Cathodoluminescence as a tool for the identification of diagenetic changes in Permian silicified wood – evidence of U and V mobility

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Permineralized fossil plant stems found in sedimentary basins have recorded original palaeoenvironmental conditions as well as later diagenetic processes (Matysová 2006, Matysová et al. 2008, 2010). A piece of silicified Lower Permian *Dadoxylon*-type wood from the Krkonoše Piedmont Basin, Czech Republic, originally found in 1910 in the vicinity of the Studenec village in Eastern Bohemia, astonishes by its peculiar hot cathodoluminescence (CL) pattern of the silica phase. X-ray diffraction proved highly crystalline quartz (SiO_2, α-quartz,) in the entire specimen. Former organic matter is now probably absent and plant anatomy is visualized mainly by a silica texture. Whereas the large proportion of the silicified sample consists of permineralized brownish secondary xylem with *dark reddish* CL emission (maximum near 643 nm) of high intensity, the minor portion is whitish, leached wood of the same taxonomic kind with a *short-lived (transient) bright blue* CL emission (near 390 nm) pointing to hydrothermal origin and very different content of CL activators/defects in the α-quartz crystal lattice (Fig.1). Furthermore, detailed petrography captured the texture of formerly slightly humified wood (textinite/ulminite-like) on the outer edge of the sample (now also emitting dark reddish CL), i.e. the wood in different oxidation stages has been silicified and later diagenetically altered. In other words, a marginal part of the wood sample had been humified (reductively degraded) before the initial stages of silicification.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA–ICP–MS) revealed differences in the chemical composition of both distinct parts of the α-quartz phase in the sample and significantly contributed to the understanding of CL signatures. The original silica with the dark reddish CL is relatively enriched in REE, Y and As (compared to chondrite). Whitish zones of leached wood are relatively depleted in U and V, and enriched in Al, Li, Rb, Cu, or Sr (Fig.2). Cation-compensated Al^{3+} centres are probably responsible for the transient blue CL of the quartz. A WDS electron microprobe analysis identified an opaque phase (under transmitted light) locally enclosing individual silicified tracheids as a solid solution among *wakefieldite–(Ce)*, *wakefieldite–(Y)* and *As-rich xenotime.* The presence of wakefieldite was also confirmed by X-ray micro-diffraction. $(Ce,Y)VO_4$, an uncommon mineral from a xenotime group, has been identified in silicified plant tissue for the first time and this discovery should be reported as unique around the world. Generally, this mineral is quite rare and not much is known about its formation.

In the given geologic area migration of vanadium- and uranium-rich basinal waters can be proposed according to many published indices. Beside Lower Permian (andesitic) volcanism, tectonic movements or Cu-ore deposits, which affected the older coarse basinal sediments with embedded silicified plant stems, either V-rich organic black shales and other V minerals, such as vesignieite $Cu_3Ba(VO_4)_2(OH)_2$, roscoelite $K(V^{III},Al,Mg)_2AlSi_3O_{10}(OH)_2$, or volborthite $Cu^{II+}{}_3V^{V+}{}_2O_7(OH)_2 \cdot 2H_2O$, have been reported by a number of local geologists. Here, the wakefieldite was most likely formed as a secondary mineral during diagenesis of silica mass, pointing to V and U mobility in both the (silicified) wood and the close proximity of the fossiliferous locality. It is obvious that during later wood alteration these elements have been

depleted from some parts of the wood (the leached zone). Surprisingly the diagenesis did not erase the original anatomic structure of the well-preserved wood.

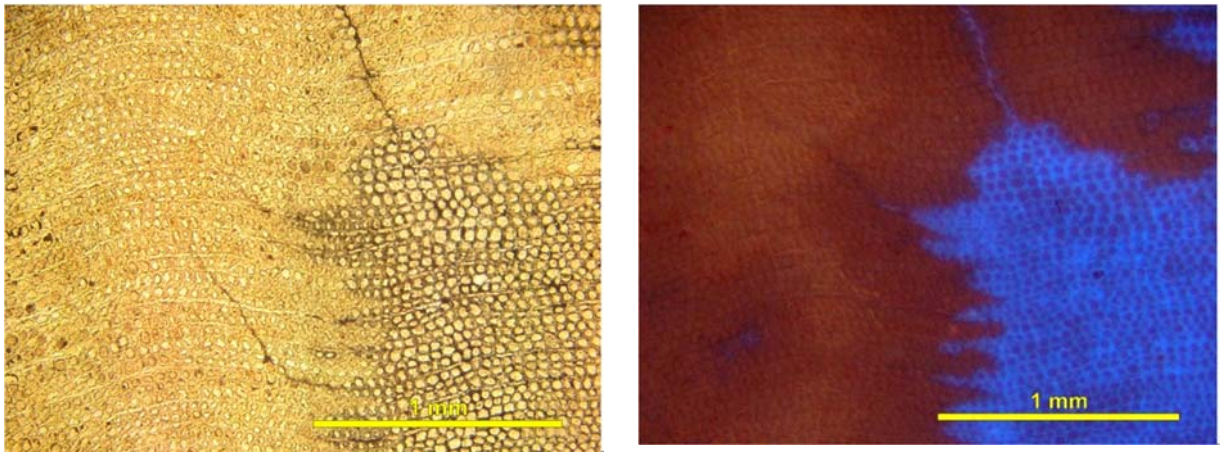

Fig.1 *Transversal cut through pycnoxylic Dadoxylon wood; slightly undulated parenchymatic rays attending rows of tracheids. Left: transmitted light, the altered leached zone is the lower right quarter (wood with dark cell walls). Right: hot cathodoluminescence, short-lived blue CL of the altered zone interferes with dark reddish CL of unaltered wood*

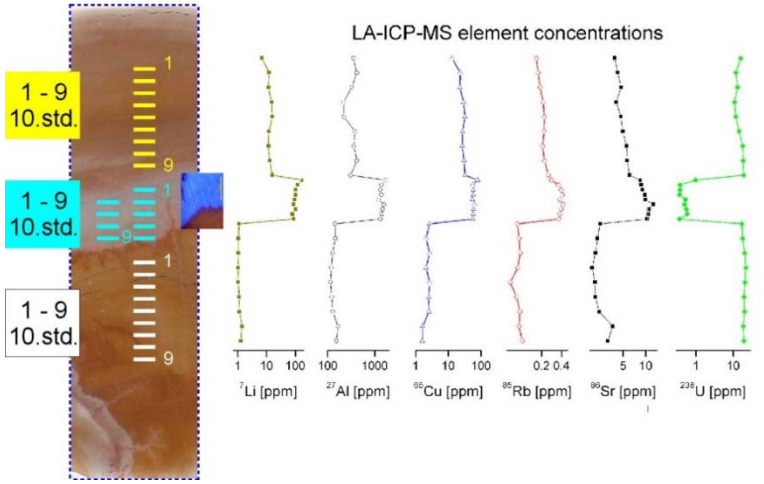

Fig.2 *Illustration of laser ablation ICP-MS measurements in line crossing all principal parts of the sample (from the top to the bottom: slightly humified wood, leached zone of well-preserved wood, and unaltered well-preserved wood). Nine lines were measured in each part followed by a reference measurement of the internal standard (^{29}Si; 10.std.). Element concentrations clearly show differences in the chemical composition of distinct parts of the α-quartz phase in the sample*

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