

Soil Biology & Biochemistry 37 (2005) 117-124

Soil Biology & Biochemistry

www.elsevier.com/locate/soilbio

## Soil carbon sequestration in phytoliths

J.F. Parr\*, L.A. Sullivan

School of Environmental Science and Management, Southern Cross University, Lismore, NSW 2480, Australia

Received 2 December 2003; received in revised form 9 June 2004; accepted 16 June 2004

#### Abstract

The role of the organic carbon occluded within phytoliths (referred to in this text as 'PhytOC') in carbon sequestration in some soils is examined. The results show that PhytOC can be a substantial component of total organic carbon in soil. PhytOC is highly resistant to decomposition compared to other soil organic carbon components in the soil environments examined accounting for up to 82% of the total carbon in well-drained soils after 1000 years of organic matter decomposition. Estimated PhytOC accumulation rates were between 15 and 37% of the estimated global mean long-term (i.e. on a millenial scale) soil carbon accumulation rate of 2.4 g C m<sup>-2</sup> yr<sup>-1</sup> indicating that the accumulation of PhytOC within soil is an important process in the terrestrial sequestration of carbon. The rates of phytolith production and the long-term sequestration of carbon occluded in phytoliths varied according to the overlying plant community. The PhytOC yield of a sugarcane crop was 18.1 g C m<sup>-2</sup> yr<sup>-1</sup>, an accumulation rate that is sustainable over the long-term (millenia) and yet comparable to the rates of carbon sequestration that are achievable (but only for a few decades) by land use changes such as conversion of cultivated land to forest or grassland, or a change of tillage practices from conventional to no tillage. This process offers the opportunity to use plant species that yield high amounts of PhytOC to enhance terrestrial carbon sequestration.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Soil organic carbon; Phytoliths; Terrestrial carbon sequestration; Occluded carbon; Organic matter decomposition

## 1. Introduction

Terrestrial carbon sequestration is fundamental to the global carbon cycle and is being utilised to counter increases in anthropogenic carbon dioxide emissions. Soil organic carbon dominates the terrestrial carbon cycle in terms of total quantity, yet the long-term sequestration of soil organic carbon is relatively low (only  $\sim 0.7\%$  of net primary production) (Schlesinger, 1990). Long-term (decades to millennia) soil organic carbon sequestration mechanisms are thought to be mainly due to the physical protection of chemically recalcitrant organic matter within organomineral complexes (Post and Kwon, 2000), and also to charcoal formation (Skjemstad et al., 1996). Although studies of terrestrial carbon sequestration have often focused on the soil organic carbon fraction, the role of the organic carbon occluded within phytoliths (i.e. PhytOC) in

E-mail address: jparr@scu.edu.au (J.F. Parr).

this process has not yet been examined. This is surprising as phytoliths generally constitute up to 3% of the total soil mass (Drees et al., 1989) and PhytOC is very stable in soil environments (Wilding, 1967; Wilding et al., 1967; Mulholland and Prior, 1993).

Phytoliths, also referred to as plant opal, are silicified features that form as a result of biomineralization within plants. Silica in the soil solution is taken up by plant roots in the form of monosilicic acid (Si(OH)<sub>4</sub>) and subsequently deposited throughout the intra- and extra-cellular structures of their leaf, stem and root systems (Siever and Scott, 1963). Piperno (1988) describes three sites of silica deposition within plant tissue: (1) the cell wall deposits, (2) infillings of the cell lumen, and (3) in intercellular spaces of the cortex. The cell wall deposits of silica often replicate the morphology of the living cells, while those forming in the lumen do not. Such silicification results in the occlusion of carbon within phytoliths (Jones and Milne, 1963). Wilding et al. (1967) considered that the occluded carbon in any phytolith was most likely the original cytoplasmic organic constituents within the plant cell around which in vivo

<sup>\*</sup> Corresponding author. Tel.: +61-2-6620-3789; fax: +61-2-6621-2669.

<sup>0038-0717/\$ -</sup> see front matter @ 2004 Elsevier Ltd. All rights reserved. doi:10.1016/j.soilbio.2004.06.013

silicification had taken place. The organic carbon content of phytoliths can be considerable: for example, the carbon content in phytoliths extracted from oats was from 5.0 to 5.8% (Jones and Milne, 1963) and Wilding et al. (1967) determined the average occluded carbon content of 20–50  $\mu$ m sized phytoliths extracted from a soil in Ohio to be 2.40%. The carbon occluded in phytoliths is highly resistant to oxidation (Wilding et al., 1967).

Whilst many plant species are effective silica accumulators, taking far more silica from the soil solution than would be expected from a consideration of both the monosilicic acid concentration in the soil solution and the transpiration rate, other plant species can effectively exclude monosilicic acid uptake (Marschner, 1995). Marschner (1995) divided the higher plants into three groups according to their silicon content (SiO<sub>2</sub>, expressed as a percentage of shoot dry weight): (1) members of Cyperaceae and wetland species of Gramineae (e.g. rice) with 10-15%, (2) dryland species of Gramineae (e.g. wheat, sugarcane) and a few dicotyledons with 1-3%, and (3) most dicotyledons, especially legumes, with <0.5%. Although silica occurs in many plants, some tree species (Sharma and Rao, 1970; Ter Welle, 1976; Bozarth, 1992) and herbaceous plants such as those of the Poaceae and Cyperaceae are generally considered the most prolific producers of phytoliths (Brown, 1984; Krishnan et al., 2000; Mehra and Sharma, 1965; Mulholland and Rapp, 1992; Parr et al., 2001a; Piperno and Pearsall, 1998; Twiss et al., 1969; Whang et al., 1998). It is also these herbaceous types that generally produce most of the cell wall deposits of silica that contain occluded carbon. As a result, long-term phytolith accumulation rates under grasslands are commonly 5–10 times greater than under forests (Drees et al., 1989).

The rate of phytolith production for a soil will also be affected by factors other than plant species including soil factors (e.g. those that affect the monosilicic acid concentration in the soil solution), climate, and geomorphology (Drees et al., 1989). Drees et al. (1989) found that concentration of phytoliths in soil varied by several orders of magnitude from one region to the next, considered to be in part due to variations in opal yields from plants from 8 to 10 kg ha<sup>-1</sup> yr<sup>-1</sup> in New Mexico (Pease and Anderson, 1969) to 300 kg ha<sup>-1</sup> yr<sup>-1</sup> in Oregon (Norgren, 1973). Although the concentration of phytoliths in soils is generally below 3% on a total soil basis (Drees et al., 1989) some soil horizons are almost completely composed of phytoliths (Riquier, 1960).

Recent studies of carbon occluded in phytoliths have concentrated on radiocarbon dating of fossil phytoliths to establish stratigraphic chronologies for archaeological and palaeobotanical research (Wilding, 1967; Wilding et al., 1967; Mulholland and Prior, 1993) or  $\delta^{13}$ C isotope values to determine palaeovegetation types based on C3 and C4 signatures (Kelly et al., 1991; Ding and Yang, 2000; Krull et al., 2003). This study examines the PhytOC fraction in some tropical and sub-tropical soils from West New Britain and Australia. Underlying the soils in West New Britain are palaeosols formed in volcanic ash layers: the chronology of these layers is well established (Machida et al., 1996) and is augmented here by carbon dating of phytoliths from selected layers. Fresh unaltered ash layers devoid of phytoliths separate the uppermost layers of each palaeosol that have been affected by the accumulation of organic matter and phytoliths (Parr et al., 2001a). Such soil chronosequences offer an ideal opportunity to examine aged PhytOC samples unadulterated by fresh additions, and to examine the stability of the PhytOC fraction in comparison to the remainder of the soil organic carbon against natural decomposition processes over many thousands of years.

#### 2. Methods and materials

### 2.1. Soil sampling sites

Soil samples were gained from six sites from the Numundo Oil Palm Plantation (Lat.:  $5^{\circ}55'S$ , Long.:  $150^{\circ}14'E$ ) on the Williamez Peninsula in West New Britain, Papua New Guinea, and a peat soil from Byron Bay (Lat.:  $28^{\circ}37'52''S$  Long.:  $153^{\circ}35'18''E$ ), in northeastern New South Wales, Australia. The Williamez Peninsula is a wet tropical environment that has been periodically exposed to volcanic activity throughout the late Quaternary period (Blake and McDougall, 1973; Machida et al., 1996) (Table 1). The Numundo sites are situated on volcanic ash deposits. A typical stratigraphy of the volcanic ash deposits and associated buried paleaosols at the Numundo sites is as shown in Fig. 1.

#### 2.2. Soil pH and carbon analysis

Soil pH was measured in a 1:5 soil:water suspension. Soil samples were mechanically milled prior to total carbon and organic carbon analysis. Total Carbon was analysed by LECO CNS 2000. The organic carbon fraction was analysed by the Walkley and Black (1934) method: as organic carbon was determined on finely-ground samples it will also include PhytOC. Soil samples for PhytOC determination were hand-milled with a mortar and pestle and the silica content isolated with Aqua Regia digest in an OI Analytical

ruore r					
Summary of the	stratigraphic	periods at	Numundo	(Torrence et	al., 2000)

Period	Stratigraphic position	Date (years before present)
3	Soil on W-K1 tephra and/or under W-K2 tephra	6000–3500
4	Soil on W-K2 tephra	3500-1800
5	Soil on W-K3 tephra	1800-1200
6	Soil on W-K4 tephra	1200-500
7	Soils associated with the W-H tephra	Less than 500
8	Modern topsoil	Less than 200



Fig. 1. Diagrammatic representation of a typical stratigraphy of the volcanic ash deposits and associated buried paleaosols at the Numundo sites (after Machida et al., 1996).

microwave sample preparation system (Parr, 2002). Sample silica residues were washed in 30% HCl, rinsed with purified water, and air-dried. The silica residues were then analysed by LECO CNS 2000 to determine the PhytOC content.

#### 2.3. Phytolith extraction and identification

Phytoliths were extracted from sediments and herbarium reference material by microwave digestion (Parr et al., 2001b; Parr, 2002). For the Numundo sites a phytolith reference collection comprising a digital image database was established from 81 plant families comprising 213 species found in the study area. A smaller version of a phytolith digital image database was also made for the Byron Bay study area from 30 species. From these data the dominant palaeovegetation types could be established. Sugarcane samples were taken from a field near the Byron Bay site and the phytolith yield determined after microwave digestion (Parr et al., 2001b, Parr, 2002) and the PhytOC content analysed by LECO CNS 2000. The biomass yield of sugarcane (Saccharum officinarum, a known silica accumulator species) in this region is  $110 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ (New South Wales Sugar Milling Cooperative, 2003).

#### 2.4. Radiocarbon dating

Radiocarbon dates were obtained at the Australian Nuclear Science and Technology Organisation by AMS

dating of fossil phytoliths recovered from the samples examined in this study. Samples were prepared by Parr at the ANTARES target preparation laboratory Sydney using standard laboratory procedures (Bird and Gröcke, 1997; Jacobsen et al., 1997).

## 3. Results

#### 3.1. Carbon forms present in the Numundo soil materials

The total carbon and organic carbon concentrations in the Numundo soil layers (Table 1) indicate that in these well-drained soils, the main organic carbon constituents were those sampled by the Walkley-Black method (i.e. readily decomposable organic matter) and that there was only minor charcoal present. Carbonates were absent from all of these Numundo soil layers: all were acidic to neutral with a pH range of 4.9–7.3 with a mean pH of 6.5.

The PhytOC concentrations of the soil layers ranged between 0.032 and 0.603% for the well-drained Numundo sites, and between 0.69 and 5.05% for the poorly drained Byron Bay soil layers. In comparison, the range of PhytOC concentrations for temperate Illinois topsoils is estimated (using the phytolith concentration data of Jones and Beavers (1964) and assuming an average carbon content of phytoliths of 2.40% (Wilding et al., 1967)) to be between 0.02 and 0.46%. It is clear from this data that PhytOC can be a substantial component of the total organic carbon within soil.

## 3.2. Abundance of PhytOC in relation to other soil organic carbon fractions

At the well-drained Numundo sites, the proportion of the PhytOC fraction to total carbon increased considerably over the last 6500 years from levels of <1.0% in one of the youngest layers, to 82% in one of the older layers, whereas the concentrations of the total carbon fraction decreased markedly over this period (Table 2). Although PhytOC was a relatively minor fraction of the soil carbon in the young (<200 years) Numundo topsoils, most of the other soil organic matter components were considerably decomposed in the older topsoils, resulting in PhytOC comprising a mean of 42% of the total carbon pool in these well-drained soils after 1000 years. At the poorly drained Byron Bay site the concentrations of the PhytOC and the other carbon fractions were high in all soil layers examined (from 4540 to 8710 yrs of age) (Table 2). In these Byron Bay soil layers the decomposition process is greatly impeded by the presence of water logged conditions resulting in the accumulation of soil organic matter over the last 8000 years and the consequent formation of peat (Table 1).

Site	Depth layer (m)	Date (years BP)	Total carbon (TC) (%)	Walkley-Black organic carbon (%)	PhytOC (%)	PhytOC/TC (%)	Soil pH
N1	0-0.05	<200#	4.439	4.022	0.032	0.72	5.6
	0.05-0.10	350#	3.003	2.872	0.058	1.93	6.3
	0.20-0.25	< 500#	1.492	1.573	0.064	4.29	6.0
	0.65-0.70	1200*	1.876	1.867	0.079	4.21	6.3
	1.10-1.15	1800*	0.820	0.820	0.091	11.09	6.7
N2	0-0.05	<200#	3.654	3.091	0.297	8.13	5.6
	0.20-0.25	651 <sup>R</sup>	1.793	1.731	0.369	20.58	6.3
	0.60-0.65	1600 <sup>R</sup>	0.426	0.326	0.207	48.59	6.9
	1.40-1.45	1800*	0.319	0.373	0.151	47.34	7.2
	2.10-2.15	3500*	0.363	0.511	0.229	63.09	7.2
N3	0-0.05	<200#	5.849	5.278	0.510	8.72	4.9
	0.30-0.35	< 500#	2.326	2.538	0.442	19.00	6.4
	0.90-0.95	1200*	0.280	0.330	0.190	67.86	7.0
	2.00-2.10	2220 <sup>R</sup>	0.348	0.558	0.287	82.47	6.7
N4	0-0.05	105 <sup>R</sup>	5.350	4.800	0.101	1.89	5.3
	0.05-0.10	460 <sup>R</sup>	2.246	2.125	0.108	4.81	5.9
	2.35-2.40	4040 <sup>R</sup>	0.226	0.426	0.046	20.35	6.8
N5	0-0.05	<200#	4.181	3.697	0.387	9.26	6.0
	0.35-0.40	< 500#	1.226	1.205	0.316	25.77	6.6
	0.70-0.75	1200*	0.639	0.675	0.279	43.66	6.9
N6	0-0.05	165 <sup>R</sup>	3.886	3.686	0.194	4.99	5.6
	0.35-0.40	1020 <sup>R</sup>	1.454	1.620	0.603	41.47	6.8
	0.65-0.70	1200*	0.758	0.836	0.235	31.00	7.2
BB	0.60-0.65	4540 <sup>R</sup>	49.30	11.93	0.959	1.95	3.1
	0.65-0.70		10.86	6.94	0.695	6.40	3.2
	0.85-0.90	5430 <sup>R</sup>	11.43	6.62	1.035	9.06	3.5
	0.90-0.95	6050 <sup>R</sup>	37.97	8.94	0.589	1.55	3.4
	1.10-1.15	6590 <sup>R</sup>	36.36	14.77	5.053	13.90	3.7
	1.15-1.20		29.25	9.71	1.970	6.74	4.4
	1.60-1.65	8710 <sup>R</sup>	14.70	6.29	0.938	6.38	5.1

Dates, carbon fractions and soil pH for soil materials at Numundo and Byron Bay

Dates are presented in years before present (BP), with AMS radiocarbon dates from fossil phytoliths<sup>R</sup>, previously established (Machida et al., 1996) radiocarbon dates\* and dates estimated by stratigraphic relationship<sup>#</sup>. PhytOC/TC is PhytOC as a percentage of total carbon.

## 3.3. Influence of plant community on PhytOC concentration in soil

There was considerable variation in the accumulation of PhytOC in the soil beneath different plant communities. Within the Numundo sites, higher concentrations of PhytOC were recorded at sites (e.g. N3 and N6) where herbaceous plants were dominant as compared to sites that had a larger arboreal component (e.g. sites N1 and N4). Although herbaceous species, particularly Cyperaceae and Poaceae are known to be prolific producers of phytoliths, there are many other plant families currently growing at the Numundo sites that contain phytoliths. A total of 81 plant families comprising 213 species found in the Numundo and Byron Bay study areas were found to contain phytoliths at various levels of abundance (Table 3) from a mere presence of silica to prolific silicification of articulated cells (Fig. 2).

The Numundo sites exhibited a greater phytolith assemblage diversity compared to the Byron Bay site. All sites had phytolith types that were representative of silica deposition in cell walls, infillings of the cell lumen, and from intercellular spaces of the cortex as described by Piperno (1988). The phytolith types that were most frequently observed in each sample studied included those that are commonly reported in Poaceae species such as, bilobates, blocks, bulliforms, elongates, prickles, saddles and also distinctive Cyperaceae phytolith types such as plates with conical decoration and those from seed cases (Fig. 2). However, many other morphotypes made up the total phytolith assemblages of these sites. For example, the Numundo samples contained arboreal types from Arecaceae and Burseraceae such as globular and spinulose spheres, as well as uncommon phytolith types similar to the Asteraceae platelets reported by Bozarth (1992) and distinctive forms found in Musaceae. The Byron Bay soil layers contained phytoliths dominantly from helophytic wetland species and had much higher PhytOC concentrations than the Numundo soil layers where the phytoliths were derived from open hemicryptophytic grassy wetland vegetation. Whether these differences were due primarily to the plant community per se or to the waterlogged conditions at the Byron Bay site that favours the preservation of organic matter is not clear.

Table 2

#### Table 3

Abundance of extracted phytoliths from herbarium specimens assessed visually on glass slides at  $400 \times$  magnification from plant species occurring at both the Numundo and Byron Bay sites

### High

Asteraceae: Vernonia cinerea (L.) Less., Blechcaceae: Blechnum indicucm Burm. F., Cyperaceae: Gahnia sieberana Kunth., Moraceae: Artocarpus cumingiana Trec., Ficus coronata Spin., Myrtaceae: Eucalyptus robusta Smith, Pandanaceae: Pandanus tectorious Solms., Poaceae: Bambusa forbesii (Ridl.) Holttum, Brachiaria brizantha (Hoscht. Ex A. Rich) Stap f., Buergersiochloa macrophylla S.T. Blake, Blumea Supp., Coix lachryma-jobi L., Hetaropogon triticus (R.Br) Stapf. Ex Cralb, Imperata cylindrica P.Beauv., Imperata exaltata (Roxb.) Brogn., Ischaemun polystachyun (L.), Polytoca macrophylla Benth., Saccharum officinarum (L.), Saccharum robustum (L.), Seteria sphacelata (K. Schum.) Stapf. & C.E. Hubb, Schizostachym brachycladum (Blanco) Mer., Themeda arguens (L.) Hack, Thysanolsara maxima (Roxb.) O.K., Pteridophyta: Diplazium esculentum (Retz.) Sw., Rubiaceae: Massaenda ferruginea K. Sch. Var. scandens Val., Timonius sp., Scrophulariaceae: Buchnera tumentosa Bl., Simaroubaceae: Ailanthus integrifolia Lamk.

Annonaceae: Annona muricata L., Arecaceae: Areca catachu L., Caryota rumphiana Mart., Cocas nucifera L. Burseraceae: Canarium indicum L., Combretaceae: Terminalia catappa L., Cucurbitaceae: Bryophyllum pinnatum (Lamk) Kurz., Luffa cylindrica (L.) Roem., Cyperaceae: Cyperus kyllingia Endl., Moraceae: Ficus nodosa Teysm. & Binn, Ficus papus Peekel, Ficus pungens Reinw. ex Bl., Myrtaceae: Eucalyptus maculata Hook., Leptospermum sp., Piperaceae: Piper betal L., Pteridophyta: Nephrolepis hirstulata (Forst.) Presl, Rubiaceae: Massaenda ferruginea K. Sch. Var. scandens Val., Rutaceae: Eucali hortensis J.R.&G. Forst., Sapotaceae: Burckella obovata (Forst.) Pierre, Simaroubaceae: Quassia indica (Gaertn.) Nooteboom Low

Acanthaceae: Hemigraphis reptans (Forst. F.) And. ex Hemsley, Amaranthaceae: Cyathula prostrata Bl., Anarcardiaceae: Dracontomelon dao (Blanco) Merr & Rolfe, Spondias dulcis Soland. ex Forst., Annonaceae: Cananga odorata Hook., Apocynaceae: Alstonia scholaris R. Br., Cerbera manghas L., Ichnocarpus frutescens (L.) R. Br., Araceae: Colocasia esculenta (L.) Schott., Schismatoglottis calyptrata (Roxb.) Zol & Mor., Pothos helwigii Engl., Araliaceae: Polyscias cummingiana (Presl.) F.-Vill., Arecaceae: Licuala peckelii Laut., Metroxylon sagu Rottb., Nypa fruticans Wurmb., Aristolochiaceae: Aristilochia tagala Cham., Barringtoniaceae: Barringtonia asiatica L., Barringtonia novae-hiberniae Laut., Boraginaceae: Cordia subcordia Lamk., Caryophyllaceae: Drymaria cordata (L.) Willd. Ex Roem & Schult., Convolvulaceae: Ipomea batatus L., Ipomea congesta R. Br., Cycadaceae: Cycus rumphii Miq., Cyperaceae: Mapanea macrocephala (Gaud.) K. Sch., Dioscoreaceae: Dioscorea pentaphylla L., Ebenaceae: Diospyros peekelii Laut., Euphorbiaceae: Macaranga aleuritoides F. Muell., Macaranga tararius (L.) Muell.-Arg., Macaranga urophylla Pax & Hoffm., Manihot esculenta Crantz., Fabaceae: Canavalia rosea (Sw.), Casia alata L., Flagallariaceae: Flagallerea gigantia Hook. f., Flagallarea indica L., Flacourtiaceae: Homalium foetidum (Roxb.) Benth., Pangium edule Reinw., Gnetaceae: Gnetum gnemon L., Gnetum latifolium L., Goodeniaceae: Scaevola taccada (Gaertn.) Roxb., Hernandiaceae: Hernandia nymphaefolia (presl) Kubitski, Lamiaceae: Ocimum basilicum L., Lauraceae: Cassytha filiformis L., Litsea grandiflora Teschn., Liliaceae: Cordyline fruiticosa (L.) A. Chev., Cordyline terminalis Kunth, Malvaceae: Hibiscus manihot L., Hibiscus tiliaceus L., Sida rhombifolia L., Marantaceae: Donax canniformis (Forst.) K. Sch., Melastomataceae: Osbeckia chinensis L., Moraceae: Artocarpus cumingiana Trec., Musaceae: Heliconia bihai L., Heliconia indica Lamk., Musa accuminata (simons), Musa becarrii(simons), Musa erecta (simons), Musa paradisica L., Musa peekellii Laut., Musa schizocarpa (simons), Musa truncata var.horizontalis Holtlum., Ensete calosperma F.U.M., Myrtaceae: Syzigium bevicymum (Diels) Merr. & Perry Syzigium malaccence (L.) Merr. & Perry, Nyctaginaceae: Pisonia longirostris Teys. & Binn., Orchidaceae: Dendrobium bifalce Lindl., Dendrobium peekelii schltr., Piperaceae: Piper mestorii F.M. Bail., Piper peekelii C. DC., Pittosporaceae: Pitosporum ferrugineum Ait., Podocarpaceae: Dacrycarpus imbricatus Bl., Proteaceae: Banksia sp., Pteridophyta: Bolbitis quogana (Gaud.) Ching, Rhamnaceae: Alphitonia macrocarpa Mansf., Alphitoria molaccana Reiss. ex Endl., Rhizophoraceae: Brugiera gymnorrhiza (L.) Lamk, Rhizophora apiculata Bl., Rosaceae: Cyolendophora laurina (A. Gr.) Kosterm., Rubus rosaefolius Sm., Rubiaceae: Uncaria bernaysii F. Muell., Sapindaceae: Pometia pinnarta J.R. & G. Forst., Scrophulariaceae: Lindernia crustaceae (L.) F. Muell., Solanaceae: Datura metal L., Solanum erianthum D. Don., Solanum torvum Sw., Sterculiaceae: Heritiera littoralis Dryand ex W. Ait., Kleinhohia hospita L., Melochia odorata L. f., Urticaceae: Dendrocnide warburgii (Winkl.) Chew, Leukosyke capitellata Poir., Pipturus argenteus (Forst.) Wedd., Verbenaceae: Premna serratifolia L., Xanthorrhoeaceae: Xanthorrhoea resinosa Pers.

High: >66% cover of slide, Medium: >33 to <66% cover, and Low: >1 to <33% cover.

#### 3.4. PhytOC accumulation rates

The annual PhytOC accumulation rate over the last 200 years at Numundo can be reasonably estimated for the dated topsoil layers (0–0.05 m) at the N4 and N6 sites both of which have AMS radiocarbon dates from phytoliths. Assuming a bulk density of 1.5 Mg m<sup>-3</sup> for the Numundo soils, the estimated PhytOC accumulation rate for N4 is 0.72 g C m<sup>-2</sup> yr<sup>-1</sup>, whereas for N6 the estimated PhytOC accumulation rate is 0.88 g C m<sup>-2</sup> yr<sup>-1</sup>. Assuming a bulk density of 1.0 Mg m<sup>-3</sup> for the peat soil, for the BB 0.85–0.90 m layer, with an accumulation duration of 620 years, the estimated annual PhytOC accumulation rate is 0.84 g C m<sup>-2</sup> yr<sup>-1</sup>.

The phytolith yield of the sugarcane crop grown near the Byron Bay site was 594 g m<sup>-2</sup> yr<sup>-1</sup>. With a mean organic carbon content within the phytoliths of 3.039%, the PhytOC yield of this sugarcane crop was  $18.1 \text{ g C m}^{-2} \text{ yr}^{-1}$ .

This PhytOC yield is over an order of magnitude greater than the PhytOC accumulation rates for the vegetation growing at the Numundo and Byron Bay sites.

## 4. Discussion

#### 4.1. Resistance of PhytOC against decomposition

Relative to the other soil organic carbon constituents, PhytOC was highly resistant against decomposition in the well-drained Numundo soil environments. Although <10% of the total carbon pool in the contemporary topsoils (with ages of <200 years), the resistance of PhytOC against decomposition processes resulted in PhytOC comprising up to 82% (with a mean of 42%) of the total carbon pool in the buried topsoils after 1000 years of decomposition.



Fig. 2. Fossil phytoliths from the 160–170 cm depth layer of the Byron Bay site dated c.  $8710\pm50$  BP. From A, top left articulated phytoliths and B, top right a seed coat phytolith from a Cyperaceae sp. possibly *Gahnia sieberana* Kunth.. Bottom left C, a bulliform phytolith that resembles those found in Phragmites sp. and D bottom right, a cerate longcell phytolith.

# 4.2. Long-term rate of soil carbon sequestration in phytoliths

The estimated annual PhytOC accumulation rates from the tropical sites (i.e. Numundo) and the sub-tropical site (i.e. Byron Bay) were remarkably similar being the range of 0.72–0.88 g C m<sup>-2</sup> yr<sup>-1</sup>. For comparison, the PhytOC accumulation rate for two temperate soils can be estimated (using the phytolith accumulation data of Jones and Beavers (1964) for the Joy and Cisne soils of 15 g m<sup>-2</sup> yr<sup>-1</sup> and an average carbon content of phytoliths for similar soils in Ohio of 2.40% by Wilding et al. (1967)) to be 0.36 g C m<sup>-2</sup> yr<sup>-1</sup>. These PhytOC accumulation rates are between 15 and 37% of the estimated global mean long-term soil carbon accumulation rate of 2.4 g C m<sup>-2</sup> yr<sup>-1</sup> over the last 10,000 years (Schlesinger, 1990) indicating that in the soils examined PhytOC accumulation is an important process in the long-term sequestration of terrestrial carbon.

### 4.3. Implications for soil carbon turnover models

Soil organic carbon sequestration mechanisms operating over decades to millenia are currently thought to be mainly due to the physical protection of chemically recalcitrant organic matter within organo-mineral complexes (Post and Kwon, 2000), and possibly also to charcoal formation (Skjemstad et al., 1996): the role of PhytOC has not been considered (e.g. Swift, 2001). This is most likely due to the widespread adoption of physical fractionation procedures to define the various soil organic carbon pools in soil organic carbon turnover models. Whilst these procedures have distinct advantages in integrating aspects of the structural and functional properties of soil organic carbon (Christensen, 1996) they do not directly identify nor quantify the PhytOC pool. Given the amount of PhytOC that can accumulate in soil and the stability of this PhytOC against decomposition, it is likely that for many soil materials, PhytOC will constitute a considerable portion of the passive (i.e. old or inert) carbon pool component contained in most soil organic carbon turnover models. Such a passive carbon pool (although not identified by physical fractionation procedures (Post and Kwon, 2000)) has been postulated in order for these models to show agreement with <sup>14</sup>C measurements (Harrison et al., 1993).

## 4.4. Management of PhytOC in soil

The calculated PhytOC accumulation rates in this study are much smaller than the mean carbon sequestration rates calculated for the conversion of formerly cultivated agricultural land to either forest or grassland of  $33.5 \text{ g} \text{ Cm}^{-2} \text{ yr}^{-1}$  (Post and Kwon, 2000) and that resulting from a change of tillage practices from conventional to no tillage of 50.7 g C  $m^{-2}$  yr<sup>-1</sup> (West and Post, 2002). However, the periods of carbon sequestration resulting directly from such land use changes are only for a short duration and carbon sequestration ceases whenever the new soil total carbon equilibrium is established (e.g. within a few decades in the case of the change of tillage practices (West and Post, 2002)). In contrast the data presented here indicates that sequestration of carbon within PhytOC will continue for millenia. In addition, the data presented here demonstrates that whilst most of the carbon sequestered in the short-term by land use changes such as afforestation will be prone to decomposition should that land use change in the future, the accumulation of PhytOC represents a more stable form of sequestered soil carbon.

The difference between plant species (or vegetation types) in their ability to produce PhytOC represents an opportunity to select and grow plant species that yield high amounts of PhytOC in order to enhance long-term terrestrial carbon sequestration. For example, the phytOC yield of the sugarcane crop grown near the Byron Bay site (i.e.  $18.1 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) is comparable to the shortterm rates of carbon sequestration achievable by land use changes such as conversion of cultivated land to forest or grassland (Post and Kwon, 2000), or a change of tillage practices from conventional to no tillage (West and Post, 2002). This data clearly demonstrates that there is an opportunity to enhance both short- and long-term carbon sequestration by cultivation of high PhytOC yielding plant species. This opportunity will be maximised if the other factors affecting phytolith yield from plants, as well as those that enhance phytolith stability in the soil environment, are also optimised. Many of the species known to be prolific producers of phytoliths are economically important plants such as barley, maize, rice, sorghum, sugarcane and wheat (Lanning et al., 1980; Piperno and Pearsall, 1993; Pearsall et al., 1995; Marschner, 1995; Zhao et al., 1998; Yeo et al., 1999).

Afforestation or reforestation of land have both been recently suggested (Fang et al., 2001) to provide benefits in terms of increased carbon sequestration. However, as the long-term phytolith accumulation rates under grasslands are commonly 5–10 times greater than under forests (Drees et al., 1989), the short-term (i.e. decades) carbon sequestration benefits provided by afforestation or reforestation may need to be balanced against a substantially lowered long-term carbon sequestration by PhytOC accumulation under forests.

## 5. Conclusions

The results demonstrate for the soils examined that

- PhytOC can be a substantial component of soil organic carbon;
- (2) PhytOC is highly resistant to decomposition in the soil environment;
- (3) The accumulation of PhytOC is an important process in the terrestrial sequestration of soil carbon;
- (4) The potential exists to greatly enhance PhytOC production and accumulation and as a consequence increase the terrestrial sequestration of carbon.

#### References

- Bird, M.I., Gröcke, D.R., 1997. Determination of the abundance and carbon isotope composition of elemental carbon sediments. Geochimica et Cosmochimica Acta 61, 3413–3423.
- Blake, D.H. McDougall, I., 1973. Ages of the Cape Hoskins volcanoes, New Britain, Papua Guinea. The Journal of the Geological Society of Australia 20, 199–204.
- Bozarth, S.R., 1992. Classification of opal phytoliths formed in selected dicotyledons native to the Great Plains, in: Rapp, G.J., Mulholland, S.C. (Eds.), Phytolith Systematics Emerging Issues. Society for Archaeological Sciences, New York, pp. 193–214.
- Brown, D.A., 1984. Prospects and limits of a phytolith key for grasses in the central United States. Journal of Archaeological Science 11, 345–368.
- Christensen, B.T., 1996. Matching measurable soil organic matter fractions with conceptual pools in simulation models of carbon turnover: revision of model structure, in: Powlson, D.S., Smith, P., Smith, J.U. (Eds.), Evolution of Soil Organic Matter Models. NATO ASI Series 1, vol. 38. Springer, Berlin, pp. 144–160.
- Ding, Z.L., Yang, S.L., 2000. C3/C4 vegetation evolution over the last 7.0 Myr in the Chinese Loess Plateau: evidence from pedogenic carbonate δ13C. Palaeogeography, Palaeoclimatology and Palaeoecology 160, 291–299.
- Drees, L.R., Wilding, L.P., Smeck, N.E., Senkayi, A.L., 1989. Silica in soils: quartz, and disordered silica polymorphs, in: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments, second ed. Soil Science Society of America, Madison, WI, pp. 471–552.
- Fang, J., Chen, A., Peng, C., Zhoa, S., Ci, L., 2001. Changes in forest biomass carbon storage in China between 1949 and 1998. Science 292, 2320–2322.
- Harrison, K.G., Broeker, W.S., Bonani, G., 1993. The effect of changing land use on soil radiocarbon. Science 262, 725–726.
- Jacobsen, G.E., Hua, Q., Tarshishi, F., Fink, D., Hotchkis, M.A.C., Lawson, E.M., Smith, M.A., Tuniz, C., 1997. AMS radiocarbon analysis of microsamples. Handbook of The Sixth Australian Archaeomety Conference, Sydney, Australia 1997 pp. 36–37.
- Jones, R.L., Beavers, A.H., 1964. Aspects of catenary and depth distribution of opal phytoliths in Illinois soils. Soil Science Society of America Proceedings 28, 711–712.
- Jones, L.H.P., Milne, A.A., 1963. Studies of silica in the oat plant. Plant and Soil 43, 207–220.
- Kelly, E.F., Amundson, R.G., Marino, B.D., Deniro, M.J., 1991. Stable isotope ratios of carbon in phytoliths as a quantitative method of monitoring vegetation and climate change. Quaternary Research 35, 222–233.

- Krishnan, S., Samson, N.P., Ravichandran, P., Narasimhan, D., Dayanandan, P., 2000. Phytoliths of Indian grasses and their potential use in identification. Botanical Journal of the Linnean Society 132, 241–252.
- Krull, E.S., Skjemstad, J.O., Graetz, D., Grice, K., Dunning, W., Cook, G.D., Parr, J.F., 2003. <sup>1313</sup>C-depleted charcoal from C3 and C4 grasses and the role of occluded carbon in phytoliths. Organic Geochemistry 34, 1337–1352.
- Lanning, F. C., Hopkins, T. L. Loera, J. C., 1980. Silica and ash content and depositional patterns in tissues of mature Zea mays L. plants. Annals of Botany 45, 549–554.
- Machida, H., Blong, R.J., Specht, J., Moriwaki, H., Torrence, R., Hayakawa, Y., Talai, B., Lolok, D., Pain, C.F., 1996. Holocene explosive eruptions of Witori and Dakataua caldera volcanoes in WNB, Papua New Guinea. Quarternary International 34–36, 65–78.
- Marschner, H., 1995. Mineral Nutrition of Higher Plants, second ed. Academic Press, London. 889pp.
- Mehra, P.N., Sharma, O.P., 1965. Epidermal silica cells in the Cyperaceae. Botanical Gazette 126, 53–58.
- Mulholland, S.C., Prior, C.A., 1993. AMS radiocarbon dating of phytoliths, in: Pearsall, D.M., Piperno, D.R. (Eds.), MASCA Research Papers in Science and Archaeology. University of Pennsylvania, Philadelphia, pp. 21–23.
- Mulholland, S.C., Rapp, G.J., 1992. A morphological classification of grass silica bodies, in: Mulholland, S.C., Rapp, G.J. (Eds.), Phytolith Systematics: Emerging Issues. Plenum Press, New York, pp. 65–89.
- New South Wales Sugar Milling Cooperative Industry Information, 2003. Retrieved November 17th 2003 from http://www.nswsugar.com.au/ PAGES/INDUSTRY.HTM
- Norgren, A., 1973. Opal phytoliths as indicators of soil age and vegetative history. PhD Dissertations. Oregon State University, Corvallis, OR, Dissertation. Abstracts International 33, 3421B.
- Parr, J.F., 2002. A comparison of heavy liquid floatation and microwave digestion techniques for the extraction of fossil phytoliths from sediments. Review of Palaeobotany and Palynology 120, 315–336.
- Parr, J.F., Lentfer, C.J., Boyd, W.E., 2001a. Spatial analysis of phytolith assemblages at an archaeological site in West New Britain, Papua New Guinea. Terra Australis 17, 125–134.
- Parr, J.F., Dolic, V., Lancaster, G., Boyd, W.E., 2001b. A microwave digestion method for the extraction of phytoliths from herbarium specimens. Review of Palaeobotany and Palynology 116, 203–212.
- Pearsall, D.M., Piperno, D.R., Dinan, E.H., Umlauf, M., Zhao, Z. Benfer, J., 1995. Distinguishing rice (Oryza sativa Poaceae) from wild Oryza species through phytolith analysis: results of preliminary research. Economic Botany 49, 183–196.
- Pease, D.S., Anderson, J.U., 1969. Opal phytoliths in Bouteloua Eriopoda Torr. roots and soils. Soil Science Society of America Proceedings 33, 321–322.
- Piperno, D.R., 1988. Phytolith Analysis: An Archaeological and Geological Perspective. Academic Press, London.
- Piperno, D. R. Pearsall, D. M., 1993. Phytoliths in the reproductive structures of Maize and Teosinte: implications for the study of Maize evolution. Journal of Archaeological Science 20,337–362.

- Piperno, D.R., Pearsall, D.M., 1998. The silica bodies of tropical American grasses: morphology, taxonomy, and implications for grass systematics and fossil phytolith identification. Smithsonian Institution Press, Washington, DC.
- Post, W.M., Kwon, K.C., 2000. Soil carbon sequestration and land-use change: processes and potential. Global Change Biology 6, 317–327.
- Riquier, J., 1960. Les phytoliths de certain sols Tropicaux et des podzols. Transactions of the Seventh International Congress of Soil Science, Madison, WI, IV, pp. 425–431.
- Schlesinger, W.H., 1990. Evidence from chronosequence studies for a low carbon storage potential of soils. Nature 348, 232–234.
- Sharma, M., Rao, K.R., 1970. Investigations into the occurrence of silica in Indian timbers. Indian Forester 96, 740–754.
- Siever, R., Scott, R.A., 1963. Organic geochemistry of silica, in: Berger, I.A. (Ed.), Organic Geochemistry. Pergammon Press, Elmsford, NY, pp. 579–595.
- Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., McClure, S.G., 1996. The chemistry and nature of protected carbon in soil. Australian Journal of Soil Science 34, 251–271.
- Swift, R.S., 2001. Sequestration of carbon by soil. Soil Science 166, 858-871.
- Ter Welle, B.J.H., 1976. Silica grains in woody plants of the neotropics, especially Surinam. Leiden Botanical Series 3, 107–142.
- Torrence, R., Pavlides, C., Jackson, P., Webb, J., 2000. Volcanic disasters and cultural discontinuities in the Holocene of West New Britain, Papua New Guinea, in: McGuire, W.G., Griffiths, D.R., Handcock, P.L., Stewart, I.S. (Eds.), The Archaeology of Geological Catastrophes. Geological Society, Special Publications, London, pp. 225–244.
- Twiss, P.C., Suess, E., Smith, R.M., 1969. Morphological classification of grass phytoliths. Soil Science Society of America Proceedings 33, 109–115.
- Walkley, A., Black, I.A., 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Science 37, 29–38.
- West, T.O., Post, W.M., 2002. Soil organic carbon sequestration by tillage and crop rotation: a global data analysis. Soil Science Society of America Journal 66, 1930–1946.
- Whang, S.S., Kim, K., Hess, W.M., 1998. Variation of silica bodies in leaf epidermal long cells within and among seventeen species of Oryza (Poaceae). American Journal of Botany 85, 461–466.
- Wilding, L.P., 1967. Radiocarbon dating of biogenetic opal. Science 156, 66–67.
- Wilding, L.P., Brown, R.E., Holowaychuk, N., 1967. Accessibility and properties of occluded carbon in biogenic opal. Soil Science 103, 56–61.
- Yeo, A. R., Flowers, S. A., Rao, G, Welfare, K., Senanayake, N. Flowers, T. J., 1999. Silicon reduces sodium uptake in rice (Oryza sativa L.) in saline conditions and this is accounted for by a reduction in the transpirational bypass flow. Plant, Cell & Environment 22, 559.
- Zhao, Z., Pearsall, D. M., Benfer, R. A. J. Piperno, D. R., 1998. Distinguishing rice (Oryza sativa Poacea from wild Oryza species through phytolith analysis, II: Finalized method. Economic Botany 52, 134–145.