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CHEMICAL PRODUCTS TRACEABILITY ON TREATED BAMBOO

Antonio L. Beraldo^{a*}; Gisleiva C. S. Ferreira^a

^aSchool of Agricultural Engineering – Campinas State University - UNICAMP
beraldo@agr.unicamp.br, gisleiva@agr.unicamp.br

*Faculdade de Engenharia Agrícola – Universidade Estadual de Campinas.
CEP – 13083-875 - Campinas – SP – Brasil

Abstract: Bamboo is raw-material available mainly in tropical developing countries. Low-density and flexibility are the main advantages of bamboo compared with conventional materials. However, concerning to its natural durability the majority of bamboo species are decay susceptible, mainly due to borer and termite attacks.

Several treatments can be applied to bamboo culms or to bamboo strips. Salt solutions, such as CCA (chromium, copper and arsenic) or CCB (chromium, copper and bore) are the principal chemical products employed to prevent bamboo decay. The effectiveness of these treatments was evaluated by means of the total amount of chemicals products retained in bamboo culm. In the other hand, few investigations report chemical products detection along the bamboo anatomical elements. Strips from *Bambusa tuldoidea* Munro were soaked in CCB solutions (31.75% of Cr, 13% of Cu and 5.25% of B) with 10% concentration. It was also evaluated the influence of the elapsed time between strips cutting and soaking. Chemical products traceability was performed by scanning electronic microscopic (SEM). Results obtained confirm a non uniform distribution of chromium and copper oxides along the bamboo anatomical elements.

Keywords: *bamboo, chemical treatments, traceability, SEM.*

INTRODUCTION

Bamboo is a very important raw material for several applications in tropical regions. However, despite its availability, bamboo still is a non dependable material since its engineering properties change with time and it can be strongly affected by decay.

Like most lignocellulosic materials, several bamboo species show poor decay resistance. Several factors are responsible for the magnitude of the bamboo decay, such as, specie considered, season of the year, climatic conditions (temperature and relative humidity) and applications (KUMAR et al. [1]). Protection by design is a strategy to enhance bamboo durability (LIESE [2]).

Large amounts of starch (2.0% to 6.0%, according CNBRC - China National Bamboo Research Center [3]) in the parenchyma cells are very attractive for fungi and powder-post beetles (KUMAR et al. [1]). This last one can attack freshly felled bamboo culms and the severity of attack mainly depends on the starch content (LIESE [2]). Culms or strips obtained from seasoned bamboo (generally with less starch content) or from those felled 2-3 months after sprouting normally are more durable.

Bamboo treatments are ranged in two categories: natural or non-chemical and chemical (with or without pressure). HIDALGO LOPEZ [4] reported several natural treatments. Chemical treatments are normally more effective, but environmental control contamination is a problem. Eco-friendly wood (or bamboo) preservers using naturally available plants by-products with less toxicity are under investigation.

Green round bamboos normally are treated by soaking or by Boucherie method while dry bamboos are treated by soaking or in autoclave.

Compared with hardwoods and softwoods, bamboo is quite different and its anatomic structure is more regular (CNBRC [3]). The absence of the ray cells in bamboo is a drawback in terms of the effectiveness of the chemical solution transfers.

Chemical treatment effectiveness depends on several factors, mainly the bamboo anatomy, age (strong correlation with starch content), thickness, length, density, moisture content, etc.

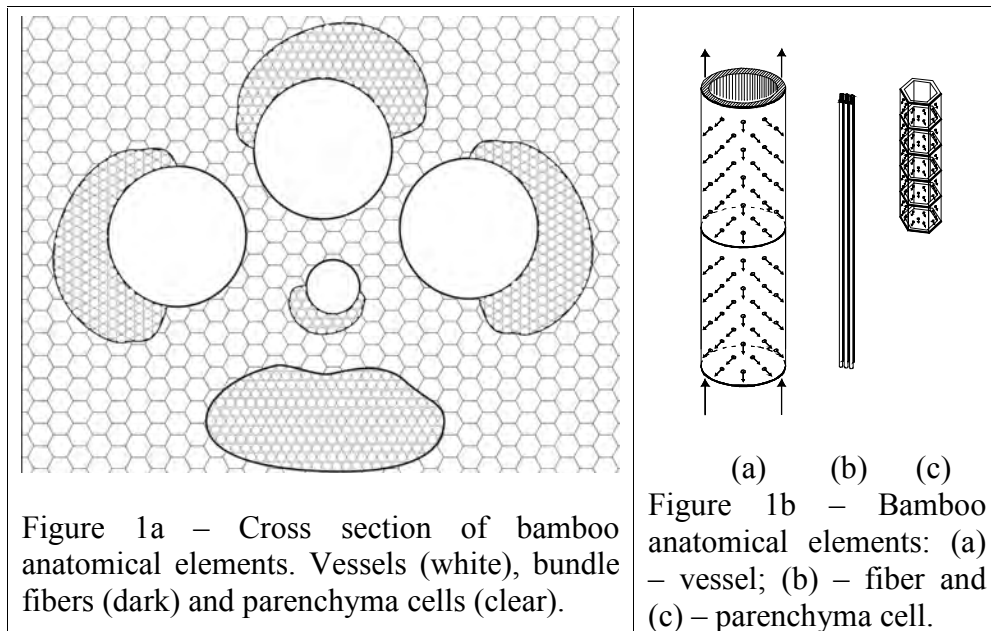
Treatment performance depends on preservative penetration into the treated material. Soaking requires a long process time which is faster for green bamboo than for the dried ones (HIDALGO LOPEZ [4]).

LIESE [2] reported that axial diffusion is faster (for about 20 times in bamboo dried) than in the others anatomical directions (radial and tangential). The treatability of dried bamboo is more difficult because sap can precipitate in the vessels blocking the flow. Pit channels in the parenchyma cells and the entrapped air in various bamboo tissues are responsible for the poor penetration (KUMAR et al. [1]).

Average content of vessels, parenchyma cells and bundle fibers are 10%, 50% and 40%, respectively (LIESE [2]); for 33 bamboo species, similar results were 6.1%, 52.8% and 40.8%, respectively (CNBRC [3]). Despite its small variation in surface, vessel diameter average changes across the wall according to their position: outer (28 μ), middle (87 μ) and inner (98 μ). So, in a preliminary analysis it can be expected that the chemical solution flow occurs more

effectively at the inner zone. This fact can be advantageous because this region, richer in starch content is attacked faster (LIESE [2]).

In the internodes the vessels are isolated from each other by the parenchyma cells (Figure 1a). Treatment effectiveness depends on the magnitude of a lateral flow by penetration (diffusion) from the vessel to the others anatomical elements. Vessels are easily permeable, but lateral flow is restrained because the absence of ray cells (KUMAR et al. [1]). Pits located at vessel walls have an important function in promoting the lateral flow (Figure 1b).



Source: BERALDO et al. [5]).

LIESE (1959) apud KUMAR et al. [1] reported the importance of the vessels on chemical solution distribution to the surrounding tissues. Untreated pockets, mainly in the parenchyma cells, are vulnerable to attacks. Scanning electronic microscope (SEM) analysis applied to pressure treated bamboo corroborated this hypothesis. A heterogeneous chemicals distribution was observed in several samples. Chemical elements were detected only in the vessels (BERALDO et al. [5]).

METHODOLOGY

Five years old green culms from *Bambusa tuldoidea* Munro were selected for this research. Splits of 2 cm width and 50 cm high, from the internodes, were obtained. Splits were identified as bottom, middle and top, according to their position along the culm. Three replicates of splits were treated by soaking in a commercial salts solution (10% concentration). Preservative concentration must be greater for green bamboo than air dried ones, according to HIDALGO LOPEZ [4]. A solution of sodium dichromate (31.75%), copper sulfate (13.00%) and boric acid (5.25%) was prepared.

To evaluate the effectiveness of the treatment applied to the green bamboo splits it was selected some combinations of factors, such as, culm position, time elapsed after telling the culm and soaking duration (Table 1). After soaking, splits were air dried in room conditions during two

months, in order to fix the preservative. One specimen (#01) without treatment was select as reference for scanning electronic microscope (SEM) analysis.

Table 1 – Factors evaluated on bamboo treatment.

Split Specimen	Position in the culm	Time after tell (h)	Treatment time (h)
#03	Bottom	0	6
#10	Bottom	0	24
#21	Bottom	0	48
#29	Bottom	0	168
#47	Bottom	24	24
#57	Bottom	24	48
#13	Middle	0	24

From each treated strip it was cut one sample measuring 4.0 cm in length, 1.5 cm in width and 0.5 cm in height. The samples were divided into 4-6 parts parallels to the fibers direction, using a sharp blade (Figure 2).

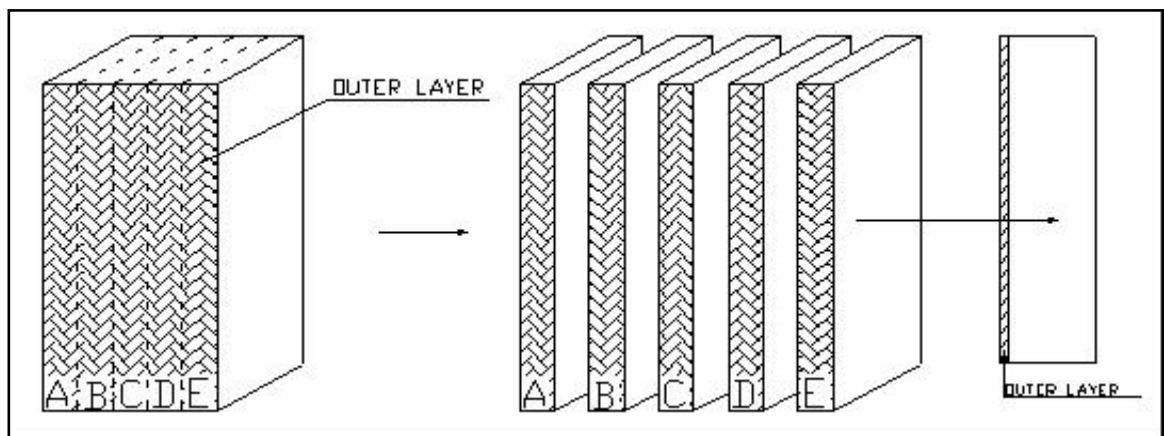


Figure 2 – Samples preparation for SEM analysis.

In preparing for the SEM the bamboo strips were covered by a thin gold film and the analysis was performed in a LEO-430 apparatus. Samples were analyzed along the direction parallel to the fibers. Three to seven points corresponding to different anatomical constituents (vessels, parenchyma and fibers) were selected for each image. Then chemical elements percentages were automatic detected in these points by the software. SEM analysis was applied to survey the chemical solution concentration across the bamboo sample and as a qualitative comparison. Boron compounds were not detected by this procedure.

RESULTS AND DISCUSSION

Bamboo treatment effectiveness is not so simple to explain in terms of the chemical elements traceability, because the variability of the culms in terms of its anatomical elements (vessels, parenchyma and fibers) and the effect of others parameters, such as, age, sampling position (bottom, middle and top), drying duration etc.

SEM analysis of the bamboo samples were automatically reported by the software as oxides contents. Figure 3 shows the natural bamboo composition. CO₂ content is over 90% for the seven points selected. Calcium and magnesium oxides were also detected in some points. Potassium (0.82%) and phosphorus (0.16%) oxides were also presented in the analysis reported by CNBRC [3]. Gold oxide contents (1% to 6%) were detected due to the SEM sample preparation (Table 2).

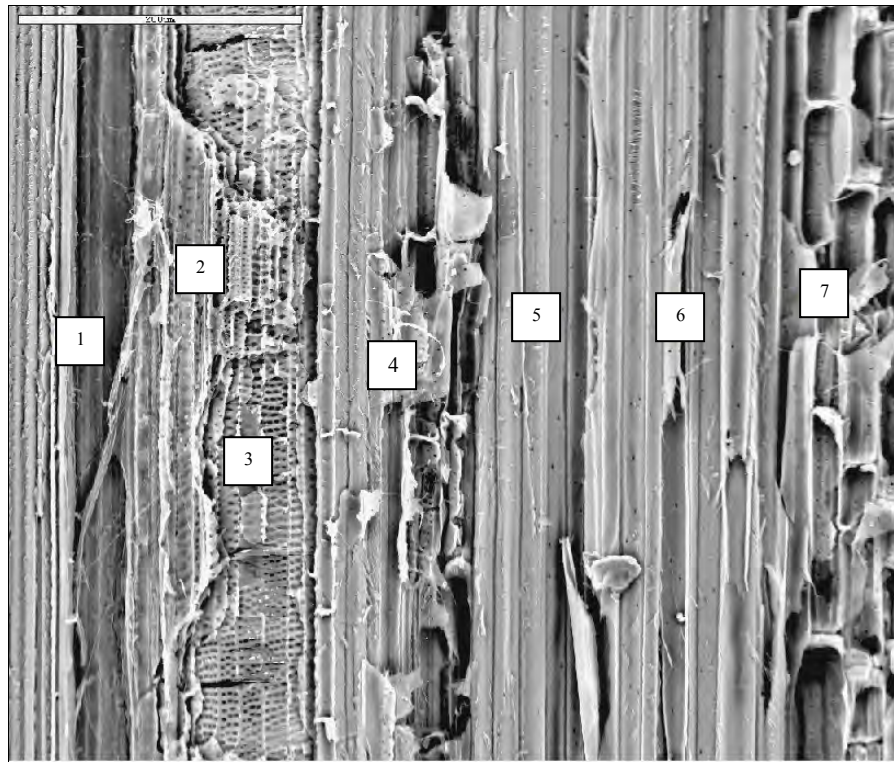


Figure 3 - Sample #01 Layer A – *Bambusa tuldooides* reference. 500X.

Table 2 - Oxides contents on *B. tuldooides* reference.

BT			A2				
Points	P1	P2	P3	P4	P5	P6	P7
CO ₂	93.90	97.51	97.95	97.88	92.96	96.01	98.43
MgO	-	0.47	0.12	0.12	-	0.19	0.12
CaO	1.52	0.22	0.05	0.08	0.20	0.10	0.04
Au ₂ O ₃	3.00	1.60	1.82	1.77	5.95	3.40	1.28

Figures 4-10 corresponding to 3-4 strips layers shows the pattern of all treatments applied to the bamboo as related in Table 1. Global data were presented in Annex.

Samples #03 – 0 h/6 h

The potassium content detection can be explained as a contaminant present in sodium dichromate used in the solution or as a natural compound present in bamboo, as reported by CNBRC [3]. Therefore, it seems to be more adequate to perform the analysis based on the presence of the others metals oxides. Chromium and copper oxides were scarcely detected mainly in points belonging to the layers A and B (Figure 4).

Sample #10 – 0 h/24 h

For layer A, analysis at points 1 and 4 (white spots in the images) showed greater chromium and copper oxides contents. Iron oxide at point 4 was also very high, denoting a possible sample contamination. For layer C oxides were absents. Small oxides contents were detected on layer F (Figure 5).

Sample #21 0 h/48 h

Copper oxide was not detected at layers C and F. Oxides distribution remains non uniform, despite 48 h treatment (Figure 6).

Sample #29 – 0 h/ 168 h

Normally for longer time treatment duration it can be expected a better oxides detection. Despite chromium and copper oxides being detected in almost of all the points, the treatment would be considered as effective only on layer E, at points 1 and 2, and in smaller degree at point 5 (Figure 7).

Sample # 47 – 24 h/24 h

For layer A (except point 3) there was a higher iron oxide content explained by a possible sample contamination. Chromium oxide was well detected for all of the points in the 4 layers. Copper oxide was detected in all of the points at layer F. Despite the large occurrence of white spots at layer A copper oxide was not detected (Figure 8).

Sample #57 – 24 h/48 h

Compared with the precedent sample it was expected that this treatment with greater duration time the oxides contents would be higher. However, results obtained did not confirm this hypothesis. Copper oxide was only detected at four points at layer D; chromium oxide also was poorly detected at all of the layers analyzed. This could be explained because culms probably were quite anatomically different or their drying time (24 h) inhibited solution absorption by the bamboo layers. Partial vessels sap blockage was reported by KUMAR et al. [1] (Figure 9).

Sample #13 – 0 h/ 24 h – Position: middle region of the culm

Data obtained were compared with those from sample #10 (same condition, bottom culm region). It can be observed that for both conditions at layer C oxides were not well detected. Oxides

contents at layers A and E were higher for bottom than from intermediate culm position. This can be explained because greater diameter vessels better the solution flows (LIESE [2] (Figure 10).

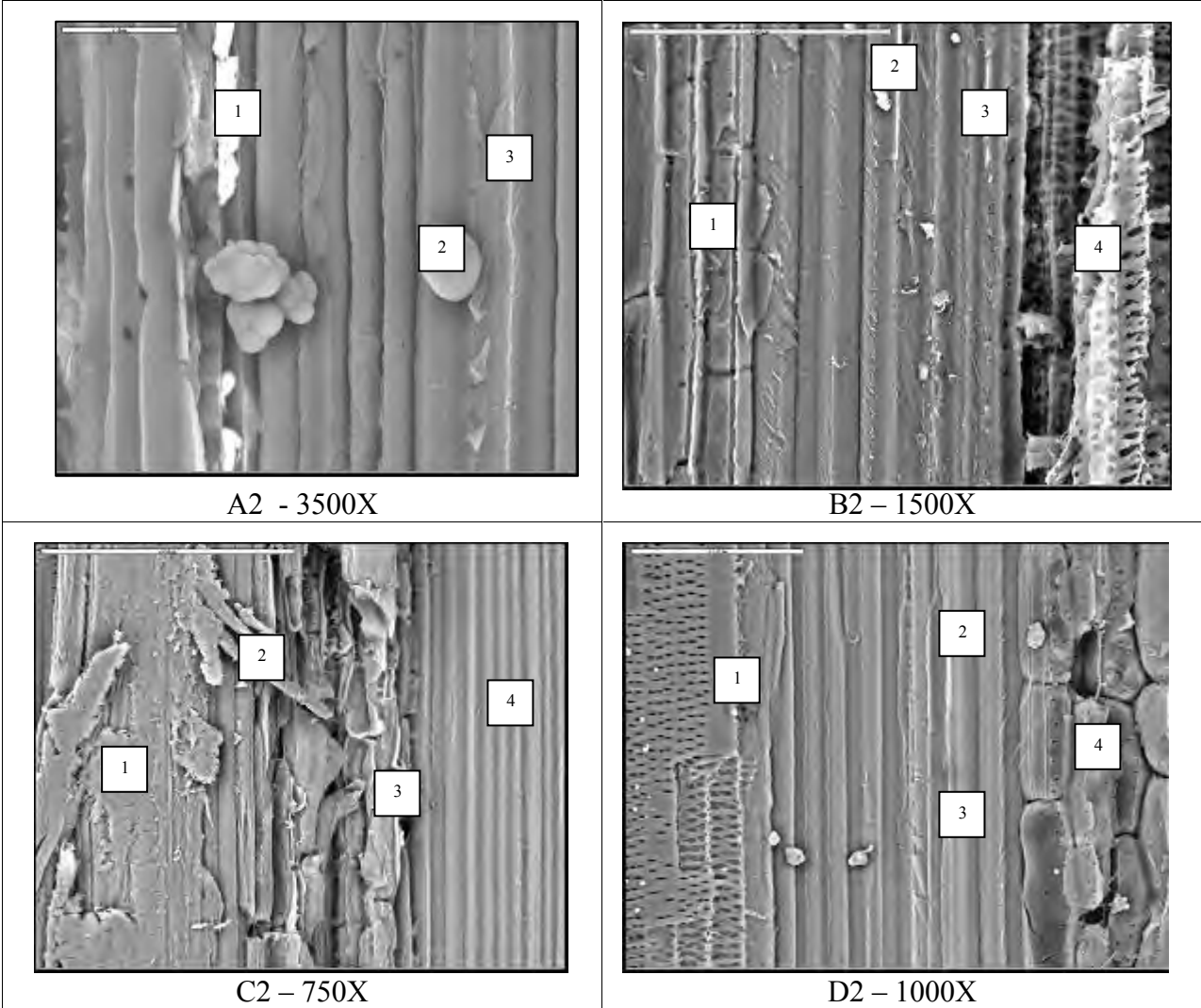
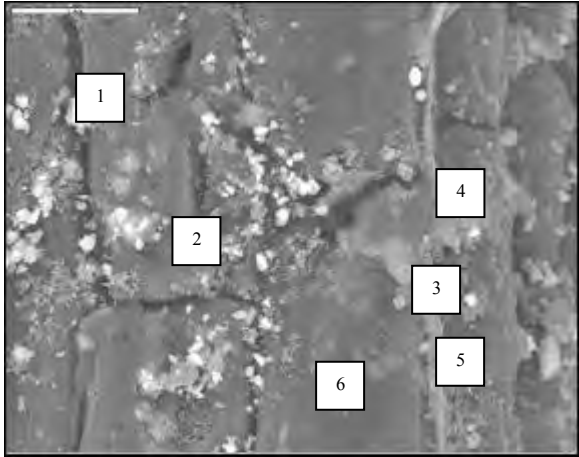
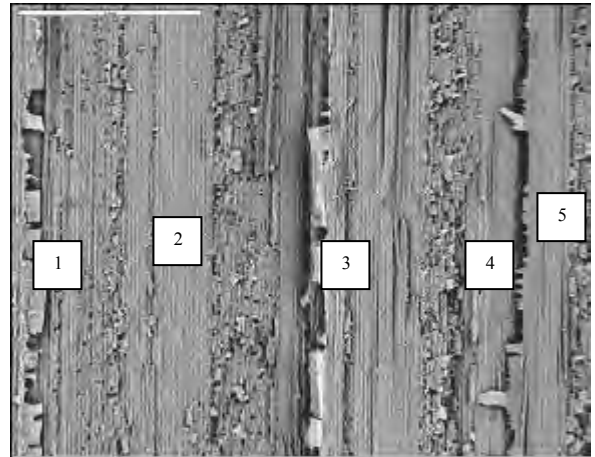


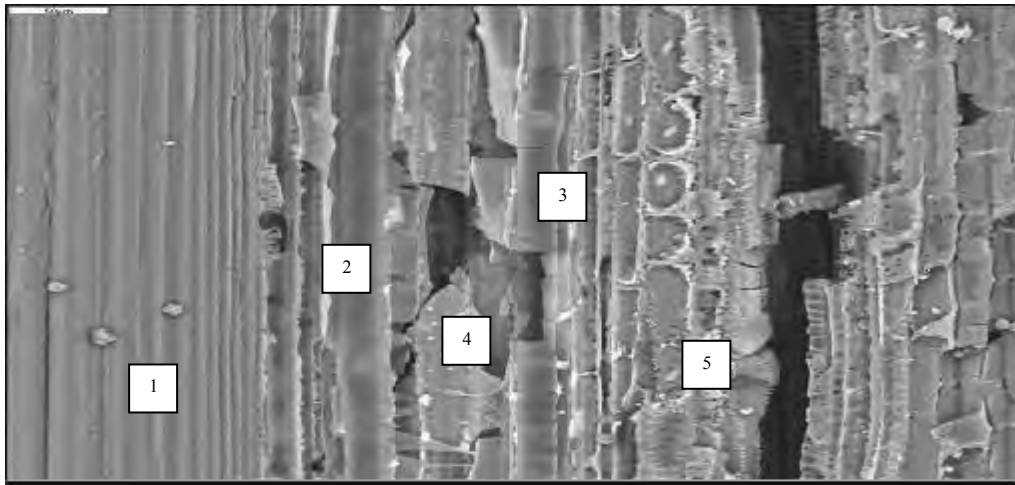
Figure 4 – Sample #03. 0 h/6 h.



A3 - 1000X

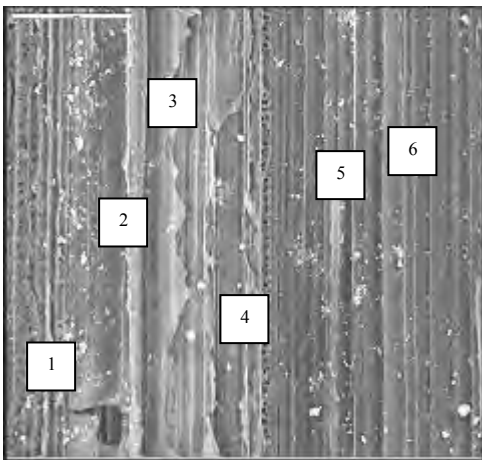


C3 - 630X

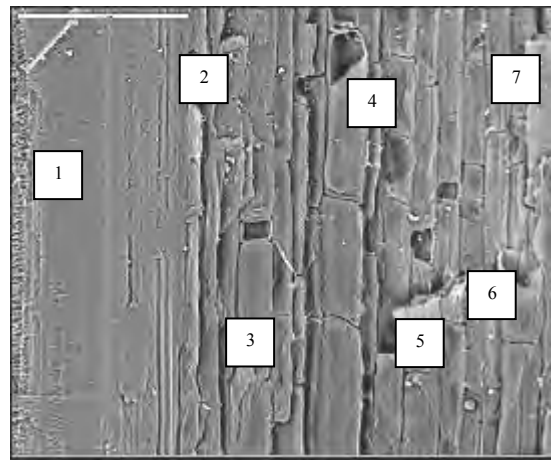


F2 - 630X

Figure 5 - Sample # 10. 0 h/24 h.



A3 - 800X



C2 - 500X

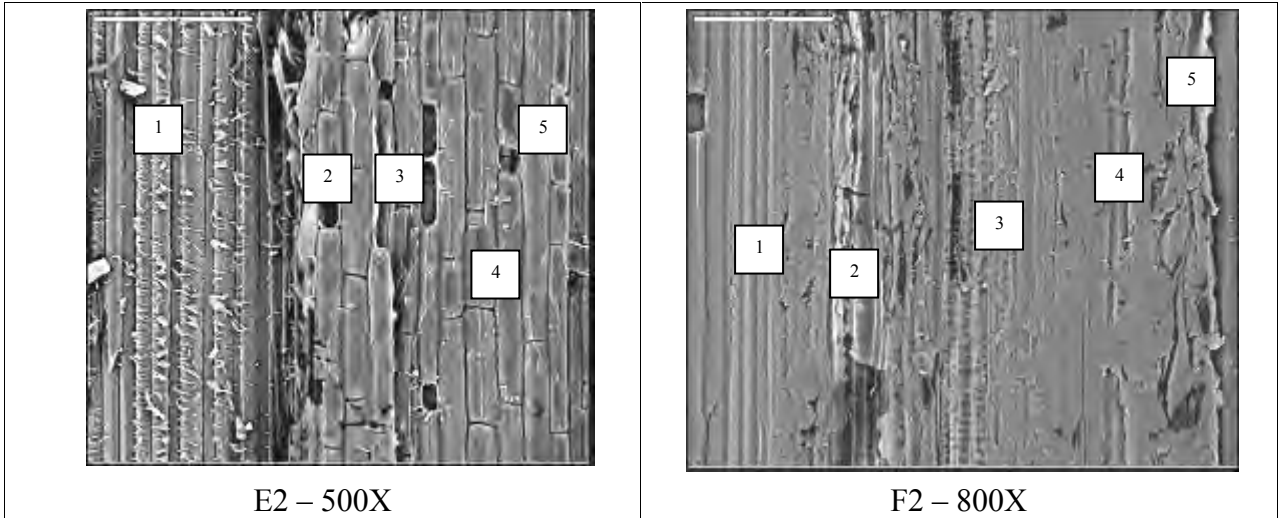


Figure 6 – Sample #21. 0 h/48 h.

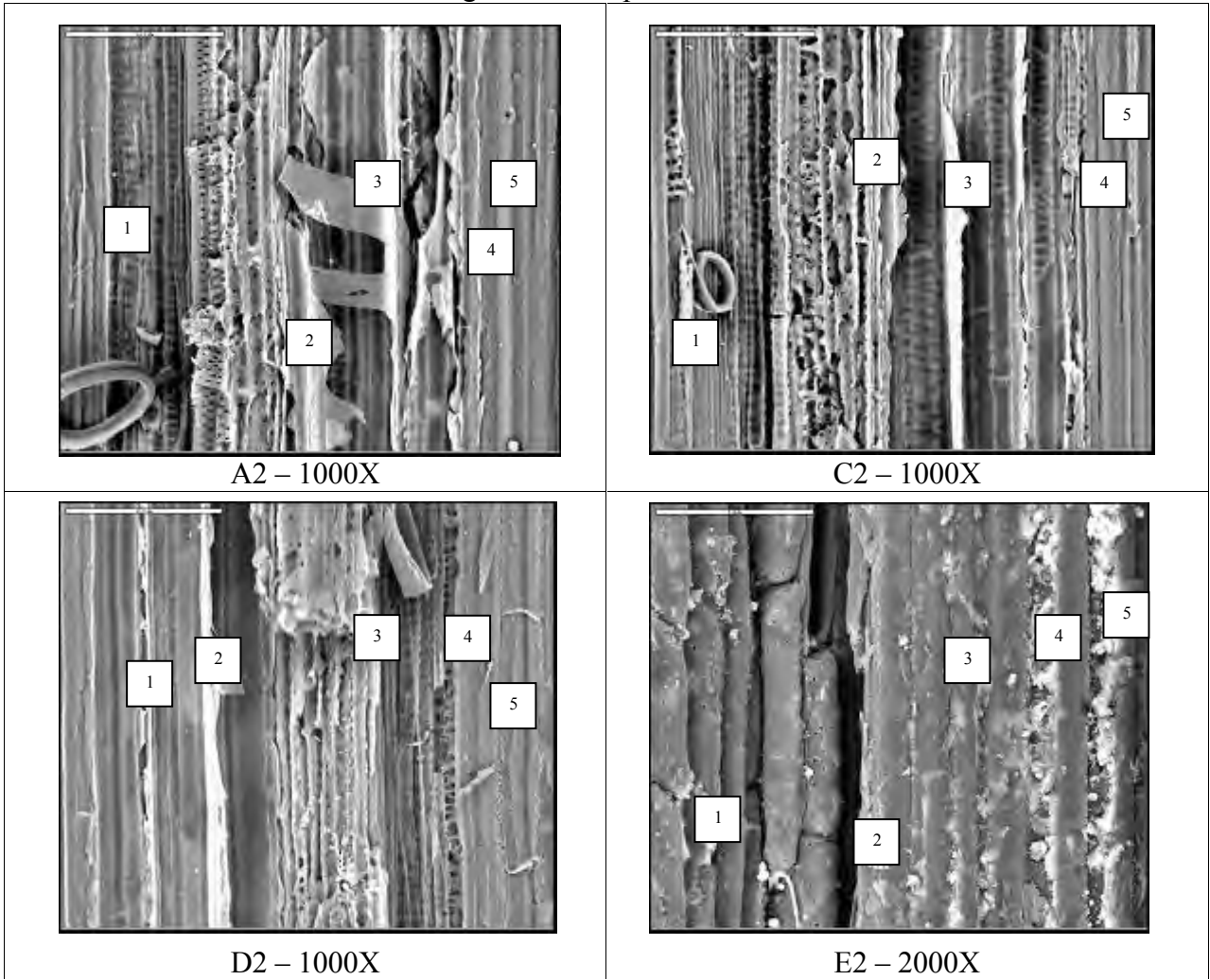


Figure 7 – Sample #29. 0 h/168 h.

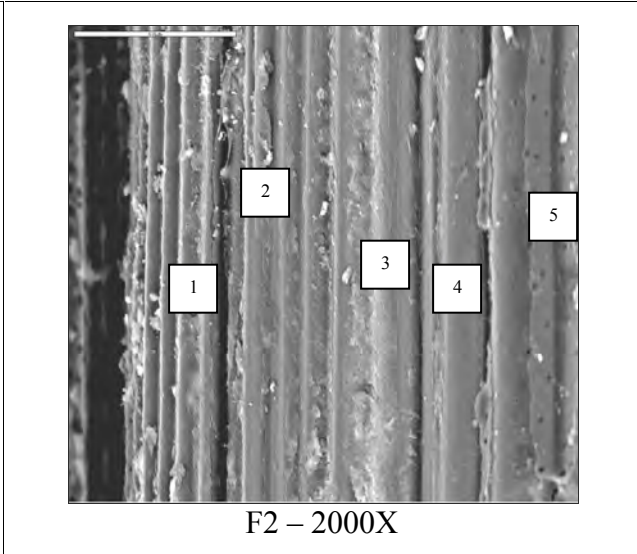
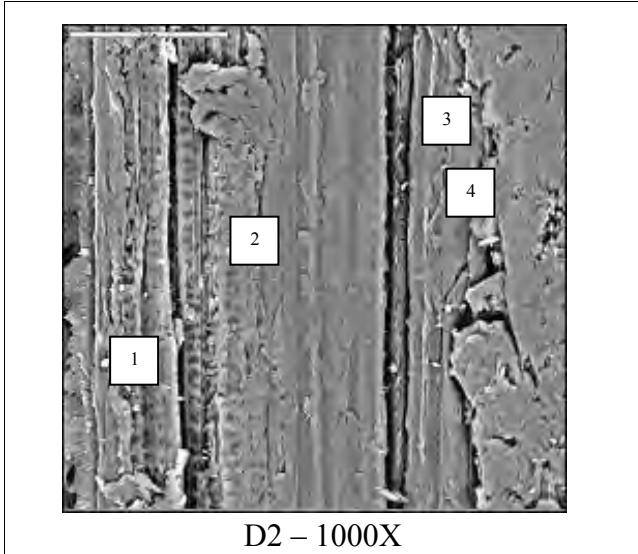
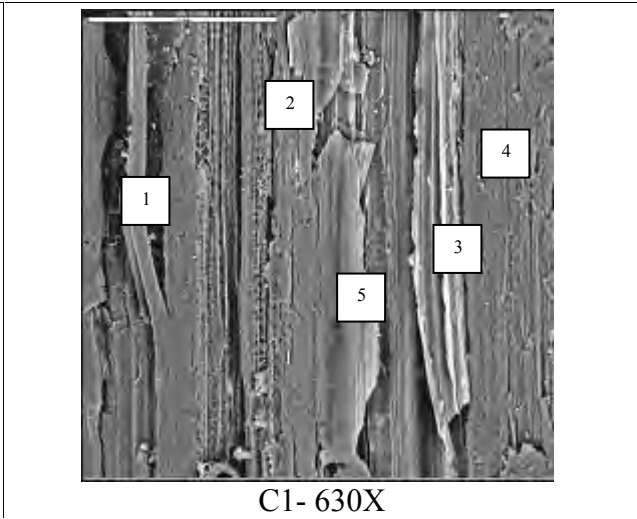
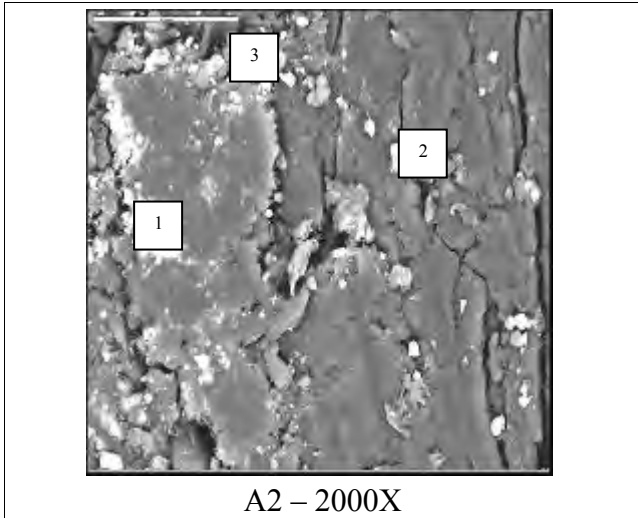
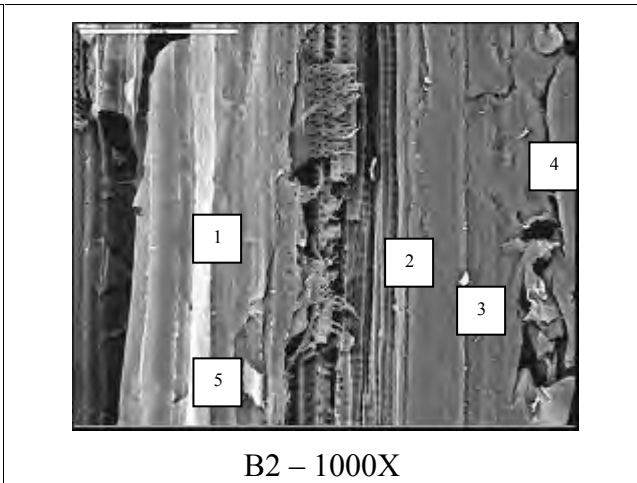
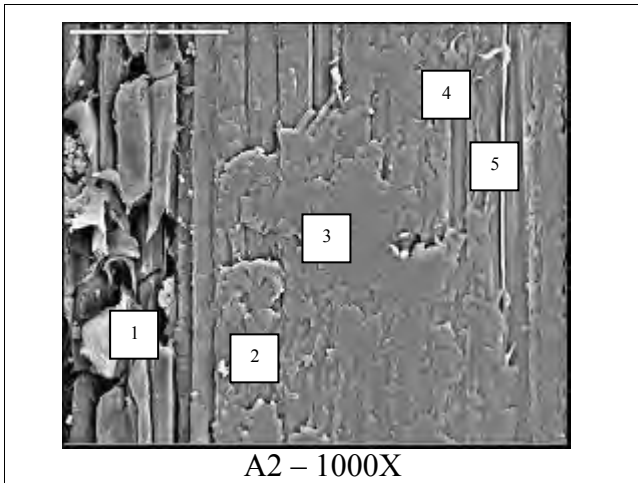


Figure 8 – Sample #47. 24 h/24 h.



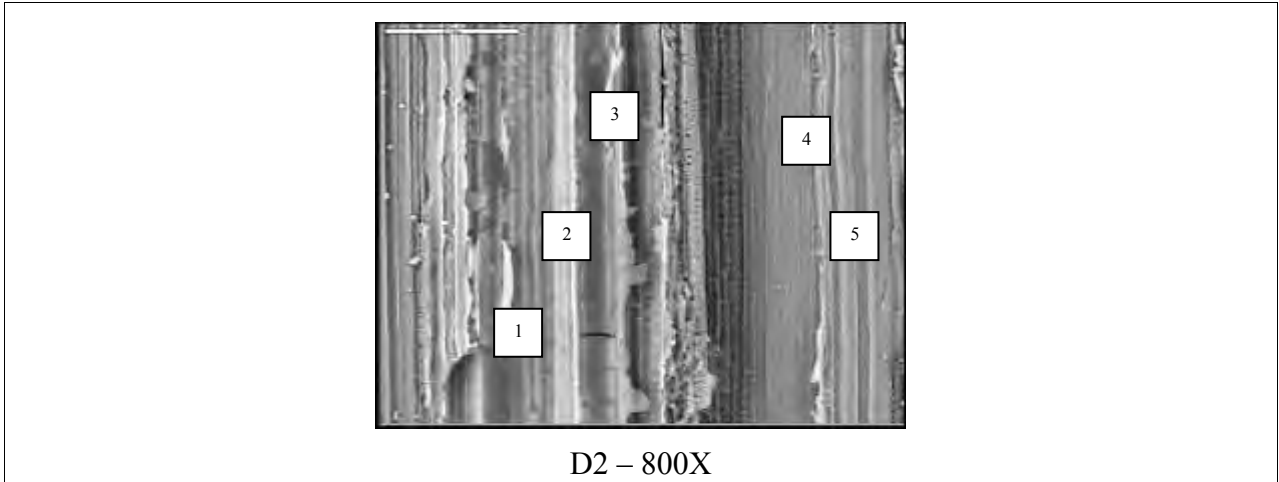


Figure 9 – Sample #57. 24 h/48 h.

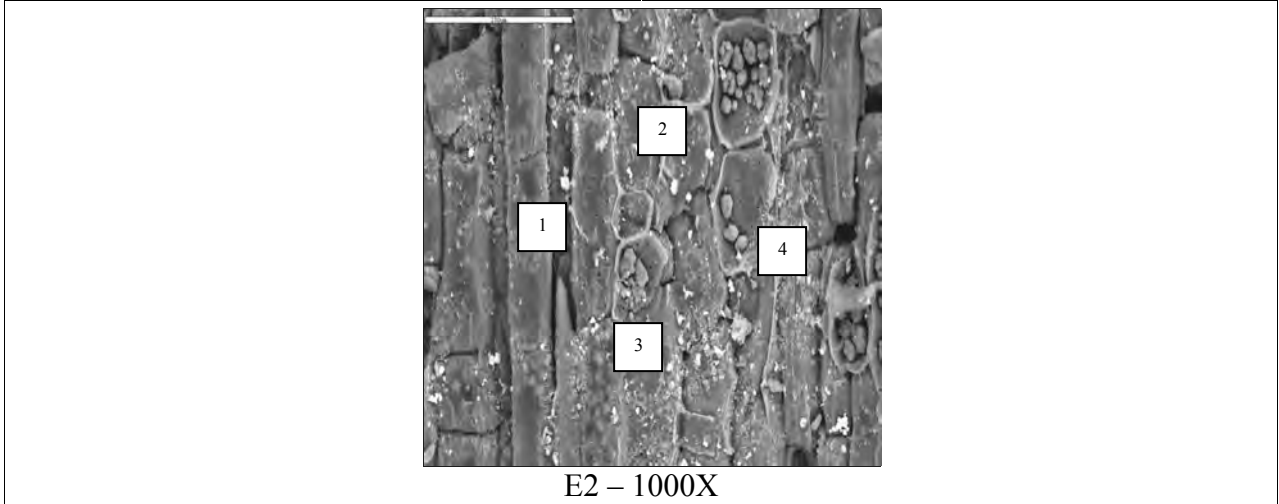
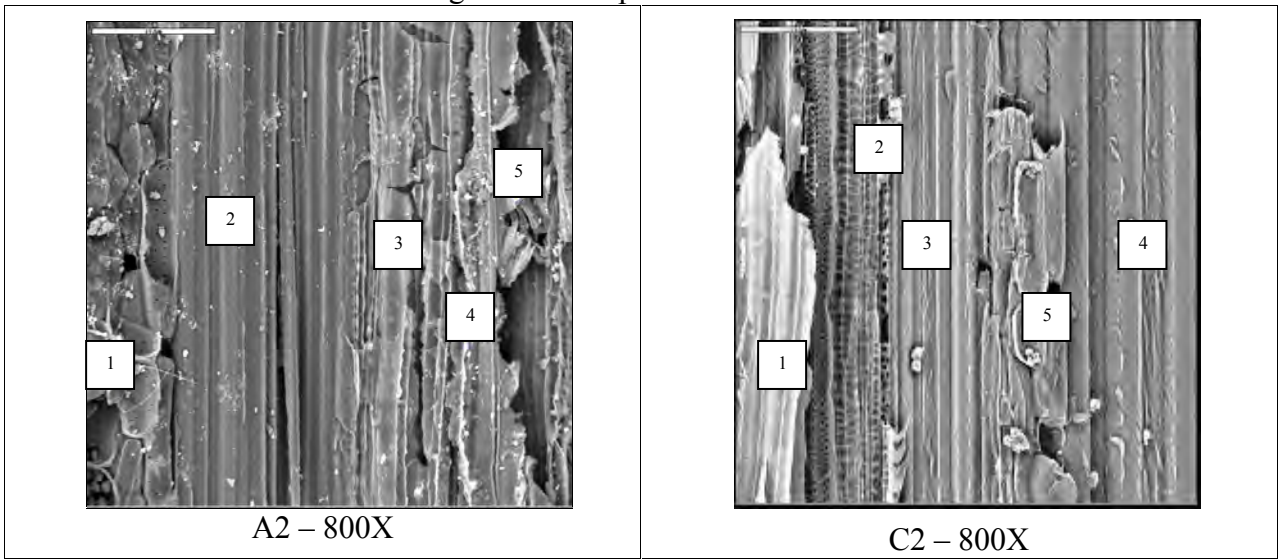


Figure 10 – Sample #13. 0 h/24 h. Culm middle region.

CONCLUSIONS

Chemical elements traceability evaluated by SEM with respect of oxides contents showed a non homogeneous distribution along the samples. In the majority of the samples, oxides were scarcely detected on bamboo. Chemicals products contents analysis was not conclusive with respect to the effect of the duration treatment or the interval after bamboo telling. It can be concluded that parenchyma cells were not protected against decay.

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ANNEX – Oxides detected by SEM on bamboo.

3	A2				B2				C2				D2			
Point	P1	P2	P3	P1	P2	P3	P4	P5	P1	P2	P3	P4	P1	P2	P3	P4
CO2	81.50	98.69	98.12	94.61	96.87	97.66	95.10	95.83	96.85	93.97	96.69	92.60	96.88	98.49	93.63	97.89
MgO	-	-	-	-	0.12	-	0.11	0.13	-	-	-	-	0.07	-	-	-
SO3	6.61	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SiO2	-	-	-	-	0.78	0.11	2.44	0.54	-	-	-	-	-	-	-	-
K2O	10.31	-	0.91	0.52	0.47	0.16	0.43	0.45	0.98	2.76	0.68	2.77	0.84	0.63	1.99	0.49
FeO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CaO	0.26	-	-	-	-	-	0.78	1.07	-	-	-	-	-	-	-	-
Cr2O3	0.18	-	-	-	0.17	-	0.08	-	-	-	-	-	-	-	-	-
CuO	-	-	-	-	0.27	-	-	0.10	-	-	-	-	-	-	-	-
Au2O3	-	1.16	0.58	4.72	1.26	1.98	0.99	1.82	1.63	2.31	2.45	3.42	1.96	0.56	3.83	1.38

10	A3						C3						F2			
Point	P1	P2	P3	P4	P5	P6	P1	P2	P3	P4	P5	P1	P2	P3	P4	P6
CO2	70.39	92.33	77.04	50.69	82.65	94.24	93.58	96.30	97.16	98.04	98.58	94.80	91.33	94.30	91.52	93.02
MgO	-	-	-	-	-	-	-	0.07	0.05	0.05	-	-	0.29	0.34	0.43	0.17
SO3	0.83	-	-	1.68	0.76	0.30	-	-	-	-	-	-	-	-	-	1.39
SiO2	0.28	0.13	0.39	3.05	0.48	0.08	-	-	-	-	-	-	-	0.28	0.30	0.22
K2O	0.80	0.70	0.60	2.32	1.01	0.65	0.84	0.59	0.53	0.59	0.40	1.43	2.19	2.43	2.92	1.59
FeO	1.51	-	0.54	9.47	1.37	-	-	-	-	-	-	-	-	-	-	-
CaO	0.15	-	6.37	0.25	0.07	-	-	-	-	-	-	-	0.25	0.30	0.30	0.41
Al2O3	0.13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr2O3	7.22	2.60	1.78	13.53	4.60	1.82	0.18	-	0.09	-	-	-	1.06	0.98	1.83	0.30
CuO	16.73	1.19	1.28	13.41	3.99	0.56	-	-	-	-	-	-	0.64	0.61	1.61	0.18
Na2O	-	-	-	-	-	-	-	-	-	-	-	-	0.13	0.22	0.29	-
Au2O3	1.84	2.92	2.34	5.30	4.94	2.23	5.18	2.88	2.01	1.12	0.85	2.84	3.82	0.19	0.44	2.43

21				A3					C2				E2					F2		
Point	P1	P2	P3	P4	P5	P6	P1	P2	P3	P4	P5	P2	P3	P4	P6	P1	P2	P3	P4	P5
CO2	93.83	92.82	93.36	95.12	97.92	97.79	96.97	93.43	93.31	95.44	96.07	94.28	90.35	75.38	92.99	97.86	93.20		97.73	94.8
MgO	0.06	0.07	-	-	-	-	-	0.12	-	-	0.06	-	-	-	-	-	0.08	-	-	-
SiO2	0.22	0.23	0.12	0.11	0.05	0.04	-	0.14	0.13	-		0.11	0.25	0.23	-	-	0.12	-	-	-
K2O	1.21	1.66	1.38	1.00	0.43	0.25	0.81	1.18	1.33	0.82	0.68	-	0.93	0.67	0.64	0.28	1.45		0.59	1.93
FeO	0.41	0.15	0.07	0.18	-	0.07	-	-	-	-	-	-	0.17	0.41	-	-	-	-	-	-
CaO	0.04	0.06	0.05	0.08	-	-	-	0.09	-	-	0.06	-	-	-	-	-	0.32	-	-	-
Al2O3	-	-	-	-	-	-			-	-	-	-	0.19	-	-	-	-	-	-	-
Cr2O3	0.88	1.15	0.97	0.93	0.21	0.13	0.16	0.12	-	-	-	0.34	0.48	8.58	0.36	-	0.36	-	-	-
CuO	0.91	1.14	0.91	0.86	0.19	-	-	-	-	-	-	0.28	0.47	10.46	0.40	-	-	-	-	-
Na2O	0.14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Au2O3	2.13	2.43	2.91	1.44	0.93	1.59	1.56	4.63	4.99	3.54	2.94	4.37	6.93	4.02	5.40	1.74	4.21		1.48	2.48

29			A2						C2				D2				E2			
Point	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P1	P2	P3	P4	P5		
CO2	96.22	90.86	87.87	88.07	96.58	97.48	95.74	86.75	98.24	97.01	93.01	90.91	86.07	72.72	68.04	97.21	97.02	89.36		
MgO	-	-	-	0.06	-	0.13	0.06	0.29	-	-	0.10	0.11	0.19	-	-	-	-	-		
SiO2	0.11	-	2.10	-	-	0.06	0.05	-	0.08	-	0.07	0.07	0.26	0.51	0.34	0.06	0.05	0.26		
K2O	0.74	2.29	0.25	0.33	0.28	0.69	0.52	2.76	0.24	0.39	0.91	0.99	1.51	0.82	0.33	0.31	0.22	0.43		
FeO	-	-	3.37	3.22	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
CaO	-	-	-	0.30	-	0.15	0.08	0.49	-	-	0.12	0.11	0.56	0.09	-	-	-	-		
Al2O3	-	-	3.09	2.22	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Cr2O3	0.72	1.66	0.46	0.22	0.15	0.72	0.33	2.51	0.07	0.13	1.12	1.15	2.71	7.59	6.59	0.73	0.87	3.86		
CuO	0.42	0.45	0.52	0.20	-	0.25	0.12	0.61	-	-	0.37	0.39	1.58	14.12	20.15	0.88	1.23	4.24		
Na2O	-	0.29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
TiO2	-	-	0.29	0.18	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
ZnO	-	-	-	0.74	-	-	-	-	-	-	0.50	0.47	0.32	0.51	1.69	-	-	-		
Au2O3	1.60	4.21	1.96	2.17	2.76	3.09	2.95	5.64	1.20	2.21	3.68	5.67	6.61	3.21	2.41	0.54	0.41	1.38		

47			A2			C1						D2				F2			
Point	P1	P2	P3	P4	P2	P3	P4	P5	P1	P2	P3	P4	P1	P2	P3	P4	P5		
CO2	59.93	56.02	96.77	68.44	91.48	90.89	97.94	95.34	90.14	76.86	95.42	98.04	97.79	97.52	97.31	97.94	97.53		
MgO	-	-	0.10	-	-	-	-	-	0.10	0.12	0.06	0.09	-	-	-	-	-		
SO3	-	-	-	-	-	0.54	-	-	-	8.57	-	-	-	-	-	-	-		
SiO2	0.38	0.25	0.09	0.20	0.71	0.55	-	0.37	0.79	0.28	0.12	0.08	0.08	0.19	0.13	0.07	0.08		
K2O	0.90	0.72	1.67	0.29	2.39	4.04	0.37	1.27	1.02	5.64	1.30	0.83	0.27	0.34	0.38	0.27	0.27		
FeO	36.32	39.95	0.16	29.74	-	-	0.05	-	0.42	-	-	0.08	-	0.10	0.18	0.06	0.05		
CaO	-	0.10	0.10	-	-	-	-	0.05	0.27	4.28	0.06	-	-	-	-	-	-		
Al2O3	-	-	-	-	-	-	-	-	0.69	-	-	-	0.04	0.08	-	-	-		
Cr2O3	0.15	0.15	0.19	0.11	0.89	1.29	0.03	0.43	1.38	0.74	0.13	0.13	0.45	0.82	0.53	0.32	0.31		
CuO	-	-	-	-	0.68	0.86	-	0.23	0.89	0.38	-	-	0.12	0.19	0.38	0.17	0.16		
Na2O	-	-	-	-	-	-	-	-	0.54	-	-	-	-	-	-	-	-		
MnO	-	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
ZnO	-	-	-	-	0.26	-	-	-	-	-	-	-	-	-	-	-	-		
Au2O3	1.75	2.03	0.43	1.00	2.82	0.89	1.36	1.90	3.33	2.69	2.53	0.54	1.10	0.57	0.91	1.04	1.51		

57			A2					B2					D2		
Point	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5
CO2	96.77	96.55	98.36	97.62	97.05	93.76	95.75	94.79	94.29	92.14	93.18	91.51	93.69	95.19	97.37
MgO	0.07	-	-	-	-	0.12	0.29	-	0.12	0.13	0.17	0.27	0.20	0.11	-
SiO2	0.04	-	-	-	-	1.17	-	0.05	-	2.61	0.28	0.30	0.44	-	-
K2O	0.34	0.29	0.50	0.48	0.40	0.89	0.66	0.57	0.74	0.94	1.42	1.96	1.86	0.51	0.32
FeO	-	-	-	-	-	-	-	-	0.09	-	-	-	-	-	-
CaO	-	-	-	-	-	0.17	0.20	0.04	0.07	0.14	-	0.22	0.18	0.06	-
Al2O3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr2O3	-	-	-	-	-	0.23	0.19	-	-	0.26	0.71	2.13	1.03	0.52	0.15
CuO	-	-	-	-	-	-	-	-	-	-	0.22	0.57	0.41	0.19	-
Na2O	0.09	0.08	0.08	0.08	0.07	-	-	0.11	0.09	-	-	-	-	-	-
Au2O3	2.56	2.84	0.80	1.59	2.27	3.44	2.67	4.14	4.24	3.55	3.72	2.74	1.87	3.32	1.97

13			A2					C2					E2	
Point	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4
CO2	94.89	98.00	-	86.78	90.98	96.28	96.16	97.54	98.05	94.45	97.63	95.36	89.79	86.55
MgO	-	-	-	0.23	0.10	-	-	-	-	-	0.02	0.05	-	0.11
SiO2	0.10	-	-	5.49	1.42	0.08	0.06	-	-	-	0.10	0.65	0.15	-
K2O	0.97	0.63	-	1.45	1.96	1.09	0.68	0.44	0.39	1.83	0.66	0.57	2.12	1.98
FeO	0.25	-	-	1.59	0.52	-	-	-	-	-	0.09	0.97	-	3.72
CaO	0.05	-	-	0.03	0.15	0.12	0.07	0.03	-	-	0.02	0.07	0.18	0.23
Al2O3	-	-	-	2.04	0.20	-	-	-	-	-	-	0.06	-	-
Cr2O3	0.45	0.26	-	0.98	1.14	0.12	0.10	-	-	-	0.26	0.55	1.65	2.25
CuO	0.51	0.15	-	0.54	0.91	-	-	-	-	-	0.17	0.54	0.99	1.93
Na2O	-	-	-	-	-	0.10	-	-	-	-	-	-	-	-
P2O5	-	-	-	-	-	-	-	-	-	-	-	-	-	1.83
Au2O3	2.68	0.56	-	0.69	2.23	2.08	2.84	1.88	1.46	3.21	0.78	1.05	4.53	0.80