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## Alluvial and volcanic pathways to silicified plant stems (Upper Carboniferous–Triassic) and their taphonomic and palaeoenvironmental meaning

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#### article info abstract

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Petrographic imaging, in combination with qualitative and quantitative instrumental analyses of mineral mass, allow us to obtain material signatures of silicified plant stems that are relatively common in sediments of continental basins since the late Palaeozoic. These fossils can be found in their original strata but commonly have been removed from their environmental and stratigraphic context, redeposited, and scattered on the recent land surface after erosion of the parent rocks. Analytical data gathered from X-ray diffraction analysis, hot cathodoluminescence (CL) imaging and spectroscopy, electron microprobe analysis, Raman spectrometry, and polarised light microscopy serve to characterise material signatures of samples from basins in Brazil, Germany, the Czech Republic, Sultanate of Oman, Mongolia, Antarctica, France, and the USA. This collection includes silicified Pennsylvanian and Permian plant taxa (and a few from the Triassic) found in fluvial environments and sites influenced by volcanism with the purpose to discern fundamental material characteristics formed under particular environmental circumstances. Late Pennsylvanian and Permian silicified stems in fluvial rocks include the presence of well-crystalline quartz ( $\alpha$ -SiO<sub>2</sub>), sometimes with a trace of kaolinite, showing weak CL (mostly blue or dark reddish), occasional mosaic or patchy preservation of anatomical details, and other signs of pressure distortion of wet trunks in fluvial deposits and subsequent diagenetic recrystallisation. The presumed silica source for the initial stage of silicification was weathering of labile minerals, mostly feldspars in the alluvium. In wood from aeolian deposits, moganite in combination with goethite was detected. Based on our results, we propose that the stems were silicified in sandy or gravelly fluvial deposits, most frequently in arkoses and arkosic sands, indicators of relatively warm climate with pronounced seasonal distribution of precipitation. Excluded from this interpretation are stems silicified primarily by volcanic material; these are distinguished by a higher species diversity, silicification close to the site of growth, miscellaneous mineralogy, usually with very colourful CL shades, and the presence of metastable forms of SiO2, opal-CT or moganite. This volcanic influence on silicification mode is less clearly controlled by seasonality of precipitation or palaeoclimate itself.

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### 1. Introduction

Considering the dynamics of both endogenic and exogenic processes and the extent of geologic time, it seems astonishing that today we can

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observe three-dimensionally preserved extinct plants that lived about 300 Ma. While petrified forests have attracted the attention of the public, collectors, and scientists, their formation and relevance to deciphering palaeoenvironmental conditions have not been satisfactorily understood. Considerable progress is apparent in the last few decades due to more intensive interdisciplinary research (e.g., [Witke](#page--1-0) [et al., 2004; Parrish and Falcon-Lang, 2007\)](#page--1-0). After carbonisation (coalification), permineralisation (mainly silicification) is the most common mode of Palaeozoic and Mesozoic plant fossilisation.

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Permineralisation of plant stems by carbonates (calcification), although less common, is known from Mississippian–Pennsylvanian limestones and fluvial deposits (e.g., [Brown et al., 1994; Falcon-Lang and Scott,](#page--1-0) [2000\)](#page--1-0), and from the well-known coal balls from the Pennsylvanian of Euramerica (e.g., [Snigirevskaya, 1972; DiMichele and Phillips, 1994\)](#page--1-0). Further examples of plant permineralisation, such as phosphatisation, fluoritisation, pyritisation, goethitisation or preservation by Mn-rich solutions, have also been mentioned (e.g., [Buurman, 1972; Jefferson,](#page--1-0) [1987; Grimes et al., 2002; Nowak et al., 2005; Polgári et al., 2005; Chaney](#page--1-0) [et al., 2009](#page--1-0)). Nevertheless, silicified stems are the most resistant to weathering and hence have the highest preservation potential. It has already been proposed that silicified wood denotes a certain palaeoclimatic meaning (e.g., Skoč[ek, 1974; Lefranc, 1975; Beauchamp, 1981;](#page--1-0) [Fielding and Alexander, 2001; Wagner and Mayoral, 2007; Colombi and](#page--1-0) Parrish, 2008; Matysová et al., 2009; Mencl et al., 2009), which should be further elaborated.

There are several environmental settings leading to silicification of plant stems. Impregnation of wood in association with hot springs via filling cell space by microspheres of opal-A has been performed experimentally and is well documented (e.g., [Akahane et al., 2004;](#page--1-0) [Channing and Edwards, 2004](#page--1-0)); opal-A is further converted to opal-CT and finally to quartz ([Stein, 1982; Rodgers et al., 2004\)](#page--1-0). This process is not very likely to produce basin-wide correlated fossiliferous strata such as those, e.g., in the Czech Pennsylvanian basins (e.g., Skoč[ek, 1970,](#page--1-0) 1974; Peš[ek et al., 2001; Matysová et al., 2008; Mencl et al., 2009\)](#page--1-0). A different situation in the fossil record was an almost complete burial of plants in growth position (in situ) or at least in taphonomic proximity to volcanic material (e.g., [Sigleo, 1979; Noll and Wilde, 2002; Witke et al.,](#page--1-0) [2004; Rössler, 2006; Wagner and Mayoral, 2007](#page--1-0)), which, possibly with associated co- and post-volcanic hydrothermal fluids, produced mainly quartz, sometimes with metastable silica polymorphs such as moganite [\(Witke et al., 2004\)](#page--1-0), but also minerals such as  $CaF<sub>2</sub>$  or phosphates of uranium and rare earth elements (e.g., [Götze and Rössler, 2000; Witke](#page--1-0) [et al., 2004; Matysová et al., 2009\)](#page--1-0), which are not formed in fluvial environments. The earliest stages of silicification were described in tree trunks buried by lahars after the eruptions of Mt. Helens ([Karowe and](#page--1-0) [Jefferson, 1987](#page--1-0)), indicating that complete silicification in a temperate climate would happen very slowly after burial by fine sediments. Additionally, silicified logs are occasionally found on the top of lignite layers [\(Weibel, 1996; Fairon-Demaret et al., 2003](#page--1-0)) and rarely also in marly marine sediments, e.g. in the Liassic of Europe ([Philippe and](#page--1-0) [Thevenard, 1996](#page--1-0)).

Silicified stems are most common in permeable sandy or gravelly fluvial strata which have no obvious association with volcanic material but which contain indicators of periodically variable groundwater levels ([Parrish and Falcon-Lang, 2007\)](#page--1-0). They are particularly common in coarse-grained fluvial facies (e.g., Skoč[ek, 1970, 1974; Del](#page--1-0) [Fueyo et al., 1995; Weibel, 1996; Fielding and Alexander, 2001; Pe](#page--1-0)šek [et al., 2001; Diéguez and López-Gómez, 2005; Matysová et al., 2008;](#page--1-0) [Mencl et al., 2009](#page--1-0)), and in associated overbank fines [\(Rössler, 2006;](#page--1-0) [Artabe et al., 2007\)](#page--1-0). The question is whether these permineralisations provide information about the original palaeoclimatic conditions.

The aim of this work is to compare available geological, sedimentological, mineralogical, and palaeobotanical data about silicified stems from several selected localities, in order to produce a 'test set' to evaluate further specimens from other localities or with uncertain original provenance and geological settings. Opal and moganite phases have been examined in silicified stems to test whether their presence is related to the age of the specimens (e.g., [Stein, 1982; Moxon, 2002;](#page--1-0) [Moxon and Ríos, 2004; Moxon and Reed, 2006\)](#page--1-0) or to the mode of silicification (e.g., [Heaney, 1995](#page--1-0)). Cathodoluminescence (CL) imaging was utilised following initial investigations by[Götze and Rössler \(2000\),](#page--1-0) [Witke et al. \(2004\), Matysová et al. \(2008\), and Mencl et al. \(2009\),](#page--1-0) and spectral analyses of CL emissions were added by [Matysová et al. \(2009\).](#page--1-0) We interpret these signatures in terms of palaeoenvironmental reconstruction [\(Golonka and Ford, 2000](#page--1-0)), similar to the way that CL of quartz is used as a tool for provenance analysis (e.g., [Götze, 2000; Götze](#page--1-0) [and Zimmerle, 2000; Boggs et al., 2002; Boggs and Krinsley, 2006\)](#page--1-0).

Skoč[ek \(1974\)](#page--1-0) hypothesised that silicified stems, frequently found in transitional formations from Pennsylvanian rocks of Central Bohemian Basins, especially between grey and red units, are markers of relatively fast aridisation. [Mencl et al. \(2009\)](#page--1-0) found that silicified stems, preserved in late Palaeozoic fluvial deposits of the Czech basins, occurred in periods of (seasonally) dry climate that fit into the environmental changes inferred by Opluš[til and Cleal \(2007\)](#page--1-0). These interpretations can only be valid if the silicification was not caused by hot springs, burial by volcanic material, or any other phenomena not implicitly related to the given palaeoenvironment. To unequivocally discriminate silicification regimes, in this paper we detail the mineralogy of a collection of stems silicified in alluvial sediments and compare their material signatures to those fossilised in the vicinity of volcanism. The results of this research suggest that stems silicified in fluvial sediments represent environmentally sensitive indicators which have previously been under-utilised in palaeoclimatic and palaeoenvironmental reconstructions.

#### 2. Materials and methods

Optical microscopes (an Olympus BX-51 and BX-60) were used for microscopic observations of standard (polished) thin sections (transverse, tangential and radial longitudinal cuts) in transmitted (PPL) and polarised (XPL) light. An Olympus BX-51M microscope was used for observing polished sections in reflected light.

Cathodoluminescence imaging was performed with a hot cathode CL microscope Simon-Neuser HC2-LM (Faculty of Science, Masaryk University, Brno, Czech Republic), allowing light microscopy and cathodoluminescence imaging without sample readjustment. The electron gun was operated at 14 kV with a current density 10–40 μA/ mm<sup>2</sup> in vacuum ( $10^{-6}$  bars) and luminescence images taken by a digital camera (Olympus C-5060). CL spectra were acquired with a hot cathode CL microscope HC1-LM (TU Bergakademie Freiberg, Germany) connected to an Acton Research SP-2356 digital, triplegrating spectrograph with a Princeton Spec-10 CCD detector (wavelength calibration by a Hg-halogen lamp) by a silica fibre guide. Thin sections were carbon coated to prevent build up of electrical charge. Spectral analysis was performed after conversion to wave numbers by deconvolution to Gaussian bands using the OriginPro 7.5 (OriginLab, USA). The procedure served to separate spectral components; mean luminescence maxima were recalculated to wavelengths and discussed (see also [Müller et al., 2002, 2003\)](#page--1-0).

X-ray powder diffraction was performed with a conventional D5005 diffractometer (Bruker-AXS). Planar fragments obtained during production of thin sections for microscopy and imaging were analysed. The diffraction patterns were evaluated by X'Pert HighScore (PANalytical) using the PDF-2 database and identification was confirmed and complemented by quantitative analysis using Rietveld code Topas (Bruker). The Rietveld code produces an estimate of mean coherence length (MCL) of quartz, and size of quartz crystal domains without crystallographic defects.

If necessary, mineral admixtures were identified by electron microanalysis using conventional electron microscopes, i.e., a Cameca SX 100 with a WDS detector and a high resolution CL detector (Faculty of Science, Masaryk University, Brno, Czech Republic) or a Cambridge CamScan with an EDS detector and micro-analytical system LinkISIS 300 (Faculty of Science, Charles University, Prague, Czech Republic). Raman spectrometry (Institute of Chemical Technology, Prague, Czech Republic) was used particularly to detect the presence of moganite, goethite, and organic matter. Jobin Yvon model Labram HR with a confocal Olympus microscope worked with an excitation laser (532 nm) with an input power of 50 mW. Spectra were measured under power of 5 mW, with 30 s data acquisition and 30 spectra accumulation.

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