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Early entombment within silica minimizes the molecular degradation of microorganisms during advanced diagenesis

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ABSTRACT

Most ancient organic microfossils delicately preserved in 3D have been found in cherts. Although entombment within silica has been shown to promote morphological preservation, the impact of early silicification on the molecular evolution of fossilized microorganisms during burial remains poorly constrained. Here, we report results of advanced fossilization experiments performed under pressure (250 bars) and temperature (250 °C) conditions typical of sub-greenschist facies metamorphism for different durations up to 100 days on microorganisms experimentally entombed (or not) within a silica gel. The experimental residues have been characterized using XRD and XANES spectroscopy. The present study demonstrates that entombment within silica limits the degradation of microorganism molecular signatures, likely through specific chemical interactions, despite the progressive conversion of silica into quartz during the experiments. Extrapolation of the present results suggests that such protection may persist during geological timescales. The present experimental study provides molecular evidence that, in addition to morphologies, cherts may support the chemical preservation of remains of ancient life. The present results thus constitute a step forward towards the reconstruction of the original chemistry of putative fossilized microorganisms.

1. Introduction

Ancient organic microfossils provide a great deal of information about the evolution of cellular life on Earth. Yet, in addition to hindering their identification, the inevitable degradation of the organic molecules comprising these microorganisms over the course of geologic time likely muddles the reconstruction of their original chemistry (e.g. Bernard and Papineau, 2014; Briggs and Summons, 2014). As a result, the search for the earliest fossil evidence of life on Earth has been and is still fraught with controversies (e.g. Schopf et al., 2002; Brasier et al., 2002; Schopf and Kudryavtsev, 2012; Brasier et al., 2015; Wacey et al., 2015).

Remarkably, most of the oldest (putative) organic microfossils delicately preserved in 3D reported so far have been found in cherts (*i.e.* silica-rich rocks), (e.g. Walsh and Lowe, 1985; Ueno et al., 2001, 2006; Westall et al., 2001, 2006, 2011, 2015; Tice and Lowe, 2004, 2006; Sugitani et al., 2007, 2010, 2013, 2015a, 2015b; Glikson et al., 2008; Javaux et al., 2010; Wacey et al., 2011a, 2011b, 2012; Lepot et al., 2013). Cherts are thus now recognized as windows of exceptional morphological preservation of organic microfossils (i.e. "Bitter Springs-type preservation", sensu Butterfield, 2003; Xiao and Schiffbauer, 2009). Despite this recognition and recent analytical progress, studies addressing the molecular signatures of (putative) organic microfossils morphologically preserved in ancient cherts remain rare (e.g., De Gregorio and Sharp, 2006; Igisu et al., 2009; De Gregorio et al., 2009, 2011; Alleon et al., 2016). Intriguingly, although these (putative) microfossils have experienced diagenetic temperatures similar to overmature clay-rich gas shales, *i.e.* prehnite-pumpellyite to greenschist facies metamorphism, their molecular signatures are significantly less degraded than those of overmature kerogens (Bernard et al., 2010b, 2012a, 2012b).

A priori, silicification might be invoked as the explanation for the limited molecular degradation experienced by these microfossils during advanced (thermal) diagenesis. The critical role of authigenic mineralization (e.g.., pyritization, calcification, phosphatization, chloritization, glauconitization) in the morphological survivability of organic fossils through geological times has indeed been recognized and highlighted by many authors (e.g., Orr et al., 1998; Briggs, 2003; Briggs and Wilby, 1996; Bernard et al., 2010a; Anderson et al., 2011; Galvez et al., 2012; Kremer et al., 2012; Broce et al., 2014; Schiffbauer et al., 2014; Wacey et al., 2014; Muscente et al., 2015). Consistently, a number of experimental studies have highlighted the importance of the close association with minerals (such as sulfides, carbonates, phosphates, hydroxides, clays) for the morphological (e.g., Briggs and Kear, 1993; Briggs et al., 1993; Grimes et al., 2001; Martin et al., 2003; Wilson and Butterfield,

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2014; Iniesto et al., 2015) and chemical (e.g., Li et al., 2013, 2014; Picard et al., 2015a, 2015b) preservation/degradation of soft tissues during fossilization processes.

Silicification processes have received even more attention: silicified microbial morphologies have been studied *in situ* by many authors in modern silicifying hydrothermal systems (Walter et al., 1972; Schultze-Lam et al., 1995; Cady and Farmer, 1996; Konhauser and Ferris, 1996; Jones et al., 1998, 2001, 2003, 2004; McKenzie et al., 2001; Konhauser et al., 2001, 2003, 2004; Handley et al., 2005, 2008; Campbell et al., 2015). In parallel, a number of authors have experimentally investigated the processes of silica polymerization and precipitation in the presence of microorganisms (e.g. Fortin and Ferris, 1998; Hinman, 1990; Fein et al., 2002; Yee et al., 2003; Benning et al., 2004a, 2004b). Further, the impact of early silicification on the morphologies of microorganisms has been extensively studied through laboratory experiments conducted under various conditions, from room temperature to pressure and temperature conditions typical of diagenesis (e.g. Oehler and Schopf, 1971; Oehler, 1976a; Walters et al., 1977; Francis et al., 1978a, 1978b; Birnbaum et al., 1989; Westall et al., 1995; Phoenix et al., 2000; Toporski et al., 2002; Lalonde et al., 2005; Orange et al., 2009, 2011a, 2011b, 2012, 2013a, 2013b, 2014).

Altogether, these studies have shown that the precipitation of amorphous silica is mainly controlled by the dehydroxylation of the active hydroxyl groups present at the surface of silica (silanols) and that the rate of amorphous silica polymerization and precipitation is independent of the presence of biomass, *i.e.* that the microbial role in silicification is predominantly incidental. During silicification, microorganisms likely act as templates for the binding and nucleation of silica, even though they have only little affinity for monomeric silica. Long exposure to silicifying media eventually leads to the complete impregnation of microorganisms by silica, with cell walls and intracellular granules progressively becoming the only recognizable features. Besides the pioneering study of Oehler (1976a), which investigated the geochemical evolution of algal soluble organics (lipids and pigments) during thermal diagenesis, and the recent study of Orange et al. (2012), which documented the changes in composition of archeal soluble organics (amino acids, polysaccharides and lipids) during silicification, the above-mentioned experimental studies have all only focused on morphologies. Although these studies have highlighted the high potential of silica matrices for the morphological preservation of microfossils, i.e. that early silicification of microorganisms allows their morphological preservation, the impact of advanced (thermal) diagenesis on the molecular signatures of silicified microorganisms remains to be precisely documented. In fact, this appears as the prerequisite to, eventually, clear the way for the reconstruction of the original chemistry of putative fossilized microorganisms.

Here, we report results of advanced fossilization experiments performed on prokaryotic cyanobacteria *Gloeobacter violaceus* and eukaryotic microalgae *Euglena gracilis* that we experimentally entombed within a silica gel initially consisting of opal-A, i.e. a hydrated amorphous form of silica. Following the philosophy of Oehler (1976a), who performed fossilization experiments under pressure and temperature conditions typical of diagenesis, the present advanced fossilization experiments have been performed at 250 °C and 250 bars for different durations (1, 10 and 100 days) to simulate burial-induced diagenetic processes. These temperature conditions typical of sub-greenschist facies metamorphism are similar to those experienced by most Archean cherts (e.g., Tice et al., 2004; Sugitani et al., 2007, 2010; Glikson et al., 2008; Javaux et al., 2010; Lepot et al., 2013). Regardless its value, pressure is important as it authorizes microtextural transformation (Beyssac et al., 2003). A sample of microorganism-free silica gel and silica-free microorganisms have also been submitted to the same conditions to serve as control groups. Experimental residues have been characterized using X-ray diffraction (XRD) and synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy to document both mineralogical and organic geochemical evolution of these silicified microorganisms. The present results demonstrate that silica restrains the molecular degradation of microorganisms during experimental fossilization at 250 °C and 250 bars and still offers effective protection even after the conversion of silica into quartz. Extrapolating the present results suggests that the mechanism of impeding chemical degradation via silica emplacement may be relevant in fossilization of organic materials over geological timescales.

2. Methods

2.1. Selected microorganisms

Although most experimental silicification studies have been historically performed on cyanobacteria (Oehler and Schopf, 1971; Oehler, 1976a; Walters et al., 1977; Francis et al., 1978a, 1978b; Phoenix et al., 2000; Yee et al., 2003; Benning et al., 2004a; Benning et al., 2004b; Orange et al., 2013a, 2013b), the response to silicification of a wide range of microorganisms has also been investigated, including other bacteria, either Gram-positive (Fortin and Ferris, 1998; Fein et al., 2002; Orange et al., 2014) or Gram-negative (Birnbaum et al., 1989; Fortin and Ferris, 1998; Toporski et al., 2002; Lalonde et al., 2005), archaea and viruses (Orange et al., 2009, 2011a, 2011b, 2012), and eukaryotes (Walters et al., 1977; Francis et al., 1978a, 1978b; Westall et al., 1995).

Here, we selected two strains of unicellular oxygenic photosynthetic microorganisms for advanced fossilization experiments: the prokaryotic cyanobacteria *Gloeobacter violaceus* (PCC 7421) and the eukaryotic microalgae *Euglena gracilis* (n°1224-5d - Cambridge). Fresh *G. violaceus* exhibit purple spherical cells of about 1 μm in diameter, while fresh *E. gracilis* cells are green and approximately 30 μm in length and 10 μm in width (Fig. 1). Obviously, these two strains have not been selected to exemplify all prokaryotic and eukaryotic microorganisms, but rather to serve as two different well-known precursors for the present experiments.

G. violaceus are believed to have diverged phylogenetically prior to the endosymbiotic event responsible for the apparition of the first

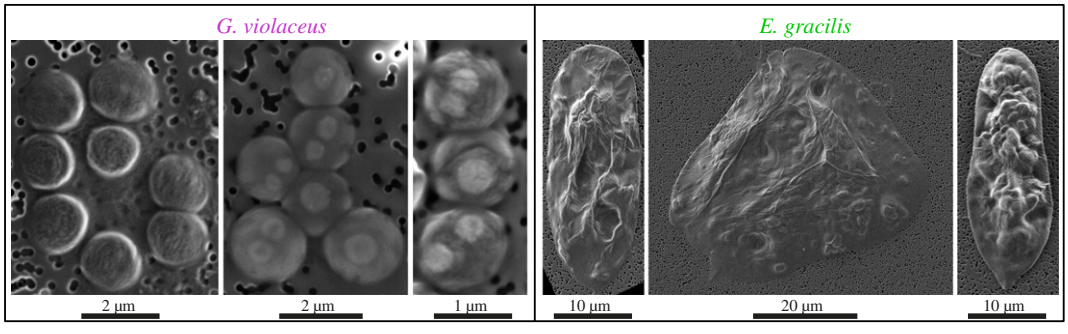

Fig. 1. Scanning electron microscopy observations of the selected microorganisms (*G. violaceus* on the left, *E. gracilis* on the right).