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CHAPTER ELEVEN

C0055

Genomics, Lifestyles and Future Prospects of Wood-Decay and Litter-Decomposing Basidiomycota

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Contents

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Abstract

Saprobic (*saprotrophic* and *saprophytic*) *wood-decay fungi* are in majority species belonging to the fungal phylum Basidiomycota, whereas *saprobic plant litter-decomposing fungi* are species of both the Basidiomycota and the second Dikarya phylum Ascomycota. Wood-colonizing white rot and brown rot fungi are principally polypore, gilled pleurotoid, or corticioid Basidiomycota species of the class Agaricomycetes, which also includes forest and grassland soil-inhabiting and litter-decomposing mushroom species. In this chapter, examples of lignocellulose degradation patterns are presented in the current view of genome sequencing and comparative genomics of fungal wood-decay enzymes. Specific attention is given to the model white rot fungus, lignin-degrading species *Phanerochaete chrysosporium* and its wood decay-related gene expression (transcriptomics) on lignocellulose substrates. Types of fungal decay patterns on wood and plant lignocellulose are discussed in the view of fungal lifestyle strategies. Potentiality of the plant biomass-decomposing Basidiomycota species, their secreted enzymes and respective lignocellulose-attacking genes is evaluated in regard to development of biotechnological and industrial applications.

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1. INTRODUCTION: PLANT AND SOIL ORGANIC MATTER

p0005 Of the annual input of atmospheric carbon, the majority of the accumulation of CO_2 is generated by natural decomposition of organic matter. In terrestrial environments, one-third of the organic carbon pool is present in the structural components of living organisms, mainly plants and microbes, while two-thirds of the organic carbon is fixed in nonliving biomass. The dead organic substances are either compact plant lignocelluloses or soil organic matter of diverse composition. In order to initiate degradation and modification of these complex organic carbon pools, and thereby promote cycling of carbon and other nutrients in particular in the forest ecosystems, robust and versatile bioconversion reactions have evolved in the fungal lineages.

s0010

1.1. Organic matter and Earth's carbon cycle

p0010 Organic carbon pool reservoirs on Earth consist of fossil fuels, soil organic carbon, terrestrial biosphere and the ocean biosphere and dissolved organic compounds. Fossil fuels account for over 4000 Gtn (gigatons) by mass of the carbon pool, while terrestrial biomass—consisting of living and dead organisms and soil-stored organic carbon—accounts for 2000 Gtn (Falkowski et al., 2000). Most of the terrestrial biosphere-fixed organic carbon is stored

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in dead biomass (1200 Gtn), while living plants and other organisms sum up to 1/3 of the terrestrial organic carbon pool (Falkowski et al., 2000; Prentice et al., 2001). Au3

p0015 Woody plants (trees, shrubs and lianas) account for 75% of stored terrestrial plant carbon (Horwarth, 2007). Tree-filled forests and wooded lands cover together 40% of the Earth's land area (over 9% of the planet's surface) making a sum of over 5×10^9 ha. This accounts for a global volume of ca. 540×10^9 m^3 of growing wood stock making a biomass of over 600 Gtn (in dry matter) of living wood (sum of above- and belowground wood) (FAO, 2010). Dead wood biomass reaches 67 Gtn in the manageable forests (FAO, 2010). It has been estimated that it takes about 10 years for plants to recycle their carbon, when their respiration (CO_2 formation) is subtracted from their gross primary production of organic carbon compounds by CO_2 fixation via photosynthesis (Horwarth, 2007). In forest ecosystems, turnover rates for complete degradation of the woody components and soil humified matter may reach up to thousands of years. In order to allow short-term carbon cycling in tree-based forest ecosystems, organisms specialized in conversion and degradation of all the components of wood lignocellulose, the wood-decay Basidiomycota fungi, play a crucial role.

p0020 More than 90% of the input of atmospheric carbon (in CO_2) is generated by natural decomposition of organic matter (Falkowski et al., 2000; Prentice et al., 2001). However, two-thirds of the terrestrial organic carbon is fixed in organic compounds of nonliving biomass. Of the dead organic carbon substances, the largest proportions are trapped in forest ecosystems in dead wood *lignocellulose* and *soil organic matter* (*SOM*). Wood lignocellulose is a compact composite of plant cell wall cellulose, hemicelluloses and lignin (see later). SOM on the contrary is a diverse term embracing both aboveground and belowground organic matter, such as forest tree and other plant-derived litter (leaves, needles, sticks, branches, hay and seeds), plant root exudates and rhizosphere microbes, dead plant roots, dead animals and microbes and humic substances composed of dead wood lignin-derived phenolic compounds, aliphatic chains and a substantial amount of nitrogen heterocyclic compounds such as pyrrole and pyridine rings (Horwarth, 2007).

p0025 Of the heterogeneous SOM, the humic substances are the most persistent reservoir of trapped carbon in the soil ecosystems and thereby generate an important carbon sink in the Earth's carbon cycle (Falkowski et al., 2000; Horwarth, 2007). SOM contains 3× more carbon than what exists in the atmosphere or is fixed in the biomass of living plants. Degradation of mostly plant-derived organic matter is the key process to release other nutrients than

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carbon (nitrogen, phosphorous, mineral cations and sulphur) for use by soil microorganisms and plant roots. In these processes, soil-inhabiting litter-decomposing species play key functional roles.

s0015 1.2. Structure of plant biomass and lignocellulose

p0030 In forests ecosystems, the majority of SOM is derived from trees as dead wood lignocellulose derived from fallen trunks and branches, stumps and roots and littered leaves and needles. In grasslands, plant coverage is principally composed of nonwood species, and dead plant biomass is thereby dominated by grass-type litter lignocellulose. Most of the SOM consists of insoluble large polymers from the plant matter including polysaccharides (cellulose, hemicellulose, starch and pectin), lipids and waxes, proteins, nucleic acids, lignin and phenolic compounds (Horwarth, 2007). Of these macromolecules, lignin is the most recalcitrant for decomposition due to its aromatic and heterogeneous structure of various interlinkages and side groups and varying number of phenylpropanoid subunits.

p0035 The significance of the saprobic plant biomass-degrading Basidiomycota is seen in the evolution of their ability to completely decompose the tough woody (xylem) tissue lignocellulose. Lignocellulose composite forms the building material of the plant secondary cell walls and is composed of the polymeric polysaccharides cellulose, hemicelluloses and pectins and aromatic lignin heteropolymers (Bidlack, Malone, & Benson, 1992; Eriksson, Blanchette, & Ander, 1990; Sjöström, 1981). The long cellulose chains are arranged in packed microfibrils that are differentially orientated in the plant cell wall layers. Between these partially crystalline microfibril threads, hemicellulose units attach aromatic lignin moieties, thus generating a complex and rigid structure of the carbohydrate polymers (Fig. 11.1).

p0040 In trees, the amount of cellulose is 40–50% of the wood dry weight, and hemicelluloses and lignin each account for 15–30%, depending on the plant species and tissue (Eriksson et al., 1990; Sjöström, 1981). Cellulose is a homopolymer of β-1,4-glycosidic interlinked D-glucopyranoses forming up to 8000–10,000 unit long chains, which are tightly packed by hydrogen bonding in 40 chain bundles (microfibrils) (Bidlack et al., 1992; Sjöström, 1981). In plant cell walls, the orderly packed and crystalline cellulose microfibrils are embedded by hemicellulose–lignin matrix in several layers (Fig. 11.1). Angiosperm hemicelluloses are mainly xylans (β-1,4-D-xylopyranose chains), often acetylated methylglucurono-β-D-xylans, and some glucomannans (β-1,4-linked D-glucopyranose-D-mannopyranose

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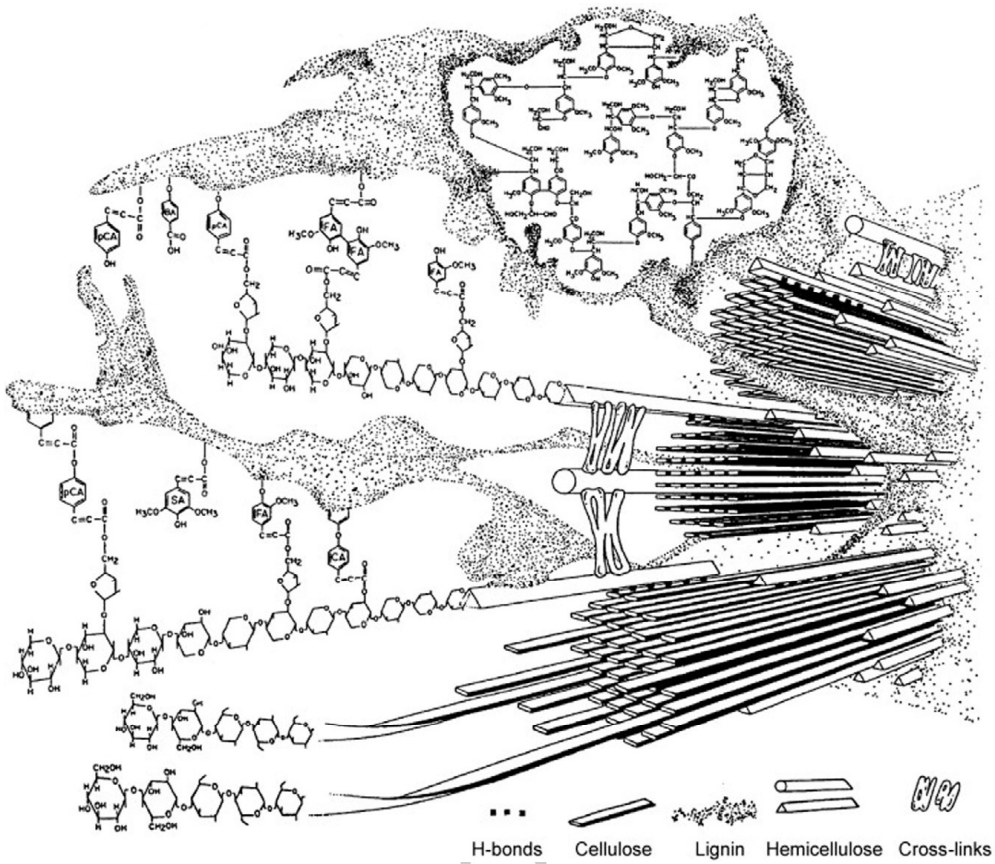

f0005 **Figure 11.1** Plant lignocellulose. Schematic view of the lignified secondary cell wall molecular structure for grass plants. Polymeric cellulose microfibrils (linear polymers) are tightly packed in ordered layers surrounded by branched hemicellulose chains and aromatic lignin heteropolymers. Cross-links between hemicellulose chains and between hemicelluloses and lignin moieties (by ester and ether linkages) are depicted. *Picture according to the original illustration (Bidlack et al., 1992) is reprinted from* Current Opinion in Biotechnology, *Martínez, Ruiz-Dueñas, Martínez, del Río, and Gutiérrez (2009), Copyright (2009), with permission from Elsevier.*

chains). Coniferous gymnosperm hemicelluloses mainly comprise galactoglucomannans (glucomannan chains including α-1,6-linked galactose units). In addition to galactoglucomannans, coniferous softwood contains arabinoglucuronoxylan (Sjöström, 1981). Typical features for hemicelluloses are branching, partial acetylation of the sugar units and cross-linking also to other lignocellulose components. The hemicellulose backbones are substituted with a variety of carbohydrate monomers such as D-galactose, D-xylose, L-arabinose and D-glucuronic acid. Grass hemicelluloses are chemically diverse containing various pentose sugar units and more cross-linking, for example, by L-arabinofuranoses in arabinoxylans

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and to pectin (α-1,4-galacturonan and other D-galacturonic acid-containing branched polysaccharide chains) (Fig. 11.1). Grass hemicelluloses also contain covalent ester and ether bonds to ferulic and *p*-coumaric acid lignin monomers (Bidlack et al., 1992).

p0045 Lignin is an aromatic, non-polysaccharide heteropolymer of phenylpropanoid monolignol (*p*-coumaryl, feruloyl and sinapyl alcohol) subunits (Fig. 11.1). The degree of polymerization—number of interlinked phenylpropanoid units—as well as type of covalent linkages and amount of methyl-ether side groups is a highly variable characteristic of lignin depending on plant species and cell wall localization (Sjöström, 1981; Vanholme, Demedts, Morreel, Ralph, & Boerjan, 2010). The most condensed lignin is present in the middle lamellae interconnected to plant primary cell wall pectins and in gymnosperm softwood to xyloglucan hemicellulose. Xyloglucan is also synthesized in tension wood in angiosperm trees (Mellerowicz, Immerzeel, & Hayashi, 2008). The various ether and C–C bond interlinkages are formed via enzyme-catalysed radical coupling upon lignin biosynthesis (Vanholme et al., 2010). This chemical heterogeneity makes lignins difficult to degrade by hydrolytic enzyme attack. The most efficient degraders of this persistent component of the plant cell wall lignocellulose complex are the white rot wood decay Basidiomycota species of the systematic class Agaricomycetes, which are able to decompose not only cellulose and hemicelluloses but also the recalcitrant lignin polymers.

p0050 In addition to the lignocellulosic complex, plant cell walls contain proteins (enzymes and structural proteins), monomeric lignin precursors and other phenolic compounds and branched pectin polysaccharides (Eriksson et al., 1990; Sjöström, 1981). Pectin, lignin and hemicellulose fill the cell corners and interlayers forming the so-called middle lamellae in mature xylem cells (wood tissue). Thus, the compact wood composite structure is formed. Tree stems (trunks) include chemically distinct vertical compartments, starting from the bark outer layers, followed by living phloem and cambial wood tracheid-forming cells and then the innermost dead wood cell xylem compartments of sapwood and heartwood, including rays of living parenchyma cells. In conifers, resin ducts dissect the inner wood compartments horizontally.

s0020 2. WOOD AND LITTER DECAY AND FUNGAL LIFESTYLES

p0055 Four main patterns of fungal decay of wood may visually be recognized: white rot, brown rot, soft rot and blue stain. The wood white and brown rot-causing species belong to Basidiomycota, whereas soft rot and

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blue stain fungi represent species of Ascomycota. In the forest ecosystems, decomposition of plant litter is in turn due to diverse species of fungi representing both Basidiomycota and Ascomycota.

2.1. White rot

p0060 White rot-decayed wood is fibrous, soft and white to yellow in colour and often contains darks manganese deposits. The typical wood-decay white rot fungi are Basidiomycota Agaricomycetes species, mainly classified to the order Polyporales (Table 11.1), which colonize wood trunks forming protruding brackets or resupinate corticioid fruiting bodies (basidiocarps). A few gilled pleurotoid basidiocarp-forming species (e.g. species of *Pleurotus* and *Lentinula*) in other orders of Agaricomycetes are efficient colonizers of dead wood such as tree stumps resulting with white rot. A general feature of the white rot fungi is the production of an array of lignin-degrading peroxidases (PODs) together with multicopper oxidase (MCO) laccases and H_2O_2-generating enzymes (Table 11.2). Some wood-decay fungi are severe tree pathogens ~~(Table 11.1)~~, in particular the conifer pathogenic species of the genus *Heterobasidion* ~~(see Chapter 16)~~. Au4

p0065 According to recent large fungal comparative genomics studies and molecular evolutionary calculations, the crucial ability to degrade lignin and cause wood white rot appeared to the ancestral agaricomycetes fungal species at the same time when the large organic carbon deposits of the Carboniferous era, resulting from massive land plants of that time, started to decline about 290 million years ago in the beginning of the Devonian era (Floudas et al., 2012; Horwarth, 2007). Based on evolutionary analysis, the key genes for lignin-degrading ability, which are coding for the secreted class II peroxidase (POD) enzymes, emerged in the ancient agaricomycetes at the same time. Apparently, the first lignin-degrading enzymes were manganese-oxidizing peroxidases (MnPs) evolved from a single, more simple generic peroxidase-encoding gene (Floudas et al., 2012). Since then, after several gene duplications, a multitude of lignin-degrading peroxidases divided to various subfamilies (short-MnPs, long-MnPs, atypical MnPs, VPs and LiPs; Table 11.2) and specific functions have appeared in the white rot agaricomycetes species (Floudas et al., 2012; Ruiz-Dueñas et al., 2013).

2.2. Brown rot

p0070 Brown rot-decayed wood is dry, brown, powdery, and cracking to cubicles. Brown rot wood decay fungi are mainly Polyporales species, apparently

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t0005 **Table 11.1** Fungal decay of wood and lignocellulose: Basidiomycota model species and decay features

Decay type	Fungal species	Systematics	Growth substrate in nature	Specific features
Wood white rot	*Phanerochaete chrysosporium* G, S, B	Phanerochaetaceae, Polyporales, Agaricomycetes, Basidiomycota	Coniferous wood chips, lignocellulose composts	Model white rot fungus, lignin depolymerizing, cellulose decay, first Basidiomycota species genome sequenced; secretes PODs and CAZymes
	Gelatoporia (*Ceriporiopsis*) *subvermispora* G, S, B	Phanerochaetaceae, Polyporales, Agaricomycetes, Basidiomycota	Dead coniferous wood (esp. spruces), fallen trunks, burned wood	Selectively lignin-degrading, biopulping fungus, rare species found in boreal forests; secretes PODs and laccase
	Trametes versicolor G, S, B	Polyporaceae, Polyporales, Agaricomycetes, Basidiomycota	Dead deciduous and angiosperm tree wood, stumps and fallen trunks	Common species in temperate climate zones, model white rot fungus; secretes PODs, laccases, CAZymes; medicinal
	Heterobasidion annosum s.l., *H. parviporum*, *H. irregulare* G, P, S	Bondarzewiaceae, Russulales, Agaricomycetes, Basidiomycota	Conifers (pines, spruces, firs), deciduous trees, attacks living trees and seedlings	Species complex, tree pathogens, common in boreal and temperate zone forests; secretes laccases and PODs

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Table 11.1 Fungal decay of wood and lignocellulose: Basidiomycota model species and decay features—cont'd

Decay type	Fungal species	Systematics	Growth substrate in nature	Specific features
Wood brown rot	*Fomitopsis pinicola* G, P, S	Fomitopsidaceae, Polyporales, Agaricomycetes, Basidiomycota	Norway spruce, Scots pine, silver birch	Typical brown rot–causing fungus, may be pathogenic and kill young trees, common in boreal forests
	Serpula lacrymans G, S	Serpulaceae, Boletales, Agaricomycetes, Basidiomycota	Wooden houses and constructs, moisture-damaged buildings, timber, planks	Causes destructive dry rot in buildings, more rare in nature, nonpathogenic in soil and tree roots
	Coniophora puteana G, S	Boletaceae, Boletales, Agaricomycetes, Basidiomycota	Stumps of conifers and deciduous trees, timber, wood constructs	Tolerates cold, grows well in humid constructs and cellars, may cause destruction
Wood soft rot	*Phialophora* sp., *Scytalidium* sp., *Paecilomyces* sp. S, P, B	Dothideomycetes, Leotiomycetes, Eurotiomycetes, Ascomycota	Unprotected wood constructs, moisture-damaged buildings, wood chip composts	Soften surface of timber and planks, some species generate microhyphae, cellulose
	Xylaria hypoxylon, *X. polymorpha*, *X. longipes* S	Xylariaceae, Xylariales, Sordariomycetes, Ascomycota	Stumps, wood chips and sticks on soil, mulch and detritus	Soften pieces of wood, polysaccharide decay, partial modification of wood lignin

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Table 11.1 Fungal decay of wood and lignocellulose: Basidiomycota model species and decay features—cont'd

Decay type	Fungal species	Systematics	Growth substrate in nature	Specific features
Wood blue stain	*Ophiostoma* sp., *O. piceae* G, S, *Grosmannia clavigera* G, P	Ophiostomataceae, Ophiostomatales, Sordariomycetes, Ascomycota	Timber and felled trunks, live in resin ducts or phloem and parenchyma cells, pathogenic species attack living trees	Blue and black stain of trunks, no real decomposition of wood lignocellulose, also tree pathogenic species
Litter LDS	*Agaricus bisporus* (var. *bisporus*, var. *burnettii*) G, S, B	Agaricaceae, Agaricales, Agaricomycetes, Basidiomycota	Grasslands, cultivated on composted horse manure and straw, not on wood	Edible mushroom, commercial production worldwide, high nutritional and medicinal value; laccases and HTPs
	Volvariella volvacea G, S, B	Pluteaceae, Agaricales, Agaricomycetes, Basidiomycota	Cultivated on rice straw, slow decomposition of lignocellulose	Edible straw mushroom, commercial production in southern China and Asia; secretes laccases
	Coprinopsis cinerea G, S	Psathyrellaceae, Agaricales, Agaricomycetes, Basidiomycota	Grasslands, dung composts, high nitrogen demand, not on wood	Basidiomycota genetics model species; secretes laccases

LDS, litter-decomposing, soil-inhabiting; G, genome sequence available; S, saprotroph; P, pathogen; B, biotechnologically produced or applied species; CAZyme, carbohydrate-active enzyme; POD, class II lignin-modifying peroxidase; HTP, heme-thiolate peroxidase.

Modified from recent reviews on the topic (Lundell & Mäkelä, 2013; Lundell, Mäkelä, & Hildén, 2010).

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t0010 **Table 11.2** Oxidoreductase-encoding genes involved in lignin degradation in the genomes of plant biomass-decomposing Basidiomycota species

	Wood white rot										Litter LDS			EM	Wood brown rot						
AAs in CAZy database	***Pc***	***Gs***	***Ad***	***Ps***	***Fm***	***Ds***	***Tv***	***Sh***	***Hi***	***Sc***	***Ab***	***Vv***	***Cc***	***Lb***	***Rp***	***Fp***	***Cp***	***Gt***	***Sl***	***Wc***	***Da***
AA1 MCOs	5	9	10	13	11	13	10	20	18	6	na	na	17	15	7	7	8	4	6	5	5
AA1_1 laccase	0	7	7	12	10	11	7	15	16	2	11	11	17	9	7	5	6	3	4	3	0
AA2 PODs class II peroxidases	16	16	19	11	17	12	26	6	7	0	2	4	1	1	1	2	0	0	0	1	0
MnP (total)	5	13	6	10	16	9	13	5	6	0	2	4	0	0	0	0	0	0	0	0	0
MnP-short	0	1	0	2	3	5	13	0	6	0	2	4	0	0	0	0	0	0	0	0	0
Long	5	7	0	5	11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Extra long	0	5	0	3	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Atypical	0	0	6	0	2	0	0	5	0	0	0	0	0	0	0	0	0	0	0	0	0
VP	0	0	0	0	0	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
LiP	10	2	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Low-redox GP	1	1	11	1	1	0	0	1	1	0	0	na	1	1	1	2	0	0	0	1	0
AA3 GMC oxidoreductases																					
AA3_1 CDH	1	1	1	1	1	1	1	1	2	1	1	1	1	0	0	0	2	1	2	0	0
AA3_2 AAO/GO	4	7	0	4	2	9	3	14	12	5	10	8	18/27	7	3	1	0	2	0/6	0	0
AA3_3 AOX	1	4	3	3	2	4	4	7	16	3	na	na	0	0	1	4	2	1	1	4	1

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Table 11.2 Oxidoreductase-encoding genes involved in lignin degradation in the genomes of plant biomass-decomposing Basidiomycota species—cont'd

	Wood white rot										Litter LDS			EM	Wood brown rot						
AAs in CAZy database	***Pc***	***Gs***	***Ad***	***Ps***	***Fm***	***Ds***	***Tv***	***Sh***	***Hi***	***Sc***	***Ab***	***Vv***	***Cc***	***Lb***	***Rp***	***Fp***	***Cp***	***Gt***	***Sl***	***Wc***	***Da***
AA3_4 POX	1	na	2	0	0	0	2	0	0	1	na	na	0	0	0	0	0	0	0	0	0
AA5 radical copper-oxidases																					
AA5_1 GLOX	7	3	7	9	4	9	9	8	5	2	3	3	6	11	2	4	6	2	2	4	3
AA6 1,4-benzo-quinone reductase	4	1	3	3	3	1	1	1	2	4	4		3	2	1	1	2	3	2	1	1
AA9 (GH61) LPMO	15	9	19	14	13	15	18	16	10	22	11	26	35	5	2	4	10	4	5	2	0
DyP	0	0	11	5	3	1	2	2	1	0	0	3	4	2	0	0	0	0	0	0	0
HTP	3	9	16	8	4	4	3	10	5	3	25	na	8	5	3	4	2	6	3	5	6

Enzyme classification is following the CAZy database (http://www.cazy.org/) auxiliary activities (AAs) description when possible. LDS, litter-decomposing, soil-inhabiting saprotroph; EM, ectomycorrhizal. *Pc*, *Phanerochaete chrysosporium; Gs*, *Gelatoporia* (*Ceriporiopsis*) *subvermispora; Ad*, *Auricularia delicata; Ps*, *Punctularia strigosozonata; Fm*, *Fomitiporia mediterranea; Ds*, *Dichomitus squalens; Tv*, *Trametes versicolor; Sh*, *Stereum hirsutum; Hi*, *Heterobasidion irregulare; Sc*, *Schizophyllum commune; Ab*, *Agaricus bisporus; Vv*, *Volvariella volvacea; Cc*, *Coprinopsis cinerea; Lb*, *Laccaria bicolor; Rp*, *Rhodonia* (*Postia*) *placenta; Fp*, *Fomitopsis pinicola; Gt*, *Gloeophyllum trabeum; Sl*, *Serpula lacrymans; Wc*, *Wolfiporia cocos; Da*, *Dacryopinax* sp. MCOs, multicopper oxidases; PODs, class II heme-including peroxidases; LiP, lignin peroxidase; low-redox GP, general low-redox potential peroxidase; MnP, manganese peroxidase; VP, versatile peroxidase; GMC, glucose–methanol–choline oxidoreductase superfamily; CDH, cellobiose dehydrogenase; AAO, aryl alcohol oxidase; AOX, alcohol oxidase; POX, pyranose oxidase; GO, glucose oxidase; GLOX, glyoxal oxidase; LPMO, lytic polysaccharide monooxygenase; DyP, dye-decolorizing peroxidase, DyP-type peroxidase family; HTP, heme-thiolate peroxidase, peroxidase family 2; na, not annotated.

Data are derived from recent genomic studies (Bao et al., 2013; Chen et al., 2013; Fernandez-Fueyo et al., 2012; Floudas et al., 2012; Mäkelä et al., 2014; Martin et al., 2008; Martinez et al., 2004; Morin et al., 2012; Olson et al., 2012; Ruiz-Dueñas et al., 2013; Suzuki et al., 2012; Yakovlev et al., 2013).

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having lost their lignin-degrading POD genes and possessing only one or two genes for nonligninolytic, low-redox potential general peroxidases (Ruiz-Dueñas et al., 2013). The loss of the ancient MnP-encoding genes has apparently occurred several times in the agaricomycetes lineage (Floudas et al., 2012), thus leading to adaptation to other lifestyles than lignin degradation and white rot and resulting with either brown rot or ectomycorrhizal lifestyles (see Chapter 9). A few of the brown rot species are closely related to ectomycorrhizal species (e.g. *Serpula lacrymans* is classified to Boletales) (Eastwood et al., 2011). Brown rot fungi cause severe destruction of wood cellulose leading to brown and modified lignin residue, which also contains iron. The main mechanism for fungal brown rot destruction of wood polysaccharides is nonenzymatic attack, and oxidation and degradation proceed by Fenton chemistry producing highly reactive oxygen radicals (1) $Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^{\cdot} + H_2O$; (2) $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^+$ (Fenton, 1894; Jensen, Houtman, Ryan, & Hammel, 2001; Fig. 11.2).

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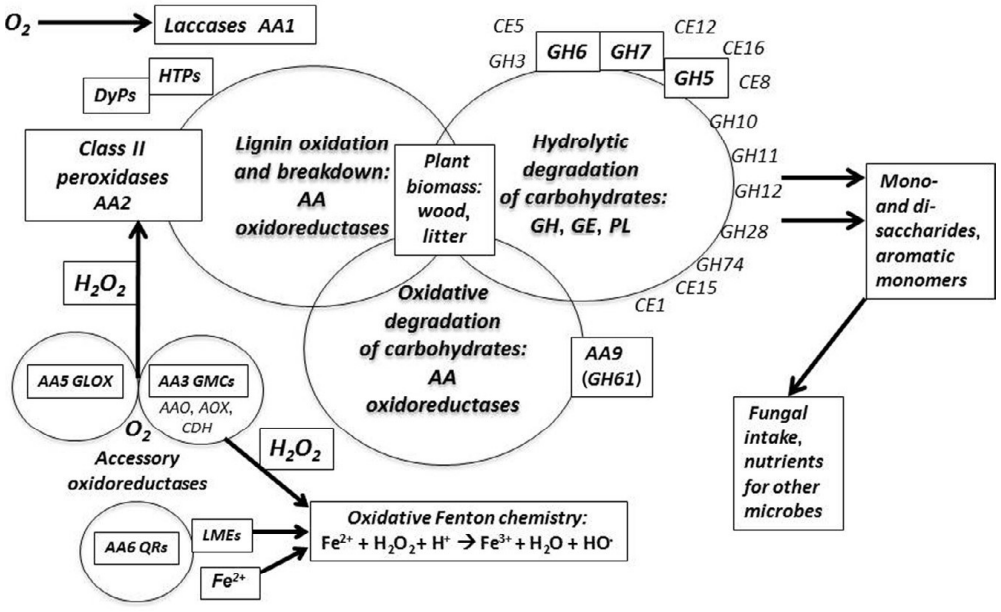

f0010 **Figure 11.2** Participation of fungal-secreted CAZy and oxidoreductase enzymes in degradation of plant biomass. Enzyme abbreviations and classes are explained in the text. LMEs, low-molecular-weight compounds; QRs, quinone reductases. *Scheme is modified from original illustration given by Dimitrios Floudas (Clark University, Worcester, MA, United States), with kind permission from the author to be used here.*

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s0035 2.3. Soft rot

p0075 Soft rot is a particular type of Ascomycota wood decay when the surface of wood material is colonized by green or dark "mould" fungi, mainly by species of the classes Sordariomycetes (genus *Trichoderma*), Dothideomycetes (*Phialophora*) and Eurotiomycetes (e.g. *Paecilomyces* ~~and~~ *Aspergillus*) (Table 11.1). In forest environments, pieces of dead wood in soil, dead tree roots, tree stumps and fallen branches may be colonized by Ascomycota species of the genus *Xylaria* causing a specific type of wood soft rot. *Xylaria* sp. decompose wood lignocellulose causing as well some degradation of wood lignin (Liers, Ullrich, Steffen, Hatakka, & Hofrichter, 2006). The "mould" Ascomycota are incapable to advance to the heartwood in dead tree trunks but may decompose cellulose and hemicelluloses of wounded or cut wood surfaces and timber. However, many wood surface soft rot fungi are efficient decomposers of plant litter (see later).

s0040 2.4. Blue stain

p0080 Blue stain fungi are Ascomycota species not destructing wood xylem lignocellulose. These fungi (e.g. species of the genera *Ophiostoma* and *Grosmannia*) are frequently disseminated as spores by wood-inhabiting beetles. Their hyphae extend in living wood trunks—thus either being pathogenic by growing in living ray parenchyma or phloem cells or being more saprobic by decomposing wood resins and waxes while growing in the resin ducts of conifers (Ballard, Walsh, & Cole, 1984; DiGuistini et al., 2011). Typical for blue stain species is the generation of dark-coloured melanins on their hyphal cell walls for protection against light, drought and host tree resistance factors. The wood-staining saprobic species *Ophiostoma piceae* is able to grow on triglycerides and oleic acid, and CAZy glycoside hydrolases are expressed on these substrates (Haridas et al., 2013). Since the blue stain species are not decomposing the main wood lignocellulose components (cellulose, hemicellulose and lignin), they are considered to be less important for wood organic carbon cycling.

s0045 2.5. Litter decomposition

p0085 Forest litter-decomposing fungi may roughly be divided into two subgroups according to their lifestyles: (i) species that colonize plant litter and debris on top of the humic organic O-layer and (ii) species that may attack smaller pieces of wood, bark, tree branches and dead tree roots. In the boreal and temperate forest ecosystems, the tree leaf litter and needle colonizers are

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mainly Ascomycota species. Litter quality, seasonal changes and variations in the top soil temperature are factors affecting litter biomass degradation rates (Prescott, 2010; Zhang, Hui, Luo, & Zhou, 2008). Extracellular hydrolytic enzyme activities are connected to soil pH, availability of nutrients (C, N and P) and microbial nutrient demand (Sinsabaugh et al., 2008). In a metaproteomic study on European forest oak leaf litter, secreted enzymes of representatives of the classes Leotiomycetes, Sordariomycetes and Eurotiomycetes dominated (80% frequency) (Schneider et al., 2012). A succession of fungi occurred to more Basidiomycota species in leaf litter sampled in spring compared to samples taken during autumn.

p0090 Fungal communities have been analysed in temperate soils of pine tree and mixed deciduous tree forests, demonstrating equal shares of Basidiomycota and Ascomycota taxonomic units (O'Brien et al., 2005). Au5 Similar results have been obtained in boreal spruce tree (*Picea abies*)-covered forest soils, where the main species identified were root endophytic Ascomycota and Basidiomycota species (Korkama-Rajala, Müller, & Pennanen, 2008). In studies using forest soil-embedded litter bags containing beech and spruce litter, it was demonstrated that Ascomycota species dominated the fungal communities (Aneja et al., 2006). The same was observed for decaying alder leaf litter in acidified streams (Clivot et al., 2013). Also in the decaying wood logs, the Ascomycota species are commonly found, together with a high variety of Basidiomycota and representatives of other fungal phyla, as is revealed by fungal community pyrosequencing metagenomic approach (Kubartova, Ottosson, Dahlberg, & Stenlid, 2012). It should be noted that soil fungal and bacterial communities are dynamic entities and variable during plant biomass degradation processes (Stursova, Zifcakova, Leigh, Burgess, & Baldrian, 2012).

s0050 3. FUNGAL ENZYMES IN DEGRADATION OF PLANT LIGNOCELLULOSE CARBOHYDRATES: GENOMIC VIEW

p0095 Due to the structural complexity of lignocellulosic plant biomass, a wide variety of carbohydrate-active enzymes and oxidoreductases are produced by fungal species to degrade the plant polysaccharides and lignin. Genomic studies have confirmed that both hydrolytic and oxidative enzyme activities are functional, together with chemical oxidation by Fenton reaction, in order to achieve efficient decay of the wood lignocellulose components (Fig. 11.2). However, depending on fungal species and lifestyles, the repertoire of enzymes and their gene numbers differs

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significantly (Tables 11.2 and 11.3). Genome sequences of plant biomass-degrading fungi have provided important molecular-level information on their strategies of biomass decay and also revealed that the fungal enzyme systems are much more diverse than was previously considered.

s0055 3.1. Carbohydrate-active enzymes

p0100 Carbohydrate-active enzymes (CAZymes) synthesize, modify or degrade plant biomass carbohydrates, such as polysaccharides and glycoconjugates. In the CAZy database (www.cazy.org; Lombard, Golaconda Ramulu, Drula, Coutinho, & Henrissat, 2013), these enzymes are classified based on their similarities in amino acid sequence, protein structure and enzymatic mechanism. Currently over 300 enzyme families can be grouped into four functional classes: glycoside hydrolases (GHs), glycosyltransferases (GTs), polysaccharide lyases (PLs) and carbohydrate esterases (CEs) based on their structural or functional domains. The role of GHs, PLs and CEs is to mediate the breakdown of polysaccharides, whereas GTs catalyse the formation of glycosidic linkages. Recently, oxidoreductases involved in lignin modification and degradation, such as laccases and class II peroxidases, have been included in the CAZy database as 10 auxiliary activity (AA) families (Levasseur, Drula, Lombard, Coutinho, & Henrissat, 2013). Comparisons of the genomic content of *wood- and litter-decomposing fungal species* have shown that there is a correlation between the number and type of CAZyme-encoding genes and the fungal capability to use various carbon sources and lignocellulosic substrates (Eastwood et al., 2011; Floudas et al., 2012).

s0060 3.2. Cellulose breakdown

p0105 Complete enzymatic hydrolysis and breakdown of cellulose chains require β-1,4-glycosidic bond-cleaving endoglucanase (EG), cellobiohydrolase (CBH) and β-glucosidase (BGL) activities. β-1,4-Endoglucanases hydrolyse noncrystalline regions of cellulose microfibrils, and the CBH enzymes attack the ends of the cellulose chains (Medie, Davies, Drancourt, & Henrissat, 2012). CBHs act in a unidirectional manner from either the reducing or nonreducing end of cellulose chains releasing disaccharide cellobiose units. Cellobiose is then cleaved to glucose by β-1,4-glucosidases, and this final step is crucial for complete hydrolysis of cellulose chains to glucose. β-Glucosidases are found in CAZy families GH1 and GH3, and in the wood-decay Basidiomycota genomes, GH3 enzymes are apparently more

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t0015 **Table 11.3** CAZy-encoding gene families in the genomes of plant biomass-decomposing Basidiomycota species

	Wood white rot										LDS			EM	Wood brown rot						
	Pc	*Gs*	*Ad*	*Ps*	*Fm*	*Ds*	*Tv*	*Sh*	*Hi*	*Sc*	*Ab*	*Vv*	*Cc*	*Lb*	*Rp*	*Fp*	*Cp*	*Gt*	*Sl*	*Wc*	*Da*
GHs																					
GH3	9	6	12	12	7	7	11	15	11	11	8	13	7	2	5	12	12	9	9	7	8
GH5	5	18	8	6	6	5	5	6	7	3	19	5	6	3	5	5	8	5	8	4	5
GH6	1	1	2	1	2	1	1	1	1	1	1	3	5	0	0	0	2	0	1	0	0
GH7	7	3	6	5	2	4	4	3	1	2	1	6	6	0	0	0	2	0	0	0	0
GH9	1	1	na	1	1	1	1	1	na	1	1	1	1	1	0	0	na	1	1	0	1
GH10	6	6	4	5	4	5	6	6	2	5	2	9	6	0	4	2	3	3	1	4	3
GH11	1	1	3	1	0	0	0	1	0	1	2	0	6	0	0	0	0	0	0	0	0
GH12	2	2	1	2	3	3	5	5	4	1	2	2	1	3	2	2	4	2	1	2	1
GH28	4	6	10	13	16	7	11	17	8	3	6	3	3	7	7	13	13	10	7	9	6
GH35	15	9	19	14	13	15	18	16	10	22	11	4	35	5	2	4	10	4	5	2	0
GH43	4	2	26	7	6	7	3	10	4	12	4	11	4	0	1	7	6	5	1	1	5
GH45	2	2	2	1	na	3	3	1	na	1	1	0	na	na	1	2	1	1	na	1	1
GH74	4	1	1	2	4	1	1	2	1	1	1	0	1	0	0	0	0	1	1	0	0
CEs																					

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Table 11.3 CAZy-encoding gene families in the genomes of plant biomass-decomposing Basidiomycota species—cont'd

	Wood white rot										LDS			EM	Wood brown rot						
	Pc	*Gs*	*Ad*	*Ps*	*Fm*	*Ds*	*Tv*	*Sh*	*Hi*	*Sc*	*Ab*	*Vv*	*Cc*	*Lb*	*Rp*	*Fp*	*Cp*	*Gt*	*Sl*	*Wc*	*Da*
CE1	4	3	3	2	0	0	3	1	1	4	2	2	3	0	0	0	0	1	0	0	0
CE16	2	5	29	8	6	10	7	10	5	10	10	0	5	3	5	11	6	6	3	6	4
CE5	0	0	3	1	0	0	0	1	0	2	6	1	6	1	0	0	1	0	0	0	0
CE8	2	2	3	6	3	3	2	4	3	2	2	2	0	4	1	2	2	2	2	1	3
CE12	0	0	1	0	2	2	0	3	2	1	3	0	1	0	0	0	0	0	0	0	0
CE15	2	2	6	2	1	2	2	1	1	2	0	0	8	0	1	1	0	1	0	1	1

For enzyme functions, see CAZy database (http://www.cazy.org/). GHs, glycosyl hydrolases; CEs, carbohydrate esterases; na, not annotated. For other abbreviations, see Table 11.2 legend.

Data are derived from recent genomic studies (Chen et al., 2013; Fernandez-Fueyo et al., 2012; Floudas et al., 2012; Hori et al., 2013; Mäkelä et al., 2014; Morin et al., 2012; Olson et al., 2012; Vanden Wymelenberg et al., 2009).

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abundant than GH1 gene models. It should be noted that β-glucosidases are also involved in the hydrolysis of other substrates (e.g. glycosides) and several of these enzymes are intracellular. It is therefore likely that only a subset of these enzymes is needed for lignocellulose breakdown. Au6

p0110 Extracellular EG activity is common in plant biomass-converting Ascomycota species (de Vries & Visser, 2001; Kluczek-Turpeinen, Maijala, Hofrichter, & Hatakka, 2007) and is reported for wood-decay white and brown rot, litter-decomposing and ectomycorrhizal Basidiomycota Agaricomycetes species (Baldrian & Valaskova, 2008; Maijala, Fagerstedt, & Raudaskoski, 1991). β-1,4-Glycosidic bond-cleaving endoglucanase activities are present in several CAZy families (GH 5, 7, 12 and 45). One of the largest GH families in the wood-decay and litter-decomposing species is GH5, which is present in variant number of gene models (3–19) in all the species sequenced (Table 11.3).

p0115 In addition to endoglucanases, GH5 also includes internal β-1,4-glycosidic bond-cleaving activities on hemicellulose substrates (xylanase and mannanase activities) and exoglucanase activity at the cellulose chain ends (Medie et al., 2012; www.cazy.org). This lack of specificity towards the polysaccharide substrate is also found in other GH families. Therefore, the function of a protein of a particular GH family cannot always be predicted from its gene model or sequence structure. Potential endoglucanase activities are as well found in CAZy families GH45 and GH12, which are present in both white and brown rot fungi (Table 11.3), but the number of gene models is lower than for GH5 and their role in wood decay is not known (Morin et al., 2012). It has been suggested that fungal GH45 and GH12 proteins may cause swelling in the lignocellulose polysaccharide complexes, thereby acting synergistically with other cellulases (Igarashi, Ishida, Hori, & Samejima, 2008; Medie et al., 2012). Fungal GH12 enzymes from Ascomycota act on xyloglucan hemicellulose, which is primarily located in the primary cell wall of wood cells. Interestingly, a single copy of a putative GH9 endoglucanase with a unique transmembrane-anchored domain is almost constitutively identified in the wood-decay white and brown rot Basidiomycota genomes (Table 11.3).

p0120 CBH activities needed for cleavage of chain ends of crystalline cellulose are found in CAZy families GH6 and GH7. Typically, only one to two gene models for GH6 (CBHII) enzymes are present in the white rot Basidiomycota (Table 11.3). For GH7 exoglucanases (CBHI), a different pattern is seen with variant gene numbers, and in the white rot model fungus *P. chrysosporium*, an expansion of GH7-encoding genes (seven to eight genes)

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was observed. The genomes of the soil-inhabiting, coprophilic Basidiomycota Agaricomycetes species *Coprinopsis cinerea* and the straw-colonizing species *Volvariella volvacea* both contain an increased number of genes for the CBHs (GH6 and GH7), which indicates substantial cellulolytic activity and decomposition ability of litter lignocellulose polysaccharides. On the contrary, loss of both CBH gene families (GH6 and GH7) is observed in the agaricomycetes brown rot species *Rhodonia* (*Postia*) *placenta*, *Fomitopsis pinicola*, *Gloeophyllum trabeum*, *Wolfiporia cocos* and *Dacryopinax* sp., and in the ectomycorrhizal species *Laccaria bicolor* (Table 11.3; Floudas et al., 2012; Martin et al., 2008). The brown rot species of the order Boletales (*Serpula lacrymans* and *Coniophora puteana*) have, however, retained their CBH gene models (Table 11.3; Eastwood et al., 2011; Kajisa, Igarashi, & Samejima, 2009).

p0125 In addition to hydrolytic enzymes, lignocellulose-degrading Basidiomycota secrete extracellular oxidative enzymes, which apparently attack on crystalline cellulose microfibril regions. These include the lytic polysaccharide monooxygenases (LPMOs, former family GH61), now reclassified to auxiliary activity CAZy family AA9, and cellobiose dehydrogenases (CDH) of family AA3 Au7 (Henriksson, Johansson, & Pettersson, 2000; Medie et al., 2012; Vaaje-Kolstad et al., 2010). AA9 LPMO gene models show significant expansions in the Basidiomycota white rot species as well as in the litter-decomposing species, and LPMO enzymes have been identified in fungal cultures on wood (Vanden Wymelenberg et al., 2011).

p0130 Combining the genomic information with gene expression studies, it may be concluded that the common ancestor of Basidiomycota Agaricomycetes was able to attack crystalline cellulose by production of the GH6 and GH7 CBHs and AA9 LPMOs, similar to the contemporary white rot species and litter-decomposing agaricomycetes soil saprotrophs. Except for *C. puteana*, the brown rot agaricomycetes genomes include AA9 gene models in lower numbers (Table 11.3), which is in line with their alternative, nonenzymatic Fenton chemistry-based oxidative destruction of cellulose.

p0135 Cellobiose dehydrogenase (CDH, CAZy family AA3) has versatile oxidoreductive activities, such as reduction of quinones and dioxygen while using, for example, cellobiose as electron donator. CDH has the combination of FAD and heme as prosthetic ligands (Henriksson et al., 2000), which is unique among extracellular enzymes. As proteins, CDHs are grouped to the glucose–methanol–choline GMC oxidoreductase superfamily of FAD-binding oxidases and dehydrogenases (Pfam family PF00732). White rot

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species have one CDH gene model (two in *H. irregulare*), whereas in some brown rot species, the gene is absent (Table 11.2).

s0065 3.3. Hemicellulose breakdown

p0140 Hydrolysis and degradation of plant hemicelluloses are more complicated due to the diverse chemical composition and presence of branched sugar units, acetyl groups and covalent cross-linkages in hemicelluloses, the latter in particular in grass plant biomass (see earlier). Due to this heterogeneity, a diverse group of backbone cleaving and debranching enzymes are needed for decomposition. According to the number of gene models, the enzymatic machinery for hemicellulose degradation is divergent between white rot and brown rot fungi. CAZy families GH10 and GH11 both contain endoxylanase activities, and GH10 enzymes are able to cleave substituted xylan backbones due to lower substrate specificity. The preferred substrates for GH11 enzymes are unsubstituted xylan chains (van den Brink & de Vries, 2011). Several genes (two to six genes, only one in *S. lacrymans*) for GH10 enzyme models are present in the wood-decay and litter-decomposing species (Table 11.3). GH11 genes are much scarcer in the wood-decay genomes with only a single gene present or being completely absent. However, in the litter-decomposing genomes, two to six genes for GH11 enzymes are depicted. A larger array of GH11 endoxylanases indicate adaptation to more efficient degradation of backbone linkages of xylan (β-1,4-D-xylopyranose chains), which is the prominent hemicellulose in grass plants and grass litter (Bidlack et al., 1992).

p0145 Xylooligosaccharides are further degraded to monosaccharides by β-xylosidases of which the majority of fungal gene models represent CAZy family GH3 (www.cazy.org; de Vries and Visser, 2004; Shallom & Shoham, 2003). Family GH3 β-xylosidases are common in Ascomycota species, whereas no such enzymes have yet been characterized from Basidiomycota. CAZy family GH43 comprises diverse enzyme activities able to cleave glycosidic linkages of hemicelluloses and pectins. Putative GH43 β-xylosidases are identified more frequently in white rot genomes (2–26 gene models) than in brown rot species (one to seven genes). A striking expansion of GH43 gene models is observed for *Auricularia delicata*, which is in correlation with its white rot decay lifestyle on wood (Table 11.3).

p0150 Xyloglucanases, which belong to CAZy families GH 5, 12 and 74 (Grishutin et al., 2004), are, for example, needed for cleavage of coniferous softwood xyloglucan hemicelluloses. White rot and litter-

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decomposing Basidiomycota possess putative GH74 enzymes (one to four genes) (Table 11.3). Most brown rot species lack genes encoding GH74, except for *G. trabeum* and *S. lacrymans*, which both possess a single gene for GH74. In contrast, gene models for GH12 enzymes are generally found in the wood-decay and litter-decomposing genomes.

p0155 In addition, other hemicellulose-degrading enzymes such as α-arabinofuranosidases (GH51 and GH54), α-glucuronidases (GH67 and GH115), acetyl xylan esterases (CE1), feruloyl esterases (CE1) and glucuronoyl esterases (CE15) are needed for cleaving of the backbone chains and branching side groups (de Vries & Visser, 2001; Saha, 2003; Shallom & Shoham, 2003). These enzyme models are found in variable numbers in the Basidiomycota genomes (Table 11.3). For instance, CE1 feruloyl esterase gene models are more general, although in low numbers (one to four genes) in the white rot and litter-decomposing species, whereas in the brown rot genomes, these genes are absent except for *G. trabeum*.

p0160 The backbone of coniferous softwood galactoglucomannan hemicellulose is cleaved by endomannanases of CAZy families GH5 and GH26, and the oligosaccharides are further cleaved to monosaccharides by β-mannosidases (family GH2) and β-glucosidases (several CAZy families). Most wood-decay fungal endomannanases are grouped in the family GH5 (Table 11.3), whereas the genes for GH26 enzymes are rare in these genomes (Floudas et al., 2012).

s0070 3.4. Pectin breakdown

p0165 CAZy glycoside hydrolases (GH families) and polysaccharide lyases (PL families) are needed for the degradation of plant biomass pectin chains. Endo- and exo-polygalacturonases of the family GH28 cleave the backbone of the smooth regions of pectin chains, whereas endo- and exo-rhamnogalacturonase (GH28), xylogalacturonase (GH28), α-rhamnosidases (GH78), unsaturated glucuronyl hydrolase (GH88) and unsaturated rhamnogalacturonan hydrolase (GH105) enzyme activities are involved in cleaving the intricate branching and hairy regions of pectins (Martens-Uzunova & Schaap, 2009). Gene models for GH28 pectinases are common in high numbers (3–17 genes) in the plant biomass-degrading Basidiomycota genomes (Table 11.3), thus indicating efficiency and flexibility in responding to different types of plant substrates containing chemically variable pectin polysaccharides. Phylogeny of GH28 protein sequences in Ascomycota and Basidiomycota species indicates enzyme

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grouping according to divergent biochemical functions, with endo-polygalacturonase and endo-rhamnogalacturonase activities forming distinct, apparently ancient clades, while the exo-polygalacturonases are more widely distributed among fungi (Saha, 2003; van den Brink & de Vries, 2011).

4. LIGNIN BREAKDOWN AND LIGNIN-MODIFYING ENZYMES

p0170 Most lignin-modifying enzymes are metal-containing oxidoreductases secreted by the wood- and litter-decaying, saprobic Basidiomycota species (Lundell et al., 2010). Oxidation and conversion of lignin even up to carbon–carbon bond cleavage and partial mineralization occur by the biochemical action of the white rot fungi (Hammel & Cullen, 2008; Hatakka & Hammel, 2010; Kirk & Farrell, 1987). Classically, laccases and class II heme-containing peroxidases were considered as lignin-degrading enzymes, but these activities may be expanded to the assisting enzymes that produce H_2O_2, oxidize aromatic alcohols or reduce or oxidize fungal-generated and lignin-derived quinones and phenols (Lundell et al., 2010; Martínez et al., 2009).

p0175 The lignin-modifying oxidoreductases are listed in the CAZy database as auxiliary activities (AA) (Levasseur et al., 2013). In addition, the oxalate-degrading enzymes may be included in the pool of enzymes regulating fungal decomposition of lignin and lignocelluloses (Mäkelä et al., 2010). Oxidation and covalent bond cleavage in lignin and its subunits are promoted by lipid peroxidation, which generates peroxyl radicals and enhances the oxidative reactions of lignin-modifying manganese peroxidases (MnPs) (Hofrichter, Lundell, & Hatakka, 2001; Kapich, Korneichik, Hatakka, & Hammel, 2010; Lundell et al., 2010).

4.1. Multicopper oxidases

p0180 Laccases of CAZy family AA1 are phenol oxidases belonging to the multicopper oxidase (MCO) superfamily (Baldrian, 2006; Hoegger, Kilaru, James, Thacker, & Kües, 2006) and are generally expressed by lignocellulose and plant biomass-degrading saprobic Basidiomycota and Ascomycota species, as well as plant pathogenic species. Four-copper-containing fungal laccases (blue laccases) are identified as gene models in the white rot and brown rot genomes, except for the white rot model species *P. chrysosporium* (Table 11.2). Expansion to over 10 laccase genes has

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occurred in the genomes of many white rot species, as well as in the litter-decomposing Basidiomycota, whereas brown rot species harness a lower number (0–7) of laccase-encoding genes. Besides laccases, the AA1 class includes other MCO enzymes such as intra- and extracellular ferro-oxidoreductases, which are important, for example, in iron homeostasis (Hoegger et al., 2006; Larrondo, Salas, Melo, Vicuña, & Cullen, 2003).

p0185 Laccases have several functional roles for fungi, not only being involved in the oxidation of extracellular phenols and toxic compounds but also participating in hyphal fusions, basidiocarp and spore formation and pigment synthesis (Baldrian, 2006; Thurston, 1994). Due to the universality of laccases and MCO enzymes in organisms—laccases are not only found in fungi but also in plants, insects, bacteria, and archaea—and their absence in the model white rot lignin-degrading genome of *P. chrysosporium*, the role of laccases in actual oxidation and degradation of lignin is not evident. Laccases are unable to directly oxidize nonphenolic, high-redox potential lignin model compounds and lignins. However, in combination with low-molecular-weight phenolic and nitrogen-substituted compounds, the laccase-mediator-system-promoted oxidation of lignin-like and larger aromatic compounds is possible (Lundell et al., 2010; Martínez et al., 2009; Morozova, Shumakovich, Shleev, & Yaropolov, 2007), and thereby, laccases may be included in the pool of lignin-modifying fungal enzymes.

s0085 4.2. Lignin-modifying class II peroxidases

p0190 The lignin-modifying fungal peroxidases (PODs) are classified in the CAZy database to the oxidoreductase family AA2. Functionally, PODs are divided to manganese-oxidizing peroxidases (MnPs), lignin peroxidases (LiPs), and versatile peroxidases (VPs), which are categorized as high-redox potential peroxidases due to their ability to abstract electrons from high-redox lignin-like aromatic substrate molecules (Hofrichter, Ullrich, Pecyna, Au8 Liers, & Lundell, 2010; Ruiz-Dueñas & Martínez, 2009). Fungal generic peroxidases (GPs) are as well heme-including enzymes but lacking the manganese binding site or protein surface redox centre, thus apparently being unable to oxidize lignin units, and are thereby referred as low-redox potential peroxidases. Fungal-secreted PODs belong to the class II heme-containing "plant peroxidases" or "nonanimal peroxidase superfamily" (Hofrichter et al., 2010; Welinder, 1992; Zamocky, Furtmüller, & Obinger, 2009), which together with the "animal peroxidases" are all grouped in the large Pfam peroxidase PF00141 protein family. Novel

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nomenclature and peroxidase enzyme grouping are emphasized in the PeroxiBase database (http://peroxibase.toulouse.inra.fr/; Oliva et al., 2009).

p0195 According to genomic data, it is evident that wood white rot lifestyle is correlated with the presence of class II lignin-modifying POD peroxidases (Floudas et al., 2012). The lignin-degrading Basidiomycota genomes possess multiple MnP-, VP- or LiP-encoding genes, whereas the brown rot genomes include only low-redox potential, nonligninolytic general peroxidases (0–2 GP genes) (Table 11.2). Several class II fungal peroxidases are structurally characterized (long-MnPs, VPs, short-MnPs, LiPs and CiP/ARP) (Hofrichter et al., 2010; Ruiz-Dueñas et al., 2013; Ruiz-Dueñas & Martínez, 2009).

p0200 Mn binding site in MnPs and VPs consists of three acidic amino acid residues (two Glu, E35 and E39, and one Asp, D179, residues in mature *P. chrysosporium* MnP1), which are crucial for hexacoordination of the Mn^{2+} ion, thereby facilitating rapid electron transfer to the heme porphyrin and oxidized ferryl iron (Gold et al., 2000; Sundaramoorthy, Gold, & Poulos, 2010). The oxalate-chelated Mn^{3+} ions act as diffusible charge transfer mediators and attack phenols and larger biopolymers, such as synthetic lignin (Wariishi et al., 1991), milled wood (Hofrichter et al., 2001), brown coal, dyes and xenobiotic compounds and wood lignin in biopulping Au9 (Hatakka & Hammel, 2010; Hofrichter, 2002; Husain, 2010; Lundell et al., 2010).

p0205 Among lignocellulose and wood-decay white rot Basidiomycota, MnPs are the most commonly discovered class II lignin-modifying peroxidases (Table 11.2). The first MnP-encoding gene developed in the early agaricomycetes lineage (Floudas et al., 2012). Later, the ancient gene diverged by gene duplications to several subfamilies of long- and short-MnP enzymes and, via emergence of a protein surface-exposed radical centre amino acid (tryptophan), to VPs and then to LiPs by modification of the Mn binding site (Ruiz-Dueñas et al., 2013). Gene expansions and functional modifications are seen in the white rot Polyporales species, and atypical short-MnP models with altered Mn binding sites are as well recognized, for example, five gene models in *Stereum hirsutum* (Ruiz-Dueñas et al., 2013).

p0210 Number and character of MnP-encoding genes vary greatly in the white rot genomes (5–16) (Table 11.3). It is noteworthy that short-MnP enzyme-encoding genes are identified in the genomes of the litter-decomposing species *Agaricus bisporus* (two genes) and straw-cultivated mushroom *Volvariella volvacea* (four genes), whereas the saprobic *C. cinerea* and the ectomycorrhizal

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species *L. bicolor* have no MnP gene models. Instead of MnP-encoding genes, the two latter genomes possess one gene encoding a general peroxidase (GP, low redox potential). The *C. cinerea* GP enzyme (CiP) has been cloned, heterologously expressed, and structurally well characterized (Hofrichter et al., 2010; Kunishima et al., 1994).

p0215 LiP is catalytically the most powerful class II fungal peroxidase with the ability to directly oxidize dimeric lignin-like model compounds at the protein surface-exposed tryptophan radical centre (Choinowski, Blodig, Winterhalter, & Piontek, 1999). LiP is expressed and secreted as sets of multiple isozymes by, for example,. *P. chrysosporium*. LiP and VP gene models are so far identified only in a few wood-decay Basidiomycota genomes. The efficient white rot lignin-degrading Polyporales species, such as *P. chrysosporium*, *Gelatoporia* (*Ceriporiopsis*) *subvermispora*, *Dichomitus squalens*, *Trametes versicolor*, *Phlebia brevispora* and *Bjerkandera adusta* (Ruiz-Dueñas et al., 2013), as well as the wood-colonizing, white rot Agaricales species *Pleurotus ostreatus* (Ruiz-Dueñas et al., 2011), all contain either LiP or VP genes. LiP-encoding gene families are significantly expanded in *B. adusta* (12 genes) (Ruiz-Dueñas et al., 2013), *P. chrysosporium* (10 genes) and *T. versicolor* (10 genes) (Table 11.3).

s0090 4.3. Other lignin-modifying, fungal-secreted peroxidases

p0220 Together with the high-redox potential class II PODs, the heme-thiolate peroxidases (HTPs) and dye-decolorizing peroxidases (DyP) may be included in the pool of fungal-secreted, heme-containing and lignin-modifying peroxidases (Hofrichter et al., 2010), since oxidation of lignin model compounds has been demonstrated for isolated HTPs and DyPs from Basidiomycota species (Liers et al., 2010; Ullrich, Nüske, Scheibner, Spantzel, & Hofrichter, 2004). HTP enzymes are characterized as either chloroperoxidases (CPOs) or aromatic universal peroxygenases (APOs and UPOs). In the Basidiomycota genomes, HTP genes are identified in highly variable numbers (3–25), whereas DyP genes are either absent (in many brown rot genomes) or present in low gene numbers (1–5) (Table 11.2). Exceptional expansion of HTP gene family is observed in the litter-decomposing Basidiomycota species *A. bisporus* (25 genes; Morin et al., 2012), and in the wood-decay white rot species *A. delicata*, expansion for both DyP and HTP gene families has occurred (Table 11.2).

p0225 *A. bisporus* HTP-encoding genes are transcribed when the fungal hyphae are colonizing humic-rich straw compost substrate, which indicates a

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particular role of these enzymes for, for example, successful growth in soil environments, which are extensive with humic substances (Morin et al., 2012). The second function for the HTP enzymes may be modification of fungal-produced secondary metabolites and bioactive compounds, such as is evident in the case of production of hypochlorite and caldariomycin by chloroperoxidase of *Caldariomyces fumago* (Osborne, Raner, Hager, & Dawson, 2006), thus protecting the fungus against other microbes in the highly competed soil environments.

s0095 ## 4.4. GMC superfamily oxidases and oxidoreductases

p0230 Extracellular generation of H_2O_2 is important for the catalysis of the class II lignin-modifying heme peroxidases and for the generation of highly reactive hydroxyl radicals via Fenton reaction (Hammel & Cullen, 2008). Copper radical oxidases (CROs, CAZy family AA5) and FAD-dependent oxidases such as the GMC (glucose–methanol–choline) superfamily oxidoreductases (CAZy family AA3) have been suggested to play a role in the production of extracellular H_2O_2 for wood-decay fungi (Martinez et al., 2004, 2009). GMC oxidoreductases are catalytically distinct from CROs including various alcohol and sugar oxidases.

p0235 Aryl alcohol oxidase (AAO; family AA3_2) is an extracellular FAD-containing GMC oxidoreductase, which is suggested to be involved in generation of H_2O_2 in the redox cycling of aromatic fungal metabolites (Gutíerrez et al., 1994). The defined role of AAO is uncertain, but it has been proposed that AAO enzymes cooperate with aryl alcohol dehydrogenases for continuous H_2O_2 supply at least in some white rot fungi such as *Pleurotus*, *Bjerkandera* and *Trametes* species (Gutíerrez et al., 1994; Martínez et al., 2009). Except for *A. delicata*, AAO gene models are identified in variant numbers (2–14 genes) in the white rot and litter-decomposing agaricomycetes genomes (Table 11.2), whereas in the brown rot genomes, the gene may be absent. The highest gene number is annotated for the litter-decomposing *C. cinerea*.

p0240 FAD-dependent alcohol oxidases (AOX; AA3_3) catalyse the oxidation of primary alcohols to corresponding aldehydes, and pyranose oxidases (POX; AA3_4) oxidize D-glucose, both enzymes generating H_2O_2 as side product (Kroutil, Mang, Edegger, & Faber, 2004; Martínez et al., 2009). In wood-decay Basidiomycota, AOX gene models (1–4) are present, whereas POX genes are only identified in a few white rot genomes (Table 11.2). Expansion of AOX gene family is observed for *S. hirsutum* (seven genes) and *H. irregulare* (16 genes).

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p0245 Glyoxal oxidase (GLOX; AA5_1) belongs to the enzyme family of copper radical oxidases (CROs) including enzymes like galactose oxidase (GAOX). GLOX reduces O_2 to H_2O_2 and it has broad substrate specificity for the oxidation of simple aldehydes, such as glyoxal and methylglyoxal, to the corresponding carboxylic acids (Whittaker et al., 1996). GLOX and GAOX are copper metalloenzymes containing an unusual free radical-coupled Cu in the active site. Predicted WSC (cell wall integrity and stress-response component) domains in GLOX proteins were suggested to be involved in carbohydrate binding, and they have been detected in three of the CRO-encoding genes of *P. chrysosporium* (Vanden Wymelenberg et al., 2006). In white and brown rot wood-decay and litter-decomposing agaricomycetes genomes, many GLOX models (two to nine genes) are depicted (Table 11.2). Interestingly, expansion to 11 GLOX-encoding model genes has occurred in the ectomycorrhizal *L. bicolor* genome.

s0100 5. *PHANEROCHAETE CHRYSOSPORIUM* AND WOOD DECAY

p0250 Due to the limited number of wood- and litter-decaying fungal genome sequences, only recently, transcriptome and proteome studies have elucidated the enzyme profiles employed for plant biomass degradation by Basidiomycota species. The first published basidiomycete genome was from *Phanerochaete chrysosporium*, which is the most intensively studied model fungus for white rot wood decay and lignin degradation (Martinez et al., 2004). *P. chrysosporium* was also the first wood-decay species subjected to thorough transcriptome and secretome studies. The initial studies were performed in carbon- and nitrogen-limited synthetic media and on cellulose (Vanden Wymelenberg et al., 2005) after which the focus has been on complex plant biomass substrates. This ground-breaking data enabled comparative transcriptome and secretome studies with other plant biomass-degrading species of Basidiomycota, such as *P. placenta*, *C. subvermispora*, *A. bisporus* and *Phanerochaete carnosa* (Fernandez-Fueyo et al., 2012; Morin et al., 2012; Au10 Suzuki et al., 2012; Vanden Wymelenberg et al., 2011). These functional studies have corroborated enzymatic and biochemical evidence of the individual and dissimilar mechanisms of lignocellulose degradation between species and their lifestyles. In addition, studies on diverse lignocellulosic substrates have revealed quick fungal physiological adaptation to changes

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in carbon and nutrient source, which is observed as altering transcript and secretome profiles.

s0105 ## 5.1. *Phanerochaete* transcriptome and secretome on lignocellulose

p0255 Seven cellulose-degrading cellobiohydrolase enzymes (CBHs from CAZy families GH6 and GH7) of *P. chrysosporium* are expressed and produced differentially on various carbon sources, demonstrating the complexity and diversity of cellulolytic strategy of the species (Broda, Birch, Brooks, & Sims, 1995; Ravalason et al., 2008; Suzuki, Igarashi, & Samejima, 2010; Vallim, Janse, Gaskell, Pizzirani-Kleiner, & Cullen, 1998; Vanden Wymelenberg et al., 2009). Cellulose induced concurrent expression of an array of cellulose-attacking genes encoding putative endoglucanases (GH5), CBHs (GH6 and GH7), xylanases (GH10 and GH11) and lytic polysaccharide monooxygenase (LPMOs, CAZy family AA9) (Vanden Wymelenberg et al., 2009). In comparison, xylan hemicellulose as carbon source stimulated production of one putative endoxylanase (GH10) and glucuronoyl esterase (CE15), as well as one CDH and several LPMOs, suggesting that these enzymes are as well involved in the degradation of a wider array of plant polysaccharides than only cellulose (Hori, Igarashi, Katayama, & Samejima, 2011). On the contrary, addition of starch (α-1,4-interlinked polymer of D-glucose) to cellulose cultures of *P. chrysosporium* repressed production of the cellulolytic and xylanolytic enzymes (Hori et al., 2011).

p0260 In comparison of *P. chrysosporium* to another species from the genus *Phanerochaete*, *P. carnosa*, production of a similar set of extracellular GH and oxidoreductase enzymes occurred in both species upon growth on spruce wood or cellulose (Mahajan & Master, 2010). However, on spruce softwood, quantitative differences in the gene expression profiles were detected between the species. CAZyme-encoding genes were expressed most abundantly by *P. chrysosporium* (Sato, Feltus, Iyer, & Tien, 2009; Vanden Wymelenberg et al., 2010), whereas in *P. carnosa*, the CAZy AA2 lignin-modifying peroxidase transcripts and H_2O_2-producing enzyme-encoding genes were upregulated (MacDonald et al., 2011). Same abundance of lignin-modifying gene transcripts over polysaccharide-related gene expression was also observed in *P. carnosa* cultures on different hardwood and softwood species (lodgepole pine, white spruce, balsam fir and sugar maple), with the highest relative transcript levels for a single gene encoding a putative LPMO (AA9) (MacDonald et al., 2011). Among the

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lignin-modifying enzymes, notable upregulation of MnP-, LiP-, GLOX- and P450 monooxygenase-encoding genes was observed. Transcripts encoding CBHs (GH6 and GH7), endoglucanase (GH5) and xylanases (GH10) were among the most abundant of the pool of cellulose and hemicellulose-degrading enzyme-expressed genes.

p0265 These data indicate that *P. carnosa* produces similar sets of carbohydrate- and lignin-attacking enzymes on angiosperm hardwood and gymnosperm softwood, but with variable levels of gene expression (MacDonald et al., 2011). While *P. carnosa* secretomes from semisolid white spruce (*Picea glauca*) and microcrystalline cellulose cultures likewise performed similar protein profiles, it was proposed that minor changes in regulation of gene expression enable the growth of *P. carnosa* on various lignocelluloses (Mahajan & Master, 2010). Among the secreted enzymes, putative mannanase (GH5), CBH (GH6 and GH7), xylanase (GH10), endoglucanase (GH16), arabinofuranosidase (GH43) and glucuronoyl esterase (CE15) proteins were detected, as well as putative LPMO enzymes supporting the combination of both hydrolytic and oxidoreductive enzyme attack for degradation of cellulose by white rot fungi. In addition, lignin-modifying MnP, LiP and H_2O_2-producing GLOX and GMC oxidoreductases were identified.

s0110 5.2. White Rot fungal secretome and selective degradation of lignin

p0270 Studies on transcriptomes and secretomes on lignocelluloses support the view of white rot species degrading cellulose by both hydrolytic and oxidoreductive extracellular reactions, which has led to a novel concept of oxidative cellulose biodegradation. For instance, *P. chrysosporium* produces the cellobiose-oxidizing CDH (AA3_1, AA8) enzyme during growth on red oakwood, wheat straw and cellulose (Salvachúa et al., 2013; Sato et al., 2009; Vanden Wymelenberg et al., 2005). In addition, peptides of CDH and LPMOs have been secreted by the white rot species *B. adusta*, *D. squalens*, *Ganoderma* sp., *P. brevispora* and *T. versicolor* in aspen cultures (Hori et al., 2013). On wheat straw, AA9 LPMO enzymes were also present in the secretomes of *P. chrysosporium* and *Irpex lacteus* (Salvachúa et al., 2013).

p0275 The sequenced genome of *Ceriporiopsis* (*Gelatoporia*) *subvermispora* and its transcriptome on aspen hardwood have given insights into the mechanism of selective lignin degradation (Fernandez-Fueyo et al., 2012). In comparison to *P. chrysosporium*, which simultaneously depolymerizes all the plant cell wall polymers, *C. subvermispora* harbours an increased number of AA2 lignin-modifying MnP-encoding genes (13; Table 11.2) of variant protein

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structures and lipid metabolism-related desaturase-encoding genes. The gene expression data emphasize the importance of the lignin-modifying oxidoreductases operating in connection to lipid peroxidation (Hofrichter et al., 2001; Kapich et al., 2010) in order to generate efficient attack against lignin moieties, together with diminished capacity for cellulose degradation, to facilitate selective white rot fungal decomposition of lignin (Fernandez-Fueyo et al., 2012).

p0280 The number and expression patterns of putative cellulase-encoding genes vary between the white rot species *P. chrysosporium* and *C. subvermispora*. For example, *P. chrysosporium* harbours seven protein models of GH7 CBHs (Table 11.3), whereas three GH7 protein models are identified for *C. subvermispora* (Fernandez-Fueyo et al., 2012). Four of the *P. chrysosporium* GH7-encoding genes were significantly upregulated in aspen-containing medium, while only one GH7-encoding gene was induced in *C. subvermispora* under similar conditions. For endoglucanases, significant increase in the amount of transcripts corresponding to two GH5 β-1-4-endoglucanases and two GH12 endoglucanases was detected in cultures of *P. chrysosporium*, while a single GH5 β-1-4 endoglucanase and GH12 endoglucanase gene were induced in the cultures of *C. subvermispora*. *P. chrysosporium* also expressed hemicellulases at a higher level when cultivated on aspen hardwood (Fernandez-Fueyo et al., 2012). Of the putative hemicellulases of *C. subvermispora*, only two to three GH5 and GH10 enzyme-encoding genes, respectively, and one gene for CE1 feruloyl esterase were upregulated. In contrast, the transcripts of genes encoding two GH5, three GH10, GH43, GH53, CE15, four GH74, one CE1 feruloyl esterase and one GH95-encoding gene transcript presented significant accumulation in the cultures of *P. chrysosporium*. The aspen culture secretomes of the two species demonstrated a higher number of CAZy GH glycoside hydrolases for *P. chrysosporium* (18) than produced by *C. subvermispora* (3), thus confirming the transcriptome data. In contrast, both species showed significant expression of multiple putative LPMO-encoding genes on aspen lignocellulose.

p0285 In respect to transcriptome features upon fungal degradation of plant biomass, upregulation of numerous HTP heme-thiolate peroxidase (over 20) and β-etherase-encoding genes was observed during mycelial growth of *A. bisporus* on litter compost (Morin et al., 2012). Gene expression pattern distinguishes this litter-decomposing species from the wood-decay white rot and brown rot species. Most possibly, expression of HTP peroxidases is a response to chemical composition of the fungal growth environment

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abundant with soil humic acids. One of the two *A. bisporus* short-MnP-encoding AA2 genes was also highly expressed on compost (Morin et al., 2012). It should be noted that over 50% of the CAZyme-encoding gene repertoire of *A. bisporus* (Table 11.3) was upregulated in the course of mycelial growth in the lignocellulose-compost cultures.

s0115 5.3. Brown rot versus white rot decay of wood

p0290 Comparative transcriptomics study of *P. chrysosporium* and the brown rot species *Postia* (*Rhodonia*) *placenta* (Vanden Wymelenberg et al., 2011) supported the biochemical evidence and divergent fungal lifestyles for wood-decay adopted for white rot and brown rot degradation of plant biomass. *P. placenta* produces oxidoreductive oxidase enzymes that putatively generate extracellular Fe^{2+} and H_2O_2, which are needed for the non-enzymatic cellulose depolymerization by Fenton chemistry (see Section 2.2). The role of fungal cellulose-cleaving GH glycoside hydrolases is therefore less significant in brown rot decay of wood compared to the so far better-characterized white rot fungal decay of lignocellulose (Martinez et al., 2009; Vanden Wymelenberg et al., 2010).

p0295 When the transcriptomes of *P. chrysosporium* and *P. placenta* were studied in semisolid hardwood aspen (*Populus grandidentata*) and softwood pine (*Pinus strobus*) cultures, a considerable difference in gene expression patterns was detected depending on the wood species (Vanden Wymelenberg et al., 2011). In addition, the transcriptome and secretome data from various lignocellulosic substrates have emphasized the importance of the AA2 oxidoreductase class II peroxidases in white rot fungal degradation of plant biomass (Salvachúa et al., 2013). Interestingly, both transcriptome and proteome studies have highlighted the importance of enzymatic, extracellular H_2O_2 production for both white and brown rot decay mechanisms (Martinez et al., 2009; Ravalason et al., 2008; Salvachúa et al., 2013; Sato et al., 2009; Vanden Wymelenberg et al., 2009, 2010).

p0300 Secretome analysis of five white rot (*B. adusta*, *D. squalens*, *Ganoderma* sp., *P. brevispora* and *T. versicolor*) and two brown rot agaricomycetes (*F. pinicola* and *W. cocos*) cultivated in liquid medium with milled aspen wood as the sole carbon source further corroborates the distinct strategies used by wood-decay fungi for degradation of plant polysaccharides (Hori et al., 2013). CAZy AA6 oxidoreductase family quinone reductases were solely present in the brown rot secretomes of *F. pinicola* and *W. cocos*, which is in accordance to results obtained for *P. placenta* on lignocellulose

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(Martinez et al., 2009; Vanden Wymelenberg et al., 2010) and supports the role of quinone reductases in brown rot Fenton chemistry (Hammel et al., 2002; Suzuki, Hunt, Houtman, Dalebroux, & Hammel, 2006). However, high expression of a single endoglucanase of CAZy family GH5 was observed for *P. placenta* on aspen and pine cultures, thus suggesting involvement of this particular enzyme in cellulose degradation by the fungus (Vanden Wymelenberg et al., 2011). In addition, putative GH28 pectinases (polygalacturonase and rhamnogalacturonase) were highly expressed in pinewood supplemented cultures of *P. placenta* (Vanden Wymelenberg et al., 2011).

p0305 Transcriptome and proteome analyses have revealed dissimilarities in wood degradation mechanisms used by the two brown rot Basidiomycota species *P. placenta* and *S. lacrymans* (Eastwood et al., 2011). *S. lacrymans* apparently employs CAZy GH glycoside hydrolases to depolymerize cellulose, whereas *P. placenta*, as is discussed earlier, degrades cellulose chains mainly nonenzymatically. When compared to glucose cultures, 21% of gene transcripts showing significant upregulation on pinewood cultures of *S. lacrymans* consisted of GH glycoside hydrolases and AA oxidoreductases. A notable increase in the transcript levels was observed for the genes encoding GH3, GH5, GH28 and GH74 enzymes and, interestingly, also for genes that encode putative AA9 LPMOs (Eastwood et al., 2011).

p0310 Several studies with *P. placenta* support the ability of brown rot Basidiomycota to modify lignin by demethylation of the lignin aromatic ring ether side groups, which is demonstrated by upregulation of specific AA3 GMC oxidoreductase superfamily methanol oxidase-encoding genes. Methanol oxidases produce H_2O_2 by oxidizing the lignin-derived methanol (Martinez et al., 2009; Vanden Wymelenberg et al., 2010). In contrast, the role of LPMOs in brown rot decay of wood remains yet unclear. Although a few AA9 LPMO-encoding gene models are present in brown rot fungal genomes (Table 11.2), the corresponding protein has so far been identified only from milled aspen wood secretome of *G. trabeum* (Floudas et al., 2012).

s0120 6. CONCLUSIONS AND OUTLOOK

p0315 As described in the previous parts of this chapter, decay of wood and leaf and forest litter is a major part of the global carbon cycle (Section 1), and fungi are the dominant players in the decomposition processes in terrestrial environments. In particular, Basidiomycota species have been shown to have a strong ability for wood and litter decay, although the physiological

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variations among them, for example, with respect to white and brown rot decay mechanism, are significant (Section 2). Studies into wood decay and litter decomposition have been performed for many decades, but the recent increase in the availability of plant biomass-degrading Basidiomycota genome sequences (Eastwood et al., 2011; Fernandez-Fueyo et al., 2012; Floudas et al., 2012; Morin et al., 2012; Olson et al., 2012; Suzuki et al., 2012) has enabled a much deeper understanding of the factors involved in the degradation processes and conversion of organic polymers and compounds. Availability of the genome sequences has not only revealed the complexity of the fungal enzyme systems (Fig. 11.2; Sections 3 and 4), but the following post-genomic approaches (transcriptomics and proteomics) have started to reveal the complex regulatory mechanisms that underlie the biological conversion processes (Section 5).

p0320 However, as most of the plant biomass-related enzymes that have been discovered in fungal genomes (Fig. 11.2) have not yet been studied biochemically or genetically, their exact roles remain speculative. While assigning the predicted genes to particular enzyme families provides a likely hypothesis about general enzymatic activity, their substrate specificity and enzyme kinetic properties remain largely unknown, which complicates envisaging their exact role in the decomposition of plant biomass. In addition, genomes of Basidiomycota species contain a significant portion of genes (20–40%) without characterized homologues, thus remaining functionally unknown, some of which appear to be specifically expressed during growth on wood or tree litter. For instance, proteomics of the wood white rot decaying species *Ganoderma lucidum*, a model polypore fungus traditionally used in the Far East for medicinal purposes, on sugar cane bagasse revealed the production of 71 proteins, comprising mainly of lignin-modifying oxidoreductase enzymes and glycoside hydrolases (Manavalan, Adav, & Sze, 2011). However, almost one-fifth of the secreted proteins were hypothetical, for which a role in plant biomass degradation is not clear. This indicates adaptations in growth strategies and biochemical mechanisms at the species level that result in this variation in saprobic lifestyles on plant biomass. To obtain a deeper understanding of theses variations, parallel genomic and post-genomic studies on taxonomically diverse Basidiomycota species are required, such as the comparative genomic saprobic agaricomycetes project (Floudas et al., 2012). Also, elucidating the role of the yet unknown and novel enzymes and assisting proteins will likely further enhance our understanding of the decay mechanisms. The presence of both brown rot and white rot species in naturally decaying wood (Ottosson, 2013;

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Ovaskainen et al., 2013) suggests that these two mechanisms in nature may act synergistically, even if they are mediated by different species.

p0325 The focus in wood decay and forest litter decomposition has so far been mainly on Basidiomycota species, largely due to their ability to also degrade the recalcitrant heteropolymer lignin, which appears to be absent in most Ascomycota species. However, ecological studies into the occurrence of fungi in wood and litter revealed that Ascomycota species are commonly found on these substrates, such as identification of several new *Penicillium* species isolated from leaf litter (Houbraken et al., 2011).

p0330 With such a common occurrence of Ascomycota naturally on plant litter, it is fair to assume that Ascomycota species participate in the overall plant biomass decomposition, although their functional role is largely unknown. Some studies addressing this have been performed in which individual fungal species have been tested for their ability to decay plant biomass substrates. Decomposition of fir needle and birch leaf litter revealed a higher ability for Basidiomycota than Ascomycota, in particular with respect to the lignin fraction (Osono & Takeda, 2006). A similar result was obtained in a study using larch needle litter (Osono, Fukasawa, & Takeda, 2003).

p0335 Based on these results, it could be hypothesized that Ascomycota species rely on Basidiomycota to degrade the plant biomass lignin fractions during decay of wood and litter, while Ascomycota mainly contribute to degradation of the plant biomass polysaccharides and other carbohydrates. However, their roles may be more complex than this. Some Ascomycota show good growth on lignin-rich substrates (www.fung-growth.org), although this may be due to residual amounts of carbohydrates or the presence of aromatic monomers and oligomers in the substrates. Also, it has been suggested that organic acids produced by fungi, such as oxalic acid, stimulate the degradation of plant biomass carbohydrates and lignin (Mäkelä et al., 2002). Many Ascomycota are good producers of organic acids (e.g. Schrickx, Raedts, Stouthamer, & van Verseveld, 1995), which could be an additional role they play in the overall decay process.

p0340 The complexity of wood and litter decay is underlined by the variety of fungal and bacterial species present in plant biomass during degradation processes. While we are starting to get a better picture of the composition of the microbial communities, and some of the key players in the degradation processes have become more evident due to the increased availability of genome sequences, we still have a long way to go in understanding the biochemical reactions as well as fungal metabolism and genetic regulation. This involves not only detailed analyses of individual organisms, such as fungal species, but

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also their interactions and ecological functions in microbial communities and in various environments, using, for example, metagenomic approaches. In nature, the combined abilities of the microbial communities create specific and overall degradation processes of the plant biomass polymers, which are more efficient than any man-made approach that has so far been designed. Unravelling these interplays and environmental conversion networks is a major challenge for future research.

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