**Protocol 2**  
Dry ashing (500°C) + acid digestion (HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>). (Combined from Kelly 1999, Parr et al. 2001, Piperno 2006).

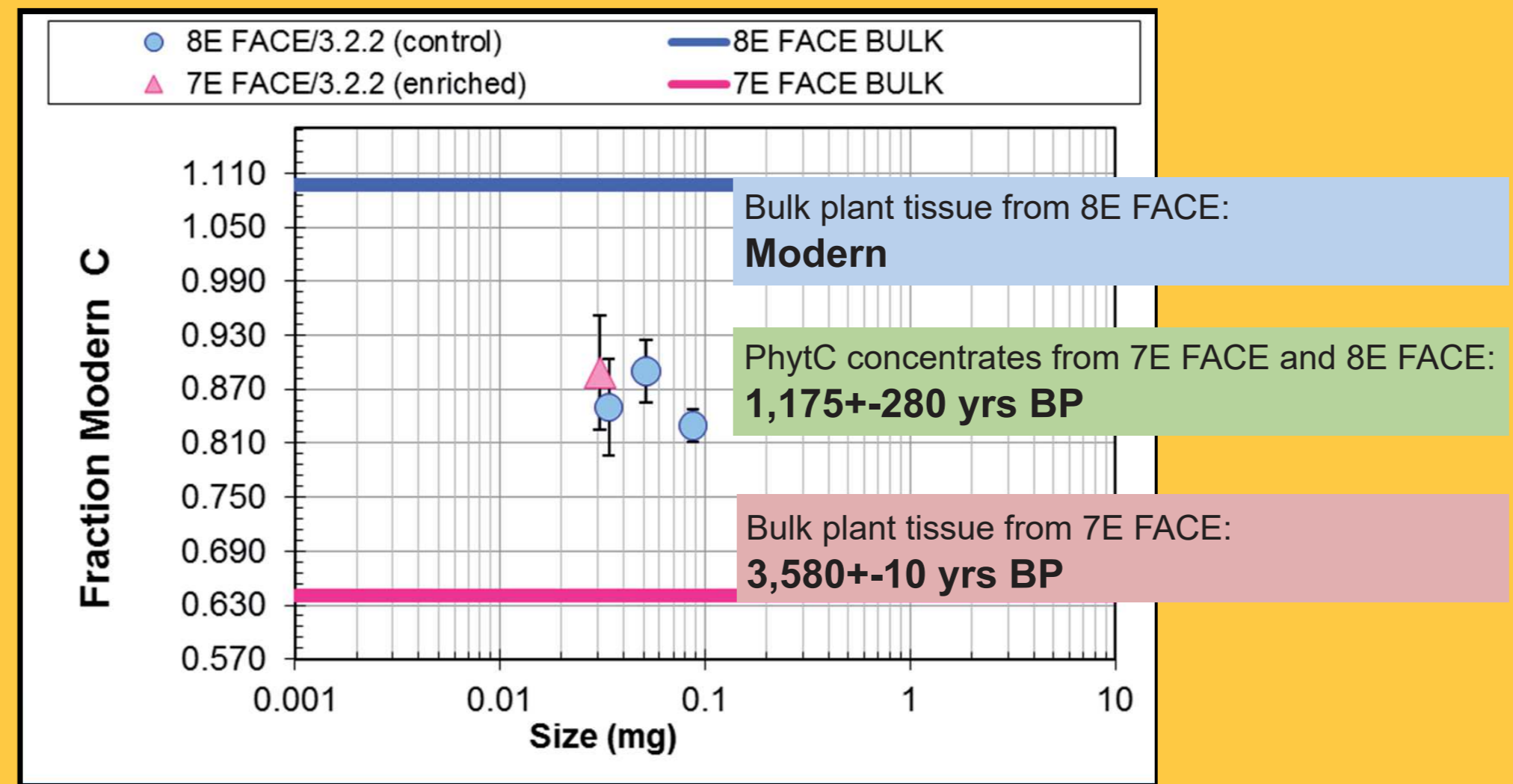
SEM images and EDS analysis of phytoliths (high peak of Si).



Phytoliths are partly dissolved.

- All particles analysed by EDS are siliceous.
- No Ca was analyzed.

**<sup>14</sup>C 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**

**14C-AMS measurements:** <sup>13</sup>C values obtained for bulk plant tissue FACE 7E and 8E are respectively -9.7 ‰ (n=2) and -11.2 ‰ (n=2) while <sup>13</sup>C 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 :

- ➔ <sup>14</sup>C analysis of FACE samples extracted using the same extraction protocols in a different lab (lab 2: UW).
- ➔ <sup>14</sup>C analysis of phytC from archaeological samples of known ages.
- ➔ <sup>14</sup>C analysis of phytC from grass planters fed by nutrients with different <sup>13</sup>C and <sup>14</sup>C values.

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