Morphology and Structure of Biomorphous Silica Isolated from *Equisetum hyemale* and *Equisetum telmateia*

Mike Neumann, Sandra Wagner, Robert Nöske, Brigitte Tiersch, and Peter Strauch

University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24 – 25, 14476 Potsdam, Germany

Reprint requests to Prof. Dr. P. Strauch. Fax: +49 (0)331 977-5054. E-mail: pstrauch@uni-potsdam.de

Z. Naturforsch. **2010**, *65b,* 1113 – 1120; received March 4, 2010

The family of horsetails (*Equisetaceae*) is characterized through their high content of silica (SiO_2), which is the highest in known vascular plants. This work has focussed on two species of this family, *Equisetum hyemale* and *Equisetum telmateia*, where the biomorphous silica is deposited basically as amorphous SiO_2 in the outer epidermis of the plants. As source of SiO_2, the original plant material was air-dried and carved or powdered. For the isolation process the biomaterial was pre-treated with aceotropic HCl. This pre-treatment has the advantage of the extraction of high amounts of the natural inorganic matrix. In a second step the organic matrix was removed by a thermal oxidative process in the temperature range of 275 – 1200 °C to isolate the biogenic silicon dioxide from the perennial plant. Parameters of time, temperature and the thermal gradient were varied to optimize the process and to get products with the highest possible surface area. Furthermore, the particle morphology of the biogenic SiO_2 from leaves and stems was examined separately. The silica deposits were characterized by optical microscopy, scanning electron microscopy, infrared spectroscopy, gravimetry, nitrogen sorption analysis, and sedimentation analysis.

Key words: *Equisetum hyemale*, *Equisetum telmateia*, Horsetail, Biomorphous Silica, Silicon Dioxide

Introduction

The family of *Equisetaceae* (horsetail) are the last descendents of an earlier group of plants, the *Sphenopsida* [1]. The genus of *Equisetum* consists of about 30 species and has its origin in the time of the Carboniferous [2]. The genus is divided into marsh and land plants [1], both being found in whole Europe. The stems are cavernous and structured in nodes and internodes. *Equisetum telmateia* achieves heights up to 200 cm, *Equisetum hyemale* are smaller with maximum heights up to 100 cm. The plants are preferrentially located at calcareous and humous soil [3].

The silicon source of plants is silicic acid in soil [4]. The availability of silica depends on the concentration and the chemical structure of the silicon compounds. Free silica is transported in the xylem through the plants and has many different tasks [5]. Silicon is quasi essential for the silicon accumulator horsetail [6]. Silicon dioxide promotes the growth and reproduction [7, 8], enhances the efficiency of photosynthesis, decreases the transpiration rate and affects the reflection of light [9, 10]. The plant stores silicon as amorphous silica or as "opal" [4]. Different studies have shown that free silica is bound at cellulose and is no more flexible after bonding. Therefore, it is no more available for the rest of the plant [11]. High concentrations of silica are found in the outer epidermis [12]. Silica concentrations in horsetail can range from 0.1 % to 10 % of dry weight [9, 13].

In history people used silica from horsetails to clean their dishware or to polish wood [5]. Today nanostructured biomorphous silica is an environmentally friendly alternative for synthetically produced silica in many ranges of materials industry [14].

The object of the present study has been the characterization of silicon dioxide isolated from *Equisetum telmateia* and *Equisetum hyemale*. We have focused our study on the morphology and structure of biogenic SiO_2. For our experiments we separated the plant material of *Equisetum telmateia* into stems and leaves and into unground and powdered samples for comparison. With *Equisetum hyemale* we varied the parameters of time, temperature and thermal gradient of the thermal oxidative process to remove the organic matrix of the plant system. The silica deposits were characterized

0932–0776 / 10 / 0900–1113 $ 06.00 © 2010 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

with optical microscopy, scanning electron microscopy (SEM/EDX), infrared spectroscopy, gravimetry, nitrogen sorption measurements (BET), and sedimentation analysis.

Experimental Section

The leaves of *Equisetum telmateia* were derived from a habitat located in Zittau (Saxony, Germany) in October 2004. One fraction of the material was milled to a diameter smaller than 250 μm, dried at 105 °C and stored at r. t. The second fraction was air-dried and stored at r. t.

Equisetum hyemale was collected in the Botanical Garden of the University of Potsdam, Germany, in October 2004 after three vegetation periods. The plants were air-dried and divided into sections with a length of about 2 – 3 cm.

All materials were pre-treated in a wet-chemical laboratory step with aceotropic HCl for 2 h at boiling temperature (aceotropic HCl/H_2O, 1 : 1). The water-washed *Equisetum* was dried at 105 °C.

Equisetum telmateia was ashed at 750 °C in an oxidative atmosphere after HCl pre-treatment [15, modified]. The percentage yields of residue were calculated. Furthermore pre-treated materials were tempered at different temperatures, *viz.* 275, 325, 375, 400, 500, 650, 700, 850, 1100, and 1200 °C with a thermal gradient of 1 K min^{-1}, and kept for 48 h at the given temperature.

Samples of *Equisetum hyemale* were tempered for 0.5, 1, 2, 4, 6, 18, 24, 48, 73, 120, 168, 240, 360, 480, 600, 840, 1080, 1200, 1320, 1440, 1560, 1680, 1800, 1914, and 2136 h after achieving the set temperature of 350 °C. The thermal gradient was 1 K min^{-1}. Other samples were heated to 350 °C for 48 h with three different thermal gradients of 0.1, 1 K min^{-1} and 8 K min^{-1}. For the maximum heating gradient at 350 °C the sample was placed directly in the preheated furnace. Furthermore, samples were tempered for 48 h with a gradient of 1 K min^{-1} at 300, 325, 350, 375, 400, 450, 500, 600, and 700 °C.

Gravimetric analysis was used to follow the loss of the organic matrix as an overall mass loss. All gravimetric analyses showed differences between the only thermolized and the HCl pre-treated biomaterial. IR spectroscopy was employed to characterize the silica and the biomaterial. An IR spectrometer 16 PC FT-IR from Perkin Elmer was used with the KBr disc technique. The discs were pressed in vacuum. The specific surface area was determined with nitrogen sorption measurements at 77 K (BET; DIN ISO 9277: 2003-05) [16]. A Quantachrome Autosorb Automated Gas Sorption System was used for the BET measurements.

The sedimentation analyses were carried out with a photoscanning sedimentograph "analysette 20" (Fritsch) for characterization of the particle size distribution of solid matter dispersed in solution. Particles in the range from 0.5 to 500 μm can be measured in relation to their sedimentation velocity. The following equation was used to calculate the sedimentation velocity: $v = (2r^2 (D_1 – D_2) g) / (9\varepsilon)$ (v = sedimentation velocity, r = particle radius, D_1 = density of the particle, D_2 = density of the solvent, g = gravitation constant, ε = viscosity of the solvent). We used water as solvent for all samples. The macroscopic structures were characterized by optical microscopy. We used reflected-light microscopy (Carl Zeiss Jena), with a magnification factor of up to 100 to describe the non-planar sample surface. For further investigations we used transmitted-light microscopy (WILL h500 Wilozyt, hund Wetzlar) with a magnification of up to 600 times. The microscopes were combined with a Nikon Coolpix-995 for picture recording.

The HCl pre-treated and for 73 h at 350 °C calcinated samples of *Equisetum hyemale* were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). For the investigations of the silicon content a cryo-field emission scanning electron microscope S-4800 (Hitachi) was used. The resolution is 1.0 nm at 15 kV and 1.4 nm at 1 kV. The EDX spectroscope was built by Thermo (Thermo-NORAN-System SIX) and equipped with a cryo-transfer system Gatan-Acto 2500-S.

Results and Discussion

For the wet-chemical pre-treatment of the biomaterials we exclusively used the method of boiling in aceotropic HCl, because this method leads to the best results. This pre-treatment of *Equisetum hyemale* and *Equisetum telmateia* reduces the inorganic matrix, which means a nearly complete loss of sodium, potassium, magnesium, calcium, and aluminum compounds [15]. The main amount of the inorganic matrix was dissolved during the following washing process with

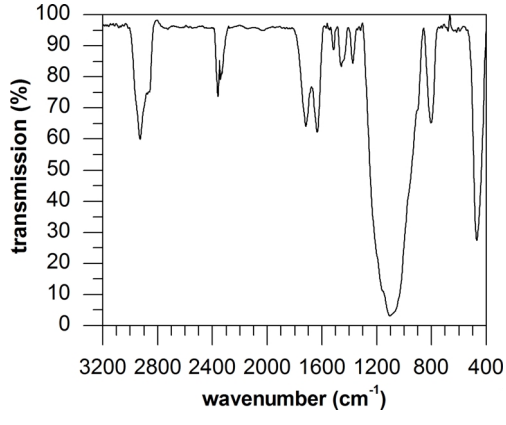

Fig. 1. IR spectrum of *Equisetum hyemale* after 2 h of treatment with boiling aceotropic HCl.

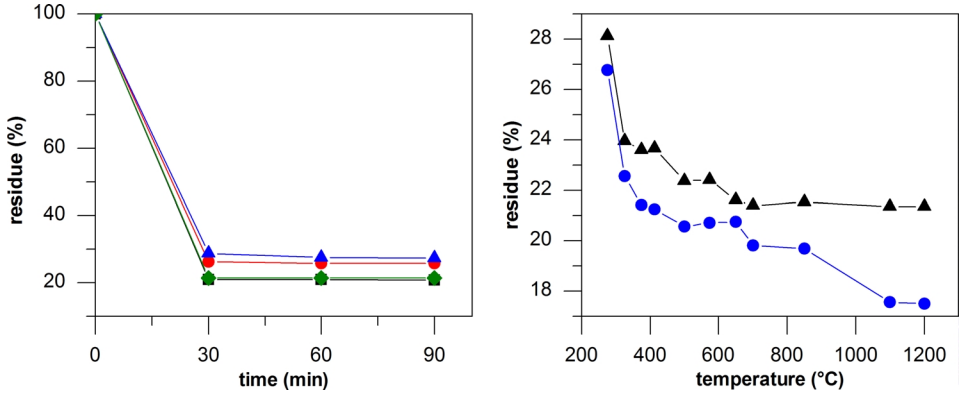

Fig. 2 (color online). Left: Residue of *Equisetum telmateia* after thermal oxidation at 750 °C: (▲) ground biomaterial, without HCl pre-treatment; (●) unground biomaterial, without HCl pre-treatment; (◆) ground biomaterial, after HCl pre-treatment; (■) unground biomaterial, after HCl pre-treatment. Right: Decomposition of the organic matrix of *Equisetum telmateia* (▲) ground and (●) unground, after treatment with boiling HCl and calcination for 48 h at different temperatures.

pure water, until the filtrate was neutral. The HCl pre-treatment causes also a partial acidic hydrolysis of the organic matrix [17]. The bonds in the cellulose network partially break and give glucose and polymers with smaller degrees of polycondensation. After boiling with HCl the biomaterials consist mainly of silicon dioxide, cellulose (about 80 %), lignin (about 5 – 20 %) and hemicelluloses [18, 19]. For *Equisetum telmateia* an average of 55 % of the original mass were found. Differences between unground leaves and powdered materials were not detected. For *Equisetum hyemale* a mass loss of 65 % was found. Fig. 1 shows the IR spectrum of a sample of *Equisetum hyemale* after HCl pre-treatment. The spectrum proves the presence of the remaining organic matrix. The absorption bands at 2923 and 2856 cm^{-1} characterize the symmetric and asymmetric CH_2 valence vibrations [20, 21]. The band for the conjugated carbonyl vibration is found at 1712 cm^{-1}, the non-inconjugated vibration at 1630 cm^{-1} [21]. The deformation vibrations of the CH groups are related to a band at 1504 cm^{-1}, those of the CH_2 groups at 1453 and 1363 cm^{-1}. All typical vibrations of silica were found in the spectra at 1098, 802 and 464 cm^{-1} [21, 22].

The organic components of the biomaterial *Equisetum telmateia* were completely degraded during calcination at 750 °C. The decomposition depends mainly on the temperature, the calcinating time and the atmosphere [23]. For the calcination we used constant temperatures and normal atmosphere (air). The mass of the remaining silica in dependency of the calcination time is shown in Fig. 2. The main loss of the organic matrix was observed during the first 30 min. Constant masses were reached after 60 and 90 min. The average residue for ground biomaterial without a HCl pre-treatment was found at 27 %, for the ground and pre-treated plant we found a residue of 21 % of the original mass.

The biomaterial *Equisetum telmateia* was also calcinated at different temperatures after pre-treatmant in boiling aceotropic HCl. The mass loss is also depicted in Fig. 2. For a complete degradation of the organic matrix we had chosen a calcination time of 48 h after reaching the appropriate temperature. All samples were heated up with a defined thermal gradient of 1 K min^{-1}. The decomposition temperature of the main organic matters are for hemicelluloses in the range of 200 – 260 °C, for cellulose 240 – 350 °C and for lignin 280 – 500 °C [23]. The mass loss for the ground and unground biomaterial is different (Fig. 2) for two reasons. First, the ground material was dried at a defined temperature of 105 °C before milling. Possibly the air-dried unground samples of *Equisetum* might contain some more water. This would result in a higher mass loss during the thermal process. Second, there are differences in the structure of the samples. The powder has a larger surface than the unground leaves, and the oxidation process is more effective for the ground material. The IR spectra (spectra not shown) showed no bands of cellulose (2900 – 2800 and 1500 – 1350 cm^{-1}) after the oxidative thermal process at 275 °C. Cellulose decomposes at temperatures between 240 and 350 °C [23]. The spectra showed the characteristic asymmetric stretching vibra-

tion at 1102 cm^{-1}, the symmetric stretching vibration at 802 cm^{-1} and the bending / deformation vibration at 469 cm^{-1} of silica, and the vibration bands of lignin at 1730, 1620 and 1010 cm^{-1} after tempering at 275 °C. For the samples calcinated at temperatures higher than 325 °C a decrease of the lignin bands could be observed. Beside the typical absorption bands of silica only the vibration band of lignin at 1620 cm^{-1} and a shoulder at 1010 cm^{-1} were found. Higher temperatures (> 400 °C) lead to the disappearence of the lignin shoulder at 1010 cm^{-1}, and a strong band of amorphous silica at 566 cm^{-1} is formed. The IR spectrum of *Equisetum telmateia* calcinated at 850 °C is different. The organic matrix is decomposed completely, and only the characteristic silica vibration bands at 1100, 800 and 469 cm^{-1} [21, 22] were found. Differences between the ground samples and the unground leaves of *Equisetum telmateia* were not detected. Obviously, the milling process had no influence on the decomposition of the organic matrix.

The samples of *Equisetum telmateia* calcinated at different temperatures in the range from 325 to 850 °C (48 h) were characterized by nitrogen sorption measurement (BET) at 77 K in order to determine the specific surface area (Fig. 3). Up to a temperature of 375 °C the biomaterial still contains large quantities of the organic matrix, resulting in a low porosity of the material and a low specific surface. The largest values of the specific surface were detected for calcination temperatures between 375 and 575 °C. The surface of the calcinated material increases up to 400 $m^2\ g^{-1}$. This effect implies the (complete) loss of celluloses and the presence of amorphous silica. A further increase of the calcination temperatures leads to crystallization, sintering and partly melting processes [10]. These effects are reflected in a significant decrease of the specific surface. The samples of ground and unground material of *Equisetum telmateia* after pretreatment with aceotropic HCl and a thermal oxidation at 575 °C show only small differences. For the ground material a specific surface area of 382 $m^2\ g^{-1}$, for the unground material of 422 $m^2\ g^{-1}$ were measured. For these samples the milling process had no significant influence on the porosity.

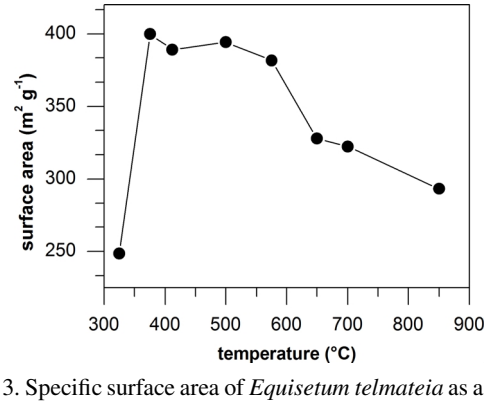

Fig. 3. Specific surface area of *Equisetum telmateia* as a function of different calcination temperatures. All samples were tempered for 48 h after HCl pre-treatment.

Table 1. d_{50} data (particle diameter) of *Equisetum telmateia* after 48 h of thermal oxidation and pre-treatment with HCl. Comparison of d_{50} data after calcination for 48 h at 850, 1100 and 1200 °C (HCl pre-treatment).

Temperature (°C)	d_{50} (μm) (ground)	d_{50} (μm) (unground)
375	11	–
575	13	14
850	15	–
1100	25	23
1200	34	37

The particle size represented by the d_{50} data and the size distribution was determined by sedimentation analysis. The measurements of ground *Equisetum telmateia* after HCl pre-treatment and thermal oxidation at temperatures between 375 and 850 °C showed no significant differences in the d_{50} data: 11.13 μm at 375 °C, 13.35 μm at 575 °C and 14.70 μm at 850 °C. Up to 850 °C the temperature has no strong influence to the particle size. However, the d_{50} data and the particle size distribution differences in the temperature range of 850 °C and 1200 °C are noticeable (Table 1). For every temperature step a significant step in the particle size of about 10 μm was observed. With increasing temperatures the silica particles start to sinter with formation of agglomerates. At 1200 °C the sedimentation velocity in water is too high to be measured, therefore, we changed the solvent to ethylene glycol. The sedimentation analysis showed no significant differences between ground and unground biomaterial. Furthermore we compared the d_{50} data of silica from ground material and unground leaves with and without HCl pretreatment. The pre-treatment with aceotropic HCl has no observable effect on the particle size. The d_{50} data are between 16 and 22 μm (not pre-treated: ground material 17 μm, unground leaves 21 μm; pre-treated: ground 18 μm, unground 19 μm).

The physiological precipitation of silica in the leaves of *Equisetum telmateia* and its function can be studied by optical microscopy. Horsetails are typical

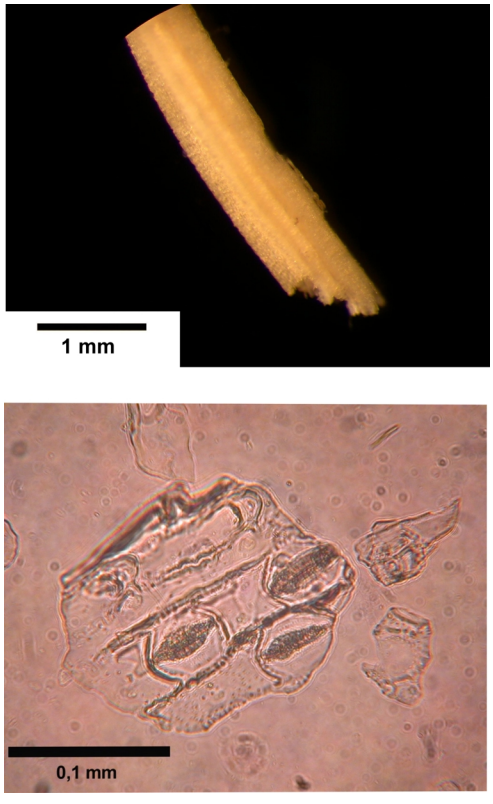

Fig. 4 (color online). (top) Optical reflected-light spectroscopy of unground leaves of *Equisetum telmateia* after HCl pre-treatment and calcination at 375 °C for 48 h. (bottom) Optical transmitted-light spectroscopy of particles from ground leaves of *Equisetum telmateia* after HCl pre-treatment and calcination at 400 °C for 48 h.

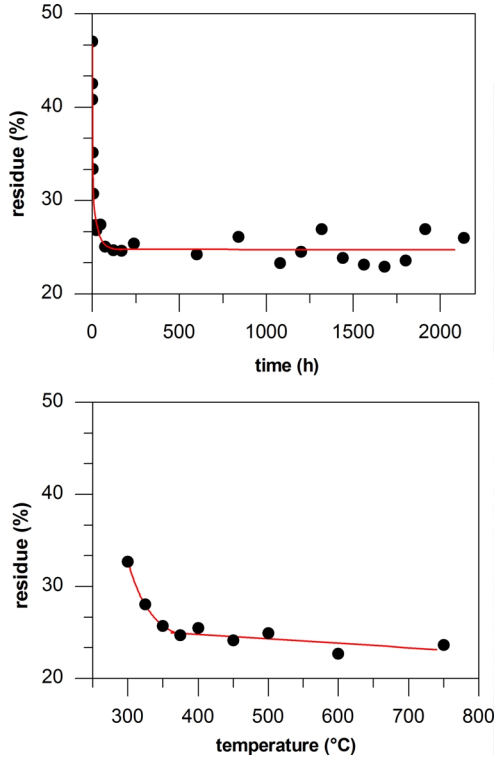

Fig. 5. Top: Gravimetric residue (•) and gravimetric average (–) of *Equisetum hyemale* as a function of time after wet-chemical pre-treatment and thermal oxidation at 350 °C. Bottom: Decomposition of the organic matrix (*Equisetum hyemale*) as a function of temperature after 48 h of thermal oxidation.

silica accumulators [10]. They assimilate silicic acid from soil and deposit it as demobilized, amorphous silica or as opal [24]. Our biomorphous silica is mainly of the amorphous form and contains only little of the opal form. The amorphous silica forms a characteristic skeleton (Fig. 4) during the decomposition of the organic matrix [5, 12]. Linkages between silicic acid and the organic polymer (cellulose and lignin) are partly broken. The deposition of silicon dioxide in leaves is mainly observed in the cells of the epidermis, the leaf veins and the closing cells [25].

To study the influence of calcination time, samples of *Equisetum hyemale* were tempered at 350 °C for up to 2136 h after achieving the appropriate temperature. Already after 18 h of thermal oxidation no significant changes in the mass loss were detected (Fig. 5), and after 120 h an equilibrium was reached. Nevertheless, we found chemical changes in the structure. An extended thermal oxidation at 350 °C results in the same decomposition of the organic matrix as a thermal process at higher temperatures (750 °C). The degradation of hemicelluloses, celluloses and lignin proceeds possibly at lower temperatures than mentioned in the literature [23]. Samples of *Equisetum hyemale* were tempered for 48 h at different temperatures between 300 and 750 °C with a heating gradient of 1 K min^{-1}. The maximum of mass loss for a constant calcination time of 48 h was detected for 600 °C (Fig. 5). At higher temperatures no further changes were observed. For short thermal treatment times (48 h) higher temperatures are necessary for the complete decomposition of all organic components [23]. The decrease of the residue mass up to 350 °C is more precipitous than at higher temperatures. The quantities of hemicelluloses and celluloses in the biomaterial are much higher than the quantity of lignin, and for lignin higher temperatures (280 – 500 °C) are required for the decomposition

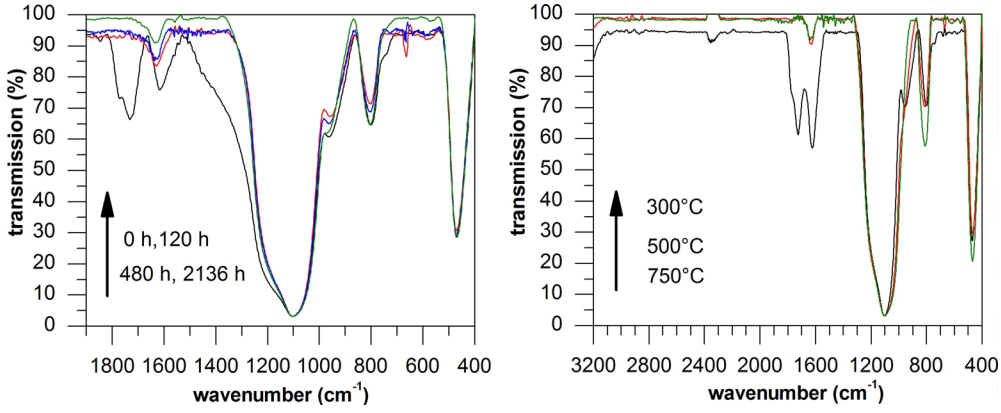

Fig. 6 (color online). IR spectra of *Equisetum hyemale* after HCl pre-treatment and calcination for 0, 120, 480 as well as for 2136 h at 350 °C (left); after 48 h of thermal treatment at 300, 500 and 750 °C (right).

than for the hemicelluloses (200 – 260 °C) and celluloses (240 – 350 °C) [23]. There is no significant influence of different heating gradients on the thermolysis of *Equisetum hyemale*. The remaining residue after 48 h of calcination at 350 °C with different gradients is nearly constant (0.1 K min^{-1}: 26 %; 1 K min^{-1}: 26 %; 7.8 K min^{-1}: 26 %, and the maximal gradient at 350 °C: 25 %).

The IR spectra of the samples after calcination times up to 2136 h (Fig. 6) show the decrease of the organic matrix. At the beginning of the calcination process at 350 °C the typical absorptions of the whole organic matrix still can be observed. The deformation vibrations at 1504 (CH group), 1453, and 1363 cm^{-1} (CH_2 groups) disappear first reflecting the decomposition of hemicelluloses and celluloses. The strong mass loss at the beginning of the thermal treatment correlates with the disappearence of the typical absorption bands of the organic matrix in the IR spectra. The carbonyl bands at 1615 (conjugated) and 1723 cm^{-1} (non-conjugated) [8, 19] decrease with increasing time, and this correlates with the decomposition of lignin. The latter has completely disappeared after 48 h, the former reaches the minimum after 120 h. All typical vibrations of silica were still present at 1102, 802, and 464 cm^{-1} [21, 22]. The IR spectrum after 2136 h of calcination shows the presence of only traces of lignin (1630 cm^{-1}). All IR spectra (Fig. 6) of the samples after 48 h of thermal oxidation at different temperatures in the range between 300 and 750 °C confirm the strong decline of the lignin bands (carbonyl bands, 1712 and 1630 cm^{-1}). The IR spectra (spectra not shown) for different thermal gradients show no significant differences between 1 K min^{-1} and the maximal gradient (the sample being placed directly into the pre-heated furnace). Only for the sample heated with a gradient of 0.1 K min^{-1} a lower mass loss was observed. Obviously, very low thermal gradients inhibit the decomposition of hemicelluloses, celluloses and lignin in *Equisetum hyemale*.

Nitrogen sorption measurements (BET) at 77 K for *Equisetum hyemale* calcinated at 350 °C, with a variation of calcination time up to 2136 h (Fig. 7) gave specific surface areas from 121 up to 418 $m^2\ g^{-1}$. Up to 24 h of calcination at 350 °C the material still contains large quantities of hemicelluloses, celluloses and lignin, which is again reflected in a reduced specific surface area, due to a reduced porosity. The largest specific surface areas were measured between 24 and

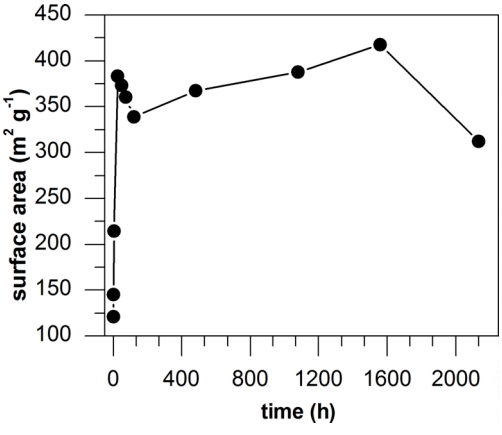

Fig. 7. Specific surface area of *Equisetum hyemale* as a function of time. All samples were calcinated at 350 °C after HCl pre-treatment.

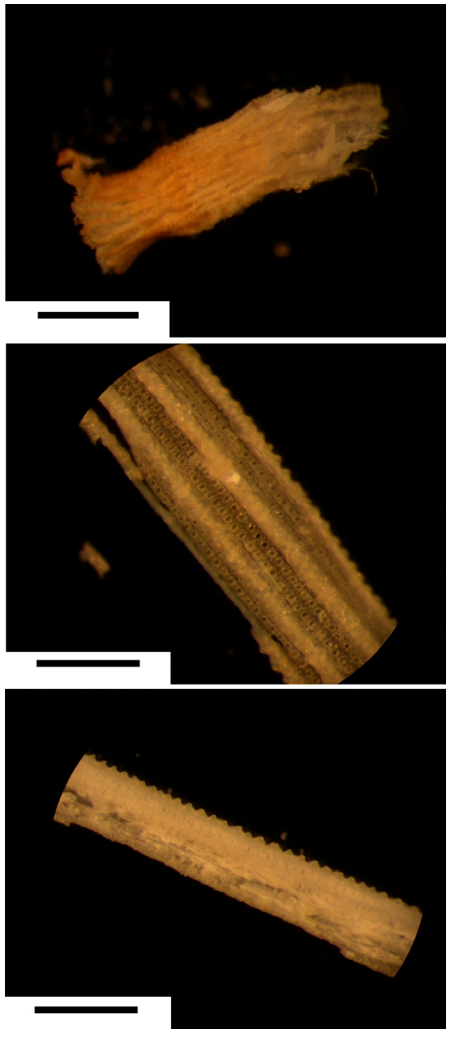

Fig. 8 (color online). Optical reflected-light spectroscopy of *Equisetum hyemale* after HCl pre-treatment and calcination at 350 °C for 120 h (top), 480 h (middle) and 2136 h (bottom). The measure bar is 1 mm in all images.

2136 h of calcination (339 – 418 $m^2\ g^{-1}$). In this time range the largest quantity of amorphous silicon dioxide with a high porosity is available. Longer thermal treatment times lead again to crystallization, melting and sintering processes [10].

The structure of *Equisetum hyemale* was also characterized by optical reflected-light microscopy after up to 2136 h of calcination at 350 °C (Fig. 8). The wet-chemically pre-treated biomaterials change their color shade from dark-brown at the beginning *via* brown, yellow, colorless to a finally snow-white end product. After 1 h of treatment the brown biomaterial starts to

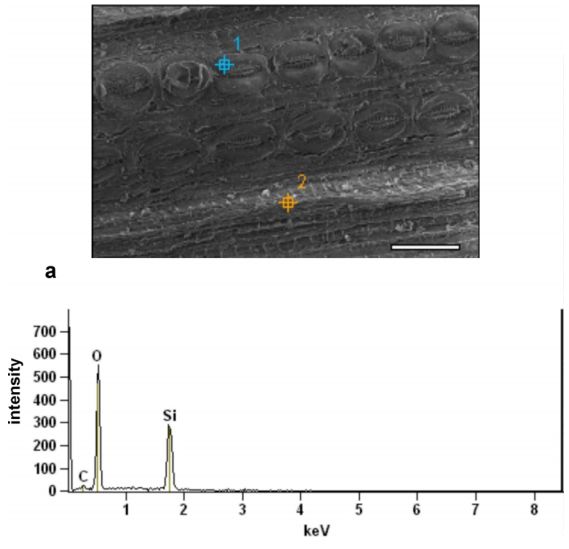

Fig. 9. SEM/EDX measurements of different areas of *Equisetum hyemale* after HCl pre-treatment and 73 h of thermal oxidation at 350 °C. The accelerating voltage was 5.0 kV. The bar is 100 μm. Top: SEM image of the sample of *E. hyemale*. The marked areas are the EDX measurement points. Bottom: EDX spectra of the measurement point 1.

brighten up, and after 73 h a colorless product is observed. Interestingly, after a long time of calcination (1800 h) the color of the silica remains unchanged. The change of color implies the oxidative degradiation process of the organic matrix to leave the silica skeleton. The best resolution was observed after longer calcination times ($>$ 1800 h).

Fig. 9 shows the SEM image and the semiquantitative analysis of a sample of *Equisetum hyemale*. The sample was pre-treated with hydrochloric acid and calcinated at 350 °C for 73 h. The image shows the basic structure of the silica deposition in the biomaterial. Two columns of stomata are flanked with epidermal layers. In EDX measurements of the stomata area (Fig. 9) carbon, oxygen and silicon can be detected. The stomata contain nearly pure silicon dioxide. The quantity of carbon (only 3.2 atom-%) is marginal and supports the gravimetric results. After 120 h of calcination time an equilibrium in the gravimetric residue was reached which contains less than 3 % carbon. For the stomata a composition of 74 atom-% oxygen and 23 atom-% silicon was measured. This atomic ratio of 0.31 for Si to O is very close to the theoretical value of 0.33 for SiO_2. The elemental analysis of the epidermal layer gave similar results as for the stomata area, *viz.* 3 atom-% for carbon, 77 atom-% for oxygen and

20 atom-% for silicon. The silicon to oxygen ratio is 0.27. The accumulation of silicon dioxide in the layer area is significantly smaller than in the stomata area. For that reason the silica distribution in *Equisetum hyemale* is not homogenous [10] and varies between the different plant components.

Conclusion

In our studies we could demonstrate that a decomposition of the organic and inorganic matrix of leaves from *Equisetum telmateia* and stems from *Equisetum hyemale* without destroying the biomorphous silica structure by a thermal oxidation process can be accomplished. In the wet-chemical pre-treatment most of the inorganic matrix is dissolved improving the purity of the remaining SiO_2. The majority of the essential inorganic compounds in plants are phosphates, carbonates and sulfates of alkali and alkaline earth ions. With these components removed, after thermal oxidation stable skeletons or small particles of silicon dioxide are obtained. In *Equisetum hyemale* the absolute content of pure silica is about 9 %, in *Equisetum telmateia* about 23 %. In both species the maximum surface area of silica is about 400 $m^2\ g^{-1}$.

The specific surface area of the silica from *Equisetum hyemale* depends significantly on the calcination time. Thermal oxidation even at moderate temperatures but over a long period results in crystallization and sintering processes decreasing the specific surface area. We have shown that thermal oxidation of hemicelluloses, celluloses and lignin in horsetails is influenced by several parameters. By optical microscopy the important role of silica as a structural element in horsetails could be demonstrated. The extraction of amorphous silica with high specific surface areas from renewable resources may be of technological importance in the future.

Acknowledgement

The authors thank Ms. Regina Rothe from the Max Planck Institute of Colloids and Interfaces (Potsdam/Golm, Germany) for nitrogen sorption measurements.

[1] H. Weymar, *Buch der Farne, Bärlappe und Schachtelhalme*, Neumann, Radebeul and Berlin, **1958**, p. 40 – 44.
[2] R. Junker, *Samenfarne, Bärlappbäume, Schachtelhalme*, Hänssler, Holzgerlingen, **2000**, p. 103.
[3] W. Meusel, J. Laroche, J. Hemmerling, *Die Schachtelhalme Europas*, A. Ziemsen, Wittenberg, **1971**, p. 5 – 6, 17.
[4] K. Mengel, E. A. Kirby, *Principles of plant nutrition*, Kluwer Academic Publishers, Dordrecht, **2001**, 643 – 649.
[5] M. G. Voronkov, G. I. Zelcan, E. Lukevits, *Silicium und Leben*, Akademie-Verlag, Berlin, **1975**, pp. 56, 77 – 91.
[6] E. Epstein, *Annu. Rev. Plant Physiol. Mol. Bio.* **1999**, *50*, 641 – 664.
[7] A. G. Sangster, M. J. Hodson, *CIBA Foundation Symposium: Silicon biochemistry*, Wiley, New York, **1986**, pp. 90 – 111.
[8] L. E. Dartnoff, G. H. Synder, *Plant. Dis.* **1992**, *76*, 1011 – 1013.
[9] E. Epstein, *Proc. Natl. Acad. Sci.* **1994**, *91*, 11 – 17.
[10] L. Sapei, N. Gierlinger, J. Hartmann, R. Nöske, P. Strauch, O. Paris, *Anal. Bioanal. Chem.* **2007**, *289*, 1249 – 1257.
[11] S. Yoshida, *Bull. Natl. Inst. Agric. Sci. B* **1965**, *15*, 1 – 58.
[12] J. D. Lewin, B. E. F. Reimann, *Annu. Rev. Plant Physiol.* **1969**, *20*, 289 – 304.
[13] J. F. Ma, E. Takahashi, *Soil, fertilizer, and plant silicon research in Japan*, Elsevier, Amsterdam, **2002**, pp. 1 – 281.
[14] L. Sapei, R. Nöske, P. Strauch, O. Paris, *Chem. Mater.* **2008**, *20*, 2020 – 2025.
[15] C. Real, M. D. Alcalá, J. M. Criado, *J. Am. Ceram. Soc.* **1996**, *79*, 2012 – 2016.
[16] P. Brunnauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *960*, 309 – 319.
[17] H. Krässig, *Cellulose, Structure, Acessibility and Reactivity*, Gordon and Breach Science Publishers, Yverdon, **1993**, pp. 215 – 277.
[18] H. Semke, Dissertation, Albert-Ludwigs-University Freiburg, Freiburg i. Br., **2001**, p. 7.
[19] R. Pastusiak, Dissertation, Technical University of Munich, München, **2003**, pp. 21 – 29.
[20] V. Trouillet, S. Heißler, U. Geckle, E. Willin, W. Faubel, *FZKA 6468*, Karlsruhe, **2000**, pp. 36 – 32.
[21] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds B*, Wiley, New York, **1997**, pp. 1 – 377.
[22] R. Ashokan, V. Gopal, K. C. Chhabra, *Phys. Stat. Sol. (a)* **1990**, *121*, 533 – 537.
[23] W. Sandermann, H. Augustin, *Eur. J. Wood Prod.* **1963**, *21*, 256 – 265.
[24] E. Bode, *Dtsch. Tierärztl. Wochenschr.* **1994**, *101*, 367 – 372.
[25] C. K. Morikawa, M. Saigusa, *Plant Soil* **2004**, *258*, 1 – 8.