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# Extracellular redox cycling and hydroxyl radical production occurs widely in lichenized Ascomycetes

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## ABSTRACT

Some free-living Ascomycetes and white and brown rot Basidiomycetes can generate hydroxyl radicals using extracellular redox cycling. However, the mechanisms of hydroxyl radical production differ between white and brown rot Basidiomycetes, and are unknown for Ascomycetes. Here, we present a survey of extracellular hydroxyl radical production by a range of lichenized Ascomycetes. Results show that given a quinone and chelated ferric ions, many lichens can readily produce hydroxyl radicals, and this is accompanied by the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . In white rot fungi, extracellular redox enzymes have been proposed to be involved in hydroxyl radical generation. However, a survey of a wide range of lichens suggests that in these fungi hydroxyl radical production does not directly correlate with the activity of laccases and peroxidases. Rather, radicals are probably produced by a mechanism like that proposed for brown rot fungi. Potential roles of hydroxyl radicals produced by lichens include the breakdown of lignocellulosic residues in the soil which may allow lichens to live a partially saprotrophic existence, the breakdown of toxic soil chemicals and the formation of an 'oxidative burst' to deter potential pathogens.

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## Introduction

Free-living fungi can produce reactive oxygen species (ROS) using extracellular redox cycling (Kerem *et al.* 1999; Cohen *et al.* 2004; Gómez-Toribio *et al.* 2009a,b; Krueger *et al.* 2015, 2016). ROS play a variety of roles in fungal biology such as the control of differentiation and defence against pathogens (Kim 2014). However, in many fungi, a key role of ROS is to breakdown lignocellulosic residues, thus facilitating

a saprotrophic lifestyle (Hammel *et al.* 2002; Baldrian 2008). In the early stages of the decay of compact higher plant tissues, conventional enzymes such as peroxidases and laccases are too large to penetrate these tissues. It has therefore been proposed that the breakdown of both lignin and cellulose requires the production of highly aggressive hydroxyl ( $\cdot\text{OH}$ ) radicals generated by 'Fenton' chemistry, essentially by reactions between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  (Arantes & Goodell 2014). The hydroxyl radical is the most aggressive non-specific oxidant in

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