

Supporting Information:

Metal Reactivity in Laboratory Burned Wood from a Watershed Affected by Wildfires

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Additional Materials and Methods.

Wood Sampling Methods. Wood samples of Ponderosa Pine, Quaking Aspen and Colorado Blue Spruce were collected from the Valles Caldera National Preserve area in New Mexico. We collected tree branches with attached twigs, leaves and needles from unburned live trees. The collected tree branches were crushed to powders using a laboratory milling machine and then oven dried for at 60°C for 48 hours before burning.

Water and Soil Sampling Methods. Surface water samples were collected as grab samples in 125 mL polypropylene bottles after three rinses. Samples for dissolved analysis were filtered through a 0.45 μm filter. Samples for metals' analysis were acidified to a pH of 2 with nitric acid. Soil samples were collected using a soil auger down to 6 inches and homogenized prior to preparation for analysis.

Solid Phase Analyses. Elemental composition and the oxidation states in the near surface (5-10 nm) were acquired using a Kratos Axis DLD Ultra X-ray photoelectron spectrometer. A monochromatic Al K α source was used, operating at 225W with no charge compensation. The Cu 2p spectra from reference Cu samples were used to identify the species of Cu present on the near surface region of the reacted ash sample. Reference Cu samples (Cu metal, Cu(I, II) oxide and Copper(II) carbonate basic) were purchased from Sigma Aldrich, Strem Chemicals and Alfa Aesar respectively. All the chemicals were >99% pure except the Copper(II) carbonate basic ($\geq 95\%$ purity). The high-resolution spectra, along with the binding energies obtained for the Cu 2p regions for these reference materials are shown in Figure S10. Curve fitting and quantification were performed using CasaXPS software. Spectra of all the samples were calibrated using gold powder deposited on each sample with respect to the Au 4f peak position at 84 eV. Electron scattering background was removed using a Shirley background; curve fitting of spectra was

done using a 70% Gaussian/30% Lorentzian [GL (30)] line shape. Qualitative mapping of the ash samples was done using an electron probe microanalyzer (EPMA) using wavelength dispersive X-ray spectroscopy (WDS). A JEOL JXA-8200 Super-Probe was used, operating at 10 kV with a 10 μm probe diameter and 30 nA probe current.

Characterization of 60°C, 350°C and 550°C samples (BET, zeta potential and C, H, N, O analysis). The Brunauer-Emmett-Teller (BET) specific surface area for the 350°C and 550°C ash samples were measured using a Gemini 2360 V5 surface area analyzer. The zeta potential of the ash samples was determined using a Malvern Zetasizer Nano-ZS equipped with a He-Ne laser (633nm) and non-invasive backscatter optics (NIBS). N and C contents (wt %) for 60°C, 350°C and 550°C samples were measured using a Costech ECS 4010 Elemental Analyzer coupled to a Thermo Fisher Scientific Delta V Advantage mass spectrometer via a CONFLO IV interface. O and H contents (wt %) were measured using a Thermo Chemical Elemental Analyzer (TCEA) coupled to a Thermo Fisher Scientific Delta V Advantage. Wt % C, H, N and O values were calculated using the Elemental Spruce Powder Standard B2213.

Table S1. Mass of wood (e.g., pine spruce and aspen) samples for **(a)** oven drying and **(b)** burning procedure of wood samples.

a)

Sample Name	Mass before oven drying at 60°C for 48 hours (g)	Mass after oven drying at 60°C for 48 hours (g)	% mass lost (moisture content)	% mass remaining due to loss of moisture content
Pine	2164	1612	25.5	74.5
Spruce	3342	2762	17.4	82.6
Aspen	2802	2173	22.4	77.6

b)

Sample Name	Mass before burning at 550°C for 4 hours (g)	Mass after burning at 550°C for 4 hours (g)	% mass remaining after burning	Mass before burning at 350°C for 4 hours (g)	Mass after burning at 350°C for 4 hours (g)	% mass remaining after burning
Pine	450.2	22.55	5.01	200.2	7.32	3.66
Spruce	450.4	17.16	3.81	200.2	6.96	3.48
Aspen	450.1	24.01	5.33	200.2	10.94	5.47

Table S2. Detection limits for analyses using: **a)** inductively coupled plasma optical emission spectrometry (ICP-OES), and **b)** inductively coupled plasma mass spectrometry (ICP-MS).

a) ICP-OES

Element	IDL (mg L ⁻¹)	MDL (mg L ⁻¹)
Al	0.0280	0.0280
Ca	0.0100	0.0100
Cu	0.0054	0.0054
Fe	0.0062	0.0062
Mg	0.0030	0.0030
Mn	0.0014	0.0014
Ni	0.0150	0.0150
Pb	0.0420	0.0420
V	0.0064	0.0064
Zn	0.0018	0.0018

b) ICP-MS

Element	IDL (mg L ⁻¹)	MDL (mg L ⁻¹)
Cu	0.004	0.009
Ni	0.006	0.02
Pb	0.0003	0.0004
V	0.006	0.01
Zn	0.04	0.1

**IDL = Instrument Detection Limit

**MDL = Method Detection Limit

Table S3. Maximum Contaminant Level (MCL) and different standards for exposure limits set by USEPA for Cr, Cu, Fe, Mn and Zn. Additionally, average concentrations of these 5 metals in natural soils (without known anthropogenic additions) are also provided for comparison with soil samples collected along the East Fork Jemez river ranges for this study.

Element	Drinking water standard- Maximum Contaminant Level (MCL) ($\mu\text{g L}^{-1}$) ²	Drinking water action level ($\mu\text{g L}^{-1}$) ³	Drinking water secondary standard ($\mu\text{g L}^{-1}$) ¹	Surface water human health for the consumption of water + organism ($\mu\text{g L}^{-1}$) ³	Aquatic Life Freshwater CMC Acute Exposure ($\mu\text{g L}^{-1}$)	Aquatic Life Freshwater CCC Chronic Exposure ($\mu\text{g L}^{-1}$)	Average concentrations of metals in non-anthropogenically affected soils in the US (mg kg^{-1}) by Burt et al. ⁵
Chromium (III)					570	74	
Chromium (total)	100						88.7
Chromium (VI)					16	11	
Copper (Cu)		1300		1300	2 ⁴	1.3 ⁴	24.7
Iron (Fe)			300			1000	19000
Manganese (Mn)			50	50			62.6
Zinc (Zn)			5000	7400	120	120	589

References

- (1) USEPA, Secondary Drinking Water Standards: Guidance for Nuisance Chemicals, accessed on Dec 22, 2017 at <https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals>
- (2) USEPA, National Primary Drinking Water Regulations, accessed on Dec 22, 2017 at <https://www.epa.gov/ground-water-and-drinking-water/table-regulated-drinking-water-contaminants>
- (3) USEPA, National Recommended Water Quality Criteria - Human Health Criteria Table, accessed on Dec 22, 2017 at <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-human-health-criteria-table>
- (4) USEPA, Fact Sheet: Draft Estuarine/Marine Copper Aquatic Life Ambient Water Quality Criteria, accessed on Dec 22, 2017 at <https://www.epa.gov/sites/production/files/2016-08/documents/copper-estuarine-marine-draft-factsheet.pdf>
- (5) Burt, R.; Wilson, M.; Mays, M.; Lee, C., Major and trace elements of selected pedons in the USA. J. Environ. Qual. 2003, 32, (6), 2109-2121.

Table S4. Acid extractable elemental content (mg kg⁻¹) for wood samples (Pine, Spruce, Aspen) at 60 °C, 350 °C and 550 °C. Data are presented as Mean $\pm$ standard deviation.

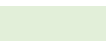
Acid Extractable Elemental Content (mg kg ⁻¹)												
Temperature: 550 °C												
Sample	Al	Ca	Cr	Cu	Fe	K	Mg	Mn	Ni	Si	Sr	Zn
Pine	4138.40	181967.73	476.16	2765.07	5050.52	78075.67	27881.15	1575.62	803.60	814.26	505.93	938.27
	$\pm$ 100.17	$\pm$ 6195.55	$\pm$ 9.12	$\pm$ 302.26	$\pm$ 767.95	$\pm$ 1781.05	$\pm$ 35.82	$\pm$ 14.15	$\pm$ 22.81	$\pm$ 93.11	$\pm$ 1.75	$\pm$ 4.94
Spruce	4734.25	164204.50	81.50	71.88	4154.38	33847.64	9807.35	3933.69	242.56	334.93	551.96	590.30
	$\pm$ 64.55	$\pm$ 3723.07	$\pm$ 1.07	$\pm$ 1.59	$\pm$ 40.74	$\pm$ 628.85	$\pm$ 106.4	$\pm$ 41.92	$\pm$ 2.91	$\pm$ 29.36	$\pm$ 6.25	$\pm$ 7.67
Aspen	177.41	307080.02	12.91	72.42	238.57	47800.02	14193.24	175.14	277.82	289.68	1372.46	1209.62
	$\pm$ 3.19	$\pm$ 4896.33	$\pm$ 2.01	$\pm$ 1.62	$\pm$ 14.5	$\pm$ 728.85	$\pm$ 129.61	$\pm$ 0.74	$\pm$ 1.64	$\pm$ 1.58	$\pm$ 15.07	$\pm$ 12.29
Temperature: 350 °C												
Pine	2384.54	122157.57	543.31	4996.51	4151.65	55823.72	19205.62	1179.05	524.65	310.14	332.28	638.32
	$\pm$ 96.48	$\pm$ 4502.43	$\pm$ 123.69	$\pm$ 261.96	$\pm$ 441.79	$\pm$ 2122.64	$\pm$ 747.69	$\pm$ 61.36	$\pm$ 101.22	$\pm$ 18.17	$\pm$ 12.89	$\pm$ 23.33
Spruce	4477.69	186287.82	112.24	81.47	3598.13	37261.72	6168.71	4760.57	266.93	322.53	646.79	799.14
	$\pm$ 175.93	$\pm$ 5459.71	$\pm$ 3.06	$\pm$ 5.42	$\pm$ 908.11	$\pm$ 1050.50	$\pm$ 48.12	$\pm$ 315.24	$\pm$ 3.04	$\pm$ 23.09	$\pm$ 27.32	$\pm$ 36.21
Aspen	184.81	294197.49	11.83	62.89	225.13	45153.30	13275.79	182.36	264.34	241.02	1390.40	1206.46
	$\pm$ 1.67	$\pm$ 1343.51	$\pm$ 0.13	$\pm$ 0.60	$\pm$ 4.72	$\pm$ 242.64	$\pm$ 73.52	$\pm$ 1.08	$\pm$ 3.52	$\pm$ 5.76	$\pm$ 3.89	$\pm$ 8.47
Temperature: 60 °C												
Pine	91.1	9364.2	4.97	58.2	114.7	8696.5	466.3	59.6	6.1	202.8	13.1	23.3
	$\pm$ 3.05	$\pm$ 220.03	$\pm$ 1.29	$\pm$ 18.24	$\pm$ 45.69	$\pm$ 35.69	$\pm$ 8.47	$\pm$ 2.81	$\pm$ 0.25	$\pm$ 11.56	$\pm$ 0.61	$\pm$ 1.81
Spruce	131.5	11294.7	12.9	4.6	198.9	8628.5	419.1	185.1	12.5	258.8	24.3	33.2
	$\pm$ 3.32	$\pm$ 248.46	$\pm$ 0.46	$\pm$ 0.31	$\pm$ 7.93	$\pm$ 28.68	$\pm$ 15.13	$\pm$ 6.5	$\pm$ 0.9	$\pm$ 1.67	$\pm$ 0.61	$\pm$ 0.4
Aspen	22.2	22359.3	5.1	5.7	22.4	9709.04	858.5	10.6	17.9	23.7	86.8	78.6
	$\pm$ 1.15	$\pm$ 565.51	$\pm$ 0.03	$\pm$ 0.88	$\pm$ 8.53	$\pm$ 25.86	$\pm$ 4.22	$\pm$ 0.15	$\pm$ 0.82	$\pm$ 3.9	$\pm$ 0.35	$\pm$ 1.49

Table S5. The Kruskal Wallis test was used to determine if significant differences exist (defined as p -value < 0.05) between the tree species (Pine, Spruce, Aspen) at three temperatures (60°C, 350°C and 550°C) with respect to acid extractable metal concentrations ($\log_{10}$ transformed). Individual contribution of the metals was not considered here due to limited number of observations ($n=3$) for each metal. No significant difference (highlighted, p -value = 0.4007 > 0.05) was observed for Pine, Aspen and Spruce at 60°C. The limitation of Kruskal Wallis test is that it does not specify which specific sample is contributing to the overall difference. To address this, Mann Whitney U test was done to do pairwise comparisons between the samples.

<u>Comparison between Pine, Spruce and Aspen at 60°C, 350°C and 550°C (n=9)</u>		
<u>Data</u>	<u>χ^2 statistic</u>	<u>p-value</u>
acid extractable element concentrations ($\log_{10}$ transformed)	89.85	4.982×10^{-4}
<u>Comparison between Pine 60, Spruce 60 and Aspen 60 (n=3)</u>		
<u>Data</u>	<u>χ^2 statistic</u>	<u>p-value</u>
acid extractable element concentrations ($\log_{10}$ transformed)	1.8293	0.4007
<u>Comparison between Pine 350, Spruce 350 and Aspen 350 (n=3)</u>		
<u>Data</u>	<u>χ^2 statistic</u>	<u>p-value</u>
acid extractable element concentrations ($\log_{10}$ transformed)	8.1227	0.01723
<u>Comparison between Pine 550, Spruce 550 and Aspen 550 (n=3)</u>		
<u>Data</u>	<u>χ^2 statistic</u>	<u>p-value</u>
acid extractable element concentrations ($\log_{10}$ transformed)	9.5225	0.00855

Table S6. The Wilcoxon rank sum test (Mann-Whitney U test) was used to do pairwise comparisons (n= 9 samples, ${}^9C_2 = 36$ combinations of pairs) of tree species (Pine, Spruce, Aspen) at 60°C, 350°C and 550°C to test for significant differences (defined as $p < 0.05$) in metal concentrations ($\log_{10}$ transformed). Individual contribution of the metals was not considered here due to limited number of observations (n=3) for each metal.

Serial No.	Pair considered	Diff.	W	p-value	Serial No.	Pair considered	Diff.	W	p-value
1	Aspen 350 – Aspen 60	1.078	990	1.20×10^{-4}	19	Pine 60 – Aspen 60	0.164	726	0.383
2	Aspen 550 – Aspen 60	1.108	991	1.15×10^{-4}	20	Spruce 60 – Aspen 60	0.331	765	0.190
3	Spruce 550 – Aspen 60	1.407	1043	8.87×10^{-6}	21	Spruce 60 – Pine 60	0.642	690	0.103
4	Spruce 350 – Aspen 60	1.477	1053	5.22×10^{-6}	22	Aspen 550 – Aspen 350	0.021	672	0.793
5	Pine 350 – Aspen 60	1.678	1080	1.18×10^{-6}	23	Spruce 550 – Aspen 350	0.401	788	0.117
6	Pine 550 – Aspen 60	1.748	1101	3.47×10^{-7}	24	Spruce 350 – Aspen 350	0.462	798	0.092
7	Aspen 350 – Pine 60	0.761	960	3.38×10^{-4}	25	Pine 350 – Aspen 350	0.532	912	2.64×10^{-3}
8	Aspen 550 – Pine 60	0.780	967	2.43×10^{-4}	26	Pine 550 – Aspen 350	0.634	927	1.45×10^{-4}
9	Spruce 550 – Pine 60	1.261	1043	3.67×10^{-6}	27	Spruce 550 – Aspen 550	0.371	775	0.155
10	Spruce 350 – Pine 60	1.284	1042	3.91×10^{-6}	28	Spruce 350 – Aspen 550	0.434	783	0.130
11	Pine 350 – Pine 60	1.413	1110	3.06×10^{-8}	29	Pine 350 – Aspen 550	0.542	911	2.75×10^{-3}
12	Pine 550 – Pine 60	1.547	1133	4.36×10^{-9}	30	Pine 550 – Aspen 550	0.651	927	1.45×10^{-3}
13	Aspen 350 – Spruce 60	0.774	903	3.73×10^{-3}	31	Spruce 350 – Spruce 550	0.043	694	0.610
14	Aspen 550 – Spruce 60	0.777	910	2.86×10^{-3}	32	Pine 350 – Spruce 550	0.140	738	0.316
15	Spruce 550 – Spruce 60	1.238	1008	2.91×10^{-5}	33	Pine 550 – Spruce 550	0.324	783	0.130
16	Spruce 350 – Spruce 60	1.235	1008	2.91×10^{-5}	34	Pine 350 – Spruce 350	0.150	713	0.470
17	Pine 350 – Spruce 60	1.339	1114	2.21×10^{-8}	35	Pine 550 – Spruce 350	0.282	761	0.207
18	Pine 550 – Spruce 60	1.431	1134	3.99×10^{-9}	36	Pine 550 – Pine 350	0.150	738	0.316

 = $p\text{-value} < 0.05$ = Significant difference

 = $p\text{-value} > 0.05$ = No significant difference

Table S7. Specific surface areas (m²/g) of the Pine, Spruce and Aspen ash samples measured by Brunauer-Emmett-Teller (BET) method.

Sample	BET Multipoint Surface Area (m ² /g)
Pine Ash 350°C	36.91
Pine Ash 550°C	294.37
Spruce Ash 350°C	20.29
Spruce Ash 550°C	124.77
Aspen ash 350°C	7.06
Aspen ash 550°C	12.9

Table S8. Elemental composition (C, H, N, O) and ratios of Pine, Spruce and Aspen samples at 60°C, 350°C and 550°C. H/C is the atomic ratio of hydrogen to carbon; O/C is the atomic ratio of oxygen to carbon and (O+N)/C is the atomic ratio of the sum of nitrogen and oxygen to carbon.

Sample	Elemental composition				Molar H/C	Molar O/C	Molar (O+N)/C
	C (%)	H (%)	N (%)	O (%)			
Pine 60°C	52.1	6.91	0.5	37.7	1.589	0.542	0.549
Spruce 60°C	50.3	6.86	0.3	41.2	1.638	0.614	0.619
Aspen 60°C	51.1	6.87	0.4	39.4	1.615	0.578	0.585
Pine 350°C	31.8	1.10	2.4	26.9	0.414	0.634	0.699
Spruce 350°C	15.0	0.48	0.7	21.5	0.384	1.078	1.115
Aspen 350°C	14.0	0.42	0.3	28.6	0.361	1.537	1.555
Pine 550°C	16.3	0.57	0.4	21.8	0.421	0.998	1.018
Spruce 550°C	25.3	0.62	0.4	19.7	0.294	0.583	0.598
Aspen 550°C	6.1	0.26	0.4	27.1	0.513	3.326	3.379

Table S9. Atomic content for the unreacted and reacted 350 °C pine ash as determined by X-ray photoelectron spectroscopy (XPS) survey scan.

Sample	% Atomic Content		
	C 1s	O 1s	Cu 2p
Unreacted 350 °C pine ash	66.2	33.8	BDL ¹
Reacted 350 °C pine ash	73.2	26.7	0.11

¹*Below detection limit*

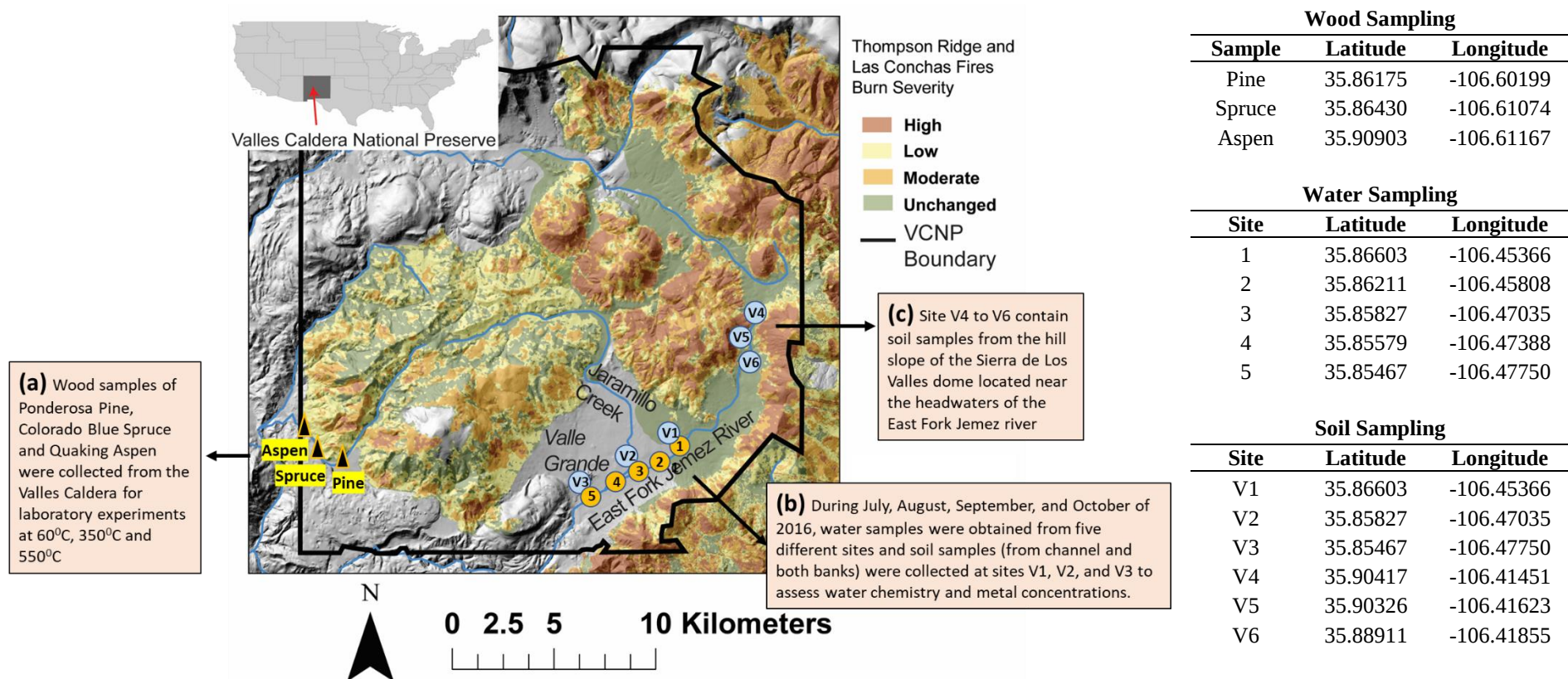


Figure S1. Map showing the sampling locations for (a) wood, (b) water and soil and (c) soil samples in Valles Caldera. The coordinates of the sampling locations are shown beside the map. This site map is adapted from the map published in a previous study by Cerrato et al.¹

Reference

- (1) Cerrato, J. M.; Blake, J. M.; Hirani, C.; Clark, A. L.; Ali, A.-M. S.; Artyushkova, K.; Peterson, E.; Bixby, R. J., Wildfires and water chemistry: effect of metals associated with wood ash. *Environ. Sci. Process. Impacts*. **2016**, *18*, (8), 1078-1089.

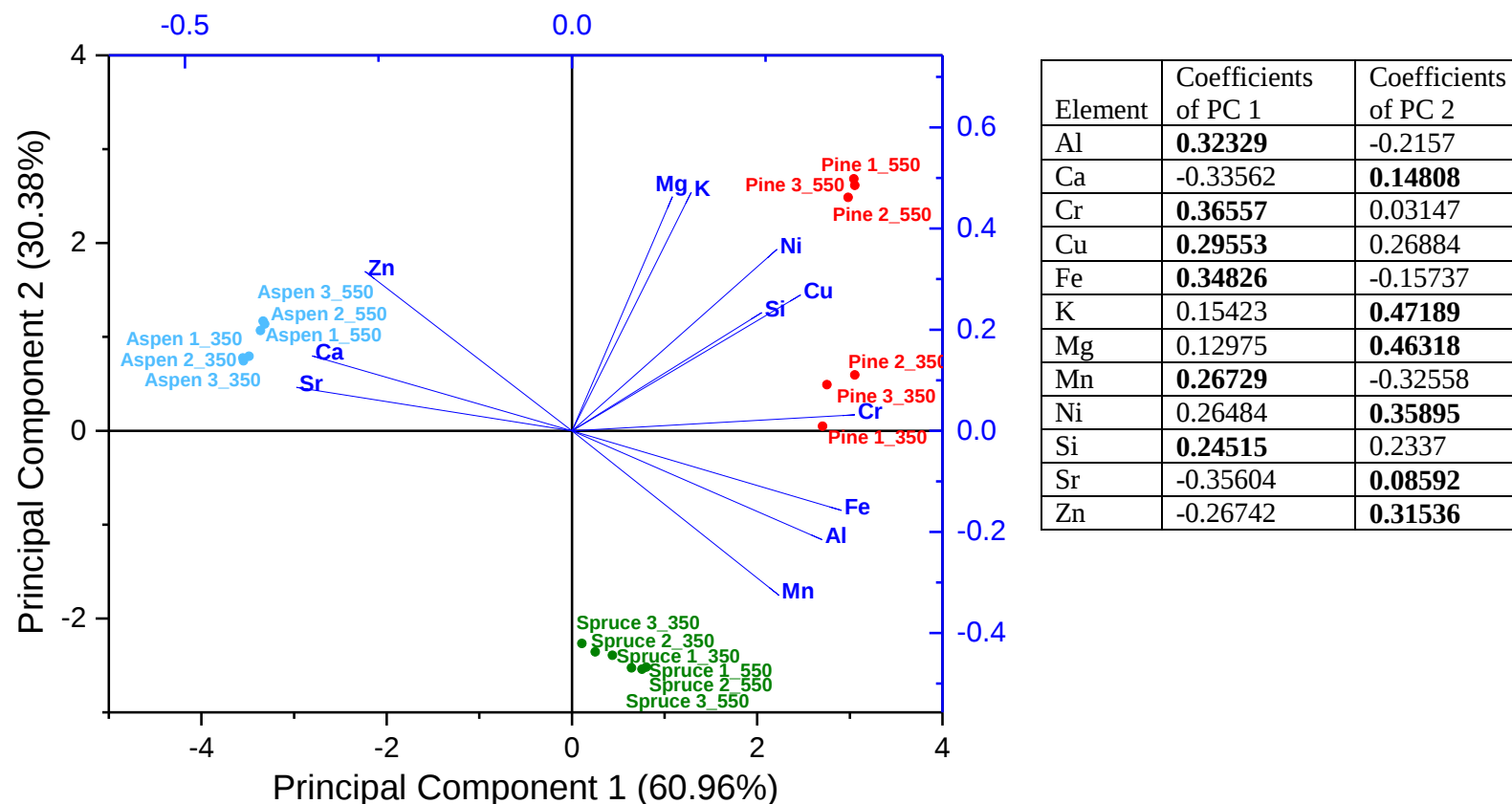


Figure S2. Principal component analysis was run on metal concentrations for 350 °C and 550 °C triplicate measurements of ash samples (Pine, Spruce, Aspen). The first two principal components explained 91.34% of the total variance. The metals such as Al, Cr, Cu, Fe, Mn and Si showed high positive loadings on PC 1; and PC 2 showed high positive loadings for the major elements (Ca, K, Mg) and metals such as Ni, Sr and Zn. Coefficients of the metals on the principal components are shown in the table. The figure also shows the component scores of the Pine, Spruce and Aspen ash samples. 350 °C and 550 °C Pine ash samples had positive scores on the both the principal components.

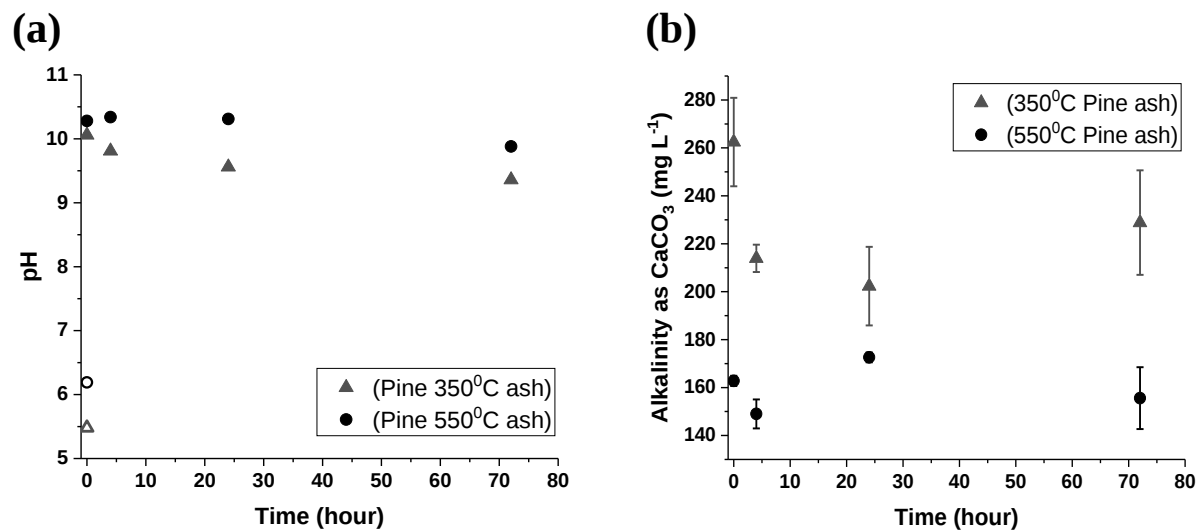
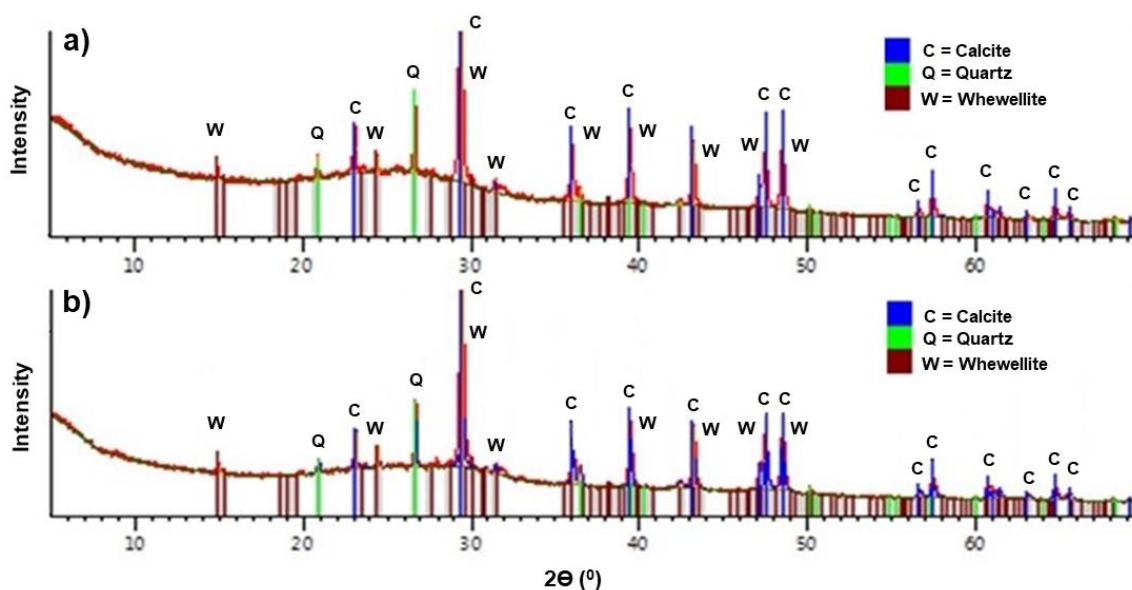


Figure S3. pH and alkalinity measured at 0, 4, 24 and 72 hours are shown in figure (a) and (b) respectively. In figure (a), the open symbols represent the pH of 18MΩ water.



Compound Name	Unreacted Ash (atomic wt.%)	Reacted Ash (atomic wt.%)
Calcite (CaCO_3)	79%	78%
Quartz (SiO_2)	12%	11%
Whewellite ($\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$)	9%	11%

Figure S4. XRD patterns of the (a) reacted and the (b) unreacted 350°C Pine ash sample from the batch sorption experiments with Cu(II). The two samples are very similar in terms of crystalline composition which is predominantly calcite (78-79 %) with lesser amounts of quartz (11-12 %) and whewellite (9-11 %).

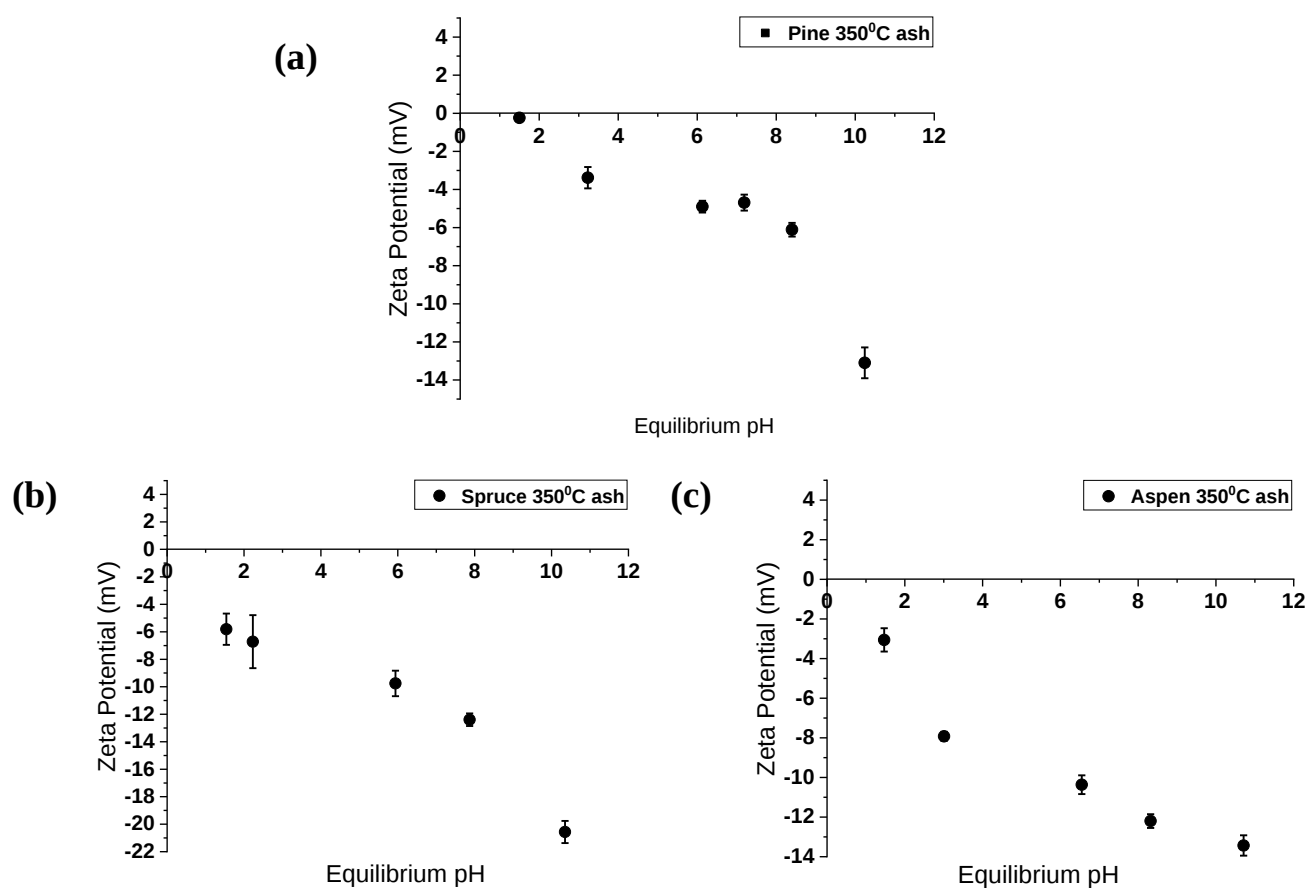


Figure S5. Zeta Potential (mV) measurements of **(a)** Pine 350°C ash, **(b)** Spruce 350°C ash and **(c)** Aspen 350°C ash in different solution pH values. The reported values are the average of three measurements.

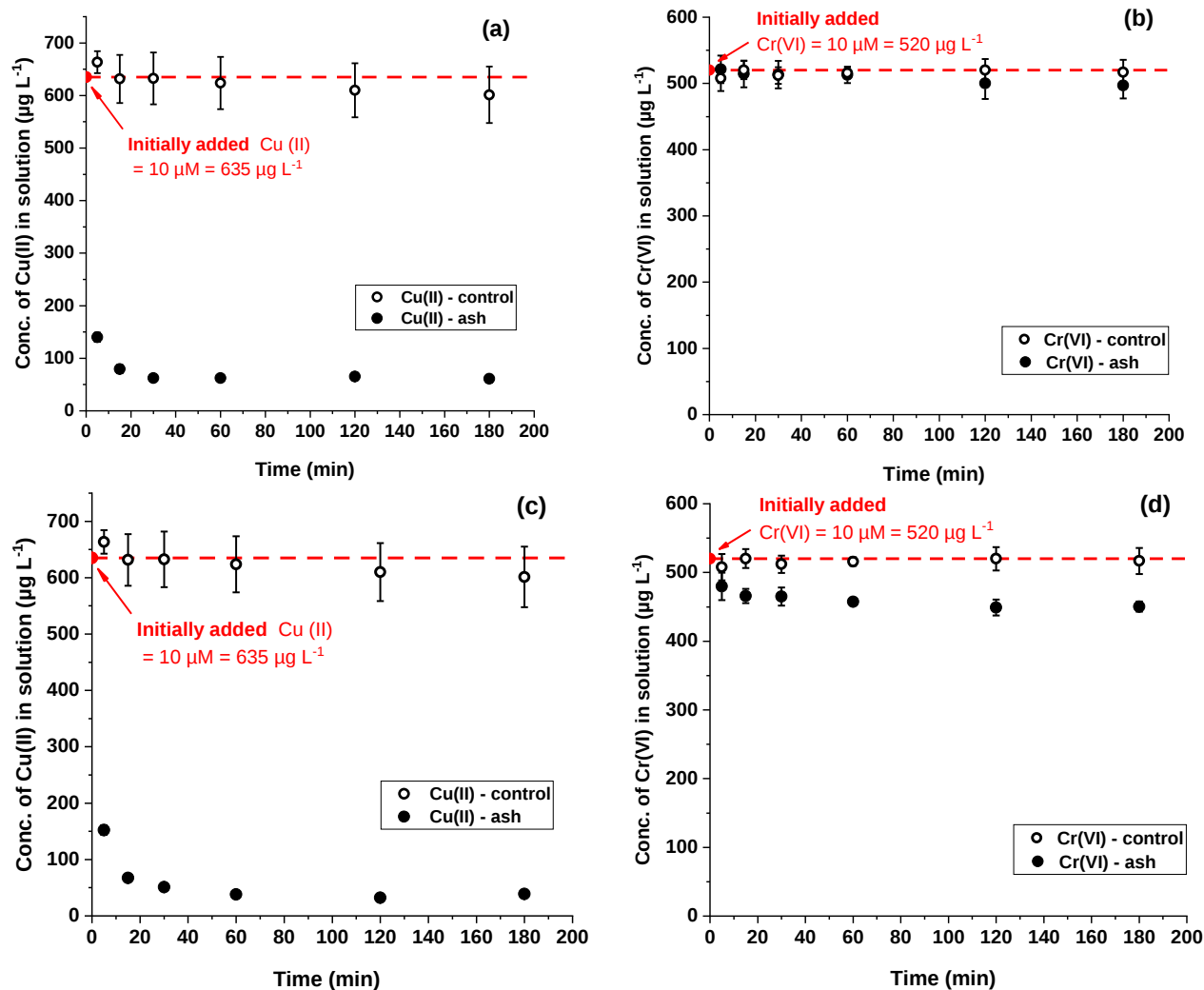
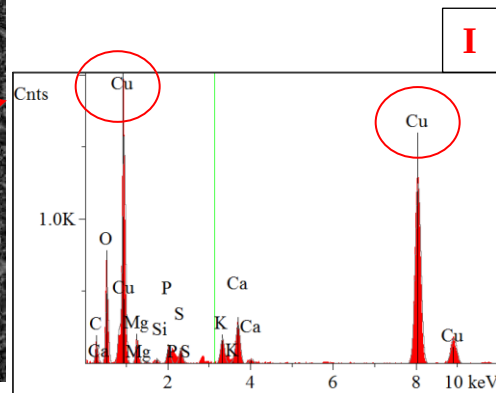
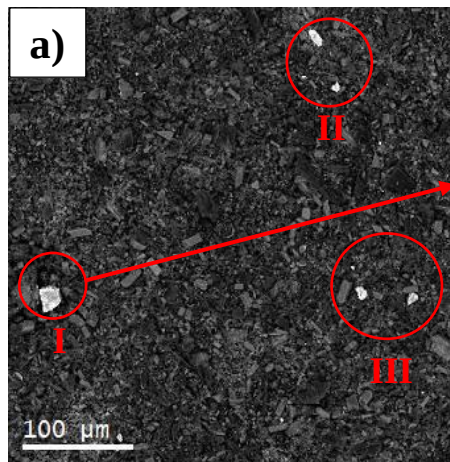


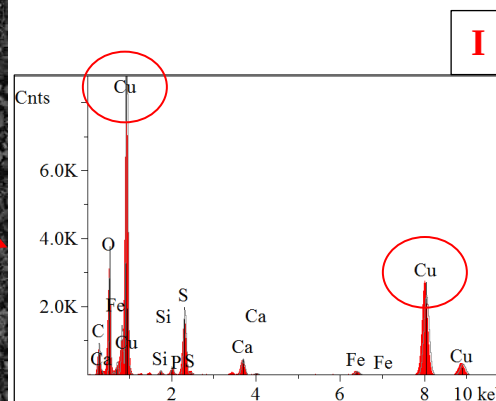
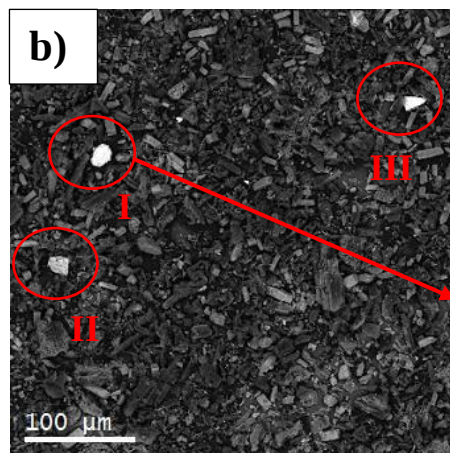
Figure S6. Results from the metal sorption experiments ($n=3$, sampling interval = 5 min, 15 min, 30 min, 1 hr, 2 hrs and 3hrs) conducted by reacting $10\ \mu\text{M}$ of **(a)** Cu(II) and **(b)** Cr(VI) separately in a solution containing 0.1g of 350°C Spruce ash with 50mL of $18\text{M}\Omega$ water. Figures **(c)** and **(d)** show the same analysis with Aspen ash. Results from the control experiments without the ash are included in all the figures.



kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 30.0

Elt.	Line	Intensity (c/s)	Conc	Units	Error 2σ*	MDL 3σ
C	Ka	36.11	7.161	wt.%	0.584	0.597
O	Ka	151.37	12.566	wt.%	0.399	0.217
Mg	Ka	53.62	2.914	wt.%	0.189	0.185
Al	Ka	4.88	0.212	wt.%	0.117	0.170
Si	Ka	10.29	0.359	wt.%	0.103	0.144
P	Ka	43.42	1.342	wt.%	0.117	0.139
S	Ka	36.71	0.984	wt.%	0.101	0.125
K	Ka	71.77	1.867	wt.%	0.115	0.125
Ca	Ka	114.96	3.089	wt.%	0.133	0.124
Cu	Ka	715.75	69.507	wt.%	0.973	0.332
Total			100.000	wt.%		

*2σ equals 95% confidence interval



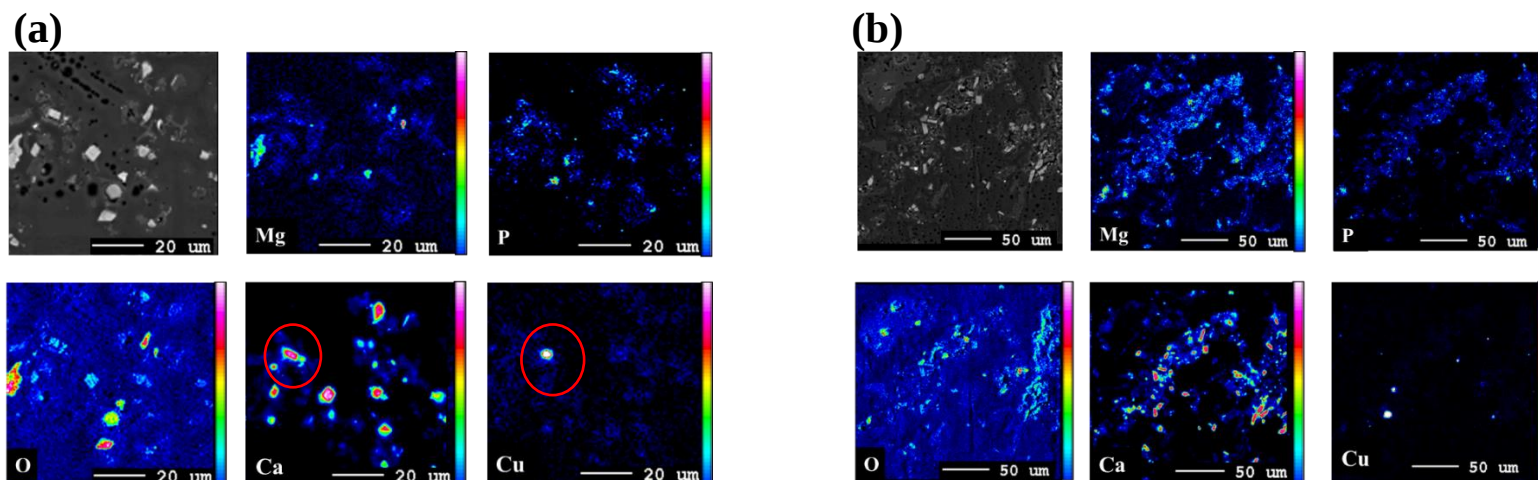
kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 30.0

Elt.	Line	Intensity (c/s)	Conc	Units	Error 2σ*	MDL 3σ
C	Ka	100.62	21.423	wt.%	0.662	0.415
O	Ka	349.71	1.326	wt.%	0.020	0.006
Si	Ka	19.73	0.588	wt.%	0.087	0.120
P	Ka	35.91	0.959	wt.%	0.084	0.108
S	Ka	324.25	7.659	wt.%	0.135	0.094
Ca	Ka	97.24	3.322	wt.%	0.132	0.140
Fe	Ka	29.62	1.173	wt.%	0.102	0.124
Cu	Ka	736.98	63.551	wt.%	0.680	0.238
Total			100.000	wt.%		

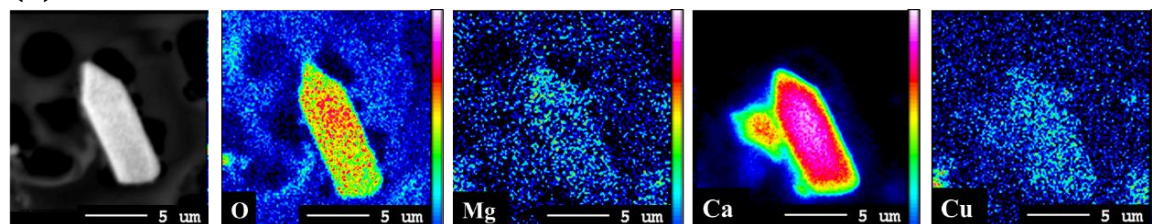
*2σ equals 95% confidence interval

Figure S7. SEM images of the (a) unreacted and the (b) reacted 350°C Pine ash from

the batch sorption experiments with Cu(II). EDS spectrum from a Cu grain on both the ash samples shows presence of Cu peaks. The atomic wt.% distribution for the respective spectrum is also shown for a specific Cu grain highlighted in red circle.



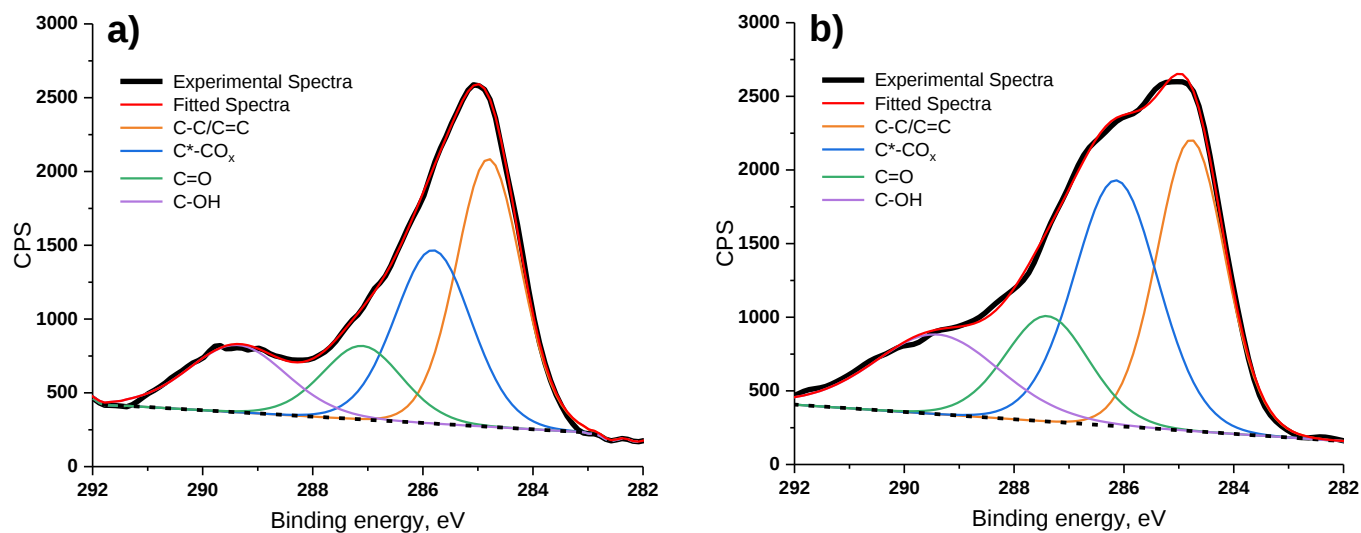
(c) Microprobe mapping of the mineralized Ca region [red circled in figure (a)] of the reacted ash



(d)	K (wt%)	Ca (wt%)	Mg (wt%)	Cu wt%	Si (wt%)	S (wt%)	P (wt%)	O (wt%)	C (wt%)	Total (wt%)
Average of 7 reference lines (Reacted sample)	0.033	16.957	0.018	0.012	0.006	0.007	0.097	46.430	14.825	78.384
Average of 7 reference lines (Unreacted sample)	0.137	17.557	0.014	BDL*	BDL	0.054	0.013	46.270	14.691	78.727

*BDL = Below detection limit at 95% confidence interval

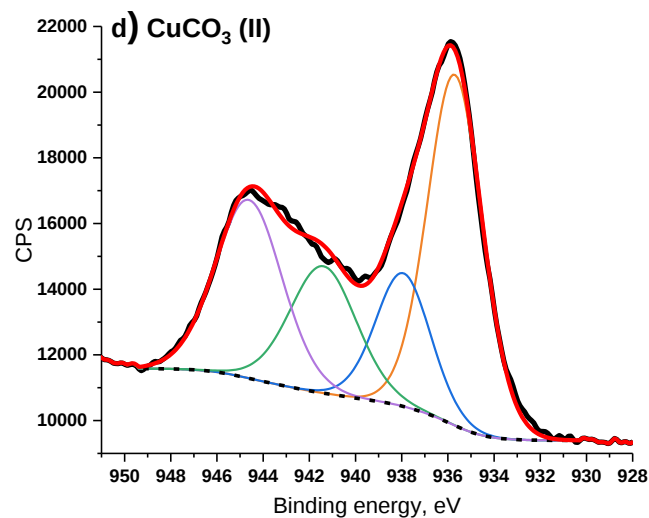
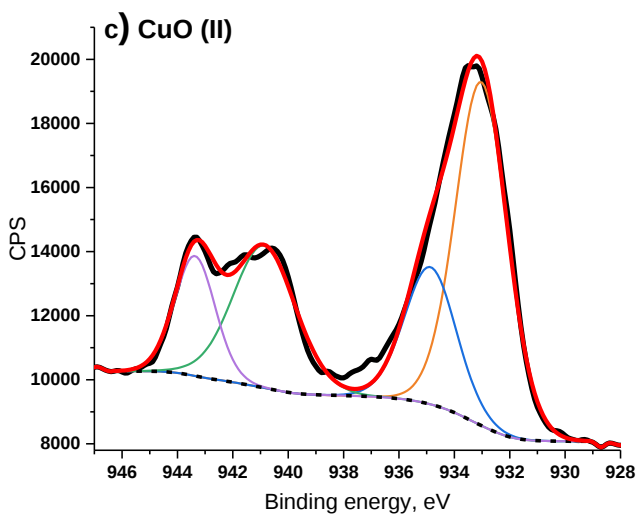
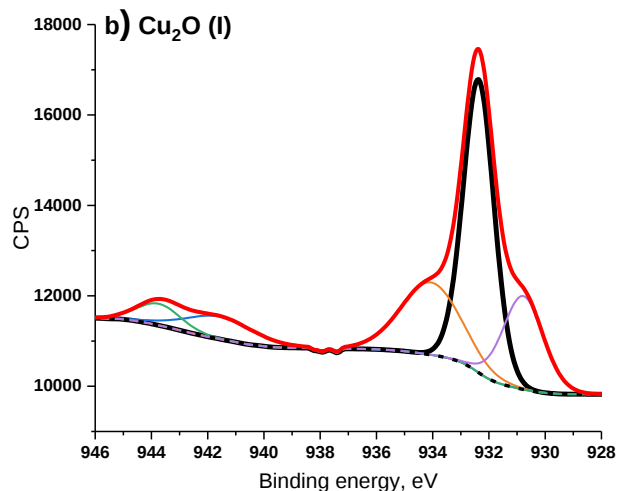
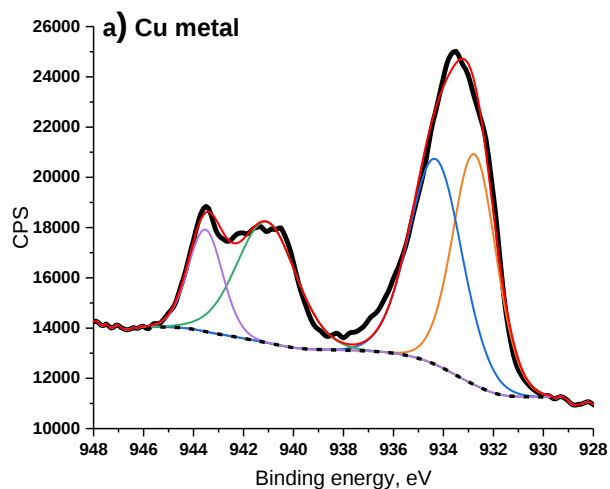
Figure S8. Microprobe mapping of Mg, P, O, Ca and Cu on the (a) reacted and (b) unreacted 350°C Pine ash. Microprobe analysis showed presence of low level of detectable Cu associated with mineralized Ca in the reacted ash, shown in figure (c). In table (d), the wt% of the elements associated with the mineralized Ca region is shown. At 95% confidence level, the Cu in the reacted sample is detectable at 0.012 wt% but below detection limit in the unreacted sample. Detection limit for Cu at 95% confidence level was 0.009 wt%.



c) Percentages of surface carbon bonds determined from curve fitting of C 1s high resolution XPS spectra

	C-C %	C*-CO _x %	C=O %	C-OH %
Binding energy, eV	285	285.6	287.5	289.5
Untreated ash	35.3	16.8	4.7	9.4
Reacted ash	25.3	24.2	11.9	11.8

Figure S9. XPS high resolution C 1s spectra for the **(a)** Unreacted 350°C Pine ash sample and **(b)** the reacted 350°C Pine ash sample. **(c)** Percent compositions of the C 1s spectra for the unreacted and the reacted ash.



(e) Binding energy values obtained for reference samples using XPS high resolution Cu 2p spectra

Reference Samples	Binding Energy (eV)
Cu metal	932.8
Cu ₂ O (I)	932.4
CuO (II)	934.9
CuCO ₃ (III)	935.7

Figure S10. XPS high-resolution Cu 2p spectra for **(a)** Cu metal, **(b)** Cu₂O (I), **(c)** CuO (II) and **(d)** CuCO₃ (II). **(e)** The binding energies obtained for the Cu 2p regions for these reference materials are shown.