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Incipient silicification of recent conifer wood at a Yellowstone hot spring

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Abstract

A branch of lodgepole pine (*Pinus contorta*) from a silica sinter apron of Cistern Spring, Yellowstone National Park, is partially mineralized with silica gel. The distribution of Si mapped in transverse sections of the branch suggests that mineralization was episodic. Early silica-rich solutions used the cellular structures in the wood as pathways, in particular the axial tracheids and rays. Later solutions infiltrated into the branch through shrinkage cracks along the decorticated branch's periphery. Among the tracheids, a distinct preference is noted for silica precipitates to line lumina of the earlywood tracheids, suggesting that this differential concentration in silica may reflect seasonal growth and water uptake in a live tree. Raman spectroscopy identifies the silica phases as amorphous silica gel. Secondary electron images of radial sections along the tracheids demonstrate that the distribution of silica is heterogeneous on a micrometer scale. Silica gel precipitates form micro spheroids with a spherical substructure that extends down to the sub-nanometer scale. All cell walls are templated with a monolayer consisting of closely spaced silica gel nano spheres around 100 nm in diameter. Transmission electron microscopy of focused ion beam sections through cell walls of partially mineralized tracheids reveals that the permineralization of cellular structures and the replacement of organic material by silica are processes that go hand in hand. The branch is dated with the ^{14}C chronometer to 140 ± 33 years, underlining that the silicification reactions that preserve wood in the fossil record can be very rapid. Textural considerations of Si distribution in the wood suggest that the early stages of silicification in this branch date from a time when the pine tree was still alive.

1. INTRODUCTION

The silicification of wood is the major preservational process of trees in the fossil record. Without silicification, much less would be known about the evolution of terrestrial plants, paleofloras, ancient forests, and paleoclimate (e.g., Daniels and Dayvault, 2006; Taylor et al., 2009). Despite considerable progress made in the past, many details of fossilization by silicification remain unanswered (Mustoe, 2008). What pathways do silica-rich solutions take in a tree when the wood is being silicified? How are silica phases precipitated once silica-bearing solutions have

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entered the wood cells? Is the commonly made distinction between permineralization, that is, the infilling of tracheids, rays, and intercellular spaces by silica precipitate, and the pseudomorphic replacement of organic material by silica justified? And last but not least, the time scale: is silicification a rapid process bound to specific events, or does it occur through slow diagenetic processes in trees buried by sediment over millions of years?

We report here the results of multiple high-resolution analyses on a branch of lodgepole pine found lying on a sinter apron of Cistern Spring in Yellowstone National Park. The branch is geologically so young (ca. 140 ± 33 years) and the organic material so well preserved that the early stages of silicification can be investigated and documented in great detail.

1.1. Location and geological setting

Cistern Spring is a small hydrothermal pool in the Norris Geyser Basin, the hottest hydrothermal area of Yellowstone National Park (Jaworowski et al., 2006). The average temperature of the surface water is 84 °C. The water is supersaturated with respect to aqueous silica species (380–430 ppm SiO_2; Fournier et al., 2002) by a factor of two to three. The high silica concentrations are acquired in 200–350 °C sub-surface reservoirs in siliceous subvolcanic rocks (Fournier and Rowe, 1966), and are kept metastably in solution when the waters ascend to the surface. The pool overflows periodically to the Southwest, depositing terrace-like siliceous sinter aprons around the pool (Guidry and Chafetz, 2002, 2003) at a rate of $\sim$5 cm year^{-1} (White et al., 1988) and killing trees in its path.

The specimen investigated is a small woody axis ca. 11 cm long and 1.5 cm in diameter. It contains 18 growth rings and is readily recognizable as lodgepole pine (*Pinus contorta* Douglas ex Louden), the dominant tree species around Cistern Spring (National Park Service, 2012). The branch is devoid of bark, but covered with a white coating. It was found lying on the surface of a sinter apron, half submerged in water, and it was not cemented onto, or incorporated into, the silica sinter. It cannot have been resting on the surface for long before it was collected, perhaps for a few months to a year; but how long exactly is difficult to reconstruct.

2. ANALYTICAL DETAILS

To identify structural elements in the wood, transverse, radial, and tangential sections were examined with an optical microscope. Two transverse sections of the branch were finely ground with 1 μm corundum sandpaper, then imaged with a JEOL JXA 8900 electron microprobe for the distribution of Si in the wood. Silicon distribution was mapped in wavelength dispersive mode at 15 kV and 15 nA with counting times on the K_α peak position of 0.5 s. Silica phases exposed on freshly broken surfaces were imaged using a CamScan MV 2300 operated at 20 kV. X-ray powder diffraction was carried out on silica deposits scraped off the branch, using a Siemens D 5000 powder diffractometer equipped with a Siemens KFL LFF Cu K_α anode run under standard conditions of 45 kV and 40 mA.

Silica deposits inside and on the outside of the branch were analyzed with Raman spectroscopy to identify the nature of the silica phases and define their degree of maturation. The Raman measurements were conducted with a high-resolution Jobin Yvon HR800 Raman system using a He–Ne (632 nm) laser as excitation source. The laser energy was $\sim$30 mW on the sample surface, low enough that sample damage was avoided. The laser was focused through a 100× objective lens with a numerical aperture of 0.9. Backscattered Raman signals were collected twice for 30 and 100 s in 180° backscattering geometry, in the wavenumber range from 200 to 1200 cm^{-1}. The scattered Raman light was dispersed by a grating of 600 grooves/mm after having passed a 200 μm entrance slit. The spectral resolution was $\sim$7 cm^{-1} in the frequency range of interest.

To document and better understand the relations between the organic substrate and silica deposits, electron-transparent focused ion beam (FIB) sections were cut from cell walls covered by silica phases. The FIB technique is a site-specific method that allows the preparation of TEM foils from the locations of interest (Wirth, 2009). The sputtering process is performed with Ga ions accelerated to 30 keV. Typical dimensions of the foils are 12 by 5 by 0.20 μm. The TEM investigations were carried out with a FEI F20 X-Twin transmission electron microscope equipped with a Schottky field emitter as the electron source, a Gatan imaging filter, a Fishione high-angle annular dark-field detector allowing for Z contrast sensitive imaging, and an EDAX X-ray analyzer with an ultra-thin window. Bright field, dark field, and high-resolution (HRTEM) images were acquired as energy-filtered images, applying a 20 eV window to the zero-loss peak of the electron energy loss spectrum.

Average silica and organic carbon concentrations of the branch were determined following microwave digestion of ground homogenized 100 mg aliquots of the wood, in a solution of 5 ml 65% HNO_3 and 0.5 ml 40% HF. The mixtures were allowed to react overnight. The resulting solutions were filtered through 2 μm Whatman 589/3 blue ribbon filter paper. Demineralized water was added to bring each solution up to 50 mL volume. The Si concentration in solution was analyzed by flame AAS using a Thermo Scientific iCE 3500 spectrometer with a nitrous oxide-acetylene flame at 251.6 nm wavelength. The relative standard deviation derived from replicate analyses of the same solutions was 5.3%. After sample treatment with mild acid to remove any carbonate carbon, bulk carbon was quantified with an Elementar Vario EL elemental analyzer following combustion of the organic material at 950 °C in pure O_2 gas. The relative standard deviation calculated from replicate analyses was less than 1%.

Two wood sample aliquots were prepared for ^{14}C analysis with accelerator mass spectrometry (AMS), using the acid–alkali–acid (AAA) extraction technique of Rethemeyer et al. (2013) and a cellulose extraction protocol modified from Leavitt and Danzer (1993). For holocellulose isolation, wood pieces were first Soxhlet-extracted using a sequence of hexane, dichloromethane, and methanol (24 h each), followed by treatment with 1% HCl (1 h at 60 °C and 10 h at room temperature) and 1% NaOH (4 h at