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Study of fossil wood by modern analytical methods: case studies

Studium fosilních dřev pomocí moderních analytických metod: případové studie

Doctoral Thesis

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Prague, May 2016

Declaration:

I claim I elaborated this PhD thesis independently and alone. All information sources and literature used are quoted namely. Neither this thesis nor its fundamental piece has been submitted to obtain other or the same academic degree.

In Prague, June 8th 2016

Signature

Preface

The presented thesis is the result of my PhD study carried out at the Institute of Geology and Palaeontology, Faculty of Science, Charles University in Prague, and at the Department of Geochemistry, Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, v.v.i., in Prague. It is a continuation of my previous work done during my master and bachelor studies at the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague. Majority of analytical data has been gained at cooperation with other research institutions, such as Masaryk University, Brno, Czech Republic, and the Technische Universität, Freiberg, Germany. The funding came from the grant project No. KJB301110704 (Grant Agency of AS CR, CR), the other financial sources are mentioned in the Acknowledgement.

The thesis is divided into 10 chapters followed by *Appendices* covering my published papers [1-5], and Suplement with lists of further work outputs and science popularisation. Chapter 1, divided into three principal subchapters, provides a general introduction to the topic. Chapter 2 introduces the main aims of the thesis and Chapter 3 briefly lists methods used in this work and in the fossil wood research generally, but particular details on the methodology applied are included in the relevant *Appendices* (published papers). Chapters 4 and 5 summarise knowledge on settings favouring natural silicification and results of experimental silicification. Chapter 6 introduces the main results of the work; it is followed by discussion (Chapter 7). Chapter 8 offers the summary of conclusions, followed by Acknowledgements (Chapter 9) and References (Chapter 10).

The time lag in the last couple of years obvious from my publication record has been caused by maternal and parental leaves. The gap in my PhD study was approved by the doctoral board in accordance with the amended Act 111/1998 Coll. on Higher Education, and the Rector's Provision no. 14/2013 adopted at Charles University in Prague on 24. 6. 2013.

It isn't easy to become a fossil. ...Only about one bone in a billion, it is thought, becomes fossilized. If that is so, it means that the complete fossil legacy of all the Americans alive today - that's 270 million people with 206 bones each - will only be about 50 bones, one-quarter of a complete skeleton. That's not to say, of course, that any of these bones will ever actually be found.

— Bill Bryson, A Short History of Nearly Everything, Broadway Books, New York, 2003

Abstract

Silicified woods belonging to the three-dimensional permineralised plants are thoroughly studied by palaeobotanists. Their importance is usually underestimated in other scientific disciplines, their mineralogy/geochemistry is poorly known in close relation to other known scientific data. Stone-like appearance and nature of silicified wood is valued mainly in mineralogical markets. Only a complex analytical view can reveal more about their taphonomic past, palaeoenvironments and mechanisms of their formation and preservation.

This PhD thesis aims to uncover the potential of instrumental analyses of permineralised woods and design remarkable procedures of observing the wood samples. I have performed petrographical and geochemical analyses and comparison of samples of the Pennsylvanian (Carboniferous) to the Late Triassic age from several localities in the Czech Republic, Germany, Brazil, Sultanate of Oman, Mongolia, USA – Arizona, France, and Antarctica.

The selected samples, in most cases taxonomically determined, were observed in qualitative and quantitative way by instrumental imaging and analytical tools. Bulk (XRD) and detailed point analyses were performed. As the samples are very old, the crystallinity of SiO_2 was high (α-quartz was their main constituent according to XRD). A rather rare metastable SiO_2 polymorph, moganite, was detected at concentration up to 20%; its presence seems to have a connection with volcanic settings or evaporitic environment.

Hot cathodoluminescence (CL) visualised most effectively the heterogeneities within the samples, distinguished different phases of silicification, secondary overprints, uncommon mineral admixtures, partial calcification or phosphatisation, and allochthonous rock/mineral grains. CL spectroscopy enabled identification of distinct CL emissions and gave precision to spectra assignment. CL has become a springboard for other instrumental point analyses (SEM/EMPA, Raman spectroscopy, LA-ICP-MS), which then led to more detailed analyses under higher magnifications. Finally, such a combination of distinct analytical techniques led to an identification of wakefieldite, a rare vanadate mineral, described in fossil wood for the first time. It was detected in a sample from the Eastern Bohemia, from a field site affected by volcanism and abundantly occurring local ore deposits. Neighbouring silicified matter with the wood structure was geochemically heterogeneous and witnessed REE's and V migration during multistep diagenetic evolution.

The unconventional approach to fossil-wood analysis allows us to distinguish alluvial and volcanic modes of silicification. It might be used as a starting point for further research worldwide that could produce a comprehensive database of materials signatures of such permineralisations. Simultaneously, the database of CL shades of mineral mass might be created to better understand the process of fossil wood silicification under distinct past environments and varying duration.

Abstrakt (in Czech)

Zkřemenělá dřeva, která se řadí mezi permineralizované rostliny v trojrozměrné podobě, jsou odjakživa předmětem studia paleobotaniků. V jiných vědních disciplínách je jejich význam obvykle podceňován, jejich mineralogie a geochemie je málo známá a tudíž není vztahována ani k dalším známým faktům z jiných oborů. Kamenný vzhled a vlastnosti zkřemenělého dřeva jsou ceněny hlavně na mineralogických burzách. Pokud chceme více pochopit tafonomii těchto dřev a mechanismus jejich vzniku a zachování a poznat paleoprostředí, ze kterého tyto fosílie pocházejí, je nutný celostní přístup.

Tato disertační práce si klade za cíl odhalit možnosti instrumentálních analýz permineralizovaných dřev a navrhnout nevšední postupy zkoumání vzorků dřev. Petrograficky a geochemicky byly analyzovány a porovnávány vzorky pennsylvanského až pozdně triasového stáří z několika lokalit z České republiky, Německa, Brazílie, Ománu, Mongolska, USA – Arizony, Francie a Antarktidy.

Vybrané vzorky, jež byly potěšinou taxonomicky určeny, byly zkoumány kvalitativně a kvantitativně s pomocí detailního zobrazování a analytických metod. Byly prováděny jejich objemové (XRD) a bodové analýzy. Vzhledem k tomu, že jsou studované vzorky vysokého stáří, krystalinita SiO_2 v nich obsaženého je taktéž vysoká (podle výsledků z rentgenové difrakce byl α-křemen převažující složkou). Celkem neobvyklý metastabilní polymorf SiO_2 – moganit – byl detekován v koncentracích do 20% a jeho výskyt pravděpodobně souvisí s vulkanismem či evaporitickým prostředím.

Jako nejefektivnější technika studia se osvědčila horká katodoluminescence (CL), jež rychle zobrazila heterogenity uvnitř vzorků, zvýraznila různé fáze silicifikace, druhotné přetisky, přítomnost neobvyklých minerálních příměsí, částečné kalcifikace či fosfatizace a alochtonní sedimentární zrna. CL spektroskopie byla použita k identifikaci různých CL emisí a přesnějšimu popisu luminiscence. Katodoluminiscence se stala odrazovým můstkem pro další instrumentální bodová měření (SEM/EMPA, LA-ICP-MS, Ramanova spektroskopie), která probíhala již detailněji a pod větším zvětšením. Díky kombinaci různých analytických technik se v jednom vzorku podařilo identifikovat wakefieldit, vzácný vanadičnan, který byl tímto ve fosilním dřevě nalezen poprvé. Vzorek pochází z východních Čech, z oblasti s doloženým vulkanismem a výskytem menších rudních ložisek. Okolní křemenná hmota se zachovanou strukturou dřeva ve vzorku vykazovala výraznou geochemickou heterogenitu a dosvědčila migraci iontů vzácných zemin a vanadu během diageneze.

Zde předložený analytický přístup k fosilním dřevům nám umožňuje rozlišit aluviální a vulkanický způsob prokřemenění (silicifikace). Mohl by být použit jako výchozí bod pro další výzkum v celosvětovém měřítku, jehož výsledkem by mohla být rozsáhlá databáze materiálových signatur takto permineralizovaných materiálů. Současně by mohla vzniknout databáze CL odstínů křemenné hmoty ve fosilních dřevech, jež by pomohla k hlubšímu porozumění procesu silicifikace dřeva probíhajícímu v různých (paleo-)environmentálních prostředích a po různě dlouhou dobu.

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Foreword

I tried to avoid perpetual explaining basic terms from miscellaneous fields covering palaeobotany, mineralogy, geochemistry, sedimentology, palaeoclimatology, taphonomy, volcanology *etc.*, that were explained in other sources many times before. Therefore I would like to refer potential readers to special literature, such as palaeobotanic "bible" by Taylor et al. (2009) or others, or references in my older partial works (in Appendices), where explanation of relevant terms can be found. Here, in the Introduction, I reviewed scientific studies in the field of fossil plant research where modern, instrumental and holistic approaches were used. However, the topic as a whole is so overwhelming that it is impossible to cover it entirely in a single thesis.

I wished for this thesis to bring new analytical views and tools to the fossil wood world, and build it on a rigid base of firmly established results. Let's call it multi- or interdisciplinary work. Only such new challenges can contribute to the general knowledge of this peculiar permineralisation plant phenomenon complicated by taphonomic and preservational bias. As everything relates to everything like in a puzzle, I wish for this thesis at least to outline the complex aspect of the "fossil wood topic", to name the main problems, to summarise my own results and put them together. Further, I tried to show which new aspects within such a complex problem of fossil wood analysis unfolded before me. As a result there are many other unanswered questions we had never thought of before, and we see that what has been done until now is still a mere drop in the ocean of the unknown.

1. INTRODUCTION

Palaeobotanists as well as broad public have been attracted to fossil plants for centuries since the fossils were discovered on the Earth's surface. Fossil plants belong to a group of body fossils, mainly in a form of adpressions, impressions, and compressions (mould or cast fossils), and they can represent various plant organs (Jones & Rowe 1999, Dernbach et al. 2002, Taylor et al. 2009). Silicified 'wood' is a different, much heavier and more robust 3D form of the so called 'permineralised' or 'replacement' fossil. This fossil form usually embodies stems, roots, or branches of arborescent plants (often only their fragments), which have been valued by human, with at least the same interest than other kinds of fossils. Their added value is beauty, especially when cut and polished. The international fossil wood market documents this phenomenon, and looking at it from a different perspective it is a huge business. These plant fossils are really old, even of the Late Palaeozoic age, where the first vegetation colonised basinal lowlands, alluvial plains, and highland areas (Falcon-Lang et al. 2009). These now extinct plants might have became silicified in two most common environments; as a part of the whole ecosystem buried *in situ* during catastrophic events (so called T^0 assemblages; see Chapter 4.1), or as individuals transported by rivers, decorticated, fragmented, perhaps scattered far away from the source locality and deposited in fluvial sediments (see Chapter 4.2) or much younger deposits (Philippe et al. 2000).

There is a large gap in scientific knowledge on these permineralised fossils. Despite the current research, there is no complete understanding of the whole silicification process. The interaction between a plant body and mineral phases, or influence of aquatic environment, volcanics, microbes *etc*. is not completely deciphered. If we knew more about it, silicified woods could be used as palaeoenvironmental indicators on a world scale. An absolute majority of scientific studies done on the "stone-like plant remains" have dealt mostly one-sidedly with systematic palaeobotany (taxonomy, anatomy, xylotomy; great summary in Taylor et al. 2009, and references therein). These fossils used to be solely utilised for palaeobotanic reconstructions since they preserved the diverse plant anatomy in a 3D form; the unique direct evidence of prehistoric vegetation existence and its physical form likely close to the real. Fortunately, in recent decades there have been a growing number of studies dealing more broadly with other branches of palaeontology *sensu lato*, such as palaeoecology, palaeoclimatology, sedimentology, or taphonomy (*e.g.*, Francis 1984, Rex 1986, Rex & Scott 1987, Fielding & Alexander 2001, Cúneo et al. 2003, Parrish & Falcon-Lang 2007, Taylor & Ryberg 2007, Wagner & Mayoral 2007, Colombi & Parrish 2008, Pfefferkorn et al. 2008, Falcon-Lang et al. 2009, Falcon-Lang et al. 2011, Rößler et al. 2012, Capretz & Rohn 2013, Luthardt et al. 2016), in which authors have worked with fossil wood in a broader sense and considered also spatial and palaeoenvironmental aspects of fossil sites.

Permineralisation is a very unique process. What did enable a plant body not to be rotten away or decomposed (recycled), but to retain roughly its original shape and internal/external features for ages? Permineralised woods often look more like a piece of stone (quartz, calcite, phosphate, pyrite, *etc*.) than a piece of plant. Scientists should pay more attention to the mineral phase or phases responsible for preserving the plant than they did earlier. Concerning silicified fossils, it is just the silica phase (SiO_2), which allowed preservation of very old parts of prehistoric plants, particularly owing to its hardness and resistivity to weathering. Quartz and other silica polymorphs (see Chapter 1.2) are thermodynamically stable under ambient environmental conditions. Even though recrystallisation in a sample might be high and fine anatomical details might not be observed clearly, the existing mineralogical phases carry information that can be interpreted in a broader context. Every mineral phase is a result of temperature-pressure-space-time conditions. Each phase has a specific chemical and isotopic composition, resulting from fluids of local specific concentrations, can contain fluid inclusions *etc.*; thus can be a valuable topic to study.

There is surprisingly a small number of scientific papers dealing with modern instrumental analysis of mineralogical phases in plant permineralisations (*e.g.*, Sigleo 1979; Scurfield 1979; Scurfield & Segnit 1984; Dietrich et al. 2000a, 2001; Götze et al. 2001; Scott & Collinson 2003; Witke et al. 2004; Polgári et al. 2005; Hatipoğlu & Türk 2009; Sweeney et al. 2009; Läbe et al. 2012) in comparison to thousands of papers published on (systematic) palaeobotany, or palynology. There are also only few studies analysing carbon content (rest) in otherwise predominantly inorganic plant silicifications (*e.g.*, Sigleo 1978; Dietrich et al. 2000b, 2001, 2013; Nestler et al. 2003; Sweeney et al. 2009). In former Czechoslovakia, Skoček (1969, 1970, 1974) did a pioneer work in this environmental/mineralogical sense. On the other hand, some modern research reports on instrumental analysis of fossil wood are too technical and do not connect the results with anatomic aspects of the fossils plants, or lack a broader context of palaeobotanical and geological background of the fossils studied (*e.g.*, Kuczumow et al. 2000, Nowak et al. 2005, Yoon & Kim 2008).

1.1 PALAEOBOTANIC ASPECT

Palaeobotany is a well-established scientific discipline with rich history dealing with the anatomy (taxonomy, palaeoxylotomy) and bio(geo)chemistry of soft-tissue preservation and further related topics such as (palaeo-)ecology, growth ring analysis, phylogeny, ontogeny, or cladistics (Taylor et al. 2009). It uses various techniques to observe miscellaneous morphologic features of plant samples on a macro- and microscopic levels, with respect to what kind of a sample is studied and in what stratigraphic context and sedimentary environment it was found. Permineralized plant fossils can be found *in situ* – to be (para)autochthonous in ‘T^0’s, as coal balls, or more or less transported in an allochthonous deposition (Chapter 4). Specimens of all those categories are presented in this thesis. In many aspects palaeobotany is very similar to modern botany but it significantly differs at one main point; only a mere fragment has been preserved in a representative shape from the prehistoric plant world up to now. Aptly, DiMichele & Falcon-Lang (2011, p. 599) said: ‘*The vagaries of preservation have robbed most fossil standing forests of some part of their original composition. Certain taxonomic elements are far more likely than others to be preserved standing in place, and different modes of preservation favour different degrees of fidelity between the fossil forest and its once-living progenitor*’. Thus, what has been preserved is most likely somehow altered or changed in a particular way – burdened by taphonomic history for a long time. Vast majority of the former whole is missing, though. The palaeobotanical concept of the ‘whole-plant reconstruction’ is based on connecting separate plant organs (morphotaxa) together in the way they once belonged to one particular plant body. For that reason, careful data processing from the Pennsylvanian T^0 assemblages (*in situ*, autochthonous) have significantly contributed to this concept since the earliest days of palaeobotany (more details in Taylor et al. 2009, DiMichelle & Falcon-Lang 2011, and references therein). Besides, T^0 assemblages offer clues to understanding even the coal origin.

Separately found **silicified** (or otherwise **permineralised/petrified**) pieces of 'wood' (stems, roots or branches) of Upper Palaeozoic arborescent plants represent a specific group of samples to study. They must be considered as peculiar morphotaxa (Tab. 1); usually representing the most resistant plant parts. Furthermore, there is a discrepancy in use of the term "silicified wood" for all samples in this thesis and it is used for simplification only. In palaeoxylotomy, which deals with wood taxonomy, the term **"**wood**"** means a dense secondary xylem (Matysová 2004). Permocarboniferous lycophyta, sphenofyta, ferns and medullosans had an arborescent habit and strongly resembled present day trees but their "trunks" contained much less real wood. The wood was arranged in a different way in their stems, particularly due to higher portions of parenchymatous tissues (Matysová 2006, Taylor et al. 2009; Tab. 1). All those anatomic aspects also strongly influenced the preservation potential of these plants (DiMichelle & Falcon-Lang 2011). Cordaites and primitive conifers were primitive gymnosperms, which had homogeneous (homoxylic) wood consisting of pitted tracheids similar to contemporary gymnosperm trees. In this thesis the term 'fossil, petrified or permineralised wood' is used generally as the name for a fossilised piece of stem or trunk. It follows that in some cases it can be taxonomically incorrect (for instance a piece of "petrified wood" of *Psaronius* is in fact a piece of stem consisting of a large root mantle and a small stem (dictyostele) in the centre, which contains only little real wood cells. A detailed palaeobotanical background and description of studied 'stem types' was presented in Matysová (2006) and it is briefly mentioned here in Tab. 1. Some other morphotaxa have been added lately, such as *Vertebraria* roots from Antarctica [4]. Concerning both the complex taphonomy and fossilisation themselves (see Chapter 1.3), not all features observed by the naked eye or under the microscope must always correspond to the original plant morphology or anatomy. Therefore, we do ask '*To what extent was the anatomy preserved? Is it enough for assigning our sample to a particular (morpho)taxon?*' Sometimes, plant anatomic features can be partially damaged by herbivors or detritovors (plant-animal interactions; *e.g.*, Falcon-Lang et al. 2015). In spite of those uncertainties, the 3D fossilized samples are very valuable to process and are not completely understood yet.

In palaeobotany, fossil woods can provide a good proxy also for palaeoclimatic interpretations, such as the studies on C isotopes (Poole et al. 2004) or growth rings anatomy (Karowe & Jefferson 1987, Taylor & Ryberg 2007) and searching via statistics for possible seasonalities. For instance, Francis (1984) or Falcon-Lang et al. (2011) observed tree rings of coniferopsids (the Upper Jurassic in southern England, and the Pennsylvanian in New Mexico, USA) that confirmed seasonally dry (semi-arid) conditions. Taylor & Ryberg (2007) indicated on the basis of tree rings analysis of silicified Antarctic wood samples a more mature forest in the Triassic than the Permian and seasonal response to climate valid for Permian specimens.

Table 1. Main morphotaxa studied in the thesis.

Arborescent plants	Morphotaxon	Stem type	Note	Demonstration	Studied in paper
horsetails (Equisetophyta) sphenopsids	***Arthropitys* GOEPP. *Calamites***	**arthrostele** with a pith cavity (=parenchymatous tissues in the centre of the stem)	having hollow central areas and massive cylinder of secondary xylem and secondary bark		[1], [3], [4] ,
tree ferns Marattiales	***Psaronius* COTTA**	**polycyclic dictyostele** clothed in a **strong accumulation of adventitious roots (root mantle**)	very heterogeneous structure, no secondary xylem, can have epiphytic plants preserved in the root mantle		[1], [4]
seed ferns, medullosans **pteridosperms**	***Medullosa* COTTA**	**cylindrical stele of several segments, multisegmentary monostele** of various kind	secondary xylem in individual segments		[1], [4]
Gymnosperms coniferous trees, cordaitaleans	***Agathoxylon* HARTIG**	eustele with **dense secondary (pycnoxylic) xylem**	dense wood, woody trunks, homogeneous (homoxylic) wood consisting of pitted tracheids		[1], [2] , [4], [5]

Which questions can we ask concerning palaeobotany of silicified (permineralised) wood?

Was the sample found in situ = T° assemblages, in (para)authochthonous, or allochthonous position?

If allochthonous, it must be a separate silicified (permineralised) piece of stem/wood (root or branch)...

To what extent anatomy is preserved? Are soft-tissues preserved?

What morphotaxon is it? (taxonomy, palaeoxylotomy) Are any other fossils around? What kind of?

Do we know anything about palaeoecology and biogeochemistry of the sample?

Do we find any epiphytic plants or plant-animal interactions within our sample?

Can we find any signs of rotting or other processes in plant tissues before silicification took place?

1.2 Mineralogic and Petrographic aspects

Minerals present within the plant fossil are identified and described using imaging and analytical tools (see Chapter 3). Mineralogy and petrography cover here a completely distinct part of the story than palaeobotany, dealing with inorganic components in the same sample. This topic goes hand in hand with one of the following chapters, *i.e.* permineralisation or silicification as a sort of fossilisation process.

What can we ask concerning mineralogy and petrography of silicified (permineralised) wood?

What kind of minerals the fossil consist of? What is their texture?

Are there any primary and secondary phases? Can we distinguish them?

From what environmental conditions the specimen comes from?

Can we recognise any volcanic or alluvial proxies?

Are there any authigenic minerals present? Any metastable phases present (SiO_2 - moganite)?

Are there any inclusions in quartz? Of what kind?

Are there allochthonous sedimentary grains? ('taphonomic/mineral pockets'?)

Can we decipher taphonomy from a rate of recrystallisation, metasomatic changes, diagenetic overprints?

What does isotope geochemistry show? (it is not part of this thesis)

Have silicified woods something in common with agates or cherts?

Can we use analytical data from agates for comparison with silicified wood and in what extent?

Mineralogy of SiO_2 polymorphs and their occurrence in silicified/permineralised wood

Group of quartz (SiO_2) – *thermodynamically stable forms*

A diagram of the stability of SiO_2 forms under p-T conditions is shown in Fig. 1. In the Late Palaeozoic fossil wood, the absolutely prevailing phase is low-temperature **α-quartz** (trigonal) [1], [2], [3], [4], [5]. It transforms at 573°C into **ß-quartz** (hexagonal), than above 870°C into high-temperature **ß-tridymite** (monoclinic) and above 1470°C into high-temperature **ß-cristobalite** (cubic). Mitchell (1967) studied low-temperature tridymite pseudomorphs of wood in Virginian Lower Cretaceous sediments. Mitchell & Tufts (1973) described wood opal as a tridymite-like mineral. The fibrous, microcrystalline variety of α-quartz is **chalcedony**, sometimes with a mixture of opal and water. High-pressure SiO_2 forms (coesite, stishovite, lechatelierite) occur mainly in impactites and have not been described in fossil wood. Läbe et al. (2012) found low-density (gaseous) inclusions in primary α-quartz inside the adventitious roots of *Psaronius* tree ferns from Chemnitz, Germany. The inclusions evidenced rather rapid mineralisation likely occurring at higher temperatures when H_2O was in the vapour stability field.

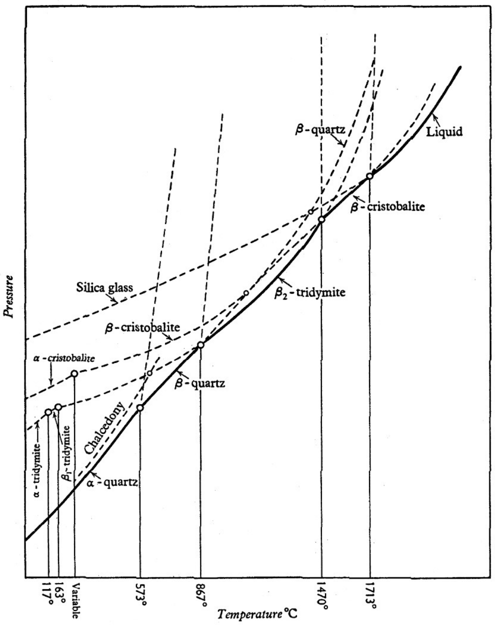

Figure 1. Phase diagram for SiO_2 (according to Deer et al. 1963).

Metastable forms of silica (Fig. 2) have different stoichiometry than quartz. The most common is **opal** ($SiO_2 \cdot n\ H_2O$), consisting of amorp-hous SiO_2, tridymite and cristobalite (Heaney 1993). **Moganite** is a peculiar metastable polymorph of SiO_2. It is fibrous, spherulitic and microcrystaline. It is gray as chalcedony and was first described in ignimbrite from Mogan (South Gran Canaria, Spain). It often occurs in association with chalcedony. This poly-morph has a structure in which slabs of left- and right-handed quartz alternate at the unite-cell scale along {101}, periodically repeating (Miehe & Graetsch 1992, Heaney 1993, Götze et al. 1998).

Metastable phases are generally stabilized by low activity of solvent water, because then Oswald ripening is decelerated, by steric hindrance in compact solid bodies, or by inhibitors of crystal-lisation: species (chemi)sorbed on exter-nal surfaces of the metastable phase slow down recrystallisation. In coincidence of these factors, metastable phases can exist for a long period of time. Mineralogy of SiO_2 and its classification was perfectly processed by Götze (2012).

Geochemistry of SiO_2 was widely discussed in Matysová (2006). Briefly, the solubility product (25°C) of crystallic quartz is much lower ($K_{sp}=10^{-3.7}$) than that of amorphous SiO_2 ($K_{sp} = 10^{-2.71}$). Amorphous SiO_2 has much higher solubility than crystallic quartz (Fig. 3). Various SiO_2 phases can be well-distinquised by, for instance, XRD (Fig. 4) or Raman (moganite; [4]).

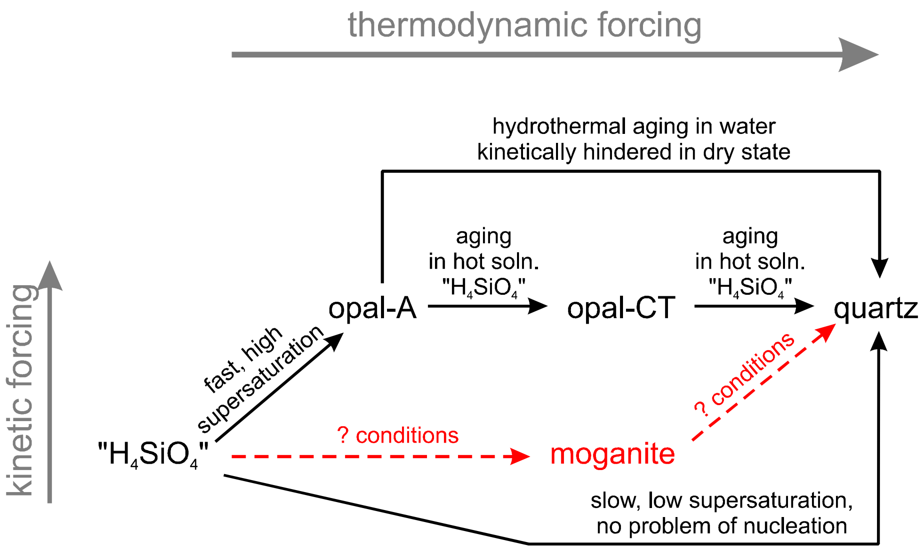

Figure 2. Crystallization of metastable silica polymorphs and quartz. Moganite formation and stability are poorly understood.

Classification of quartz in a plant cell according to morphology and crystal size

The final structure of silicified matter in fossil wood is influenced by crystallization and maturation of inorganic SiO_2 as much as by the original morphology and anatomy of the extinct plant. The plant remains served as 'biotemplates' for petrificaction. Weibel (1996) suggested that petrified wood cells can be classified as four textural types according to a crystal size of permineralising agent and crystal's spatial arrangement in the studied plant cell:

- polyblastic type – the plant cell contains more than one crystal;
- oligoblastic type – the plant cell contains only one crystal;
- hyperblastic type – crystals grow through cell walls;
- idioblastic type – cell contains euhedral (idiomorphic) crystals.

Petrography of silica grains

As classified by Hesse (1989), Flörke et al. (1991), Götze (2012) and others (see [1], and overview in Matysová 2006), using XPL we can distinguish several morphological types of silica crystals in silicified wood:

Uniform granular isometric types of quartz: microcrystalline quartz or "**microquartz**" (5-20 μm), and macrocrystalline quartz or "**megaquartz**" (20-2000 μm). All these types of silica crystals usually vary both in size and shape. Megaquartz can be further subdivided into two size ranges (20 to 50 μm and bigger).

Fibrous types of quartz: spherulitic chalcedony, quartzine, lutecite, zebraic chalcedony or microflamboyant quartz.

- „**Chalcedony** *sensu stricto*" (length-fast chalcedony) is the most abundant variety among fibrous quartz types. It contains 1-2% vol. of H_2O. The fiber elongation is perpendicular to the crystallografic axis c (ε). Heaney (1993) says it is microcrystalline (<1 μm) fibrous quartz, of which the (concentric) finely laminated variety is agate (Götze 2011). Agate can be colourful. In silicified wood agate is often present as a void-filling texture. In most cases fiber bundles of chalcedony growth from crystallisation cores on inner wall surfaces (in voids), from which they radially diverge (Flörke et al. 1991). The so called 'chalcedonic overlays' commonly confine primary and secondary pores as isopach rims. In the polarized light they look like groups of brownish laminas (probably containing laminas of small inclusions) related to each other. Usually, crystallisation starts with spherulitic growth and then turns to fibrous. In voids, chalcedony fibers often turn to macrocrystalline quartz. Both chalcedony and agate-like structures are very common in silicified wood.
- **Quartzine** (length-slow chalcedony) is long-fibrous quartz with fiber orientation parallel with crystallographic c axis and concerning the occurrence in fossils this form has been described as a secondary fill of former fossil mass (Hesse 1989).

The terminology used for description, morphology and size of SiO_2 crystals (PPL/XPL observations) is used in the text further and in all papers (Appendices). Concerning the texture of silicified tissues, terms like a polyblastic, oligoblastic, hyperblastic, idioblastic type are used. Concerning the morphology of SiO_2 crystals and their aggregates, terms like microcrystalline, macrocrystalline, euhedral (idiomorph), mosaic quartz, or chalcedony are used.

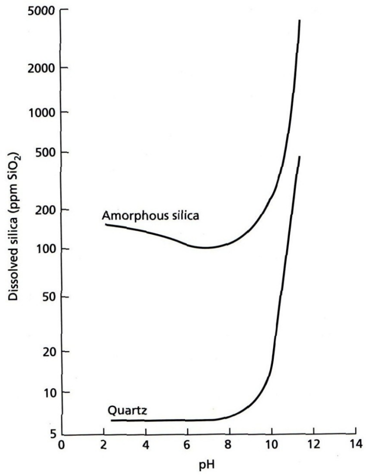

Figure 3. pH solubility diagram

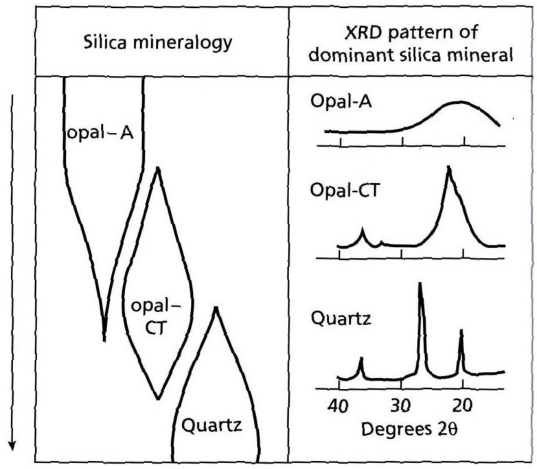

Figure 4. Diffractograms of the main SiO_2 phases.

1.3 Wood Fossilisation

Fossilisation is a complex process converting organic remains into fossils (Buurman 1972, Jones & Rowe 1999, Dernbach et al. 2002, Taylor et al. 2009). In reality fossilisation might be a combination of two or more similar or different processes or they can run close to each other (Sweeney et al. 2009, DiMichelle & Falcon-Lang 2011). In the research of fossilisation mechanisms we several times stand on frontiers of disciplines. To understand the fossilisation reactions we would often need to go down to the level not only of a particular wood cell or cell wall layers but even into the level of molecules and its derivates (*e.g.,* Jefferson 1987, Karowe & Jefferson 1987, Ballhaus et al. 2012). Wood is a complex and quite resistant structure mostly composed of cellulose, hemicellulose, and lignin and all these components can enter the fossilisation reaction in a different manner under different conditions (Poole et al. 2004). There are two fundamental types of fossilisation concerning plants: carbonatisation and petrifaction.

1.3.1 Carbonisation = Coalification

It is a complex process coming through biochemical and geochemical phases and resulting in origin of **peat, lignite, coal**, or **anthracite** (Taylor et al. 1998). It runs under stable humid (semi humid) climate. Classification of coalification products is well-developed and for instance petrography of individual macerals on a microscale level follows the strict rules (*e.g.*, Kwiecińska & Petersen 2004, Sýkorová et al. 2005). Slightly different is charcoalification, when wood is turned into **charcoal** during wildfires (Falcon-Lang & Scott 2000, Uhl et al. 2004, Scott & Glasspool 2005). A special case of carbonisation is known from volcanic settings: lava flows can thermally alter for instance wood in a root system of a big tree. This resulted in formation of **natural coke** (Matysová 2009 - unpublished special report I; conference abstract No. 10). Plant anatomy of affected part of plant was completely lost, only outer morphology of a root was preserved, organic matter converted through plastic stages to a natural coke of high reflectance. The process was probably very fast, degassing pores arose, and miscellaneous mineral composition was dispersed throughout the natural coke anisotropic structures (Kwiecińska & Petersen 2004).

1.3.2 Petrification and Permineralisation

The second common mechanism is fossilisation of plant material by various minerals (Buurman 1972). It is a completely different pathway (Fig. 5) but from practice we know that both processes can run practically side by side (*e.g.*, Weibel 1996, Fairon-Demaret et al. 2003, DiMichelle & Falcon-Lang 2011). Concerning the fossilisation by a mineral, there has been a terminological discrepancy in literature. Taylor et al. (2009) defined permineralisation and petrifaction as two different processes. The former process is characterised by minerals filling the cell lumina and the intercellular spaces, but do not completely replace the cell walls. All original organic matter in the plant has been replaced by minerals in the the latter process. In author's view this term discrepancy can be caused even because of a language barrier and different terms occuring in European non-English literature. Likewise, is petri-faction the same as petrification? In this work ([1], [2], [3], [4], [5]) permineralisation is strictly related to the true fossils only and is understood also in the case where the minerals fill both the cell lumina and intercellular spaces, together with replacement of the cell walls. Here very old plant material is studied, in which *de facto* no organics is present. Figuratively speaking, lignin particles could be count on the fingers of one hand. Petrifaction I understand *sensu lato* as the way of fossilisation by mineral resulting also in false fossils like casts, for example.

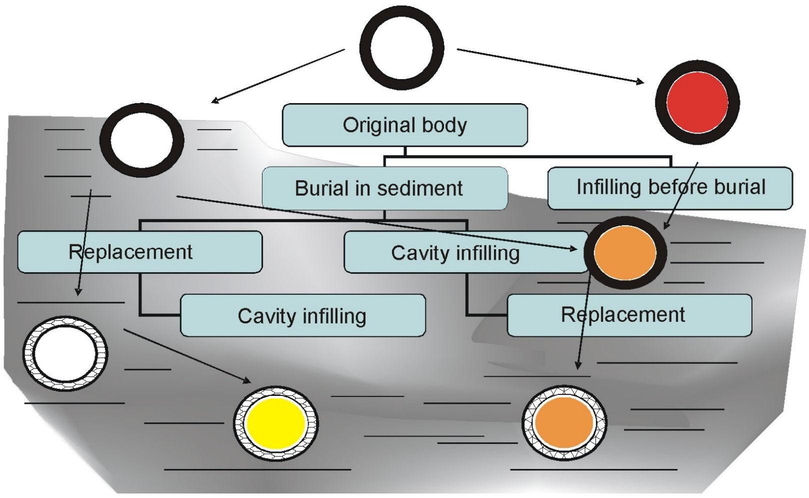

Figure 5. Origin of a fossil – basic scheme (modified according to Petránek 1993).

Basic factors which play the main role in the petrification process:

- physical characters of sediments
- individual environmental conditions
- presence of water, SiO_2 and other minerals
- temperature
- pressure
- activity of fluids
- mineral composition of sediments
- genus of plant
- tectonics (Bailey 2011)
- time

What can we ask concerning the way of plant permineralisation?

What is the permineralising agent and where does it come from?

Does the way of permineralisation have any palaeoclimatic value or significance?

Is the permineralising process known and/or is it possible to reconstruct it experimentally?

How many phases/ways of permineralisation can we distinguish?

Did the permineralisation process preserve the original plant anatomy?

Permineralisation depends on the type of mineral substance that gives the name to the process (Tab. 2):

Mineral Group	Minerals	Selected publications
Silica and silicates	Opal, hyalite, tridymite, moganite, laumontite, quartz	Skoček (1970), Buurman (1972), Rex & Scott (1987), **[1]**, **[2]**, **[3]**, **[4]**, **[5]**, Dietrich et al. (2001, 2013, 2015), Sweeney et al. (2009), Luthardt et al. (2016)
Carbonates	Calcite, aragonite, dolomite, siderite, malachite/azurite	Snigirevskaya (1972), Rex & Scott (1987), Brown et al. (1994), DiMichele & Phillips (1994), Falcon-Lang & Scott (2000), Min et al. (2001), Scott & Collinson (2003), **[1]**, **[4]**
Sulphides	Pyrite/markasite, cinnabar, galena, chalcopyrite, bornite, covellite	Kenrick & Edwards (1988), Garcia-Guinea et al. (1998), Butler & Rickard (2000), Grimes et al. (2002), Liu et al. (2002), Yamanaka & Mizota (2002), Strullu-Derrien et al. (2014)
Phosphates	Ca-phospate, apatite, phosphorite	Skoček (1969), Buurman (1972), Sweeney et al. (2009)
Sulphates	Barite, gypsum, celestite	
Iron oxides and hydroxides	Hematite, limonite, goethite, lepidocrocite	Nowak et al. (2005), Polgári et al. (2005)
Fluorides	Fluorite	Götze & Rössler (2000), Witke et al. (2004), **[4]**, Luthardt et al. (2016)
Miscellaneous	Sapperite, pitchblende, coffinite, calcium-oxide	Min et al. (2001)

Table 2. Mineralisation types of petrified wood (two left columns adapted from Polgári et al. 2005), some references added for example.

1.3.2.1 Silicification

Wood or plant permineralisation by various polymorphs of SiO_2 is one of the most abundant types of petrifactions. It concludes permeation and void-filling processes where the organic structure acts as a template for silica deposition. Some authors attempted to describe this process on the level of precise chemical reactions what is not an easy task and it is very dependent on palaeoenvironment in which all the processes had been running. It is believed that silicic acid ($H_4SiO_4^0$) in aqueous solution has a strong affinity to slightly acidic wood components and forms hydrogen bonds with hydroxy-functional groups in the molecular constituents of the cell walls (Jefferson 1987, Karowe & Jefferson 1987, Ballhaus et al. 2012). This thesis is mainly focused on silicification, but not on silicification of birds in hot springs (Channing et al. 2005).

What a kind of process the silicification is?

a] *Impermeation (void-filling) process*, *i.e.* penetration of wood by silicic acid $(H_4SiO_4)^0$ via various paths (tracheids/reticulated systems of micropores, cracks, ruptures, splits) and *subsequent precipitation*

b] *Replacement of the organic matter*

c] '*Mobility by metastability*' process, *i.e.* a diffusion process described by Landmesser (1998). This model is based on thermodynamic principles and general kinetic characters of systems with metastable substances and a slow ripening. It is a type of diffusion process of H_4SiO_4 running in pore solutions. It deals with silica transport and accumulation in geologically low temperature systems without open pathways for flowing solutions and may be considered true for silicified wood, too. It defines silica source type A and B and a relatively mature microporous silica deposit (so called 'sink'). *Silicification by diffusion* and *advection* has also been proposed by Ballhaus et al. (2012).

However, the correct option or options of silicification are still not sure. The opinion of individual researchers may have been contradictory (Mustoe 2015, Viney et al. 2016). Silicification as a process is usually too generalized. Often, some crucial steps of plant silicification itself are being simplified or biased, based on limited observations of a limited number of samples from particular environment. Main factors influencing silicification are dealt in Chapter 1.3.2.3.

1.3.2.2 Other Types of Permineralisation

Calcification (Carbonatisation)

It is permineralisation pathway quite common in seasonally dry (arid) climate. One specific category of calcification – formation of coal balls (Snigirevskaya 1972, Scott & Rex 1985, Scott et al. 1996, DiMichele & Philips 1994, Baker & DiMichele 1997, DeMaris 2000, Dernbach et al. 2002, Taylor et al. 2009) – it is beyond the scope of this thesis.

Jefferson (1987) did not study calcified wood but mentioned it in the paper. Brown et al. (1994) studied taphonomy of calcified plant fossils from the Viséan of the East Kirkton, West Lothian, Scotland. Falcon-Lang & Scott (2000) described upland ecology of some Late Carboniferous cordaitalean trees in Nova Scotia and England based on calcified plant remains. Min et al. (2001) observed excellently preserved wood cell structure with primary uranium minerals from a sandstone-hosted roll-type uranium deposit in NW China. Pitchblende and coffinite mineralized carbonized wood. Scott & Collinson (2003) used combination of non-destructive techniques (cold CL, SEM *etc.*) to study calcium-rich wood permineralisation of the Pliocene age (Dunarobba, Italy) and the Jurassic age (Swindon, UK). Nowak et al. (2005) analysed several fragments of wood also from Dunarobba, Italy and two localities in Poland. In the Dunaroba sample they found calcite(l)-goethite/hematite(w) permineralisation (l-lumina, w-wood); in Łuków, Poland sample: pyrite (l)-calcite (w), and in wood from Kwaczala, Poland: goethite(l)-silica (w). The age of the fossils was estimated as not less than 2 million years.

Phosphatisation

Although wood phospatisation is analogous to silicification, it is not as common. It was described *e.g.* by Skoček (1969) in woods from Central Bohemia, by Buurman (1972), and recently by Sweeney et al. (2009). In the Moreno Hill Formation (New Mexico) the coexistence of coal, calcified charcoal, phoshatised tissues, and prevailing silicified wood has been described. Various stages of wood degradation have been preserved in the fossils. Phosphates were also found in angiosperms and gymnosperms from outcrops of three Early Palaeocene to Late Eocene formations on Seymour Island, Antarctic Peninsula (Matysová et al. *unpublished results*). Phosphate could selectively be precipitated in woods directly from the cooler water on the bottom of the (lake) basin or from diagenetic fluids circulating in the near-surface layers of sediments. In lacustrine environment, phosphatised wood is found together with fish remains and coprolites formed of apatite (Skoček 1969).

Fluoritisation

Permineralisation by minerals such as CaF_2 has been described in wood from volcanic settings in Chemnitz in Germany (Götze & Rössler 2000, Witke et al. 2004, [4], Luthardt et al. 2016).

Pyritisation & Goethitisation

Kenrick & Edwards (1988) studied pyritised axes of Lower Devonian plants. Garcia-Guinea et al. (1998) found cell-hosted pyrite framboids in fossil woods. Butler & Rickard (2000) dealt with framboidal pyrite formation via the oxidation of iron (II) monosulfide by hydrogen sulphide. Mechanism of pyritisation (plants from Eocene London clay) was described in detail by Grimes et al. (2002). Yamanaka & Mizota (2002) observed pyrite in silicified wood with SEM and performed its S isotopic characterisation. In the vein copper deposits in Lanping-Simao basin, SW China, Liu et al. (2002) found excellent fossil wood cell texture perminera-lised by pyrite, chalcopyrite, bornite, chalcocite, with chalcopyrite being dominant (identified by SEM/EDX). Nowak et al. (2005) detected in wood samples goethite-hematite (Dunarobba, Italy), pyrite with calcite (Łuków, Poland), and goethite-silica (Kwaczala, Poland). They were gymnosperm samples from arkoses from Late Carboniferous (~ 306 millions years ago) and Permian time (286–246 millions years ago). Strullu-Derrien et al. (2014) studied narrow woody axes permineralized by pyrite (FeS_2) using standard palaeobotanical methods and created 3D images of the wood by propagation phase contrast X-ray synchrotron microtomography. Pyritisation can also be performed in laboratory (Grimes et al. 2001, Brock et al. 2006).

Manganisation

Polgári et al. (2005) described a manganised log (a piece of homoxylous wood) with limonite crust from the Mesozoic strata in Eplény mine in the Bakony Mts in Hungary. Such a peculiar fossil was regarded to be of a hydrothermal origin. The sample consisted of Sr-rich hollandite (a polymorph of Mn dioxide), accompanied by a variable amount of iron oxides (goethite) and quartz. The wood preservation was sufficient for xylotomy and taxonomomy identification; the authors described it as the Lias genus *Simplicioxylon* ANDREÁNSZKY.

1.3.2.3 Factors Influencing Silicification

Silicification of wood under natural conditions is a very complex process affected by many physical, termodynamical or biological factors not yet fully understood. Most likely, its course varies according to local macro-/micro-environmental conditions in the particular fossiliferous formation of specific composition. In literature there are repeatedly mentioned two key factors needed for silicification (Ash 1998): the **source of silica** (SiO_2, or more specificaly silicic acid, $H_4SiO_4^0$) and the **character of sedimentary environment.**

Drop in pH / gradient of the pH value from the place of mobilisation (basic-high silica mobility) to the place of silicification (acidic-low silica solubility) also plays an important role in the silicification pathway; it means transport and accumulation of silica. This pH driven diffusion pathway was experimentally verified by Ballhaus et al. (2012).

The source of Si is usually geochemically immature (poorly weathered) sedimentary component, *e.g.*, feldspars in fluvial sandstones, or volcanic material, particularly of extrusive basic rocks. It is related to SiO_2-rich weathering solutions in sedimentary units with intense chemical weathering with release of large amounts of silica (kaolinisation *etc.*). Sedimentary environment suitable for silicification is often presented as an active fluvial system or at least an environment with sufficient and fluctuating water table (see Chapter 4). It provides anaerobic conditions needed for plant tissue preservation, at least during the early stages of silicification. If some volcanic material is present, *i.e.* rather 'fast' (reactive) source of $H_4SiO_4^0$ allowing for oversaturation with respect to silica, the silicification can proceed not only in wood but also unspecifically as massive accumulation of SiO_2 in the bulk sediment, *e.g.* resulting in formation of cherts (Březinová et al. 1994, Umeda 2003) or silicified peat (Rex 1986, Taylor & Ryberg 2007, Opluštil et al. 2013, Mencl et al. 2013). Götze (2011) summarizes his observations on formation of micro-agate or agate-like structures within petrified woods. These structures are obviously cavity fills or pseudomorphs and show similarities with the agate genesis. Abundant paragenesis with calcite and fluorite seem to be a good evidence for the role of CO_2 and F^-compounds (volatile components) for the transport of material in volcanic settings (hydro-thermal). However, the process may have run even in a low-temperature regime (Landmesser 1998).

Silicification often co-occurs with charcoals or other kinds of fossilisation, *e.g.* Colombi & Parrish (2008), Sweeney et al. (2009), DiMichelle & Falcon-Lang (2011). It can be presumed that silicification of woody plants likely proceeded under variable palaeoclimatic conditions, *i.e.* sufficiently humid climate providing good conditions for plant growth, and seasonal or local dryness or fast burial in sediment preventing biological decay and accumulation of mineral components in wood (Parrish & Falcon-Lang 2007, Colombi & Parrish 2008, DiMichelle & Falcon-Lang 2011).

Comments on time factor:

It would be certainly useful to have a possibility to simulate wood permineralisation in laboratory and compare the resulting artificial model with the real one. Several studies dealing with such an ambitious topic have been published recently (*e.g.*, Götze et al. 2008, Ballhaus et al. 2012, Läbe et al. 2012, Dietrich et al. 2015; see Chapter 5). But we can hardly simulate the long time scale; time is actually one of the key factors in such a complex fossil process.

Several interesting experiments were performed dealing with time factor in natural hot springs, *i.e.*, at temperatures higher than 50°C, under extreme pH conditions and very high concentrations of H_4SiO_4. Channing & Edwards (2004) observed wood silicification in a short period of time (30 or 330 days) in hydrothermal environment of the Medusa Geyser (the Norris Geyser Basin) in Yellowstone National Park (USA). Similar, but longer experiments (7 years) were conducted by Akahane et al. (2004) in a hot spring water lake in the Tateyama Hot Spring in central Japan. Samples were immersed into the hot spring for 1, 2, 4, 5 and 7 years. Ballhaus et al. (2012) simulated silicification in laboratory in order to imitate hydrothermal conditions expected for the volcanic Chemnitz fossil site; during a time-series experiment cubes of wood over a period of 1174 h were silicified. All authors concluded that a time is likely a limiting factor for the silicification. It follows that inimitable aging of the 'bio-mineral' phases during our data processing and interpretation must be taken into consideration, together with other bias such as subsequent possible diagenetic overprints caused by syn- or postsedimentary tectonics.

2. AIMS OF THE STUDY

The aim of this PhD thesis was to overcome barrriers among disciplines to address the mineral phases in plant fossils. I studied 3D plant fossils (not casts) permineralized predominantly by SiO_2, accompanied by other mineralogical phases (iron oxides, carbonates, sulphides, fluorides, phosphates, and vanadates). The samples were fragments of stems (steles) or parts of secondary xylem of arborescent plants, such as gymnosperms – cordaitaleans or primitive conifers. These are the most commonly preserved trunks of 'Palaeozoic giants', sphenopsids, tree ferns, seed ferns *etc*. Their age was the Pennsylvanian to the Early Permian but some Early Mesozoic samples were also included.

The main aims could be defined as follows:

(i) to contribute to the understanding of petrographical, mineralogical, chemical, and CL signatures in the studied plant fossils (ideally well-classified morphotaxa) using several independent imaging and analytical techniques, such as CL, SEM, EMP, XRD, LA-ICP-MS, and Raman spectroscopy;

(ii) to clarify the relationship between the original plant anatomy and petrography-mineralogical characteristics of the inorganic matter, *i.e.*, to understand the mode of per-mineralisation;

(iii) to test CL technique limitations for silicified wood analysis;

(iv) to perform such observations (i) on specimens from several Czech and other (selected) world localities and interpret the results in accordancce with available palaeobotanical, geological, sedimentological, and paleoenvironmental data, in order to produce a 'test set' for future evaluation;

(v) to examine metastable SiO_2 phases such as opal and moganite in silicified woods, to test whether their presence is related to the specimens age or to the mode of silicification;

(vi) to investigate a very peculiar geochemical pattern of the sample E6362 noticed during master studies of Matysová (2006) and to decipher its colourful CL pattern and the probable migration of elements responsible for that pattern with leached wood parts.

Such procedure should provide some clues to palaeoenvironment under which the fossils were formed.

3. Materials and Methods

Appropriate sampling and sample preparation (Jones & Rowe 1999, Dernbach et al. 2002, Taylor et al. 2009) is as important as the subsequent analysis. We always need to decide what we want to do with the sample and where we would like to focus our further research (inspiration on research questions can be found in Bennington et al. 2009). Of course, it makes a big difference whether we have a unique museum specimen with a limitation to take the smallest volume of material sufficient for analysis (if any), or we have a possibility to do sampling during a fieldwork on our own and there is plenty of material to be hammered and consumed. Both options need a careful consideration and choice of subsequent adequate techniques. To determine basic properties of a sample we can use one particular method but usually it is better to combine several methods, even if only to check the results.

What can we ask concerning materials and methods for silicified (permineralised) wood?

Is it possible to sample also the fossiliferous sediments?

Can we have thin sections, polished sections, powder, cubes, planar fragments, acetate peels or what, and how it will fit/limit analytical methods?

What kind of imaging and analytical techniques can we apply?

What magnification we need to visualise anatomy and internal structure?

Can we use destructive methods, or only non-destructive (non-invasive) methods are allowed?

Does any method need (carbon) coating or any special pre-treatment?

How much will the analysis cost and how much can we pay for it?

How precise data will be obtained?

Can we apply cathodoluminescence microscopy and spectroscopy, and thus contribute to provenance analysis?

Can we observe the rate of recrystallisation, metasomatic changes, diagenetic overprints (taphonomy messages?)

INSTRUMENTAL METHOD	SAMPLE PREPARATION	FEATURES	PAPERS
Optical microscopy (PPL, XPL)	Thin sections	nd, i	1 - 5
Reflected light microscopy	Polished sections	nd, i	2, 4
Hot cathodoluminescence microscopy	Thin sections, carbon coated	nd, i	1 - 5
Hot cathodoluminescence spectroscopy	Thin sections, carbon coated	p, nd, ql	2, 4, 5
Scanning electron microscopy (BSE, SE)	Thin sections, carbon coated	nd, i	1 - 5
Energy dispersive spectroscopy (EDS)	Thin sections, carbon coated	p, nd, sqn	1 - 4
Electron microprobe analyses (WDS)	Thin sections, carbon coated	p, nd, qn	1, 4, 5
High resolution CL detector	Thin sections, carbon coated	I	4, 5
X-ray diffraction analysis	Powder, planar fragments	b, d/nd, qn	1, 2, 4, 5
Raman spectroscopy	Thin sections, uncoated	p, nd/μd, ql	1, 4, 5
Laser Ablation ICP-MS	Thicker thin sections (100 μm)	p, μd	5

Table 3. Imaging and analytical techniques applied on permineralised material in this thesis. Used abbreviations: nd – nondestructive, μd – microdestructive, d – destructive, i – imaging, ql – qualitative analysis, qn – quantitative analysis, sqn – semiquantitative analysis, b – bulk and p – point analysis.

Summary of methods used in this thesis is in Tab. 3. Most samples studied in this thesis came from museum and private collections. Sampling was thus limited and every step of sample processing was photo-documented. Majority of the specimens have been prepared as polished thin sections made from transverse, and where possible also longitudinal radial and tangential cuts. Analyses have always started by optical microscopy and imaging techniques (CL, SEM); point analyses were subsequently performed in areas of interest. Optical microscopy was used for both taxonomic (PPL) and petrographic (PPL/XPL) examination. Slightly thicker sections were prepared for LA-ICP-MS [5]. Bulk analyses were processed simultaneously. For XRD measurements mostly planar fragments obtained during the production of thin sections were used. Powdered samples were analysed only exceptionally. Several thick polished sections for reflected light microscopy proved to be useful. Particular instruments and techniques used, with precise determination of experimental settings are described in detail in each publication [1-5].

Overview of instrumental methods used in fossil wood analysis

An overview of techniques used in fossil wood research was published by Dietrich et al. (2015). Here I present the most common techniques including the less-known ones. Both the list of instrumental techniques and citations are outlined. Most methods are used for analysis of **inorganic** components. Other methods, such as isotope analyses (Yamanaka & Mizota 2002, Poole et al. 2004), ^{129}I dating (Jabbar et al. 2013), ^{14}C dating (Hellawell et al. 2015), mineral inclusions (Läbe et al. 2012), dendrochronologic dating and other "organic" methods are beyond the scope of this thesis.

Optical microscopy *(OM)* – the fundamental technique used in palaeobotany and mineralogy/petrography – performed with polished thin sections or acetate peels (Jones & Rowe 1999) in aim to visualise internal structure of samples;

- *transmitted (PPL) and polarised light (XPL* – "crossed nicols", used in mineralogy and petrography*)* – Buurman (1972), Scurfield & Segnit (1984), Senkayi et al. (1985), Rex (1986), Jefferson (1987), Götze & Rößler (2000), Witke et al. (2004), Parrish & Falcon-Lang (2007), Taylor & Ryberg (2007), Mustoe (2008), Sweeney et al. (2009) and lots of others;
- *reflected light (RL)* – studied polished thick sections – Sweeney et al. (2009), Rößler et al. (2012), Dietrich et al. (2013), Saminpanya & Sutherland (2013), Luthardt et al. (2016).

Cathodoluminescence microscopy and spectroscopy (CL), also available as high resolution cathodoluminescence (HR-CL) if coupled with SEM – [4, 5]. Hot CL is a very efficient method that was *de facto* introduced to fossil wood research by a German researcher Jens Götze (Götze & Rößler 2000, Götze 2012, Götze et al. 2013). CL was originally developed for petrography and provenance analysis of mineral grains of several minerals, in particular carbonates, silica, feldspars *etc*. By hot CL, even small discrepancies or multistep genesis of present SiO_2 can be distinguished that might have otherwise been described as "common quartz". CL works also for other mineral phases containing CL activators. Here I would like to emphasise the use of CL imaging, best if supplemented with CL spectra (CL spectroscopy), which can create a database of CL-active permineralised

plant samples from different localities worldwide. Accompanied by parallel results from other instrumental techniques (SEM, EPMA, XRF, LA-ICP-MS *etc.*), it is possible to describe petrography and mineralogy of the specimens (in distinct anatomical parts, if they can be differentiated), reveal growth zones, opaque minerals, minor mineral admixtures as far as concentrations of trace elements, metasomatic and diagenetic overprints;
Rex & Scott (1987), Götze & Rößler (2000), Witke et al. (2004), Götze et al. 2008), Sweeney et al. (2009), Götze (2011), Sekora (2012), Götze et al. (2012, 2013), Dietrich et al. (2015), Viney et al. (2016).

Scanning electron microscopy (SEM) – it has become a routine method used in palaeobotany for similar purposes as OM but when better spatial resolution is required (micrometer or smaller scale). Excellent results have been obtained in visualisation of plant anatomy with fractured specimens (imaging of cleaved surfaces).
Buurman (1972), Leo & Barghoorn (1976), Sigleo (1978, 1979), Scurfield & Segnit (1984), Senkayi et al. (1985), Karowe & Jefferson (1987), Jefferson (1987), Liu et al. (2002), Akahane et al. (2004), Mustoe (2008), Yoon & Kim (2008), Sweeney et al. (2009), Ballhaus et al. (2012), Läbe et al. (2012), Dietrich et al. (2013), Saminpanya & Sutherland (2013), Strullu-Derrien et al. (2014), Hellawell et al. (2015), Mustoe (2015), Viney et al. (2016), and lots of others.

Energy dispersive X-ray fluorescence spectroscopy (EDS or EDX) – semi-quantitative analysis of element composition in SEM;
Imaging in backscattered electrons (BSE or BE), or secondary electrons (SE)
Jefferson (1987), Liu et al. (2002), Witke et al. (2004), Jabbar et al. (2013), Strullu-Derrien et al. (2014).

Wavelength dispersive X-ray fluorescence spectroscopy (WDS, WDX, electron microprobe analysis or EMP): – quantitative analysis of element composition in SEM
Sigleo (1978, 1979), Läbe et al. (2012), Dietrich et al. (2013), Lo Mónaco & López (2014), Hellawell et al. (2015).

X-ray diffraction analysis (XRD) – identification of crystallinity of mineral phases;
Buurman (1972), Sigleo (1978, 1979), Senkayi et al. (1985), Březinová et al. (1994), Sweeney et al. (2009), Ballhaus et al. (2012), Saminpanya & Sutherland (2013), Lo Mónaco & López (2014), Mustoe (2015), Viney et al. (2016).

Raman spectroscopy – nearly non-destructive method (in thermally less stable specimens, *e.g.*, organic rich, the laser beam causes microdestruction comparable with the focused laser beam diameter of about a few micrometres). Contrarily to XRD the planar surface of specimens is not essential. Raman spectra may identify most mineral phases in permineralizations and some types of carbonaceous materials, exceptions are ionic compounds such as some fluorides that are not Raman active. The method has a great spatial resolution;
Dietrich et al. (2000b, 2001), Nestler et al. (2003), Witke et al. (2004), Saminpanya & Sutherland (2013), Hellawell et al. (2015).

Electron backscattered imaging and electron backscattered diffraction (EBSD) is suitable for phase analysis under conditions of SEM, or better saying for identification of crystallographic orientation of mineral grains; Dietrich et al. (2012, 2013).

Transmission electron microscopy (TEM) enables imaging of nanoparticles and sub-micron particles. Current TEM devices are often equipped with detectors for element and phase microanalysis. The bottleneck is preparation of specimens sufficiently thin to be transparent for electron beam, which still excludes TEM as a tool for routine work with mechanically resistant materials. Eicke (1952), Senkayi et al. (1985).
High Resolution TEM (HR-TEM) – it images atoms or particles of several atoms - *clusters* Hellawell et al. (2015).

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is less common but excellent method for element microanalysis with spatial resolution of a laser beam. Its detection limits are better than EDS and comparable or better than WDS; Möckel et al. (2009).

Thermogravimetry (TG) Nestler et al. (2003).

Synchotron analyses Kuczumow et al. (2000), ***X-ray Synchotron microtomography*** (PPC-SRμCT) - Strullu-Derrien et al. (2014) used propagation phase contrast. Generally, synchrotron sources of primary beams for diffraction and some spectral methods allow for microanalyses at unrivalled spatial resolution, however, the techniques are still exclusive rather than routinely used methods.

Gas chromatography-mass spectrometry (GC-MS) is suitable for identification of organic components remaining from former biological structures. Sigleo (1978, 1979).

MicroCT (high-resolution X-ray computed tomography or microtomography) and 3D visualisation - Gee (2013) applied this non-destructive imaging methods on 150 million-year-old silicified conifer seed cones as an alternative to destructive conventional thin-sectioning. MicroCT integrated with 3D segmentation and computer animation resulted in excellent 2D serial sections and segmented 3D reconstructions. Revealed characteristics led to the cone identification and understanding of the cone anatomy.

4. ENVIRONMENTAL SETTINGS FAVOURING SILICIFICATION

This chapter deals mainly with plant taphonomy. Several distinct environmental settings, in which silicified plants were discovered, are described; numerous examples can be found for instance in Taylor et al. (2009) and DiMichele & Falcon-Lang (2011). With regards to my sample set, I focus here just on characterisation of volcanic and fluvial (lacustrine) settings from which the studied specimens come. Beside that, permineralisation by silica can take place in hot springs (Akahane et al. 2004; Channing et al. 2005; Channing & Edwards 2004, 2013) marine-brackish or tidal settings (Gastaldo 1986, Philippe & Thevenard 1996, DiMichele & Falcon-Lang 2011) and in peat (Rex 1986, Taylor & Ryberg 2007, Opluštil et al. 2013, Mencl et al. 2013); these environments are beyond the scope of this thesis.

4.1 VOLCANIC SETTINGS

Fossil deposits in volcanic rocks may be formed after catastrophic events of a various intensity. They produced random snapshots from the distant past of the Earth. For palaeontologists they are of importance comparable to ancient Pompeii for anthropologists (Rößler et al. 2012, Wang et al. 2012). The so called '**T^0 assemblages**' represent fossil forests buried in place (*in situ*) retaining the life spatial arrangement as the vegetation is buried almost instantaneously (*i.e*. within minutes to days) by volcanic material. They are represented by upright trees rooted in original soils (autochthonous), or slightly displaced vegetation (paraautochthonous). The review by DiMichele & Falcon-Lang (2011) summarises available literature on the Pennsylvanian fossil plant T^0 assemblages (318-299 Ma) and assesses the significance of such kind of preservation for palaeoecology (ecology in a broader sense). 'T^0 assemblages' can preserve even the most subtle ecological details, possibly intermixing with pre-, syn- and post-eruption vegetations, and can reach over a vast area around a volcano (also over many tens of kilometres). Instructive examples are also known from the Czech Republic (West and Central Bohemia), *i.e.* Opluštil et al. (2009a,b; 2014) and Libertín et al. (2009). However, these Bohemian peat-forming forests and pioneer plant assemblages preserved *in situ* in volcanic ashes were not silicified but often preserved as coalified compressions. Similarly, Pfefferkorn & Wang (2009) described Early Permian coal-forming floras preserved as compressions from the Wuda District (Inner Mongolia, China).

Pyroclastic surge deposits (volcanic ash-falls) or lava flows

Considering the physical laws, preservation by pyroclastic surge deposits and lava flows usually operates on a more restricted spatial scale; many trees can be knocked over, charred, even moved slightly and buried. In 1978 Lockwood & Williams described so called 'lava trees' of Hawaii (lava trees and tree moulds) as indicators of lava flow directions. Karowe & Jefferson (1987) reported plant silicification caused by lahars after recurring both historic and recent eruptions of Mt St Helens volcano in the USA (36 000 years BC, 1450 to 1550 AD, 1885 and in May 1980). Most of the trees were vigorously uprooted and transported subsequently by strong mudflows on large distances (several miles), *i.e.* redeposited material – allochthonous – horizontally located trunks or stumps with disrupted root balls. In several places, upright stumps with a preserved root system were found intact (material *in situ* – with roots filled up by finely detritic material). Authors deduced that permineralisation of the wood tissue was coming up in tree trunks, which had been rapidly buried in lahar deposits (soil mixed with volcaniclastic material), probably after circa tens thousands years. Such a rapid burial provided anaerobic conditions for silicification and prevented wood from oxic decomposition. Volcaniclastic material was considered the main source of SiO_2. Different levels of ongoing wood silicification were observed on numerous sites all over the area. SEM analysis of wood fragments of trees buried by lahars revealed a very good level of tissue preservation. On the contrary, the trunks buried by volcanoclastic material in fluvial environment were very poorly preserved. Trunks buried before 1885 showed signs of starting silicification and the oldest pieces (from 36 000 years BC) had cell walls already impregnated by SiO_2. Authors also performed dendrochronological dating. Other Pennsylvanian conifer-like trees from surge-flow deposits were reported from the West Midlands of England (Galtier et al. 1992) or, Permian of China (Hilton et al. 2001, 2004). Scott & Glasspool (2005) published a study about charred stumps rooted below pyroclastic surge deposits in Montserrat. Hatipoğlu & Türk (2009) studied silicified wood of volcanic origin from the Çamlıdere–Çeltikçi–Güdül fossil forest in Ankara, Turkey. Silicified wood of Laetoli (the Pliocene) preserved by lahars was described by Bamford (2011). Březinová et al. (1994) mentioned that fossil wood in Bohemia can often be found in a direct contact with tuff (tuffite) accompanied in the same horizons with chalcedonic or quartz concretions.

Here I would like to devote the main attention to the spectacular Early Permian Petrified forest in Chemnitz in Germany (Dietrich et al. 2000a,b, 2001, 2013; Witke et al. 2004; Rößler 2006; [4]; Rößler et al. 2012; Luthardt et al. 2016), as several samples discussed in this thesis come from there. It represents a local T^0 assemblage preserved *in situ* with a rich forest flora consisting mainly of hygrophilous plants with a few mesophilous elements. The comprehensive work of Rößler et al. (2012) brought new understanding of local geology, stratigraphy, geochemistry and fossil localisation, and orientation, adding also some extraordinary finds in Chemnitz site (rooting structures of several taxa in a single horizon, foliage and reproductive organs associated with petrified stems and branches, reptile skeletons, several amphibians, diplopods, arthropods, arachnids, *etc.*). Epiphytes, lianas and other climbers, for example, may be preserved still attached to their host trees (Rößler 2000, 2006; Opluštil et al. 2007, 2009a).

A detailed three-dimensional space recording of data (in grids or clusters) was used in the excavations similarly to Opluštil et al. (2009a,b; 2014) and Libertín et al. (2009), which enabled final 3D reconstruction of plant community and modern 3D computer modelling of the whole site. New detailed sedimentological interpretation of individual units S6 to S3 (to S1), the lower part of the Zeisigwald Tuff Horizon (the upper part of the Leukersdorf Formation) and its sedimentary basement was completed (Rößler et al. 2012) and supplemented by detailed geochemical analyses of palaeosols, which may produce some palaeoenvironmental proxies (Luthardt et al. 2016). Sekora (2012) in his diploma thesis dealt with geochemical indicators of particular facies, influence of tectonics, genesis of silicified wood, geochemistry of wood haloes (wood degassing, circulation of fluid and development of bleached zones), and zoned bedrock of the Upper Leukersdorf Formation and the Zeisigwald ignimbrite. Mineralogical investigations of clay minerals, *e.g.*, the co-existence of kaolinite and smectite indicated heterogeneous geochemical environments (probably non-equilibrium conditions) as well as short transport distances. Several facts pointed to an auto-hydrothermal alteration of the pyroclastic rocks from the phreato-magmatic eruption, formation of clay mineral associations accompanied by the release of silica necessary for the wood silicification. Hydrothermal processes can be evidenced by occurrence of hydrothermal garnet (almandine Fe/Al composition) and pseudomorphs of kaolinite after garnet as well as the presence of well-ordered kaolinite, dickite and fluorite. Spectacular silicification of Chemnitz plant samples in volcanic settings inspired the team of Ch. Ballhaus to experimental silicification in his laboratory (Ballhaus et al. 2012, Läbe et al. 2012; see Chapter 5).

4.2 ALLUVIAL SYSTEMS

Rivers produce very diverse sedimentary systems on the Earth surface. Perhaps it is the reason why plant assemblages preserved in fluvial deposits are so spatially limited (few tens of square metres to few hectares at most). A proposed snapshot of the burying event takes hours to decades (DiMichele & Falcon-Lang 2011). There is a variation in the nature of the information preserved, including plants rapidly buried in place, or buried over the same extended time after death, permitting degradation of some floral elements. Usually vegetation, rivers, and sediment interact in a complex way. Floods inherent to alluvial settings have a potential to cover forested land surfaces abruptly and over vast areas. More substantial landform building events in alluvial domain can be triggered by earthquakes, compaction-induced subsidence, eustatic sea-level rise, or their combination (DiMichele & Falcon-Lang 2011).

Rivers

In dryland settings, they most commonly represent within-channel deposits (Bashforth et al. 2010, 2011), particularly of braided streams. Sigleo (1978), Karowe & Jefferson (1987), Ash & Creber (2000) and Cúneo et al. (2003) described fluvial fossilisation environment as river beds where wood bodies were rather rapidly embedded in at least several meters thick beds of coarse sediments. Owing to anaerobic conditions after wood burial, lignin and cellulose might have been preserved (Sigleo 1978, Karowe & Jefferson 1987). In the cited papers, sediments also included a portion of volcaniclastic material.

On the contrary, Fairon-Demaret et al. (2003) do not mention any volcanic material in sediment, and Weibel (1996) literally claims a total absence of volcanic material in sediment that contained permineralized wood. In both quoted cases (Weibel 1996, Fairon-Demaret et al. 2003) silicification obviously took place in fluvial environment where groundwater level fluctuations played the key role. Weibel (1996) further considered pedogenesis or chemical weathering of sediment as a probable source of silica. Diéguez & López-Gómez (2005) studied taphonomic history and fungus-plant interactions within a *Dadoxylon* trunk (Late Permian) found close to the top of a fine to medium grained subarkosic sandstone body. Colombi & Parrish (2008) studied palaeoclimate using sedimentologic analysis of the Ischigualasto Formation (the Late Triassic, Argentina) and described silicified plant remains in several taphofacies. Environments of low-sinuosity channels and crevasse-splay deposits preserved autochthonous silicified roots of low-satured, woody plants. Allochthonous horizontal or oblique silicified tree trunks (Mesozoic seed fern *Rhexoxylon pianitzkyi*) associated with charcoal fragments were found in channel bars, and autochthonous vertical silicified stumps were abundant in deposits of abandoned channels. Preservation of trunks, branches or roots significantly varied and authors mentioned amorphous silica as the main permineralizing agent, sometimes accompanied by iron oxyhydroxides. However, the methods used for mineral identification were not specified. According to the latest knowledge, the Ischigualasto Formation was deposited under a seasonal climate and unstable tectonic conditions. An occurrence of the taphofacies cited in the paper comes from a transition of the humidity peak into the dry interval of the reconstructed climatic curve. That silicification likely proceded under unstable palaeoclimatic conditions when humid climate (providing good conditions for plant growth) changed into local dryness. Plant bodies were embedded in river sediments (*in situ* or transported) and preserved by silca, accompanied by ferric oxides.

Fossil woods deposited in fluvial red beds are abundant in continental basins of the Czech part of the Bohemian Massif (Skoček 1970, 1974; Matysová 2004, 2006; Mencl 2007; Opluštil & Cleal 2007; Bureš 2011; Holeček 2011; Mencl et al. 2013a,b; Opluštil et al. 2013; Mencl 2014; Sakala 2015; Lojka et al. 2016). A significant part of this thesis is dedicated to their study, it is elaborated further; see Chapter 6 and Appendices [1], [2], [3], [4], [5].

Desert areas, coastal marine settings, lake and mass flow assemblages

Desert areas include sabkha environments and dune deposits. In desert settings of the Sultanate of Oman, silicified wood of the Permian age has been documented in Broutin et al. (1995), Stephenson et al. (2003), Berthelin et al. (2004, 2006), Hartmann et al. (2000), and [4]. Bamford et al. (2002) described fossil conifer wood from the Mesozoic of Mali, southern Sahara, and mentioned other localities, such as those in Niger, South African Karro Basin (Bamford 1999) *etc*. *Primoginkgoxylon* g. nov. (ginkgoalean wood structure) from the Triassic of Kenya (Süß et al. 2009) came from the fluvial-deltaic Mazeras Sandstone outcropping along the course of Manolo River (the Late Triassic Mazeras Formation, Mombasa Basin, SE Kenya). Francis (1984) and Falcon-Lang et al. (2011) described silicified trees from Pennsylvanian and Jurassic sabkha settings, and Parrish & Falcon-Lang (2007) from Jurassic desert margin environments (Lower Jurassic Navajo Sandstone Formation, Utah, USA). Parrish & Falcon-Lang (2007) found silicified trees of two types, conifers in growth positions associated wiht carbonate beds (*in situ*) and allochthonous assemblages (fragments of tree-trunks) in massive sandstone beds. Even though quite poorly preserved, both groups were observed as a valuable palaeoenvironmental proxy to decifer local taphonomic bias and sedimentology, *i.e.* spring-fed lakes between aeolian dunes vs dune collapse deposits, which periodically destroyed interdune stands.

5. Experimental Silicification in Laboratory Conditions

Mimicking wood silicification in laboratory is a challenging task. Whereas permineralisation is a very complex and multistage process in nature, it has to be substantially simplified in laboratory to be feasible. Regardless, experimental silicification has attracted many scientists in the last 50 years (*e.g.*, Drum 1968, Leo & Barghoorn 1976, Laroche et al. 1989, Götze et al. 2008, Ballhaus et al. 2012, Läbe et al. 2012). Recent overview was provided by Dietrich et al. (2015).

There are two possible ways we can view upon silicification in laboratory:

1. *Palaeoenviromental/natural reasoning – via* simulation of the silicification process in laboratory. Researchers attempt to decipher the complex permineralisation process of a particular natural specimen, step by step backwards. The experiments serve for deeper understanding of natural silicification. Authors usually achieved only mimicking incipient phases of permineralisation (*e.g.*, Drum 1968, Leo & Barghoorn 1976, Ballhaus et al. 2012).

2. *Technical purpose (resulting in wood-templated ceramics)* – there is an expectation to modify wood chemically to be more durable or create a new composite material for technical/consumer purposes (*e.g.*, Götze et al. 2008, Paris et al. 2013).

While the first way is not motivated by possible economic profit, the latter seems to reflect current materials research, designed for the replication of wood in order to develop hierarchical structured ceramics (Dietrich et al. 2015). 'Wood' is seen as broadly available material or a matrix for novel materials, though. Sad to say, regardless of how far the researchers have already advanced in the simulation of the natural silicification, the impact of time or nature of post-depositional changes will hardly be imitable ever. From chemical point of view, researchers have started simply with easy-to-reach sources of silica, unfortunately compounds not generally occuring in nature, such as sodium orthosilicate (Na_2SiO_4) or tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), Porosil (concentrated aqueous solution of polysilicic acids) and so on (for citations see the overview below). Still we are at the beginning of the laboratory simulation of silicification.

Short overview of artificial plant silicification in laboratory

The first well-known research paper on successful laboratory silicification of plant material was published by Drum (1968), who used fragments of birch branches (*Betula papyrifera*) immersed into a concentrated solution of sodium metasilicate ($Na_2SiO_3 \cdot 9\ H_2O$), so called 'water glass'. Water glass has highly alkaline pH of up to 14 (not common in ambient natural conditions). Such solution is quite reactive when it is infiltrated into wood, which present mildly acidic conditions. The shift in pH triggers the opal precipitation. Siliceous replicas of plant tissues were obtained after 12–24 hours of impregnation under room temperature. Opal precipitated on inner surfaces of cell walls of various sizes. The remaining organic matter was subsequently removed by oxidation using H_2CrO_4; siliceous replicas were carbon coated and observed under the electron microscope. In the late 1960s, this method provided an unusual three-dimensional image of the cellular space of the wood tissue. Leo & Barghoorn (1976) used TEOS in vacuum. When ethyl silicate reacts with water, $H_4SiO_4^0$ is released in the solution of near-neutral pH (it was closer to common natural pH values than sodium metasilicate). Leo & Barghoorn (1976) claimed that silicification proceeds from opal-A, via opal-CT to quartz; firstly cell walls permineralisation is reached, than the SiO_2 also fills the cells interiors (lumens). They first mentioned that chemical bonding of silica complexes by functional groups of the wood cells is relevant for silicification. Although their experiments ran under artificial laboratory conditions, they gained siliceous textures very similar to those found in real silicified woods. Both works of Drum (1968) and Leo & Barghoorn (1976) represented a breakthrough in the study of the plant silicification in laboratory and became the springboard for many other series of subsequent research, not only in the field of plant tissue silicification but also in contemporary nanotechnology.

Götze et al. (2008) tested several distinct methods of wood impregnation by siliceous material in laboratory to improve physical properties of wood. Experiments were conducted in glass beakers (20°C to 80°C, normal pressure) or in autoclaves (vacuum impregnation at temperatures up to 138°C, and pressures up to 12 bars). They used sodium metasilicate (Na_2SiO_3), a colloidal suspension of silica, TEOS, a mixture of TEOS with MTEOS, and silica sol with three different particle sizes as a silica source. Additionally, TEOS mixed with the alkoxides tetrapropyl zirconate (TPOZ) and tetrabutyl orthotitanate (TBOT), were used. Precursors, such as TEOS and colloidal silica proved to be suitable sources for an artificial silicification. Precursors with alkaline pH (sodium metasilicate) or low silica contents were less suitable. The use of additional silica sols, TPOZ, TBOT to precursor solutions modified the results; however, they might be a perspective alternative for future investigations. Spruce wood (with a higher proportion of large tracheids, promising higher uptake of silica into the bulk wood) proved to react better than oak wood. The advance in silicification was monitored by a set of analytical methods. For instance, both XRD and CL spectroscopy proved X-ray amorphous silica (opal-A similar to hyalite) in the wood tissue. IR measurements revealed residues of solvents left after specimen drying that indicates the process of drying and hardening was not complete. This contribution was quite chemical/technical but it also included description of the anatomical structures of wood.

Ballhaus et al. (2012) performed laboratory silicification of gymnosperm wood by volcanic glass in autoclaves. Authors intended to imitate natural silicification process under volcanic conditions. However, the experimental conditions, which are used, are very simplified in comparison to natural ones. The authors examined water/wood/basalt systems at temperature below 100ºC and tried to estimate the time needed for silicification in volcanic settings. Their first estimate was very short (tens of years). Läbe et al. (2012) tried to imitate more realistically the silicification under volcanic conditions (such as those inferred for Chemnitz locality, Germany). Using a specially developed autoclave, wood silicification has been simulated at high temperature with silica-enriched water. Temperature and pressure used in experiments could not reach more than 100 ºC and 1 atm, even though there is a presumption that in reality it should be slightly more (<2 atm) deduced from the thickness of pyroclastic material deposited in Chemnitz fossil site (12 meters). Similarly, laboratory simulations implied that silica might have been transported by an H_2O dominated vapour phase at temperatures above 100 ºC.

Hot springs environments also provide conditions suitable for 'experimental silicification' in natural supersaturated environments towards silica (Akahane et al. 2004, Channing & Edwards 2004; viz Commentary on time, p. 20).
Similarly to experimental silicification, some studies on experimental pyritisation have been published (Grimes et al. 2001, Brock et al. 2006).

6. RESULTS

My work originally commenced on isolated permineralised pieces of 'wood' from the Late Pennsylvanian, relatively common plant fossils in European Variscan orogenic belts. Their presence reflects sedimentological and ecological changes that took place around the Carboniferous-Permian transition as recorded in the continental basins of the Czech part of the Bohemian Massif (Skoček 1970, 1974; Opluštil & Cleal 2007; Opluštil et al. 2013). A detailed overview by Opluštil et al. (2013) describes red beds (coal-barren) expansion towards the drier Permian. Silicified woods deposited in fluvial red beds of the Líně Formation, Central and Western Bohemian basins *etc*. (Bureš 2011; Holeček 2011; Mencl et al. 2013a,b; Mencl 2014, Sakala 2015, Lojka et al. 2016) are listed as one of the climatically sensitive indicators. They are assumed as palaeoproxy of seasonal dry climatic phases.

The studied fossils represent remains (fragments) of stems of arborescent plants, mostly silicified (often accompanied by ferric oxides), which can be commonly found on the surface of crop fields or along small local rivers or streams, or are more hidden in woods as secondary (allochthonous) alluvium deposits. However, they can still be sometimes seen entombed in fluvial siliciclastic sediments as a part of mostly Late Pennsylvanian outcrops. My very first samples came from Eastern Bohemia. One of the well-known localities there is for instance „Kryštofovy kameny" ("Christopher's Stones") in the Intra-Sudetic Basin, CR (Matysová 2004, 2006; Mencl 2007). Even though these remarkable fossils often resemble rather a piece of quartz than a plant remnant, they have attracted attention of palaeobotanists since the earlier days of palaeobotany (H.R. Goeppert in the 19th century). However, lots of them still lack detailed palaeobotanical (taxonomic, xylotomic) description. The reason is simple; they are poorly or 'not well-enough' preserved or they have not been studied at all. Unfortunately, the days of spectacular finds of large silicified tree deposits reportedly easy to reach in the territory of the today's Czech Republic, namely in Jestřebí hory (the Hawk Mountains; Mencl 2007, 2014), have passed. Long time ago they were looted by enthusiastic traffickers or collectors and reportedly in large scale transported abroad for sale. Therefore, huge amounts of fossils potentially available for research have been lost. It was not only the plant fossils what was absolutely lost. With those huge or even smaller silicified trunks we also wasted any possibility to study complete deposit sites in a broader sedimentological and palaeoenvironmental context. Fortunately, beside the scant rest of the samples in the countryside or fossils inbuilt within local monuments, we still have some potential to study material housed in local museums, *e.g.* in Nová Paka, or in the National Museum in Prague, and, of course, appreciable amount of material is scattered in private collections.

Let's go back to the beginning; there are plenty of isolated pieces of such silicified 'woods', which nobody wanted to study any more as they were thought to have nearly none palaeobotanical value for their poor preservation and palaeoecologic isolation. Inspired by pioneer geochemical research in Germany (Matysová 2006, [1], and references therein), I began to work with 19 museum specimens; the results on 17 of them were published in [1], Table 2, p. 220. They were obtained from collections of National Museum in Prague, all originally found in Eastern Bohemia. Specifically, they came from the Late Pennsylvanian sedimentary deposits of the Krkonoše-Piedmont and Intra Sudetic basins (Matysová 2006; [1] Fig. 1, p. 218; [1] Fig. 1, p. 219).

Summary of work published in the first paper; see appendix Matysová et al. 2008 – [1]

This first paper highlights the usefulness of instrumental approach to plant fossils. It addresses the relationship between the original anatomy or internal structure of plant tissues and their specific mode of preservation in the stone-like form. In the description of plant tissue preservation by SiO_2 mass, fundamental petrographic nomenclature and morphological classification of Flörke et al. (1991) were used. According to XRD results the crystallinity index of α-quartz in the samples is high, which confirms the time/age formula: 'the older the sample, the higher the crystallinity' (Moxon 2002). The studied sample set included stem pieces of different morphotaxa (distinct systematic groups, Tab. 1), namely calamites, tree ferns, seed ferns, and cordaitaleans or primitive conifers ([1] Tab. 2, p. 220). The way of preservation of different plant cells (parenchyma, sclerenchyma, aerenchyma, tracheids) varies in the studied samples ([1] Fig. 2, p. 221).

The paper focuses on detailed microscopic observation and points out the sense of petrographic and mineralogical analyses of SiO_2 matter in silicified wood ([1] Fig. 3, p. 222). It introduces – for the first time on Czech silicified wood specimens – hot cathodoluminescence (CL), and evaluates its high potential in research of permineralised fossil plant remains from alluvial or lacustrine/alluvial environments (in contrast to wood specimens from volcanics in Germany). Hot CL proves to be an excellent analytical and imaging tool for study of relatively uniform SiO_2 matter; for that reason we propose rather low temperatures during fossil wood formation ([1] Fig. 4, p. 224). If used prior to other microanalyses (SEM/EDX, EPMA, *etc.*), CL quickly depicts heterogeneities in SiO_2 matter not visible by other techniques. Thanks to strongly contrasting CL emissions, it can visualise tiny anatomical details not noticeable by ordinary microscopy, distinguishes a specific character of mineral/rock grains trapped in "mineral pockets", reveals an incipient stage of calcification *etc*. ([1] Fig. 5, p. 226). It might be the main clue for further study of wood taphonomy and diagenesis; by visualising several stages of silicification, providing an evidence for a long transport – different grains are trapped in pockets versus grains as a part of the sediment around the fossil in a field, and so on.

Some of the main outputs of this work were closely connected with new CL results:

1. Finding of stable red CL (the primary step of silicification) and short-lived blue CL related to distorted wood parts, fractures *etc*. as a proof of secondary silicification ([1] Fig. 4, p. 224).
2. Establishment of a new CL scheme valid for majority of samples studied in our sample set (Eastern Bohemia). Every petrographic type of SiO_2 mineral present in thin sections gave own peculiar CL shade; *e.g.* microquartz – red CL, megaquartz – brownish red CL, chalcedony – pinkish-violet or bluish violet CL *etc*. ([1] Tab. 3, p. 225).
3. Taphonomic evidences such as traces of initial calcification before silicification, 'mineral pockets' *etc*. revealed ([1] Fig. 5, p. 226).

Lately, we conducted similar geochemical analyses supplemented with more detailed revision of taxonomical and geological context on gymnosperm woods from the Intra-Sudetic Basin (Mencl et al. 2009 – [2]) and calamites from the Krkonoše Piedmont Basin (Sakala et al. 2009 – [3]).

Summary of work published in the second paper; see appendix Mencl et al. 2009 – [2]

During this work we have done a closer historical insight of fossil wood findings, called 'araukarity', in the area of the 'Jestřebí hory' (the Hawk Mts) in the Czech part of the Intra-Sudetic Basin (ISB) ([2] Fig. 1, p. 270). Most of the silicified wood material comes from the Žaltman Member (mostly represented by arkoses) of the Odolov Formation, the Barruelian in age ([2] Fig. 2, p. 271). The first scientific descriptions by H. R. Goeppert come from the second half of the 19th century. The locality has been plundered since its discovery and its fate strongly resembles the fate of similar fossil wood deposit in the Kyffhäuser in Germany (Rössler 2002). In this study, we processed 14 pieces of driftwood (mere secondary xylems without branches or leaves), most of them were newly collected ([2] Table 1, p. 272; Fig. 3, p. 273) in the field, embedded in allochthonous positions, redeposited or scattered in the countryside (in the Quaternary deposits). Beside that, lots of logs are inbuilt in local monuments. According to XRD, crystallinity of SiO_2 (α-quartz) in wood samples is very high and corresponds to their high age ([2] Table 1, p. 272). In the field, palaeoflow's directions and directions of the longest axes of the stems were measured ([2] Fig. 4, p. 274) in order to reconstruct the direction of palaeostreams and the transport of the logs during deposition. We found that NW or WNW directions prevailed in fossil log orientation. Logs were shorter than axes of the bedforms (up to 10 meters) and laid almost perpendicularly to the palaeostream ([2] Fig. 4, p. 274). According to very coarse residual gravel in fluvial fossiliferous strata we suppose their transport during extreme floods.

Taxonomic revision proved to be quite difficult due to poor preservation of secondary xylem (the only preserved part of former plants) and led us to conclusion that the wood should be left in open nomenclature and ascribed as *Dadoxylon* sp. (see change in Rößler et al. 2014). We found araucarioid type of tracheids and rays ([2] Figs. 5&6, p. 275; Fig. 7, p. 276; Fig. 8, p. 277), that supports (with one *Artisia*-like pith) affinity to cordaites. Palaeobotanic observations were followed by detailed petrographical and mineralogical analyses similar as in the first paper [1]. Compared with the previous sample set in [1], a higher percentage of megaquartz domains not respecting the former wood anatomy was found ([2] Figs. 9&10, p. 278; Fig. 11, p. 279), probably due to more advanced crystal ripening.

Cathodoluminescence imaging (7 samples) was for the first time supplemented by spectral measurements (two most distinct sampels were selected), and both gave interpretable results ([2] Figs. 9&10, p. 278; Fig. 13, p. 283). In most samples, a reddish CL (primary silicification) and a short-lived blue CL (secondary overprint) prevailed. CL again revealed allochthonous sedimentary grains (K-feldspars *etc*.) or secondary minerals (clay minerals) within the wood. Unexpectedly, emission of a transient yellow CL of α-quartz in three wood samples was detected ([2] Figs. 9&10, p. 278; Tab. 2, p. 280). Prior to our study, such a short-lived yellow CL had only been known from the Permian plant samples from Chemnitz, silicified under higher temperature. Here we explain this emission also as an evidence of hydrothermal processes due to deep burial in sedimentary basins, buried wood was mechanically scarred and fractures consequently healed by a second generation of quartz under increased temperatures.

Based on our results, we suppose that the studied gymnosperm logs found in fluvial sandstones might have been fragments of cordaitalean trees once growing in the so called streamside niches, pulled downstream by heavy rains and floods, transported, decorticated, disintegrated, embedded in arkosic alluvium, and subjected to interaction with waterlogged sediment.

Summary of work published in the third paper; see appendix Sakala et al. 2009 – [3]

In this work we focused on several silicified stems of calamites coming from the Nová Paka area, the Krkonoše-Piedmont Basin (KPB). This fossil site and strata (in particular 'Balka') is supposed to be related to the volcanic Ploužnice Horizon (the Semily Formation, the Stephanian C in age). It was also confirmed by the geochemical analyses (mentioned further). Calamites represent only one part of a more diversified assemblage typical of this site, and are considered as hygrophilous elements preserved in lacustrine/fluvial environment. This site is also known for abundant finds of silicified peat (Mencl et al. 2013, Opluštil et al. 2013). Palaeobotanic revision of the selected calamite specimens led only to identification of *Arthropitys* Goeppert (details in [3]). Petrographic analysis revealed prevailing microcrystalline quartz (polyblastic textures) preserving minute anatomical details of secondary xylem of the calamite wood cylinder. Macrocrystalline quartz or spherulitic chalcedony are both present, often tissue-specific ([3] Fig. 1&2, p. 112). Sedimentary grains were abundant in central piths, where plant tissue was not preserved, or surrounded the fossil stems. CL analysis showed that the Balka samples have their specific 'geochemical signature' and are different from other samples (it is compared further in [4]). They most resemble the geochemical pattern of plant fossils known from volcanic settings. Both the published CL colour scheme [1] and the two-step silicification course (reddish CL as a proof of primary, and short-lived blue CL as a proof of secondary SiO_2 mass) are valid here. Moreover, CL in some cases highlighted really the great details of tracheids' walls, which was subsequently improved by further measurements on HR-CL [4]. In general, it seems that at Balka locality, irrespective of a generally dry climatic conditions ([2] Fig. 2, p. 271), a local assemblage was present with a predominance of hygrophilic components, for instance in shallow lacustrine or swamp environment. It is herein evidenced by remains of the Permian horsetails or findings of silicified peat.

Summary of work published in the fourth paper; see appendix Matysová et al. 2010 – [4]

Generaly speaking, we can scarcely develop any novel approach to plant fossil processing without a sufficiently broad sample collection for comparative research. We found necessary to gather adequate analytical data from permineralised fossils from both similar and contrasting localities, geological settings and specific taphonomy. The results were summarized in [4]. The set of silicified 'wood' from Krkonoše-Piedmont Basin and Intra Sudetic Basin in CR mentioned above in the first papers [1-3] was supplemented by a high number of samples from the West Bohemian Basins (WBB, CR), Tocantins (the Parnaíba Basin, Brazil), Chemnitz (the Erzgebirge Basin, Germany), the Huqf Area (the Sultanate of Oman), SW and SE Mongolia rift zone (Mongolia), Petrified Forest National Park (Arizona, USA), the Massif Central (the Autun Basin, France) and the Central Transantarctic Mountains (Antarctica) ([4] Tab. 1, p. 129; Fig. 1, p. 130).

The main attention was paid to the mineral composition of studied, mostly silicified, samples. Again, a combination of various imaging and analytical techniques (light microscopy, XRD, SEM/EDS or WDX, Raman and hot CL) was used. Observations were done in several distinct orders: first to describe microstructural features, petrographical textures, crystallite size *etc.*, then to distinguish primary and secondary phases, postdiagenetic overprints, allochthonous admixtures, and afterwards to analyse the qualitatively determined phases in a (semi-)quanti-tative way (bulk and point analyses). Bulk analyses by XRD identified quartz (α-SiO_2) as the major permineralising agent with its mean coherence length (MCL) significantly varying. Reasons for that were searched under light microscopy during petrographic analysis; it confirmed a relation to particular tissue/cell anatomy in each sample individually. In some samples, also metastable SiO_2 phases, such as moganite and opal-CT were present. Quartz was sometimes accompanied by chalcedony (of a spherulitic or zebroic type), goethite, fluorite and other mineral phases. Some of these phases were also identified by the Raman spectroscopy ([4] Fig. 2, p. 131; Fig. 3, p. 132; Tab. 2, p. 136).

CL spectral components, especially those of SiO_2 phase, and their assignment showed as a crucial analytical tool leading to deeper understanding to the silicification process ([4] Fig. 4, p. 133; Fig. 5, p. 135; Tab. 2, p. 136). Bluish and reddish CL shades of primary and secondary silica masses prevailed, respectively, but the spectrum of the gained CL signals was broader as described in more details ([4] Tab. 3, p. 138). Peculiarities, such as primarily fluoritised tissue or readable anatomy in a *Psaronius* sample otherwise unreadable (by PPL/XPL) was revealed only owing to the hot CL ([4] Fig. 7, p. 138) and attributed to the extensive observations of plant anatomy preservation, pigmentation *etc.* ([4] Fig. 6, p. 137). Therefore, both hot CL and CL spectroscopy (in combination with other methods) should be considered fundamental techniques for study of silica phases and materials features of silica mass to reveal palaeoenvironmental proxies with respect to anatomical features (taxonomy) as well as sedimentary background of each fossiliferous locality ([4] Tab. 4 & Fig. 8, p. 139). We distinguished different CL signals for samples from volcanic and/or alluvial settings, or settings with a certain influence of volcanism ([4] Tab. 4, p. 139). It is not easy to interpret CL shades and CL spectra according to standard mineralogical conventions as we balance between inorganic matter (mineral) and organic matrix (plant); both interrelated. In this point our new knowledge (newly gained CL data) begs fundamental questions about CL principles in silicified wood, *i.e.*, the presence of defects in the crystal lattice (related to the plant anatomy), the presence of CL activators/quenchers in close relation to a real arrangement of SiO_2 mass in fossil wood on a micro-level, sometimes highlighting a subcellular level (*e.g.*, different CL shades in various parts of the tracheid wall in *Arthropitys* sp. ([4] Fig. 5.A, p. 135). Some of the main outputs were also closely connected with CL results (summary in [4] Tab. 4, p. 139):

We positively distinguished diagnostic signs of:

1. **Silicification in fluvial sediments** (Fig. 6): in those fossils no metastable silica phases were detected beside dominant α-quartz, well crystalline, with rather weak CL and prevailing reddish (primary) CL and only occasional blue, blue-violet or yellow CL shades of secondary (later diagenetic) silica mass. Poor or moderate preservation of anatomy prevail, most fossils were dense pycnoxylic wood. Fossils were embedded in allochthonous positions, typically in

arkosic psamitic sediments, of which feldspars and unstable Al-silicates were proposed as the source of Si for silicification. The studied specimens of this group come from the Czech Republic, Sultanate of Oman, and Tocantins (Brazil).

2. **Silicification influenced by volcanics** (Fig. 7)**, with three subtypes:**

a. *with a direct influence of volcanism*: samples found *in situ* in (para-) autochthonous position, with higher species diversity and better preserved anatomy, CL characteristics point to hydrothermal origin of the mineral mass ([4] Tab. 2, p. 136; Tab. 4, p. 139). Beside α-quartz, further minerals and metastable SiO_2 polymorphs are common, documenting a multistage process of silicification, primary mass commonly emits a yellow CL attributed to hydrothermal quartz, secondary overprints are marked by a short-lived blue CL. Fluoritisation is frequent. Type locality is Chemnitz, Germany.

b. *fluvial facies associated with volcaniclastic components*: mineralogical and CL patterns are similar to volcanic subtype (a), anatomy is better preserved than from fluvial settings without volcanic components. The studied specimens of that group were from Arizona, Mongolia, and Antarctica.

c. *lacustrine facies associated with volcanic activity*: the fossils from lacustrine settings represent a hygrophilous flora of a higher diversity. Secondary overprints (silica with short-lived blue CL) are common. Type locality is Balka, the Krkonoše Piedmont Basin (CR), also bearing silicified peat.

Silicified plant stems may therefore serve as palaeoenvironmental and potentially stratigraphic indicators and CL characteristics points to specific conditions of the fossil wood formation. In the continental basins of the Czech Republic the fossil wood is often found in certain strata that bear indications of seasonal climates during fossil permineralisation (they alternate with coal-bearing strata representing interpreted as formed under more stable humid climate).

Our interpretation on palaeoenvironment based on silicified stems preserved in the late Palaeozoic fluvial deposits of the Bohemian basins are in accordance with conclusions of Opluštil & Cleal (2007). They characterised environment in individual strata in Bohemian basins where silicified stems were found; they occurred during periods of (seasonally) dry climate. Skoček (1970, 1974) and then Opluštil et al. (2013) believed that silicified stems, frequently found between grey and red units in the continental Bohemian basins of the Pennsylvanian age are markers of relatively rapidly increasing aridity.

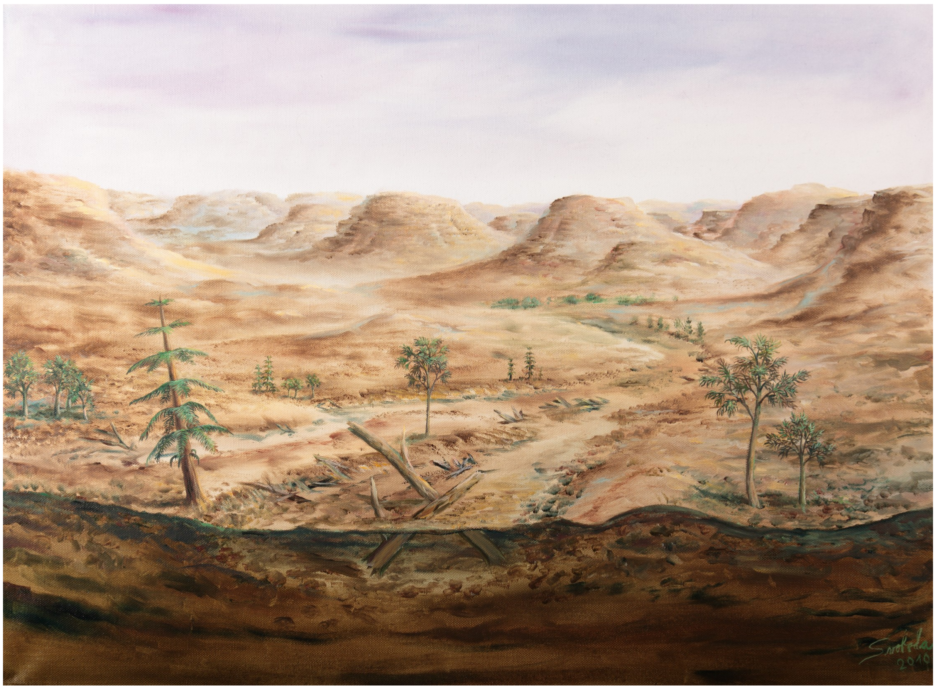

Figure 6. Artistic reconstruction of wood deposition and silicification in river sediments in allochthonous positions. Some individual gymnosperm-like trees are fluvially transported by downpours or massive floods. The trees are decorticated and disintegrated during the transport (painted by ©Jiří Svoboda).

Figure 7. Artistic reconstruction of plant burial by volcanic fall-out, under which various plants as a whole ecosystem is preserved *in situ* during catastrophic event accompanied by fires, lahars, tectonic movements, and hydrothermal phenomena (painted by ©Jiří Svoboda).

The last paper deals only with the sample E6362 and it is a follow-up of the analytical work published in papers [1] and [4].

Summary of work published in the fifth paper; see appendix Matysová et al. 2016 – [5]

We obtained unexpected results from study of a single specimen of a silicified *Agathoxylon*-type wood of the Lower Permian age from the Krkonoše-Piedmont Basin (CR) ([5] Fig. 1, p. 2). It was found in 1910 in the vicinity of Studenec Village in the Eastern Bohemia ([5] Fig. S1). X-ray diffraction identified well-crystalline quartz (α-SiO_2) in the specimen bulk. In contrast to other samples it had strikingly different cathodoluminescence (CL) pattern of the silica phase ([5] Fig. 5, p. 10). Whereas the large proportion of the sample consists of brownish silicified secondary xylem with intense dark reddish CL emission (maximum at 643 nm), the minor portion of the xylem is whitish, “bleached”, with short-lived (transient) bright blue CL emission under electron beam. The CL maximum at 390 nm points to a hydrothermal origin and very different content of CL activators/defects in α-SiO_2 crystal lattice. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) revealed striking differences in the chemical composition of α-SiO_2 phases of both brownish and whitish parts of the sample ([5] Tab. 1, p. 6-7). The silica phase is enriched in REE, Y and As. Whitish zones (“bleached” wood) are depleted in U and V, and enriched in Al, Li, Rb, Cu, and Sr ([5] Fig. 9, p. 15). We suppose that for instance sodium impurities (66 ppm Na) in brownish wood detected by LA-ICP-MS might be precursors for the so called NBOHC (activator for reddish CL). On the other hand, cation-compensated Al^{3+} centres $[AlO_4/M^+]^0$, considered as activators for short-lived blue CL (secondary overprint), are confirmed by substantially higher concentrations of Al^{3+} and Li^+ ([5] Fig. 9, p. 15, Table 1, p. 6). Both are very typical hydrothermal elements, as are Rb, Cu, and Sr.

The SEM observations enabled to distinguish primary and secondary mineral phases and identified a vanadate rich conglomerate embedded in the silica mass ([5] Figs. 3-4, p. 8-9). An EMP/WDS analysis ([5] Tab. 3, p. 12-13) identified the conglomerate as a solid solution of wakefieldite–(Ce) and wakefieldite–(Y) [(Ce,Y,Nd)VO_4], accompanied by the As-rich xenotime-(Y); both minerals locally enclose individual silicified tracheids. X-ray micro-diffraction also confirmed the presence of wakefieldite ([5] Fig. S4) as well as the Raman analysis ([5] Fig. 6, p. 10; Tab. 2, p. 11). Such rare mineral conglomerate has been identified in a silicified plant for the first time. Chemical variability among larg-size Y-Ce-Nd and tetrahedral P-As-V cations in wakefieldite and xenotime were presented in [5] (Fig. 7, p. 14). Wakefieldite-(Y), wakefieldite-(Ce) and As-bearing xenotime-(Y) with slightly variable distribution of REEs ([5] Fig. 10, p. 16) were obviously formed in the silicified wood lately during diagenesis as their precipitation in exogenic environment can hardly be expected. The mechanism of the vanadate formation and its relationship with local volcanism is discussed in [5]. Concerning the uranium, only brownish wood parts (quartz) are enriched in U, up to 19 ppm. We hypothesise that redox sensitive elements, in particular U and V, were acumulated by the organic remnants in fossil wood. The course of complex fossilization of the studied sample is schematized in [5] (Fig. 11, p. 17).

7. DISCUSSION FOLLOW-UP SINCE 2010

All results (Chapter 6) have been discussed properly in Appendices [1] - [5]. To avoid repetition, I have chosen a non-traditional discussion form here. The papers [1] - [4], which form the fundament of this thesis, have been cited by geologists describing fossiliferous localities worldwide, the environment of the Bohemian basins and other miscellaneous topics. This part of the thesis is an overview of quotations of our work (Tab. 4 – Appendices).

A multi-focus research in our work [4] has been appreciated by Luthardt et al. (2016), who studied sedimentology, geochemistry and palaeobotany of palaeoclimatic and site-specific conditions in the early Permian fossil forest of Chemnitz. The main reason of mentioning our work is the description of environments favourable for silicification. Alluvial sediments, *i.e.*, porous coarse-grained feldspathic sandstones and conglomerates, are typical environment of seasonally dry to semi-arid environments, in which fluctuating water table is the main pre-requisite for wood silicification; cited also by DiMichele & Falcon-Lang (2011), Falcon-Lang et al. (2012), Capretz & Rohn (2013), Opluštil et al. (2013), Tavares et al. (2014), Falcon-Lang et al. (2015), Neregato et al. (2015), and Lojka et al. (2016). The permineralisation was probably enabled by the marked seasonal alternation of dry and humid intervals (Opluštil et al. 2013, Tavares et al. 2014, Neregato et al. 2015). Weathering of unstable minerals (mostly feldspars) is presumed as the silica source for the initial stage of silicification (Ballhaus et al. 2012, Läbe et al. 2012, Saminpanya & Sutherland 2013), in which precipitation of silica in plant cells resulted because of very local pH drops related to CO_2 releases by initial decomposition (Falcon-Lang et al. 2012, Capretz & Rohn 2013, Neregato et al. 2015). Our research on fossil wood from the uppermost Gharif sandstones (Sultanate of Oman) [4] rich in feldspar was cited by Heward & Penney (2014). Silicified prostrate stems lacking bark, branches or roots (without parent palaeosols), are good indicators of transport prior to final burial (Jeong et al. 2014), and are assumed, in accordance to our opinion, as palaeo-proxy of seasonal dry climatic phases. Climatic and biotic changes around the Carboniferous/Permian boundary recorded in continental basins of the Czech Republic, which described fluvial red beds (coal-barren) expansion towards the drier Permian was reviewed by Opluštil et al. (2013). Opluštil et al. (2013) concurred with our interpretation [4] that silicified stem assemblages from Ploužnice Horizon can became silicified in lacustrine environment under direct influence of volcanism. This may indicate a temporary co-existence of dryland and wetland assemblages in lowlands of continental basins during the early Gzhelian (the Stephanian C in regional European stratigraphy).

The presence of moganite (metastable polymorf of SiO_2) as a possible proxy for volcanic influence on silicification [4] was cited by Saminpanya & Sutherland (2013), who studied silica phase-transformations (influences of heating, weathering and dissolution) during diagenesis within petrified woods found in fluvial deposits from Thailand–Myanmar. They processed relatively young (0.7-0.9. Ma?) wood samples found in recent fluvial deposits at several localities. Their redeposition is very likely, however. XRD measurements determined mostly quartz and opal CT in samples. Raman microprobe analyses additionally identified moganite and opal (in 3 different cases). Under the SEM they found evidences of quartz crystals with resting structures of opal-CT lepidospheres (transformation of opal-CT to quartz). It is still difficult to say if the higher crystallinity of some their samples is a result of more developed process (in the sense of aging by Moxon (2002), or it is caused by the difference in dissolved silica concentration available for silicification in fossiliferous strata.

Saminpanya & Sutherland (2013), Mencl et al. (2013b), and Lo Mónaco & López (2014) also cites [4] in listing of main geological environments for wood silicification (fluvial vs. volcanic).

Itoh et al. (2013) studied diagenesis of silicic species during examination of the Si state in fossilized sclerotium. They used micro-X-ray diffraction to search for the presence of crystalline quartz, which was not confirmed in diffractograms, compared to our data [4].

Even from our work it is obvious that fossilisation is a very complex process, which was further confirmed by other authors (Dietrich et al. 2013, Elliott & Foster 2014, Tavares et al. 2014). Detailed preservation of cellular structures was discussed by Elliott & Foster (2014). Tavares et al. (2014) and Neregato et al. (2015) quoted our work on Lower Permian samples from Parnaíba, Tavares et al. (2014) in the sense that cell wall remnants are unusual in fluvial deposits without volcaniclastic input, except for stems from Tocantins. D'Rozario et al. (2011) quoted our petrographic, CL and XRD analysis on Bohemian samples of *Psaronius* where we described the fine grained mineral matrix [1]. Silicification is certainly enhanced by the presence of volcanics with abundant sources for silica-rich fluids (DiMichele & Falcon-Lang 2011, Channing & Edwards 2013, Elliott & Foster 2014, Luthardt et al. 2016). In Chemnitz, we found domains with fluoritisation in silicifications, which were evlauated by Götze et al. (2012) in their study on the role of fluids in the formation of agates.

Advantages of CL technique with respect to fossil wood research were quoted in D'Rozario et al. (2011) and Götze et al. (2013), and CL application on samples from Parnaíba Basin was mentioned by Neregato et al. (2015). Dietrich et al. (2013) in their review on natural and artificial silicification covered all used techniques employed in our work.

Note on taxonomic nomenclature:
Genus *Dadoxylon* Endl. mentioned in our work [1] - [4], was redefined in 2014. This should be further on referred to as *Agathoxylon* Hartig (Rößler et al. 2014).

8. Conclusions

(i) The combination of imaging (PPL/XPL, CL, SEM/BSE/SE) and analytical techniques (XRD, Raman, EMP/WDS, LA-ICP-MS *etc.*) is a very useful and effective in the study of silicified (permineralised) plant remains, providing a good estimate on the fossilisation mode occurring in various depositional environments; still there are open questions related to the process of conversion of soluble silica species to solid silica mass and a specific role of plant tissue in this conversion.

(ii) According to specific anatomical arrangement of the plant tissues in stems of the most common Palaeozoic (now extinct) arborescent plants, the samples (mostly parts of stems/trunks) were classified to distinct 'stem types'. Individual plant tissues showed to have specific resistance to destruction and were permineralised accordingly, dependent on local palaeoenvironment conditions. The arrangement of various morphological types of SiO_2 (micro- and macrocrystalline quartz, microcrystalline and spherulitic chalcedony and agate-like structures) appeared to be associated with the original plant tissue anatomy down to cell level. However, wide intra- and inter-specimen variations in the way of duplicating the original plant anatomy by silica or other mineral phases have been found. Generaly, polyblastic textures of microcrystalline quartz (many crystals in one cell) preserved the original structure of plant tissues the best. Due to strong recrystallisation, almost no organic remains, some samples from alluvia were barely recognizable as wood remains.

(iii) Hot cathodolominescence (CL) proved to be an efficient and fast imaging method, particularly if CL microscopy is supplemented by CL spectroscopy to avoid possible uncertainties in the assignment of yellow, orange-reddish, and bluish luminescence shades to hydrothermal quartz with yellow or bright blue CL shades. CL is the best method used prior to further analyses. CL can highlight various heterogeneities, such as variable genesis of SiO_2 phases (cannot be visualized by PPL or SEM), relicts of carbonates, unexpected presence of allochthonous detrital grains *etc.*, as well as the minute differences in the character of individual layers of tracheid cell walls. CL provided direct evidence for the existence and variability of these layers in the Late Palaeozoic plants. Two basic approaches to the interpretation of CL colours were established; 1. The individual shade of CL corresponds to the morphological and genetic types of silica; 2. Silicification was proven to be a multi-phase process.

(iv) A large 'test set' of the Late Pennsylvanian-Early Mesozoic silicified woods from the Czech Republic, Tocantins (Brazil), Chemnitz (Germany), the Huqf Area (Oman), SW/SE Mongolia rift zone (Mongolia), Petrified Forest National Park (Arizona, USA), the Autun Basin (France) and the Central Transantarctic Mountains (Antarctica) was analysed and evaluated. On the basis of detailed instrumental analysis, in the sense (i), we distinguished diagnostic signs of:

1. *Silicification in fluvial sediments:* the Czech Republic, Oman, and Tocantins (Brazil).

2. *Silicification under influence of volcanics*:

    a. with a direct influence of volcanism: Chemnitz (Germany);

b. fluvial facies associated with volcaniclastic components: Arizona, Mongolia, and Antarctica;

c. lacustrine facies associated with volcanic activity: Balka, the Krkonoše Piedmont Basin (CR).

We came to conclusion that silicified woods can serve as palaeoenvironmental and potentially stratigraphic indicators – stems deposited in the late Palaeozoic fluvial arkosic sediments of the Bohemian basins correspond to periods of (seasonally) dry climate, and CL characteristics points to specific conditions of the fossil wood formation. Other samples can be compared with these results in future.

(v) Metastable SiO_2 phases, such as moganite, were detected by XRD and Raman spectroscopy. Moganite content was up to 5% in the specimens from Autun (France), Arizona (USA), and Chemnitz (Germany), but as much as 5 – 20% was detected in the wood from the Saiwan locality in Oman, and from Mongolia wood. In the Saiwan specimen, goethite was observed as the primary mineral that preserved parts of original wood structures, while silica (moganite and quartz) was the filling agent present around, and lacked any plant anatomical features. Moganite appears to be an indicator of volcaniclastic influence during silicification, *i.e.* its presence seems to be related to the mode of silicification rahter than to the age of the specimens;

(vi) The piece of silicified wood E6362 came from alluvial deposits of a tectonically and volcanically active area in the Krkonoše Piedmont Basin (CR) at the Carboniferous/Permian boundary. The silicification and diagenesis was multi-step, pointing to a hydrothermal overprint during the later diagenesis. The variegated CL shades of quartz are attributable to miscellaneous CL activators in the crystal lattice. The unique presence of the wakefieldite and xenotime directly associated with silicified wood has not been reported before. After partial dissolution, wakefieldite was established as another phase and supports changing of redox conditions and intensive migration and redistribution/reprecipitation of V, U, As, REEs in the aquatic fossiliferous environment during successive steps of diagenesis of the fossil. The complex fossilization course has been schematically drawn.

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10. References

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List of Appendices

(Papers 1-2, and 4-5 are published in international journals with IF, viz Tab. 4 below)

[1] **Matysová, P.***, Leichmann, J., Grygar, T. & Rößler, R., 2008. Cathodoluminescence of silicified trunks from the Permo-Carboniferous basins in eastern Bohemia, Czech Republic. *European Journal of Mineralogy* 20 (2), 217–231 (15). ISSN: 0935-1221. doi:10.1127/0935-1221/2008/0020-1797.

[2] Mencl, V., **Matysová, P.*** & Sakala, J., 2009. Silicified wood from the Czech part of the Intra Sudetic Basin (Late Pennsylvanian, Bohemian Massif, Czech Republic): systematics, silicification and palaeoenvironment. *Neues Jahrbuch für Geologie und Palaontologie-Abhandlungen* 252 (3), 269–288. ISSN: 0077-7749. doi:10.1127/0077-7749/2009/0252-0269.

[3] Sakala, J.*, Mencl, V. & **Matysová**, **P.**, 2009. Nové poznatky o svrchně karbonských prokřemenělých stoncích stromovitých přesliček z Novopacka. (New data on Upper Carboniferous silicified stems of calamites from the Nová Paka region). *Zprávy o geologických výzkumech v roce 2008*, 111–113. Česká geologická služba, Praha. ISSN 0514-8057. ISBN 978-80-7075-738-3. (*in Czech with English abstract*)

[4] **Matysová**, **P.***, Rössler, R., Götze, J., Leichmann, J., Forbes, G., Taylor, E.L., Sakala, J. & Grygar T., 2010. Alluvial and volcanic pathways to silicified plant stems (Upper Carboniferous–Triassic) and their taphonomic and palaeoenvironmental meaning. *Palaeo-geography, Palaeoclimatology, Palaeoecology* 292, 127–143. doi:10.1016/j.palaeo.2010.03.036.

[5] **Matysová**, **P.***, Götze, J., Leichmann, J., Škoda, R., Strnad, L., Drahota, P. & Matys Grygar T., 2016. Cathodoluminescence and LA-ICP-MS chemistry of silicified wood enclosing wakefieldite – REEs and V migration during complex diagenetic evolution. *European Journal of Mineralogy.* doi:10.1127/ejm/2016/0028-2556.

#	Paper/Year	International Journal with IF	IF (2014)	IF *5 year*	Citations on WOS (up to 18th May 2016)	Citations without self-citations of author and any co-author
[1]	Matysová et al. 2008	*Eur. J Mineral.*	*1.483*	*1.513*	10	6
[2]	Mencl et al. 2009	*N. Jb. Geol. Paläont. Abh.*	*0.519*	*0.791*	8	5
[4]	Matysová et al. 2010	*Palaeogeogr. Palaeoclimatol. Palaeoecol.*	*2.339*	*2.942*	23	16
[5]	Matysová et al. 2016	*Eur. J Mineral.*	*1.483*	*1.513*	-	-

Table 4. Scientometry up to May 18th 2016.

Appendices

[1]

Matysová, P., Leichmann, J., Grygar, T. & Rößler, R., 2008. Cathodoluminescence of silicified trunks from the Permo-Carboniferous basins in eastern Bohemia, Czech Republic. *European Journal of Mineralogy*, 20 (2), 217–231 (15). ISSN: 0935-1221. doi:10.1127/0935-1221/2008/0020-1797.*

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[2]

Mencl, V., Matysová, P. & Sakala, J., 2009. Silicified wood from the Czech part of the Intra Sudetic Basin (Late Pennsylvanian, Bohemian Massif, Czech Republic): systematics, silicification and palaeoenvironment. *Neues Jahrbuch für Geologie und Palaontologie-Abhandlungen* 252 (3), 269–288. ISSN: 0077-7749. doi:10.1127/0077-7749/2009/0252-0269. *

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[3]

Sakala, J., Mencl, V. & Matysová, P., 2009. Nové poznatky o svrchně karbonských prokřemenělých stoncích stromovitých přesliček z Novopacka. (New data on Upper Carboniferous silicified stems of calamites from the Nová Paka region). *Zprávy o geologických výzkumech v roce 2008*, 111–113. Česká geologická služba, Praha. ISSN 0514-8057. ISBN 978-80-7075-738-3. (*in Czech with English abstract*). *

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[4]

Matysová, P., Rössler, R., Götze, J., Leichmann, J., Forbes, G., Taylor, E.L., Sakala, J. & Grygar T., 2010. Alluvial and volcanic pathways to silicified plant stems (Upper Carboniferous–Triassic) and their taphonomic and palaeoenvironmental meaning. *Palaeogeography, Palaeoclimatology, Palaeoecology* 292, 127–143. doi:10.1016/j.palaeo.2010.03.036.*

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[5]

Matysová, P., Götze, J., Leichmann, J., Strnad, L., Škoda, R., Drahota, P. & Matys Grygar, T., 2016. Cathodoluminescence and LA-ICP-MS chemistry of silicified wood enclosing wakefieldite – REEs and V migration during complex diagenetic evolution. *European Journal of Mineralogy*. doi:10.1127/ejm/2016/0028-2556 *

SUPLEMENT

List of further papers in journals (covered by WOS)

Sýkorová, I.*, Havelcová, M., Trejtnarová, H., **Matysová**, **P**., Vašíček, M., Kříbek, B., Suchý, V. & Kotlík, B., 2009. Characterization of organic matter in dusts and fluvial sediments from exposed areas of downtown Prague, Czech Republic. *International Journal of Coal Geology* 80, 69–86. doi:10.1016/j.coal.2009.08.004.

Suchý, V.*, Dobeš, P., Sýkorová, I., Machovič, V., Stejskal, M., Kroufek, J., Chudoba, J., Matějovský, L., Havelcová, M. & **Matysová**, **P**., 2010. Oil-bearing inclusions in vein quartz and calcite and, bitumens in veins: Testament to multiple phases of hydrocarbon migration in the Barrandian basin (lower Palaeozoic), Czech Republic. *Marine and Petroleum Geology* 27, 285–297. doi:10.1016/j.marpetgeo.2009.08.017.

Lojka, R.*, Sýkorová, I., Laurin, J., **Matysová**, **P**. & Matys Grygar, T., 2010. Lacustrine couplet-lamination: evidence for Late Pennsylvanian seasonality in central equatorial Pangae (Stephanian B, Mšec Member, Central and Western Bohemian basins). *Bulletin of Geosciences* 85 (4), 709–734. Czech Geological Survey, Prague. ISSN 1214-1119. doi:10.3140/bull.geosci.1210.

Havelcová, M.*, Sýkorová, I., Bechtel, A., Mach, K., Trejtnarová, H., Žaloudková, M., **Matysová**, **P**., Blažek, J., Boudová, J. & Sakala, J., 2013. “Stump Horizon” in the Bílina Mine (Most Basin, Czech Republic) — GC–MS, optical and electron microscopy in identification of wood biological origin. *International Journal of Coal Geology* 107, 62–77. doi:10.1016/j.coal.2012.09.008.

List of further reviewed publications (Science popularisation):

Matysová, **P**.*, Mencl, V. & Sakala, J., 2007. Permineralized trunks of the Krkonoše-Piedmont Basin (Czech Republic), Permineralizovaná dřeva Podkrkonošské pánve. VENTS 2007. *Sborník Muzea Českého ráje*, Turnov. *Acta Musei Turnoviensis* 2, 16–19, 35–38. ISBN 80-239-6435-6.

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List of unpublished special reports:

I. **Matysová**, **P**., 2009. REPORT: Petrographical and geochemical analyses of Jambi Wood, 35 pp. *For:* Isabel M. van Waveren, National Museum of Natural History, Naturalis, Leiden, The Netherlands.

II. **Matysová**, **P**.* & Sýkorová, I., 2009. Provedení speciálních mineralogických rozborů 13 vzorků mineralizované uhelné hmoty z lomu Bílina a Libouš dle přiložené specifikace – r. 2009. Závěrečná zpráva, 77 pp. *For:* K. Mach, North Bohemia Mines, j.s.c., Bílina Mines, Bílina, Czech Republic. *(in Czech)*

List of selected conference abstracts and talks (speaker)

1) **Matysová, P.**, Mencl, V. & Sakala, J., 2007. *Dadoxylon* type of wood from the Czech part of the Intrasudetic basin, (Late Pennsylvanian, NE Bohemia, Czech Republic): a preliminary report. *Book of Abstracts of SÉMINAIRE INTERNATIONAL, Palaeobotany and the Evolution of Plants: Current issues*, Paris, COLLÈGE DE FRANCE, 23.-25.5. 2007, p. 30.
2) **Matysová, P.**, Leichmann, J., Mencl, V. & Sakala, J., 2007. *Imaging* paleozoických a mezozoických silicifikovaných dřev pomocí katodoluminiscence s horkou katodou. *Sborník abstrakt a Exkurzní průvodce 3. sjezdu České geologické společnosti, Volary*, 19.-22.9. 2007, p. 50.
3) Mencl, V., **Matysová, P.** & Sakala, J., 2008. An overview of fossil wood record of the Krkonoše-Piedmont and the Intra Sudetic basins with respect to its stratigraphical position, *Volume of abstracts, 11th Coal Geology Conference, 26.-30.5. 2008*, Charles University in Prague, Faculty of Science, p. 18.
4) **Matysová, P.**, Mencl, V., Sakala, J. & Grygar, T., 2008. Stratigraphical and palaeoenvironmental comparison of fossil wood record in Czech and German Permocarboniferous Basins with the help of instrumental analysis. *In*: Štamberg, S. & Zajíc, J. (Eds.): *Faunas and palaeoenvironment of the Late Palaeozoic – Special Publication to „5th Symposium on Permo-Carboniferous Faunas“,* Museum of Eastern Bohemia at Hradec Králové, 7.-11.7. 2008, Hradec Králové, p. 25. ISBN 978-80-85031-78-2.
5) **Matysová, P.**, Grygar, T., Leichmann, L., Rößler, R., Götze, J. & Forbes G., 2008. Can instrumental analysis and imaging help to extract paleoenvironmental information from silicified stems? *TERRA NOSTRA 2008/2, IPC-XII / IOPC-XIII Bonn, Germany 2008 Abstract volume*, p. 185 [455]. 30.8.-5.9. 2008, Bonn, Germany. ISSN 0946-8978.
6) Mencl, V., **Matysová**, **P**. & Sakala, J., 2008. Fossil wood record of the Krkonoše-Piedmont and the Intra Sudetic Basins with respect to its systematical affinity. *TERRA NOSTRA 2008/2, IPC-XII / IOPC-XIII Bonn, Germany 2008 Abstract volume*, p. 188 [463]. 30.8.-5.9. 2008, Bonn, Germany. ISSN 0946-8978. *(poster)*
7) **Matysová, P.** & Grygar, T., 2008. How to reconstruct Upper Palaeozoic climate: Silicified woods as a part of basinal sediments in equatorial Pangaea and their preliminary comparison with Omani specimens. Geological society of Oman (*Invited speach as a part of cooperation with PDO/GSO and a field trip for silicified woods*).
8) **Matysová, P.**, Götze, J., Forbes, G., Leichmann, J., Rößler, R. & Grygar, T., 2009. Decoding Environmental Conditions During Silicification of plant stems in Equatorial Pangaea and Oman by Cathodoluminescence Imaging and Analysis. *In: Conference on Micro-Raman Spectroscopy and Luminescence Studies in the Earth and Planetary Sciences*, p. 57–58. LPI Contribution No. 1437, Lunar and Planetary Institute, Houston. ISSN No. 0161-5297. 2.-4.4. 2009, Mainz, Germany. *Supplemented abstract.*
9) **Matysová, P.**, Götze, J., Forbes, G., Leichmann, J., Rößler, R. & Grygar, T., 2009. Analyses and cathodoluminescence imaging & spectroscopy on petrified wood –

palaeoenvironmental significance. *15. Tagung Festkörperanalytik*, 12.-16.7. 2009, Technische Universität Chemnitz, Germany, p. 26. *Invited lecture.*

10) **Matysová, P.**, Sýkorová, I., Booi, M., Crow, M.J. & van Waveren, I.M., 2009. Instrumental imaging and analysis of Early Permian fossilized plants from Sumatra: comparison of thermally altered and silicified wood. *Joint 61st ICCP/26th TSOP meeting, Gramado/Porto Alegre/Brazil, Sep 19th-26th 2009, Advances in Organic Petrology and Organic Geochemistry*, p. 31. *Best Student Paper Award 2009 (TSOP)*

11) Sýkorová, I., Havelcová, M., **Matysová**, **P**., Trejtnarová, H., Mach, K., Šulc, A. & Čermák, I., 2009. Optical and electron microscopy and GC/MS studies in identification of tree stumps from the Bílina open cast mine, Most Basin, Czech Republic. *Joint 61st ICCP/26th TSOP meeting, Gramado/Porto Alegre/Brazil, Sep 19th-26th 2009, Advances in Organic Petrology and Organic Geochemistry*, p. 88.

12) **Matysová, P.**, Götze, J., Leichmann, J., Škoda, R., Strnad, L. & Drahota, P., 2013. Cathodoluminescence as a tool for the identification of diagenetic changes in Permian silicified wood – evidence of U and V mobility. *Book of Abstracts, CORALS 2013*, Conference on Raman and Luminescence Spectroscopy, July 3rd-6th 2013, Vienna, Austria, 77–78.

Appendix

What feels like a permineralized wood?

A Fossilization Recipe
by Petra Matysová

'Take remains of a plant body, in this case a large stem, trunk or big roots or branches would be the best, and replace their fresh organic matter for rigid mineral mass, no matter how much uniform it will be. Choose one of the conditions that will conserve such plant/mineral forms, or enable their slight changes through time that lead to a far heterogeneous composition; the more miscellaneous diagenesis the better. It might be either water forces in rivers with a high energy, or floods themselves that can transport anything of a various size and embed it in a sedimentary sequence, far away from the original place of growth. It might also be the strength coming up from volcanoes followed by lahars or ash-falls, both resulting in preservation of pieces of plants originally growing within reach. Then you can chose whether you make this process true in the place the plant once grew (*in situ*) or mystify the whole situation more by a random transport. Then add resistance to the nascent fossil against the weathering as much as possible. During or afterwards this long taphonomic process shake it with tectonics; bury it or lift it up under locally precise temperature and pressure conditions. One day, after millions or many thousands of years, a human comes to a place where a piece of "enigmatic and old" wood is unexpectedly revealed by natural phenomena or human activity on a ground surface, and 'the story of deciphering both the basic plant material and every single item of the entire fossilisation process can begin'. How much can we trace from such a fossil?

'*The gift of fantasy has meant more to me than my talent for absorbing positive knowledge.*'
Albert Einstein

'*Imagination is more important than knowledge.*'
Albert Einstein

'*A scientist in his laboratory is not a mere technician: he is also a child confronting natural phenomena that impress him as though they were fairy tales.*'
Marie Curie