



Beyond the green: understanding the evolutionary puzzle of plant and algal cell walls

Title	Beyond the green: understanding the evolutionary puzzle of plant and algal cell walls
Author(s)	Popper, Zoë A.; Tuohy, Maria G.
Publication Date	2010-04-26
Publisher	American Society of Plant Biologists
Repository DOI	10.1104/pp.110.158055

Running Head: Plant and algal cell wall diversity

Corresponding Author:

Zoë A Popper

Botany and Plant Science, School of Natural Sciences, National University of
Ireland Galway, Ireland

Tel: +353 91 49 5431

E-mail: zoe.popper@nuigalway.ie

Research category: Invited Update article for Plant Cell Wall Focus Volume

Beyond the green — understanding the evolutionary puzzle of plant and algal cell walls

Zoë A Popper ^a, Maria G Tuohy ^b

^a Botany and Plant Science, School of Natural Sciences, National University of Ireland Galway, Ireland

^b Molecular Glycobiotechnology Group, Biochemistry, School of Natural Sciences, National University of Ireland Galway, Ireland

Financial source: This work was supported by a NUI Galway Millennium Grant to ZAP.

Corresponding author: Zoë A Popper

E-mail address: zoe.popper@nuigalway.ie

Abstract

Plant-environment interactions have been shown to impact directly on the composition of the plant cell wall such that within a single plant the optimal wall composition can vary depending on the developmental stage or tissue type. Diversity in composition also exists between different plant species in a way that can be mapped to key events in land plant evolution including terrestrialisation and vascularisation. However, land plants are not the only photosynthetic organisms to have a cell wall. In fact most photosynthetic organisms, with the exception of the Euglenozoa and some wall-less green algae, have a cell wall; perhaps afforded by virtue of being autotrophic. Photosynthetic organisms originate either from a primary (red and green algae and land plants) or a secondary endosymbiotic (brown algae) event. These endosymbiotic events are thought to have been accompanied by the transference of genes that were either already involved in wall biosynthesis or were subsequently co-opted into the synthesis of cell wall polymers. Emerging evidence suggests that some wall components have ancient origins, some are innovations within a particular lineage, and others have evolved several times. In this update the diversity and patterns of occurrence of specific wall components, along with mechanisms of their biosynthesis, will be discussed in combination with genetic data to support the hypothesis that diversity in extant photosynthetic organisms is a reflection of a medley of evolutionary mechanisms.

Introduction

Niklas (2000) defined 'plants' as 'photosynthetic eukaryotes' thereby including brown, red and green macro- and micro-algae. These groups share several features including the presence of a complex, dynamic and polysaccharide-rich, cell wall. Cell walls in eukaryotes are thought to have evolved by lateral transfer from cell wall producing organisms (Niklas, 2004). Green and red algae originate from a primary endosymbiotic event with a cyanobacterium, which is thought to have occurred over 1500 million years ago (Palmer et al., 2004). Even though extant cyanobacteria have cell walls which are based on a peptidoglycan-polysaccharide-lipo-polysaccharide matrix, and thus differ markedly from the polysaccharide-rich cell walls of plants, there is preliminary evidence that they may contain some similar polysaccharides (Hoiczky and Hansel, 2000) and genes already involved in polysaccharide synthesis or those subsequently co-opted into wall biosynthesis may have been transferred during endosymbiosis. Independent secondary endosymbiotic events subsequently gave rise to the Euglenozoa (which lack cell walls) and brown algae (which have cell walls) (Palmer et al., 2004). Investigations of the diversity of wall composition, structure and biosynthesis which include algae may therefore lend new insights into wall evolution (Niklas, 2004).

Algal cell wall research, in common with that of land plants, has focussed on commercially important species and polysaccharides thus the most well described algal wall components include the commercially and ecologically important laminarans, carrageenans, fucans and alginates (Mabeau and Kloareg, 1997; Campo et al., 2009). However, there are over 35,600 species of seaweed and their cell wall components exhibit enormous diversity (reviewed by Painter, 1983, Kloareg and Quatrano, 1998 and De Reviere, 2002). Even though distinct suites of polysaccharides are known to occur in different taxa such that algal cell wall profiles can be used as taxonomic markers (Parker, 1970; Domozych et al., 1980) some wall components have a wider distribution and are also found in other organisms including land plants.

Renewed interest in plant and algal cell wall composition (Popper and Fry, 2003; Popper and Fry 2004; Niklas, 2004; Vissenberg et al., 2005; Van

Sandt et al., 2007; Fry et al., 2008a and b; Popper, 2008; Sørensen et al., 2008), perhaps driven by potential industrial applications (Pauly and Keegstra, 2008) and a desire to better understand cell wall functions (Niklas, 2004), has been facilitated by the development of several techniques capable of screening cell wall polymers. Increased information has added detail to the diversity known to exist in cell wall composition, generated as organisms adapted to specific niches (Sarkar et al., 2009). However, it is also becoming apparent that similarities, as well as differences, exist between plant and algal cell walls. Examination of the patterns of occurrence of wall components suggests that existing diversity is therefore likely to be a result of a variety of different evolutionary scenarios.

A question of origin

Investigation of the occurrence of wall components and the genes involved in their biosynthesis may suggest whether they are innovations within a particular lineage or have a more ancient origin. Mechanisms of cell wall biosynthesis may have evolved several times, from diversification of gene families, have been retained from ancestral organisms or have been acquired through horizontal gene transfer. Whilst horizontal gene transfer is a rare event (Becker and Marin, 2009) several endosymbiotic events gave rise to photosynthetic organisms (Fig. 1; Keeling et al., 2004; Palmer et al., 2004) and could have been accompanied by transfer of wall biosynthesis genes (Niklas, 2004). It could therefore be expected that some cell wall genes and their products are common to both algae and plants. However, it is likely that the majority of land plant cell wall components are the products of directly inherited genes which have diversified within a particular lineage (Yin et al., 2009).

Convergent evolution — several routes result in similar wall components

The recent discovery of lignin in the cell walls of a red alga, *Calliathron cheilosporioides* (Martone et al., 2009) was surprising for a number of reasons. Most significantly, lignin is normally found in vascular plant cell walls (Table 1) which probably last shared a common ancestor with red algae over a billion years ago (Martone et al., 2009). Furthermore, recorded diversity in

wall composition is usually at a more subtle level and tends to mirror known taxonomic groups, for example the presence of acidic sugar residues in bryophyte xyloglucans (Peña et al., 2008). Thus the existence of a cell wall component in two groups as distantly related as red algae and vascular plants leads us to consider how this may have occurred.

There are several evolutionary scenarios which could explain the occurrence of lignin in red algae and vascular plants; 1) lignin could have evolved independently in both lineages; 2) ancient algal genes leading to lignin biosynthesis could have been co-opted during the evolution of vascular plants (Niklas and Kutschera 2009 and 2010); 3) the lignin biosynthesis pathway may have existed before divergence of the embryophytes and subsequently lost from green algae (Xu et al., 2009); or 4) genes for lignin biosynthesis could have been transferred from one organism to another (Niklas, 2004). Lignin is composed of mono-lignol units. Within vascular plants gymnosperm lignins are composed almost entirely of guaiacyl (G) units whereas angiosperm, lycopod (Jin et al., 2005) and *Calliathron* lignins additionally contain syringyl (S) lignin (Martone et al., 2009). However, S lignins in lycopods and angiosperms, which diverged ~400 million years ago, are derived via distinctly different biosynthetic pathways implying that S units evolved in both plant groups via convergent evolution (Weng et al., 2008 and 2010). Martone et al., (2009) suggest that S-lignin in *Calliathron* could represent another example of convergent evolution; deduction of the lignin biosynthesis pathways in *Calliathron* could lend support to this theory. Conversely, if lignin was discovered in other algal groups it could suggest that lignin biosynthesis in land plants has a more ancient origin.

Another potential example of convergent evolution is (1→3),(1→4)-β-D-glucan (MLG), which has been reported from; lichens (Olafsdottir and Ingolfsdottir, 2001; Honegger and Haisch, 2001); fungi (Burton and Fincher, 2009; Pettolino et al., 2009); green algae (Eder et al., 2008); horsetails (Fry et al., 2008a; Sørensen et al., 2008); and Poales (Trethewey, 2005)(Table 1).

Within land plants MLG was only recently discovered in horsetails (Fry et al., 2008a; Sørensen et al., 2008) and was previously thought to have a restricted taxonomic distribution occurring only in members of the Poales (Trethewey et al., 2005) which last shared a common ancestor with the

horsetails over 370 million years ago (Bell and Hemsley, 2000). However, two independent groups, using several methods, concurrently discovered MLG in *Equisetum* cell walls. Fry et al., (2008a) digested horsetail wall preparations with an MLG-specific enzyme (lichenase, E.C.3.2.1.73) (Parrish et al., 1960). Quantification of the resulting oligosaccharides by high-pressure liquid chromatography revealed that *Equisetum* cell walls contain MLG at levels equal to or greater than that found in members of the Poales (Fry et al., 2008a). The presence of MLG in *Equisetum* cell walls was further supported, and localized within the wall, by monoclonal antibody (mAb)-labelling (Sørensen et al., 2008) with an mAb which has a high degree of specificity to MLG (Meikle et al., 1994). The existence of MLG in horsetails was also found to be correlated with the occurrence of a wall-remodelling enzyme capable of grafting MLG to xyloglucan (Fry et al., 2008b).

The cellulose synthase-like gene families CslF, CslH and CslJ have been shown to be involved in MLG synthesis in grasses (Richmond and Somerville, 2000; Burton et al., 2006; Burton et al., 2008; Doblin et al., 2009). Since these gene families appear to have diverged from within other cellulose synthase-like gene families (Yin et al., 2009) after horsetails had diverged from the lineage which eventually lead to the Poales (Fig. 1)(Yin et al., 2009) it seems likely that MLG arose independently in horsetails and Poales. The existence of an MLG-like polysaccharide in several groups of only distantly related photosynthetic organisms, putatively including the brown algae (Popper et al., unpublished data, Table 1), many of which existed prior to the divergence of the CslF, CslH and CslJ (Yin et al., 2009) further supports multiple origins of the polymer (Burton and Fincher, 2009).

Whilst the mode of MLG synthesis may be different in Poales and *Equisetum* it is of interest to note that the plants share some common morphological and biochemical features. Poales and horsetails exhibit similar body plans (Niklas, 2004). Additionally, they are both known to accumulate silica in their walls (Hodson et al., 2005) which Fry et al., (2008a) suggested may be correlated with the presence of MLG. If this were the case it could be expected that liverworts, which have the highest relative mean shoot concentration of silica in land plants, could also contain MLG (Hodson et al., 2005). In fact, lichenase digestion of a cell wall preparation from the leafy

liverwort *Lophocolea bidentata* has indicated that at least some liverworts may contain a polysaccharide similar to MLG (Popper and Fry, 2003). A Si-transporter and mutants deficient in Si-accumulation have been discovered in rice (Ma et al., 2006). If these plants exhibited alterations in MLG amount or deposition patterns this would lend support to an interaction between MLG and Si.

Diversification within a lineage

Perhaps the best examined cell wall biosynthetic genes are members of the cellulose synthase superfamily which appears to have diversified within the land plant lineage to give nine cellulose synthase-like (Csl) families and one cellulose synthase (CesA family)(Yin et al, 2009).

Cellulose is the most abundant naturally occurring polymer (Hess et al., 1928) and has a widespread distribution being found in plants (Brown, 1985), algae (Naylor and Russell-Wells, 1934), bacteria (Roberts et al., 2002), cyanobacterium (Nobels et al., 2001), and tunicates (Kimura and Itoh, 1995). In land plants cellulose may account for 20–50% w/w (and in specialised cell walls such as cotton fibres up to 98% w/w) of the wall whereas in red algae, it may only account for 1–8% w/w (Kloareg and Quatrano, 1988). CesAs are widespread among eukaryotes and prokaryotes (Tsekos, 1999; Roberts et al., 2002; Roberts and Roberts, 2009) but those which form rosette terminal complexes have only been sequenced from the land plant lineage (Yin et al., 2009) and probably evolved after the divergence of the land plant from the chlorophytes (Yin et al., 2009; Fig. 1). Cellulose in the chlorophyta, and red and brown algae is synthesised by CesA genes whose origin pre-dates that of the plant-specific CesA genes (Yin et al., 2009) and whose products form linear terminal complexes (Tsekos, 1999). Roberts et al., (2002) suggested that observed differences in cellulose microfibril diameter between different cellulose-containing organisms (Nobels et al., 2001) could, at least partially, be as a result of known differences in arrangement of terminal complexes (Tsekos, 1999).

Mannans and glucomannans are synthesised by CslAs (Dhugga et al., 2004; Liepman et al., 2005; Goubet et al., 2009). Whilst CslAs appear to be absent from green algae (Yin et al., 2009) these algae contain a specific Csl

family which is most homologous to land plant CslA and CslC families (Yin et al., 2009)(designated CslA/CslC in Fig. 1). Since mannans are known to occur in green algae including *Codium fragile* (Estevez et al., 2009) and *Acetabularia acetabulum* (Dunn et al., 2007) the products of CslA/CslC could be responsible for mannan synthesis. CslA/CslC appears to be absent from brown and red algae (Yin et al., 2009) (Fig. 1) suggesting that an absence of reports for mannans in brown algae (Table 1) could be due to a lack of the required biosynthetic machinery. However, some red algae have been reported to contain mannans (Percival et al., 2001). The genes responsible for mannan synthesis in red algae may not be CslAs or their sequences may differ significantly from CslAs such that they were not detected in the screen used by Yin et al. (2009). *Ostreococcus*, an ancient member of the 1,500 million year old green lineage and the smallest known eukaryote (Derelle et al., 2006), was the earliest diverging organism found to contain CslA/CslC (Yin et al., 2009). Although *Ostreococcus* is wall-less the existence of the products of CslA/CslC may be involved in cell-surface glycosylation which Palenik et al., (2003 and 2007) suggest may help disguise them from grazers. Taken in the context of a lack of all other plant-like Csl genes (Yin et al., 2009), the existence of a gene responsible for mannan synthesis in green algae and the subsequent evolution of a specific family of CslA genes suggests that the presence of mannan in their cell walls could have facilitated the success and diversification of green algae.

Ancient origins

Xylans represent a case for the possibility that some plant cell wall components are derived from genes that existed before the divergence of green and red algae. Xylans are found ubiquitously in vascular plants and appear to be present in hornworts (Carafa et al., 2005), charophycean green algae (CGA) (Domozych et al., 2009), chlorophytes and red algae (Lahaye et al., 2003); suggesting that they have a cosmopolitan distribution among cell walls of photosynthetic organisms (Table 1). Xylans can either be (1→3) or (1→4)-linked. Painter (1983) hypothesised that red algae were at an evolutionary branch point as some red algae including the relatively basal *Bangia fuscopurpurea* are composed of (1→3) linkages while others, such as

the more recently diverged *Palmaria palmata*, have been suggested to contain both (1→3) and (1→4) linkages in the same molecule (Turvey and Williams, 1970). Potentially, green algae and land plants derived the genes for (1→4)-β-D-xylan synthesis from red algae. Additionally, whilst many land plant cell wall polysaccharides appear to be synthesised by Csl's which diverged after green algae (Yin et al., 2009; Fig. 1) evidence for the involvement of Csl's in xylan biosynthesis appears to be lacking (Zhou et al., 2006). Instead a large number of glycosyl transferases including; FRA8 (GT47; GT numbers refer to those designated by the CAZy database, <http://www.cazy.org>; Cantarel et al., 2009), IRX8 and PARVUS (GT8), and IRX9 and IRX14 (GT43) are implicated (Brown et al., 2005 and 2007; Lee et al., 2007; Peña et al., 2007; York and O'Neill, 2008). Querying the CAZy database (<http://www.cazy.org>; Cantarel et al., 2009) reveals that *Ostreococcus* (the smallest known eukaryote and a member of the prasinophycean green algae) appears to lack members of the GT43 family (Hashimoto et al., 2009) thought to be involved in xylan backbone synthesis (Lee et al., 2007). *Ostreococcus* contains several other glycosyl transferases (<http://www.cazy.org>; Cantarel et al., 2009) which could have a role in xylan synthesis including; GT8 (which is involved in glucuronoxylan synthesis, Lee et al., 2007) and GT4, which includes a 1,4-β-D-xylan synthase (EC 2.4.2.24; Bailey and Hassid, 1966), thus supporting an origin for xylan biosynthesis which predates the land plant lineage.

Another group of wall components which appear to have ancient origins are arabinogalactan proteins (AGPs); a group of proteoglycans which exhibit considerable structural and functional diversity and are thought to occur ubiquitously in land plants (Basile, 1980; Basile et al., 1989; Pennell et al., 1989; Knox et al., 1991; Lee et al., 2005). However, they may be much more widely distributed. Immunolabelling and chemical analyses have suggested their occurrence in the CGA (McCann et al., 2007; Domozych et al., 2009), and chlorophytes (Stanley et al., 2005; Eder et al., 2008; Estevez et al., 2009). We have also detected AGPs in extracts from red and brown algae using the radial gel diffusion assay (Popper et al., unpublished data). At least some AGP functions may be conserved between taxa; localisation of AGPs in the utricle apical zone in *C. fragile* (Estevez et al., 2009) may suggest a role in

tip growth which correlates with their reported involvement in tip growth of moss protonemata (Lee et al., 2005).

The model organism, *Chlamydomonas*, which is a flagellated green alga, has walls which are substantially different from those of land plants not least because they seem to lack cellulose (Roberts, 1974). Instead the major wall components are layers of crystalline arabinose-rich hydroxyproline-rich glycoproteins (Miller et al., 1974; Roberts, 1974; Bolling et al., 2007). However, closer examination of the *Chlamydomonas* glycoproteins shows that they appear to share some features with AGPs including conservation of an inner core of two arabinose residues linked to hydroxyproline (Bollig et al., 2007). This lends support to the argument for a degree of conservation between plant and algal wall components. It also highlights the need for extensive sampling as some green algae share other wall features with land plants (Fig 1).

Possible innovations

RGII is perhaps the most distinct example of an innovation in wall composition to have occurred in land plants. It has a highly conserved structure and is present in all vascular plants (Match et al., 1996) but if present in extant bryophytes it constitutes less than 0.025% w/w of the wall (Matsunaga et al., 2004). Since RGII has not been detected in green algae (Domozych et al., 1980; Becker et al., 1994 and 1998) it seems likely that its occurrence in land plants could be correlated with specific evolutionary pressures potentially related to terrestrialisation. However, the ability to make some of the relatively unusual monosaccharide residues present in RGII, such as 3-deoxy-D-manno-2-octulosonic acid (Kdo) (York et al., 1985), may have deeper origins. Most members of the prasinophyceae have scales or a theca (wall) containing Kdo (York et al. 1985; Becker et al., 1991; Domozych et al., 1991). CMP-Kdo synthetase (CKS) is responsible for generating the activated sugar donor CMP-Kdo required for synthesis of wall polymers containing Kdo and sequences for the CKS gene are present in every major plant group including mosses (Royo et al., 2000). Neither Kdo nor CKS has been found in animals or yeasts. However, they are both present in gram negative eubacteria (Royo et al., 2000) where they probably represent an example of

horizontal gene transfer either from the bacteria to the plant or, more unusually, from the plant to the bacteria (Royo et al, 2000). It is of interest to note that a putative Kdo transferase gene (AtKDTA)(Séveno et al., 2010) has recently been characterised. However, AtKDTA appears to represent an example of a gene that was not transferred from a bacterium (in this case the ancestor of mitochondria) to a plant following an endosymbiotic event. The evidence for this is that AtKDTA synthesises a protein which localises to the mitochondria, where Séveno et al. (2010) hypothesise that it may be involved in synthesis of a lipid A-like molecule. More significantly, in terms of plant cell wall synthesis, AtKDTA null mutants appear to have an unaltered phenotype and conserved RGII structure and amount implying that AtKDTA is unlikely to be involved in RGII synthesis (Séveno et al., 2010).

Xyloglucan may also represent a relatively recent innovation. It is present in all land plants (Popper and Fry, 2003; Popper and Fry, 2004) and immunolabelling suggests that it may be present in some members of the CGA (Ikegaya et al., 2008; Domozych et al., 2009). Occurrence of xyloglucans in other photosynthetic organisms is unknown (Table 1). In addition the enzymes involved in xyloglucan synthesis appear to have continued to diversify within the land plants. This is suggested by the discovery that moss and liverwort xyloglucans contain galacturonic acid and are structurally distinct from xyloglucans synthesised by vascular plants and hornworts (Peña et al., 2008). There are also several xyloglucan side-chains which may be restricted to the relatively recently diverged Asteridae (Hoffman et al., 2005). Furthermore, activity of the enzyme xyloglucan endotransglucosylase (XET), involved in xyloglucan modification (Thompson and Fry, 2001) and consequently plant growth and differentiation (Vissenberg et al., 2005), was found in the chlorophyte, *U. linza*, but appeared to be absent from red and brown algae (Van Sandt et al. 2007). This suggests that xyloglucan or a structurally similar polysaccharide does not occur in the cell walls of either red or brown algae.

Pectins or pectin-like polymers appear to have a relatively cosmopolitan occurrence and are found in red and green algae as well as land plants (Painter, 1983; Domozych et al., 2007; Eder and Lütz-Meindl, 2008). A polysaccharide has even been isolated from the cyanobacterium

Microcystis flos-aquae which contains the monosaccharide residues galacturonic acid, rhamnose, mannose, xylose, glucose and galactose in a similar molar ratio to that found in pectin, although the degree of structural similarity has not been determined (Plude et al., 1991). However, arabinans might be expected to be a land plant innovation. Specifically, they could be predicted to occur only in hornworts and vascular plants because they have been implicated in stomatal opening (Jones et al., 2005). However, LM6, a mAb which recognises short linear stretches of arabinosyl residues, not only labels guard cell walls (Jones et al., 2005) but has also been found to bind to *Chara* cell walls (Domozych et al., 2009). The recruitment of arabinans in guard cell function might therefore be an example of co-option in function of a pre-existing wall polymer.

Sampling cell wall diversity

Correlating the occurrence of genes and wall components with phylogenies, as given for CesA and Csl's (Fig. 1), undoubtedly has the potential to reveal new insights into wall evolution. However, as discussed by Sørensen et al. (2010) it is dependant on adequate sampling. This could be approached by the detailed analysis of representative plants but screening may help to optimise which plants are selected for further analysis. With conservative estimates of 260,000 vascular plant species alone (Judd et al., 2002; AGP, 2003) investigation of the cell wall composition of photosynthetic organisms necessarily demands a high throughput approach (Sørensen et al., 2010). The total number of samples is further expanded by taking into consideration variation between tissues and with stage in the life cycle (Sørensen et al., 2010). For example, based on analysis of the products released by enzyme digestion of vegetative cells xyloglucan was thought to be absent from *Chara* (Popper and Fry, 2003). However, more recent evidence provided by mAb labelling suggests that xyloglucan may occur in the walls of *Chara* antheridia (Domozych et al., 2009). Additional evidence will be necessary to determine whether xyloglucan actually does occur in *Chara* cell walls because although an anti-xyloglucan mAb was capable of recognising and binding to an epitope present in *Chara* cell walls that epitope could be part of a polymer which is not xyloglucan.

Several techniques have been developed which could greatly facilitate investigation of wall diversity, including Fourier-transform Infrared microspectroscopy (FT-IR) (Mouille et al., 2003), Oligosaccharide Mass Profiling (OLIMP) (Obel et al., 2006) and Comprehensive Microarray Polymer Profiling (CoMPP) (Willats et al., 2002; Sørensen et al., 2008).

FT-IR is capable of generating a fingerprint which can distinguish between *Arabidopsis* mutants with altered cellulose, pectin and xyloglucan compositions (Mouille et al., 2003). This method could be extended to profile different taxa. However, peaks may shift depending on molecular interactions and the environment within the wall (Kačuváková et al., 2000); a phenomenon which is likely to be even more pronounced between distantly related taxa making unambiguous peak assignment and attribution difficult.

OLIMP utilises highly specific hydrolases to digest wall components (Obel et al., 2006). The digestion products are then analysed by MALDI-TOF-MS and structural differences are indicated by changes in observed ions (Obel et al., 2006). This method has been applied to the investigation of *Arabidopsis* cell wall polysaccharides (Obel et al., 2006; Gille et al., 2009) but could be extremely valuable for screening for the existence of structural differences between polysaccharides within diverse plant taxa. Polysaccharides with unknown or unusual structures could then be subjected to further and more detailed methods of analysis. However, structural analysis of a cell wall component, using OLIMP, is dependant on its ability to be hydrolysed and in some taxa a wall component could be present but resist hydrolysis. We recently found that several species of brown algae can be labelled with a mAb which has a high specificity for (1→3),(1→4)-β-D-glucan (Meikle et al., 1994; Popper et al., unpublished data). In addition polysaccharides extracted from the wall using strong alkali could be digested with lichenase. But, digestion of brown algal cell walls with lichenase prior to labelling did not prevent the anti-MLG mAb from binding (Popper et al., unpublished data). It seems likely that digestion was prevented by the presence of high concentrations of wall-bound phenolic compounds (Schoenwaelder and Clayton, 1999; Schoenwaelder and Clayton, 1998) which have been shown to inhibit enzyme activity (Barwell et al., 1989; Shibata et al., 2003).

To date CoMPP is the technique which has been most extensively applied toward screening cell wall diversity (Sørensen et al. 2008) and has already resulted in some interesting discoveries such as the presence of MLG in *Equisetum* (horsetail) cell walls (Sørensen et al., 2008) as discussed earlier.

Using, CoMPP an indication of the likely presence of specific cell wall components within a particular plant species, tissue, or developmental stage is dependant on the reaction of extracted wall components with mAbs or carbohydrate binding molecules (CBMs)(Moller et al., 2007). Thus availability of mAbs and CBMs currently limits the full potential of CoMPP. Increased numbers of mAbs, which are continuing to become available (Pattathil et al., 2010), will increase the power of CoMPP and greatly facilitate analysis of cell wall diversity. The majority of cell wall specific-mAbs were generated against polysaccharides isolated from flowering plant cell walls but there are exceptions including those generated against polysaccharides from brown seaweeds (Vreeland, 1972; Vreeland et al., 1982; Vreeland et al, 1984). Furthermore, each mAb detects a specific epitope wherever it occurs although interpretation may be complicated by the fact that the epitope recognised by a mAb can exist in different wall components in different taxa.

CoMPP is frequently followed by more extensive characterisation of the cell wall using a variety of techniques to both confirm and add detail to the initial results (Sørensen et al., 2008; Sørensen et al., 2010). *In situ* methods enable investigation of the wall components in their native environment facilitating exploration of their intramural associations.

One of the most frequently used *in situ* methods is labelling using mAbs or CBMs. This method can map the tissue specific location of cell wall components and when used in concert with advanced microscopy techniques such as electron tomography can even enable three-dimensional visualization of a component within the wall (Mastrorarde, 1997; Otegui et al., 2001; Otegui and Staehlin, 2004; Segui-Simarro et al., 2004;). It has been found that the presence of high concentrations of pectin can mask, or prevent, mAb-labelling of xyloglucan (Marcus et al., 2008). Whilst the phenomenon of masking complicates interpretation of mAb-labelling it also yields details regarding interactions between wall components which can be unveiled by a strategy

which combines specific enzyme digestion with mAb-labelling (Marcus et al., 2008). Further complications could arise from the presence of cell wall components which render hydrolytic enzymes inactive. However, mAb-labelling can also be combined with a variety of chemical pre-treatments; incubation of *Fucus* sections in EDTA prior to mAb-labelling was found to improve antibody penetration (Vreeland et al., (1984).

Conclusion

Becker and Marin (2009) stated that they were 'convinced that many plant 'innovations' will actually turn out to be innovations of the streptophyte algae' whereas Niklas (2004) suggested that some plant cell wall features may have even deeper roots and share origins with more ancient algal ancestors. Both hypotheses may be true for different wall components.

Despite the fact that the chlorophytes and streptophytes (land plants and CGA) last shared a common ancestor 725–1200 million years ago (Becker and Marin, 2009), it appears that through a combination of shared ancestry and convergent evolution they have some common cell wall characteristics. They also share some wall features with red and brown algae (summarised in Table 1) to which they are even more distantly related (Yoon et al., 2004). Therefore, whilst cell wall differentiation may have been of high adaptive importance (Stebbins, 1992), it appears that a degree of conservation also exists. Further characterisation of plant and algal cell wall polysaccharides and the enzymes which synthesise them may reveal the existence of core features common to eukaryotic cell walls, despite the presence of different co-occurring cell wall components and diverse intramural interactions.

Acknowledgements

We thank the editor and reviewers for their helpful comments and suggestions and David Domozych, Iben Sørensen and William Willats for allowing us to read a pre-edition of 'How did plant cell walls evolve?'

Literature Cited

- Andrew IG, Little JWL** (1997) A xyloglucan isolated in etiolated seedlings of *Pinus radiata*. *Phytochemistry* **46**: 203–207
- Angiosperm Phylogeny Group** (2003) An update of the Angiosperm Phylogeny Group for the orders and families of flowering plants: APGII. *Bot J Linn Soc* **141**: 399–436
- Bacic A, Harris PJ, Stone BA** (1988) Structure and function of plant cell walls. P297–371 In *The biochemistry of plants. Volume 14: Carbohydrates*. Editor J Preiss. Academic Press, San Diego
- Bailey RW, Hassid WZ** (1966) Xylan synthesis from uridine-diphosphate-D-xylose by particulate preparations from immature corncobs. *PNAS* **56**: 1586–1593
- Baldan B, Andolfo P, Navazio L, Tolomio A, Mariani P** (2001) Cellulose in algal cell wall: an '*in situ*' localization. *Eur J Histochem* **45**: 51–56
- Barwell CJ, Blunden G, Manandhar PD** (1989) Isolation and characterization of brown algal polyphenols as inhibitors of α -amylase, lipase and trypsin. *J App Phycol* **1**: 319–323
- Basile DV** (1980) A possible mode of action for morphoregulatory hydroxyproline-proteins. *Bull Torr Bot Club* **107**: 325–338.
- Basile DV, Kushner BK, Basile MR** (1989) A new method for separating and comparing arabinogalactan proteins in the *Hepatica*. *Bryologist* **90**: 401–4
- Becker B, Becker D, Kamerling JP, Melkonian M** (1991) 2-Keto-sugar acids in green flagellates: a chemical marker for prasinophyte scales. *J Phycol* **27**: 498–504
- Becker B, Marin B, Melkonian M** (1994) Structure, composition, and biogenesis of prasinophyte cell coverings. *Protoplasma* **181**: 233–244
- Becker B, Melkonian M, Kamerling JP** (1998) The cell wall (theca) of *Tetraselmis striata* (Chlorophyta): macromolecular composition and structural elements of the complex polysaccharides. *J Phycol* **34**: 779–787
- Becker B, Marin B** (2009) Streptophyte algae and the origin of the embryophytes. *Ann Bot* **103**: 999–1004

- Bell PR, Hemsley AR** (2000) Green plants: their origin and diversity. Cambridge University Press, Cambridge, UK
- Bollig K, Lamshöft M, Schweimer K, Marnier F-J, Budzikiewicz H, Waffenschmidt S** (2007) Structural analysis of linear hydroxyproline-bound O-glycans of *Chlamydomonas reinhardtii* — conservation of the inner core in *Chlamydomonas* and land plants. *Carbohydr Res* **342**: 2557–3566
- Bourne EJ, Brush P, Percival E** (1969) The active carbohydrate metabolites of the brown seaweed, *Fucus vesiculosus*. *Carbohydr Res* **9**: 415–422
- Bremner I, Wilkie KCB** (1971) The hemicelluloses of bracken. II. A galactoglucomannan. *Carbohydr Res* **20**: 193–203
- Brown DM, Zeef LAH, Ellis J, Goodacre R, Turner SR** (2005) Identification of novel genes in Arabidopsis involved in secondary cell wall formation using expression profiling and reverse genetics. *Plant Cell* **17**: 2281–2295
- Brown DM, Goubet F, Wong VW, Goodacre R, Stephens E, Dupree P, Turner SR** (2007) Comparison of five xylan synthesis mutants reveals new insight into the mechanisms of xylan synthesis. *Plant J* **52**: 1154–1168
- Brown RM Jr** (1985) Cellulose microfibril assembly and orientation: recent developments. *J Cell Sci Suppl* **2**: 13–32
- Burton RA, Wilson SM, Hrmova M, Harvey AJ, Shirley NJ, Medhurst A, Stone BA, Newbigin EJ, Bacic A, Fincher GB** (2006) Cellulose synthase-like *CsIF* genes mediate the synthesis of cell wall (1,3;1,4)- β -D-glucans. *Science* **311**: 1940–42
- Burton RA, Jobling SA, Harvey AJ, Shirley NJ, Mather DE, Bacic A, Fincher GB** (2008) The genetics and transcriptional profiles of the cellulose synthase-like HvCsIF gene family in barley (*Hordeum vulgare* L.). *Plant Physiol* **146**: 1821–33
- Burton RA, Fincher GB** (2009) (1,3;1,4)- β -D-Glucans in the cell walls of the Poaceae, lower plants, and fungi: a tale of two linkages. *Mol Plant* **2**: 873–82

- Campo VL, Kawano DF, Da Silva DB Jr, Carvalho I** (2009) Carrageenans: biological properties, chemical modifications and structural analysis — a review. *Carbohydr Polymers* **77**: 167–180
- Cantarel BL, Coutinho PM, Rancurel C, Bernard T, Lombard V, Henrissat B** (2009) The Carbohydrate-Active EnZymes database (CAZy): an expert resource for glycogenomics. *Nucleic Acids Res* **37**: D233–238
- Carafa A, Duckett JG, Knox JP, Ligrone R** (2005) Distribution of cell-wall xylans in bryophytes and tracheophytes: new insights into basal interrelationships of land plants. *New Phytol* **168**: 231–40
- Carpita NC, Defernez M, Findlay K, Wells B, Shoue DA, Catchpole G, Wilson RH, McCann MC** (2001) Cell wall architecture of the elongating maize coleoptile. *Plant Physiol* **127**: 551–65
- Chodat F, Cortesi R** (1939) Sur la coloration des membranes de mousses. *Compt Rend Soc Phys Nat Genève* **5C 21**: 58–61
- Currie HA, Perry CC** (2007) Silica in plants: biological, biochemical and chemical studies. *Ann Bot* **100**: 1393–1389
- Delwiche CF, Graham LE, Thomson N** (1989) Lignin-like compounds and sporopollenin in *Coleochaete*, an algal model for land plant ancestry. *Science* **245**: 399–401
- De Reviere B** (2002) *Biologie et phylogénie des algues*. Tome 1. p144–165. Belin, Paris
- Derelle E, Ferraz C, Rombauts S, Rouzé P, Worden AZ, Robbens S, Partensky F, Degroeve S, Echeynián S, Cooke R, Saeys Y, Wuyts J, Sabbart K, Bowler C, Panaud O, Piégu B, Ball SG, Ral J-P, Bouget F-Y, Piganeau G, De Baets B, Picard A, Deldseny M, Demaille J, Van de Peer Y, Moreau H** (2006) Genome analysis of the smallest free-living eukaryote *Ostreococcus tauri* unveils many unique features. *PNAS* **103**: 11647–11652
- Dhugga KS, Barreiro R, Whitten B, Stecca K, Hazeebrook J, Randhawa GS, Dolan M, Kinney AJ, Tomer D, Nichols S, Anderson P** (2004) Guar seed β -mannan synthase is a member of the cellulase synthase super gene family. *Science* **303**: 363–366
- Doblin MS, Pettolino FA, Wilson SM, Campbell R, Burton RA, Fincher GB, Newbigin E, Bacic A** (2009) A barley *cellulose synthase-like CSLH*

- gene mediates (1,3;1,4)- β -D-glucan synthesis in transgenic *Arabidopsis*. PNAS **14**: 5996–6001
- Domozych DS, Stewart KD, Mattox KR** (1980) The comparative aspects of cell wall chemistry in the green algae (chlorophyta). J Mol Evol **15**: 1–12
- Domozych DS, Wells B, Shaw PJ** (1991) The basket scales of the green alga *Mesostigma viridae*: chemistry, immunology and ultrastructure. J Cell Sci **100**: 297–407
- Domozych DS, Serfis A, Kiemle SN, Gretz MR** (2007) The structure and biochemistry of charophycean cell walls. I. Pectins of *Penium margaritaceum*. Protoplasma **230**: 99–115
- Domozych DS, Sørensen I, Willats WGT** (2009) The distribution of cell wall polymers during antheridium development and spermatogenesis in the charophycean green alga, *Chara corallina*. Ann Bot **104**: 1045–56
- Dunn EK, Shoue DA, Huang X, Kline RE, Mackay AL, Carpita NC, Taylor IEP, Mandoli DF** (2007) Spectroscopic and biochemical analysis of regions of the cell wall of the unicellular ‘mannan weed’, *Acetabularia acetabulum*. Plant Cell Physiol **48**: 122–33
- Edashige Y, Ishii T** (1996) Structures of cell-wall polysaccharides from suspension-cultured cells of *Cryptomeria japonica*. Mokuzaï Gakkaishi **42**: 895–900
- Eder M, Lütz-Meindl U** (2008) Pectin-like carbohydrates in the green alga *Micrasterias* characterized by cytochemical analysis and energy filtering TEM. J Microscopy **231**: 201–214
- Eder M, Tenhaken R, Driouich A, Lütz-Meindl U**. 2008. Occurrence and characterization of arabinogalactan-like proteins and hemicelluloses in *Micrasterias* (Streptophyta). J Phycol **44**: 1221–34
- Estevez JM, Fernández PV, Kasulin L, Dupree P, Ciancia M** (2009) Chemical and in situ characterization of macromolecular components of the cell walls from the green seaweed *Codium fragile*. Glycobiology **19**: 212–28
- Fincher GB** (2009) Revolutionary times in our understanding of cell wall biosynthesis and remodelling in the grasses. Plant Physiol **149**: 27–37

- Fry SC, Nesselrode BH, Miller JG, Mewburn BR** (2008a) Mixed-linkage (1→3, 1→4)-β-D-glucan is a major hemicellulose of *Equisetum* (horsetail) cell walls. *New Phytol* **179**: 104–15
- Fry SC, Mohler KE, Nesselrode BHWA, Franková L** (2008b) Mixed-linkage β-glucan: xyloglucan endotransglucosylase, a novel wall-remodelling enzyme from *Equisetum* (horsetails) and charophytic algae. *Plant J* **55**: 240–52
- Fu H, Yadav MP, Nothnagel EA** (2007) *Physcomitrella patens* arabinogalactan proteins contain abundant terminal 3-O-methyl-L-rhamosyl residues not found in angiosperms. *Planta* **226**: 1151–24
- Geddes DS, Wilkie KCB** (1971) Hemicelluloses from the stem tissues of the aquatic moss *Fontinalis antipyretica*. *Carbohydr Res* **18**: 333–335
- Geddes DS, Wilkie KCB** (1972) A galactoglucomannan from the stem tissues of the aquatic moss *Fontinalis antipyretica*. *Carbohydr Res* **23**: 349–357
- Gille S, Hānsel U, Ziemann M, Pauly M** (2009) Identification of plant cell wall mutants by means of a forward chemical genetic approach using hydrolases. *PNAS* **106**: 14699–704
- Gómez Ros LV, Galbaldón C, Pomar F, Merino F, Pedreño and Ros Barceló** (2007) Structural motifs of syringyl peroxidases predate not only the gymnosperm-angiosperm divergence but also the radiation of tracheophytes. *New Phytol* **173**: 63–78
- Goubet F, Barton CJ, Mortimer JC, Yu X, Zhang Z, Miles GP, Richens J, Liepman AH, Seffen K, Dupree P** (2009) Cell wall glucomannan in *Arabidopsis* is synthesised by CSLA glycosyltransferases, and influences the progression of embryogenesis. *Plant J* **60**: 527–38
- Gunnison D, Alexander M** (1975) Basis for the resistance of several algae to microbial decomposition. *Appl Microbiol* **29**: 729–738
- Hasegawa M, Higuchi T, Ishikawa H** (1960) Formation of lignin in tissue culture of *Pinus strobus*. *Plant Cell Physiol* **1**: 173–182
- Hashimoto K, Tokimatsu T, Kaeano S, Yoshizawa AC, Okuda S, Goto S, Kanehisa M** (2009) Comprehensive analysis of glycosyltransferases in eukaryotic genomes for structural and functional characterization of glycans. *Carbohydr Res* **344**: 881–887

- Hess K, Haller R, Katz JR** (1928) Die chemie der zellulose und ihrer Begleiter. Akademische Verlagsgesellschaft, Leipzig
- Hodson MJ, White PJ, Mead A, Broadley MR** (2005) Phylogenetic variation in the silicon composition of plants. *Ann Bot* **96**: 1027–1046
- Hoffman M, Jia Z, Peña MJ, Cash M, Harper A, Blackburn AR II, Darvill A, York WS** (2005) Structural analysis of xyloglucans in the primary cell walls of plants in the subclass Asteridae. *Carbohydr Res* **115**: 1826–40
- Hoiczuk E, Hansel A** (2000) Cyanobacterial cell walls: news from an unusual prokaryotic envelope. *J Bacteriol* **182**: 1191–1199
- Honegger R, Haisch A** (2001) Immunocytochemical location of the (1,3)(1,4)-beta-glucan lichenin in the lichen-forming ascomycete *Cetraria islandica* (Icelandic moss). *New Phytol* **150**: 739–46
- Ikegaya H, Hayashi T, Kaku T, Iwata K, Sonobe S, Shimmen T** (2008) Presence of xyloglucan-like polysaccharide in *Spirogyra* and possible involvement in cell-wall attachment. *Phycol Res* **56**: 216–22
- Jones L, Milne JL, Ashford D, McQueen-Mason SJ** (2003) Cell wall arabinan is essential for guard cell function. *PNAS* **100**: 11783–11788
- Judd WS, Campbell CS, Kellogg EA, Stevens PF, Donoghue MJ** (2002) *Plant Systematics: a phylogenetic approach*. Sinauer Associates Inc. Sunderland, Massachusetts, USA
- Keeling PJ** (2004) Diversity and evolutionary history of plastids and their hosts. *Am J Bot* **91**: 1481–93
- Keeling P, Leander BS, Simpson A** (2009) Eukaryotes. Eukaryota, organisms with nucleated cells. <http://tolweb.org/Eukaryotes/3/2009.10.28> in The Tree of Life Web Project, <http://tolweb.org/>
- Kimura S, Itoh T** (1995) Evidence for the role of the glomerulocyte in cellulose synthesis in the tunicate *Metandrocarpa uedai*. *Protoplasma* **186**: 24–33
- Kloareg B, Quatrano RS** (1988) Structure of the cell walls of marine algae and the ecophysiological functions of the matrix polysaccharides. *Oceanogr Mar Biol Ann Rev* **26**: 259–315
- Knox JP, Linstead PJ, Peart J, Cooper C, Roberts K** (1991) Developmentally regulated epitopes of cell surface arabinogalactan proteins and their relation to root pattern formation. *Plant J* **1**: 317–26

- Lahaye M, Rondeau-Mouro C, Deniaud E, Buléon** (2003) Solid-state ^{13}C NMR spectroscopy studies of xylans in the cell wall of *Palmaria palmata* (L. Kuntze, Rhodophyta). *Carbohydr Res* **338**: 1559–69
- Lee C, O'Neill MA, Tsumuraya Y, Darvill AG, Ye Z-H** (2007) The irregular xylem9 mutant is deficient in xylan xylosyltransferase activity. *Plant Cell Physiol* **48**: 1624–1634
- Lee KJD, Sakata Y, Mau S-L, Pettolino F, Bacic A, Quatrano RS, Knight CD, Knox JP** (2005) Arabinogalactan proteins are required for apical cell extension in the moss *Physcomitrella patens*. *Plant Cell* **17**: 3051–65
- Lewis NG** (1999) A 20th century roller coaster ride: a short account of lignification. *Curr Opin Plant Bio* **2**: 153–162
- Liepmann AH, Wilkerson CG, Keegstra K** (2005) Expression of cellulose synthase-like (Csl) genes in insect cells reveals that CslA family members encode mannan synthases. *PNAS* **102**: 2221–26
- Loopstra CA, Sederoff RR** (1995) Xylem-specific gene expression in loblolly pine. *Plant Mol Biol* **27**: 277–291
- Love J, Percival E** (1964) The polysaccharides of the green seaweed *Codium fragile*. Part III. A β -1 \rightarrow 4-linked mannan. *J Chem Soc* 3345–3350
- Ma JF, Tamai K, Yamaji N, Mitani N, Konishi S, Katsuhara M, Ishiguro M, Murata Y, Yano M** (2006) A silicon transporter in rice. *Nature* **440**: 688–691
- Ma JF, Yamaji N** (2006) Silicon uptake and accumulation in higher plants. *Trends in Plant Science* **11**: 1360–1385
- Mabeau S, Kloareg B** (1997) Isolation and analysis of the cell walls of brown algae: *Fucus spiralis*, *F. ceranoides*, *F. vesiculosus*, *F. serratus*, *Bifurcaria bifurcata* and *Laminaria digitata*. *J Exp Bot* **38**: 1573–1580
- Mackie IM, Percival E** (1959) The constitution of xylan from the green seaweed *Caulerpa filiformis* *J Chem Soc* 1151–1156
- Marcus SE, Verhertbruggen Y, Hervé C, Ordaz-Ortiz JJ, Farkas V, Pedersen HL, Willats WG, Knox JP** (2008) Pectic homogalacturonan masks abundant sets of xyloglucan epitopes in plant cell walls. *BMC Plant Biology* **8**: 60

- Martone PT, Estevez JM, Lu F, Ruel K, Denny MW, Somerville C, Ralph J** (2009) Discovery of lignin in seaweed reveals convergent evolution of cell wall architecture. *Curr Biol* **19**: 169–75
- Mastrorade DN** (1997) Dual-axis tomograph: an approach with alignment methods that preserve resolution. *J Struct Biol* **120**:343–352
- Matoh T, Kawaguchi S, Kobayashi M** (1996) Ubiquity of a borate-rhamnogalacturonan II complex in the cell walls of higher plants. *Plant Cell Physiol* **37**: 636–640
- Matsunaga T, Ishii T, Matsumoto S, Higuchi M, Darvill A, Albersheim P, O'Neill MA** (2004) Occurrence of the primary cell wall polysaccharide rhamnogalacturonan II in pteridophytes, lycophytes, and bryophytes. Implications for the evolution of vascular plants. *Plant Physiol* **134**: 339–51
- McCann A, Benanti G, Knox JP, Popper ZA** (2007) The occurrence of arabinogalactan proteins in charophytes (stoneworts). *Physiol Plant* **130**: Abstract 125
- Meikle PJ, Hoogenraad NJ, Bonig I, Clarke AE, Stone BA** (1994) A (1,3;1,4)-beta-glucan-specific monoclonal antibody and its use in the quantification and immunocytochemical location of (1,3;1,4)-beta-glucans. *Plant J* **5**: 1–9
- Miller DH, Mellman IS, Lamport DTA, Miller M** (1974) The chemical composition of the cell wall of *Chlamydomonas gymnogama* and the concept of a plant cell wall protein *JCB* **63**: 420–429
- Mouille G, Robin S, Lecomte M, Pagent S, Höfte H** (2003) Classification and identification of Arabidopsis cell wall mutants using Fourier-transform Infrared (FT-IR) microspectroscopy. *Plant J* **35**: 393–404
- Moller I, Sørensen I, Bernal AJ, Blaukopf C, Lee K, Øbro J, Pettolino F, Roberts A, Mikkelsen J, Knox JP, Bacic T, Willats WGT** (2007) High-throughput mapping of cell wall polymers within and between plants using novel microarrays. *Plant J* **50**: 1118–28
- Morrison JC, Greve LC, Richmond PA** (1993) Cell wall synthesis during growth and maturation of *Nitella* internodal cells. *Planta* **189**: 321–328
- Naylor G, Russell-Wells B** (1934) On the presence of cellulose and its distribution in the cell walls of brown and red algae. *Ann Bot* **48**: 635–641

- Niklas KJ** (2000) The evolution of plant body plans — a biomechanical perspective. *Ann Bot* **85**: 411–438
- Niklas KJ** (2004) The cell walls that bind the tree of life. *Bioscience* **54**: 831–841
- Niklas KJ, Kutschera U** (2009) The evolutionary development of plant body plans. *Functional Plant Biology* **36**: 682–695
- Niklas KJ, Kutschera U** (2010) The evolution of the land plant life cycle. *New Phytol* **185**: 27–41
- Nobels DR, Romanovicz DK, Brown RM Jr** (2001) Cellulose in cyanobacteria. Origin of vascular plant cellulose synthase? *Plant Physiol* **127**: 529–542
- Obel N, Erben V, Pauly M** (2006) Functional wall glycomics through oligosaccharide mass profiling. In: *The science and lore of the plant cell wall: Biosynthesis, Structure and Function*. Edited by Hayashi T. Boca Raton: BrownWalker Press, pp258–66
- Olafsdottir ES, Ingolfsson K** (2001) Polysaccharides from lichens: structural characteristics and biological activity. *Planta Med* **67**: 199–208
- O’Sullivan C (1882)** α and β amylan: constituents of some cereals. *J Chem Soc* **41**: 24–32
- Otegui MS, Mastrorade DN, Kang BH, Bednarek KY, Staehelin LA** (2001) Three-dimensional analysis of syncytial-type cell plates during endosperm cellularisation visualised by high resolution electron tomography. *Plant Cell* **13**: 2033–51
- Otegui MS, Staehelin LA** (2004) Electron tomographic analysis of post-meiotic cytokinesis during pollen development in *Arabidopsis thaliana*. *Planta* **218**: 501–15
- Painter TJ** (1983) Algal polysaccharides p195–285. In: *The Polysaccharides*. Vol 2. G. O. Aspinall (ed.). Academic Press, New York
- Palenik B, Brahansha B, Larimer FW, Land M, Hauser L, Chain P, Lamerdin J, Regala W, Allen EE, McCarren J, Paulsen I, Dufresne A, Partensky F, Webb EA, Waterbury J** (2003) The genome of a motile marine *Synechococcus*. *Nature* **424**: 1037–1024
- Palenik B, Grimwood J, Aerts A, Rouzé P, Salamov A, Putman N, Dupont C, Jorgensen R, Derelle E, Rombouts S, Zhou K, Otiillar R, Merchant**

- SS, Podell S, Gaasterland T, Napoli C, Gendler K, Manuell A, Tai V, Vallon O, Piganeau G, Janeck S, Heijde M, Jabbari K, Bowler C, Lohar M, Robbens S, Werner G, Dubchak I, Pazour GJ, Ren Q, Paulsen I, Delwiche C, Schmutz J, Rothsar D, Van de Peer Y, Moreau H, Grigoriev IV** (2007) The tiny eukaryote *Ostreococcus* provides genomic insight into the paradox of plankton speciation. *PNAS* **104**: 7705–7710
- Palmer JD, Soltis JE, Chase MW** (2004) The plant tree of life: an overview and some points of view. *Am J Bot* **91**: 1437–45
- Parker BC** (1963) Translocation in the giant kelp *Macrocystis*. *Science* **140**: 891–92
- Parker BC** (1970) Significance of cell wall chemistry to phylogeny in the algae. *Annals of the New York Academy of Sciences* **175**: 417–427
- Parrish FW, Perlin AS, Reese ET** (1960) Selective enzymolysis of poly- β -D-glucans and the structure of the polymers. *Can J Chem* **38**: 2094–104
- Pattathil S, Avci U, Baldwin D, Swennes AG, McGill JA, Popper Z, Bootten T, Albert A, Davis RH, Chennareddy C, Dong R, O’Shea B, Rossi R, Leoff C, Freshour G, Nava R, O’Neil M, York WS, Hahn MG** (2010) A comprehensive toolkit of plant cell wall glycan-directed monoclonal antibodies. *Plant Physiol*
- Pauly M, Keegstra K** (2008) Physiology and metabolism ‘tear down this wall’. *Curr Opin Plant Biol* **11**: 233–235
- Peña MJ, Zhong R, Zhou G-K, Richardson EA, O’Neill MA, Darvill AG, York WS, Ye Z-H** (2007) *Arabidopsis* irregular xylem8 and irregular xylem9: implications for the complexity of glucuronoxylan biosynthesis. *Plant Cell* **19**: 549–563
- Peña MJ, Darvill AG, Eberhard S, York WS, O’Neill MA** (2008) Moss and liverwort xyloglucans contain galacturonic acid and are structurally distinct from xyloglucans synthesised by hornworts and vascular plants. *Glycobiology* **18**: 891–904
- Pennell RI, Knox PJ, Scofield GN, Selvendran RR, Roberts K** (1989) A family of abundant plasma membrane-associated glycoproteins related to the arabinogalactan proteins is unique to flowering plants. *J Cell Biol* **108**: 1967–77

- Percival E, Rupérez P, Fulgencio S-C** (2001) Dietary fibre and physicochemical properties of Spanish seaweeds. *European Food Research and Technology* **212**: 349–54
- Peter G, Neale D** (2004) Molecular basis for the evolution of xylem lignification. *Curr Opin Plant Biol* **7**: 737–742
- Pettolino F, Sasaki I, Turbic A, Wilson SM, Bacic A, Hrmova M, Fincher GB** (2009) Hyphal cell walls from the plant pathogen *Rhynchosporium secalis* contain (1,3;1,6)- β -D-glucans, galacto- and rhamnomannans, (1,3;1,4)- β -D-glucans and chitin. *FEBS J* **276**: 4122–33
- Plude JL, Parker DL, Schommer OJ, Timmerman RJ, Hagstrom SA, Joers JM, Hnasko R** (1991) Chemical characterization of polysaccharide from the slime layer of the cyanobacterium *Microcystis flos-aquae* C3-40. *Applied and Environmental Microbiology* **57**: 1696–1700
- Popper ZA, Fry SC** (2003) Primary cell wall composition of bryophytes and charophytes. *Ann Bot* **91**: 1–12
- Popper ZA, Sadler IH, Fry SC** (2004) 3-O-Methyl rhamnose in lower land plant primary cell walls. *Biochem Syst Ecol* **32**: 279–289
- Popper ZA and Fry SC** (2004) Primary cell wall composition of pteridophytes and spermatophytes. *New Phytol* **164**: 165–74
- Popper ZA** (2008) Evolution and diversity of green plant cell walls. *Curr Op Plant Biol* **11**: 286–92
- Ragan M** (1984) *Fucus* 'lignin': a reassessment. *Phytochem* **23**: 2029–2032
- Richmond T, Somerville C** (2008) The cellulose synthase superfamily. *Plant Physiol* **124**: 495–8
- Roberts AW, Roberts E, Delmer DP** (2002) Cellulose synthase (CesA) genes in the green alga *Mesotaenium caldariorum*. *Eukaryotic Cell* **1**: 847–55
- Roberts AW, Roberts E** (2004) Cellulose synthase (CesA) genes in algae and seedless plants. *Cellulose* **11**: 419–35
- Roberts E, Roberts AW** (2009) Cellulose synthase (CesA) genes in the red alga *Porphyra yezoensis* Ueda. *J Phycol* **43(S1)**: 42
- Roberts K** (1974) Crystalline glycoprotein cell walls of algae: their structure, composition and assembly. *Phil Trans Royal Soc Lond B* **268**: 129–146

- Royo J, Gómez E, Hueros G** (2000) CMP-KDO synthetase a plant gene borrowed from Gram-negative eubacteria. *Trends in Genetics* **16**: 432–433
- Sapei L, Gierlinger N, Hartmann J, Nöske R, Strauch P, Paris O** (2007) Structural and analytical studies of silica accumulation in *Equisetum hymale*. *Analytical and Bioanalytical Chemistry* **389**: 1249–1257
- Sarkar P, Bosneaga E, Auer M** (2009) Plant cell walls throughout evolution: towards a molecular understanding of their design principals. *J Exp Bot* **60**: 3615–3635
- Schoenwaelder MAE, Clayton MN** (1998) Secretion of phenolic substances into the zygote wall and cell plate in embryos of *Hormosira* and *Acrocarpia* (Fucales, Phaeophyceae). *J Phycol* **34**: 969–80
- Schoenwaelder MAE, Clayton MN** (1999) The presence of phenolic compounds in isolated cell walls of brown algae. *Phycologia* **38**: 161–66
- Schultz CJ, Johnson KL, Currie G, Bacic A** (2000) The classical arabinogalactan protein gene family of Arabidopsis. *Plant Cell* **12**: 1751–1768
- Segui-Simarro JM, Austin JR II, White EA, Staehelin LA** (2004) Electron tomographic analysis of somatic cell plate formation in meristematic cells of Arabidopsis preserved by high-pressure freezing. *Plant Cell* **16**: 836–56
- Séveno M, Séveno-Carpentier E, Voxeur A, Menu-Bouaouiche L, Rihouey C, Delmas F, Chevalier C, Driouich A, Lerouge P** (2010) Characterization of a putative 3-deoxy-D-manno-2-octulosonic acid (Kdo) transferase gene from Arabidopsis thaliana. *Glycobiology* doi: 10.1093/glycob/cwq011
- Shibata T, Nagayama K, Tanaka R, Yamaguchi K, Nakamura T** (2003) Inhibitory effects of brown algal phlorotannins on secretory phospholipase A2s, lipoxygenases and cyclooxygenases. *J App Phycol* **15**: 61–66
- Shibuya N, Misaki A** (1978) Structure of hemicellulose isolated from rice endosperm cell wall — mode of linkages and sequences in xyloglucan, β -glucan and arabinoxylan. *Agric Biol Chem* **42**: 2267–2274
- Shimokawa T, Ishii T, Matsunaga T** (1999) Isolation and structural characterization of rhamnogalacturonan II-borate complex from *Pinus densiflora*. *J Wood Sci* **45**: 435–439

- Simpson TL, Volcani BE** (1981) Silicon and siliceous structures in biological systems. Springer, New York
- Sørensen I, Pettolino FA, Wilson SM, Doblin MS, Johansen B, Bacic A, Willats WGT** (2008) Mixed-linkage (1→3),(1→4)-β-D-glucan is not unique to the Poales and is an abundant component of *Equisetum arvense* cell walls. *Plant J* **54**: 510–21
- Sørensen I, Domozych D, Willats WGT** (2010) How did plant cell walls evolve? *Plant Physiol*
- Stanley MS, Perry RM, Callow JA** (2005) Analysis of expressed sequence tags from the green alga *Ulva linza* (Chlorophyta). *J Phycol* **41**: 1219–26
- Stebbins GL** (1992) Comparative aspects of plant morphogenesis: a cellular, molecular and evolutionary approach. *Am J Bot* **79**: 589–98
- Timell TE** (1962) Studies on ferns (Filicineae). Part 1. The constitution of a xylan from cinnamon fern (*Osmunda cinnamomea*). *Svensk Papperstidning* **65**: 122–125
- Thompson JE, Fry SC** (2001) Restructuring of wall-bound xyloglucan by transglycosylation in living plant cells. *Plant J* **26**: 23–34
- Tsekos I** (1999) The sites of cellulose synthesis in algae: diversity and evolution of cellulose-synthesising enzyme complexes. *J Phycol* **35**: 635–55
- Trethewey JAK, Campbell LM, Harris PJ** (2005) (1→3),(1→4)-β-D-Glucans in the cell walls of the Poales (*sensu lato*): an immunogold labelling study using a monoclonal antibody. *Am J Bot* **92**: 1669–83
- Turvey JR, Williams EC** (1970) The structure of some xylans from red algae *Phytochem* **9**: 2383–2388
- Van Holst G-J, Clarke AE** (1985) Quantification of arabinogalactans-protein in plant extracts by single radial gel diffusion *Analytical Biochemistry* **148**: 446–450
- Van Sandt VST, Stieperaere H, Guisez Y, Verbelen J-P, Vissenberg K** (2007) XET activity is found near sites of growth and cell elongation in bryophytes and some green algae: new insights into the evolution of primary cell wall elongation. *Ann Bot* **99**: 39–51
- Verherbruggen Y, Marcus SE, Haeger A, Verhof R, Schols HA, McCleary BV, McKee L, Gilbert HJ, Knox JP** (2009) Developmental complexity of

- arabinan polysaccharides and their processing in plant cell walls. *Plant J* **59**: 413–425
- Vissenberg K, Oyama M, Osata V, Yokoyama R, Verbelen J-P, Nishitani K** (2005) Differential expression of AtXTH17, AtXTH18, AtXTH19 and AtXTH20 genes in Arabidopsis roots. Physiological roles in specific cell wall construction. *Plant Cell Physiol* **46**: 192–200
- Vreeland V (1972)** Immunocytochemical localization of the extracellular polysaccharide alginic acid in the brown seaweed, *Fucus disticus*. *J Hist Cytochem* **20**: 358–67
- Vreeland V, Larsen B, Laetsch WM (1982)** Monoclonal antibodies to *Fucus* cell wall antigens: localization and specificity patterns (Abstr.). *J Cell Biol.* **95**: 127a
- Vreeland V, Slomich M, Laetsch WM (1984)** Monoclonal antibodies as molecular probes for cell wall antigens of the brown alga, *Fucus*. *Planta* **162**: 506–17
- Weng J-K, Li X, Stout J, Chapple C** (2008) Independent origins of syringyl lignin in vascular plants. *PNAS* **105**: 7887–7892
- Weng J-K, Akiyama T, Bonawitz ND, Li X, Ralph J, Chapple C** (2010) Convergent evolution of syringyl lignin biosynthesis via distinct pathways in the lycophyte *Selaginella* and flowering plants. *Plant Cell* www.plantcell.org/cgi/doi/10.1105/tpc.109.073528
- Werner D** (1977) Silicate metabolism. Chapter 4. In: *The Biology of Diatoms*. University of California Press, Berkeley
- Willats WGT, Rasmussen SE, Kristensen T, Mikkelsen JD, Knox JP** (2002) Sugar-coated microarrays: a novel slide surface for the high-throughput analysis of glycans. *Proteomics* **2**: 1666–71
- Xu Z, Zhang D, Hu J, Zhou X, Ye X, Reichel KL, Stewart NR, Syrenne RD, Yang X, Gao P, Shi W, Doepcke C, Sykes RW, Burris JN, Bozell JJ, Cheng Z-M, Hayes DG, Labbe N, Davis M, Stewart CN, Yuan JS** (2009) Comparative gene analysis of lignin biosynthesis gene families across the plant kingdom. *BMC Bioinformatics* **10 (Suppl 11)**: S3
- Yin Y, Huang J, Xu Y** (2009) The cellulose synthase superfamily in fully sequenced plants and algae. *BMC Plant Biology* **9**: 99

- Yoon HS, Hackett JD, Ciniglia C, Pinto G, Bhattacharya D** (2004) A molecular timeline for the origin of photosynthetic eukaryotes. *Mol Biol Evol* **21**: 809–18
- York WS, Darvill AG, McNeil M, Albersheim P** (1985) 3-Deoxy-D-manno-2-octulosonic acid (KDO) is a component of rhamnogalacturonan II, a pectic polysaccharide in the primary cell walls of plants. *Carbohydr Res* **138**: 109–126
- York WS, O'Neill MA** (2008) Biochemical control of xylan biosynthesis — which end is up? *Curr Opin Plant Biol* **11**: 258–265
- Zhou G-K, Zhong R, Richardson EA, Morrison WH II, Nairn CJ, Wood-Jones A, Ye Z-H** (2006) The poplar glycosyltransferase GT47C is functionally conserved with *Arabidopsis Fragile Fiber8*. *Plant Cell Physiol* **47**: 1229–1240

Figure legends

Figure 1: Emergence of gene families (cellulose synthase (CesA) and cellulose synthase-like (Csl)) within the cellulose synthase superfamily responsible for cellulose and hemicellulose synthesis (Yin et al., 2009) mapped on to a simplified Eukaryote phylogeny (adapted from Keeling et al., 2009; Keeling 2004; Palmer et al., 2004; Yoon et al., 2004). CesA* represents members of the cellulose synthase family whose proteins assemble into rosette terminal complexes (Yin et al., 2009). CslA/C represents a single gene which is most similar to the land plant CslA and CslC gene families (Yin et al., 2009). The dotted lines indicate secondary endosymbiosis events involving; green algae which gave rise to the Euglenozoa (.....), and red algae which gave rise to the Stramenopiles (-----) (Keeling, 2004).

Table 1: Occurrence of cell wall components in plant and algal cell walls

Plant group	Other wall components								
	Cellulose	Xylan	Mannan	Xyloglucan	RGII	(1→3),(1→4) -β-D-glucan	AGPs	Lignin	Silica
Brown algae	+ ¹					± ^{26,27}	± ³¹	- ³⁹	-
Diatoms						± ²⁶			+ ⁴⁵
Rhodophytes (red algae)	+ ¹	+ ³	+ ¹¹			-	± ³²	+ ⁴⁰	-
Chlorophytes (green algae)	+ ¹	+ ⁴	+ ¹²		* ²¹	+ ²⁸	+ ^{32,33}	- ³⁹	-
Charophycean green algae (CGA)	+ ¹	+ ⁵	+ ¹³	± ¹⁸		-	+ ³⁴	- ³⁹	-
Bryophytes (mosses, liverworts and hornworts)	+ ²	+ ⁶	+ ¹⁴	+ ^{19,20}	± ²²	-	+ ³⁵	- ^{39,41}	+ ⁴⁶
Lycopodiophytes (club mosses)	+ ²	+ ⁷	+ ¹⁵	+ ¹⁹	+ ²³	-		+ ^{42,43}	-
Equisetophytes (horsetails)	+ ²	+ ⁷	+ ¹⁵	+ ¹⁹	+ ²⁴	+ ²⁹	+ ³⁶	+ ⁴³	+ ^{46,47}
Ferns	+ ²	+ ^{7,8}	+ ^{15,16}	+ ¹⁹	+ ²⁵	-		+ ⁴³	-
Gymnosperms	+ ²	+ ⁹	+ ^{15,17}	+ ¹⁹	+ ^{24,25}	-	+ ³⁷	+ ⁴⁴	-
Angiosperms excluding Poales	+ ²	+ ⁹	+ ¹⁵	+ ¹⁹	+ ²⁵	-	+ ³⁸	+ ⁴²	-
Poalean Angiosperms	+ ²	+ ¹⁰	+ ¹⁵	+ ¹⁹	+ ²⁵	+ ³⁰	+ ³⁸	+ ⁴²	+ ^{46,48}

Footnotes:

+, component is likely to be present; ±, component may be present; -, component is likely to be absent; *, component is absent but an unusual sugar residue constituent of the wall component is present.

- 1 Baldan et al., (2001), Kloareg and Quatrano (1988), Naylor and Russell-Wells (1934).
- 2 Cellulose has been found in all land plants (Brown, 1985).
- 3 Some red algae e.g. *Bangia fuscopurpurea* xylans contain all β-D-(1→3) linkages whereas others e.g. *Palmaria palmata* may contain β-D-(1→3) and β-D-(1→4) in the same molecule (Painter, 1983).
- 4 Mackie and Percival (1959).
- 5 Methylation analysis (Morrison et al., 1993) and CoMPP (Domozych et al., 2009) indicate the presence of 4-linked xylans.
- 6 Substituted (1→4)-β-D-xylans were detected by mAb labelling in hornwort sporophytes (Carafa et al., 2005).
- 7 Detected by mAb labelling (Carafa et al., 2005).
- 8 Xylans with low levels of substitution detected (Timell, 1962).
- 9 Xylans from *Cryptomeria japonica* were chemically analysed by Edashige and Ishii (1996).
- 10 Shibuya and Misaki (1978).
- 11 Estevez et al., (2009), Dunn et al., (2007), Love and Percival (1964).
- 12 Presence of (1→4)-β-D-mannans in *C. fragile* determined by FT-IR, HMBC NMR and linkage analysis (Estevez et al., 2009).
- 13 Methylation analysis (Morrison et al., 1993) and CoMPP suggests the presence of (1→4)-mannans (Domozych et al, 2009).
- 14 Hemicelluloses from an aquatic moss, *Fontinalis antipyretica*, were biochemically analysed by Geddes and Wilkie (1971 and 1972).
- 15 Popper and Fry (2004).
- 16 Bremner and Wilkie (1971).
- 17 Andrew and Little (1997).
- 18 Presence of xyloglucan in *Chara* antheridia suggested by mAb-labelling (Domozych et al., 2009).

- 19 Determined by enzyme, followed by identification of the products by HPLC (Popper and Fry, 2003; Popper and Fry, 2004).
- 20 NMR of bryophyte xyloglucans showed them to contain acidic sugars (Peña et al., 2008).
- 21 RGII has not been detected in green algae but the prasinophytes contain monosaccharide residues normally present in RGII (Becker et al., 1991; Domozych et al., 1991; York et al. 1985).
- 22 Based on analysis of Driselase-digested material by SEC/ICP-MS bryophyte walls contain less than 1% of the total amount w/w of the RGII present in Angiosperms (Matsunaga et al., 2004).
- 23 Ferns and fern allies contain RGII at levels with that found in Angiosperms. The glycosyl sequence is conserved with the exception that an L-rhamnosyl residue is replaced in some members with 3-O-methylrhamnose (Matsunaga et al., 2004). RGII was identified and structurally analysed by ¹¹B-NMR spectra and glycosyl linkage composition by GC and GC/EI-MS of alditol acetate and trimethylsilyl methyl glucoside derivatives (Matsunaga et al., 2004). 3-O-Methylrhamnose is sugar residue which is found relatively rarely in Angiosperms but has been identified in wall preparations from ferns, fern allies and bryophytes (Popper et al., 2004) and appears to be a component of bryophyte AGPs (Fu et al., 2007).
- 24 RGII isolated by Driselase digestion followed by SEC and elucidated by ¹¹B-NMR (Shimokawa et al., 1999).
- 25 A borate-rhamnogalacturonan II complex is found ubiquitously in higher plant cell walls (Match et al., 1996).
- 26 Putative occurrence based on labelling with an anti-MLG mAb (Popper et al., unpublished data). Treatment of the brown algal cell walls with 6 M NaOH solubilised polysaccharides that were fragmented by treatment with lichenase (Popper et al., unpublished data).
- 27 Bourne et al., (1969) extracted a polymer from *Fucus vesiculosus* which could be digested by laminarinase and cellulase and appeared to be structurally similar to laminarin.
- 28 Presence in *Micrasterias* determined by mAb labelling, and specific enzyme digestion followed by HPAEC-PAD (Eder et al., 2008).

29 CoMPP, enzyme digestion followed by MALDI-TOF-MS, monosaccharide linkage analysis (Sørensen et al., 2008), specific
enzyme digestion followed by TLC and HPLC (Fry et al., 2008a).

30 Immunolabelling (Trethewey et al. 2005).

31 Putative occurrence of AGPs based on extraction (Schultz et al., 2000) and detection using radial gel permeation (Van Holst
and Clarke, 1985)(Popper et al., unpublished data).

32 mAb-labelling and extraction followed by radial gel diffusion (Eder et al., 2008).

33 Presence of AGPs in *C. fragile* determined by mAb-labelling, linkage analysis and NMR (Estevez et al., 2009).

34 Presence of AGPs in *Chara* suggested by mAb labelling (Domozych et al., 2009).

35 Basile et al., (1989).

36 Detected by mAb labelling (Verhertbruggen et al., 2009).

37 AGPs detected in loblolly pine using RNA blotting (Loopstra and Sederoff, 1995).

38 Identified by mAb labelling and biochemical characterization by GLC-MS (Pennell et al., 1989).

39 Lignin-like compounds have been reported from algae and non-vascular plants (Delwiche et al., 1989; Gunnison and
Alexander, 1975) but has not been unambiguously confirmed (Peter and Neale, 2004; Ragan, 1984; Lewis, 1999).

40 The presence of lignin (monolignols H, G and S) in the rhodophyte, *Calliathron cheilosporioides*, was determined by labelling
with polyclonal antibodies and GC-MS (Martone et al., 2009).

41 Water-extractable lignans have been detected in bryophytes (Chodat and Cortesi, 1939).

42 S-lignin occurs in lycophytes and flowering plants but biochemical evidence, including analysis of enzyme kinetic properties,
suggests it is derived through separate biosynthetic pathways in each taxa (Weng et al., 2010).

43 Based on the biochemical analyses of Gómez Ros et al. (2007).

44 Hasegawa et al., (1960).

45 Diatoms are reported to contain ~5% Si by dry weight (Werner D, 1977).

- 46 Some plants either specifically accumulate Si or have a high mean relative shoot concentration (MRSC) including; a thalloid liverwort, 5.452, *Equisetum*, 3.992, and members of the Poales, 4.167. The mean value for MRSC in plants is 0.722 (Hodson et al. 2005). The MRSC reduces as follows
liverworts>horsetails>clubmosses>mosses>angiosperms>gymnosperms>ferns (Hodson et al., 2005).
- 47 Currie and Perry (2007) and Sapei et al., (2007).
- 48 Ma and Yamaji (2006).

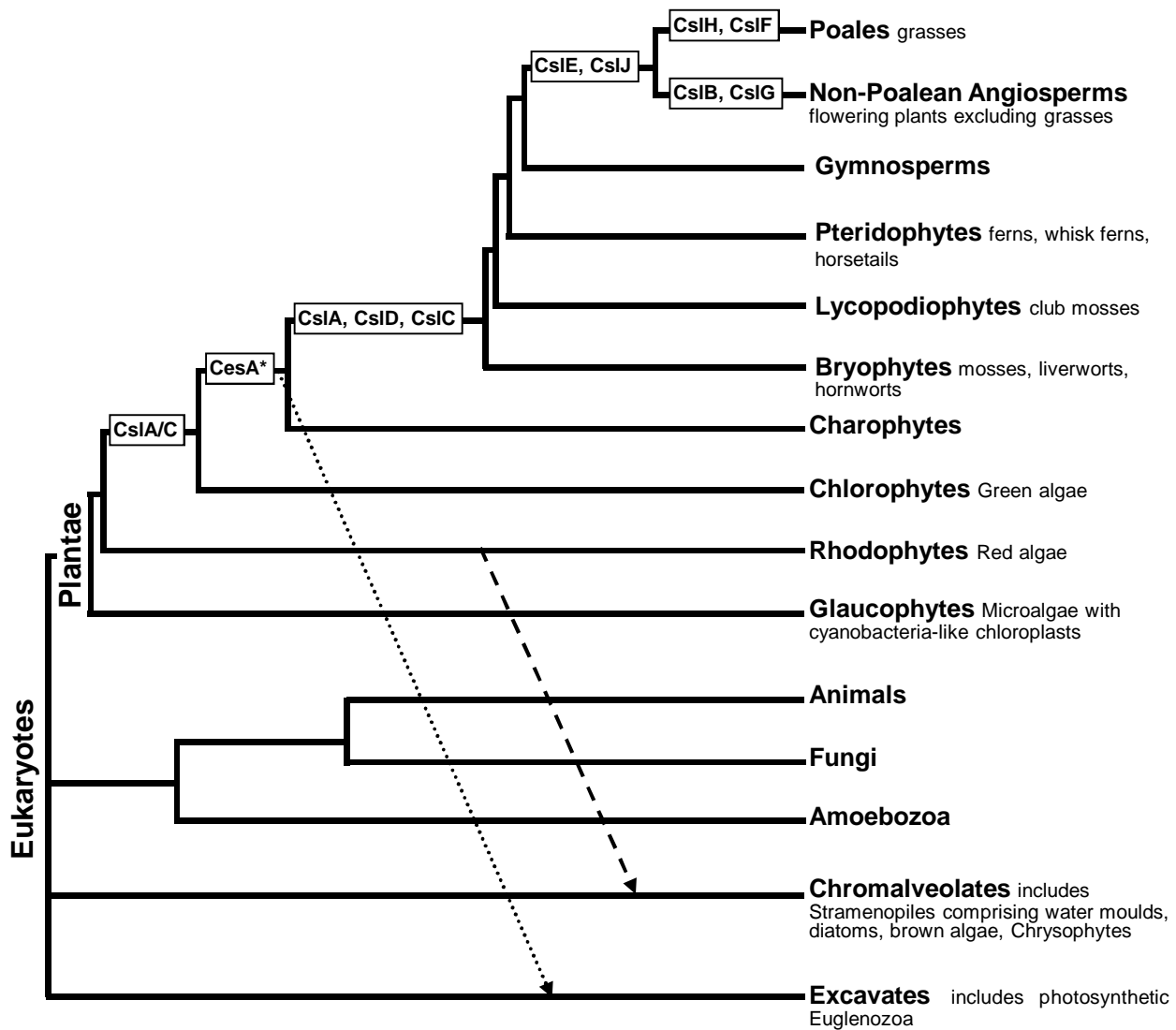


Figure 1: Emergence of gene families (cellulose synthase (CesA) and cellulose synthase-like (Csl)) within the cellulose synthase superfamily responsible for cellulose and hemicellulose synthesis (Yin et al., 2009) mapped on to a simplified Eukaryote phylogeny (adapted from Keeling et al., 2009; Keeling, 2004; Palmer et al., 2004; Yoon et al., 2004). CesA* represents members of the cellulose synthase family whose proteins assemble into rosette terminal complexes (Yin et al., 2009). CslA/C represents a single gene which is most similar to the land plant CslA and CslC gene families (Yin et al., 2009). The dotted lines indicate secondary endosymbiosis events involving; green algae which gave rise to the Euglenozoa (.....), and red algae which gave rise to the Stramenopiles (-----) (Keeling, 2004).