

# NEXAFS Investigation of Al, Fe and Mn Oxide Catalysis of the Abiotic Polyphenol-Maillard Humification Pathway

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## Introduction

In the environment, humification is pivotal in transforming biomolecules originating from organized structures typical of organisms to randomly polymerized, heterogeneous humic substances characteristic of biogeochemical systems. Humic substances are formed through both biotic (enzymatic) and abiotic (mineral) catalytic mechanisms. Soil mineral colloids, in particular metal oxides,

can catalyze synthetic humification reactions, by acting as an electron acceptor and accelerating oxidative polymerization reactions. The Maillard reaction, involving condensation between sugars and amino acids, and the polyphenol polymerization pathway are regarded as important pathways in natural humification. The Maillard reaction and integrated abiotic polyphenol-Maillard humification pathways have only recently been studied using birnessite ( $\delta$ - $MnO_2$ ) as a catalyst [1, 2]. The influence of poorly ordered Al and Fe oxides on these humification pathways has not been investigated until now. Near edge X-ray absorption fine structure (NEXAFS) spectroscopy is an indispensable tool to study the speciation of C, N, O and metals in organo-mineral samples.

## Science

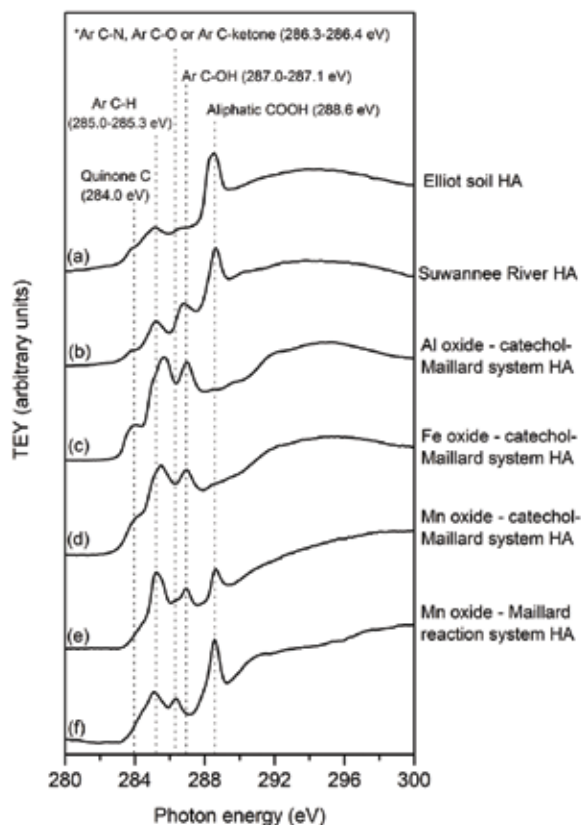
The objective of our study was to compare the catalytic effect of poorly-ordered Al, Fe and Mn oxides on the Maillard and integrated polyphenol-Maillard humification pathways. We employed C, N, O and Al *K*-edge, and Al, Fe and Mn *L*-edge NEXAFS spectroscopy to characterize the reaction products. We also compared natural humic acids (HA) with the HA extracted from our reaction systems.

A number of treatments containing Maillard reagents (0.05 mole glucose and 0.05 mole glycine) with or without polyphenol (0.05 mole catechol) in the presence of poorly-ordered Al, Fe or Mn oxides, and absence of mineral catalyst, were incubated under environmentally relevant conditions, i.e., pH 7.0 and 45° C. Sterile conditions were maintained throughout the incubation period. After 15 days, the solid residue was separated from the supernatant and the resultant humic acid (HA) fraction was isolated from the supernatant. The speciation of C, N, O, Al, Fe and Mn was investigated in the solid residues and/or HA fractions from selected reaction systems using C, N, O and Al *K*-edge and Al, Fe and Mn *L*-edge NEXAFS at the Canadian Light Source on the SGM and PGM

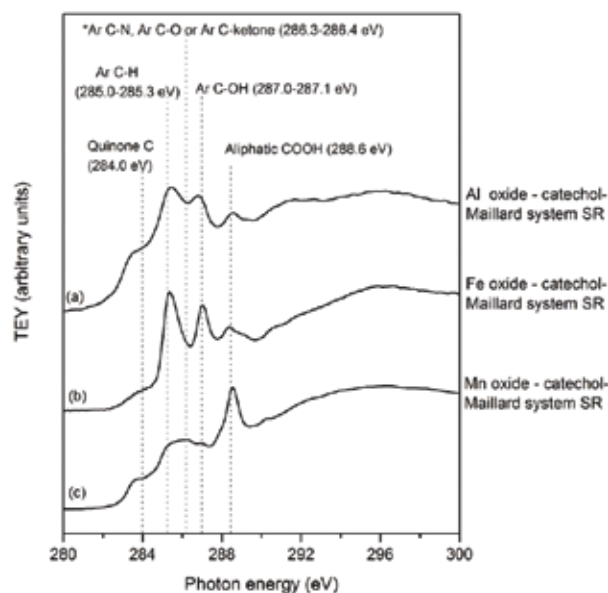
beamlines. Samples containing C were mounted on gold-coated silicon wafers. Samples which were not investigated for C were mounted on carbon tape. A number of reference compounds (IHSS Elliott soil and Suwannee River HA standards,  $AlPO_4$ , pseudoboehmite, gibbsite) were used. Selected highlights of the results are discussed below.

## Results and Discussion

The metal oxides substantially influenced the chemical nature of the resultant humic products from the supernatant (Figure 1) and solid residues (Figure 2). The humic products from the systems catalyzed by Mn oxide had a much higher content of aliphatic carboxylic groups than those from the Al and Fe oxide-catalyzed systems. This is due to the lower electronegativity of Mn and the higher redox potential of the Mn oxide system compared to Fe or Al oxide systems.

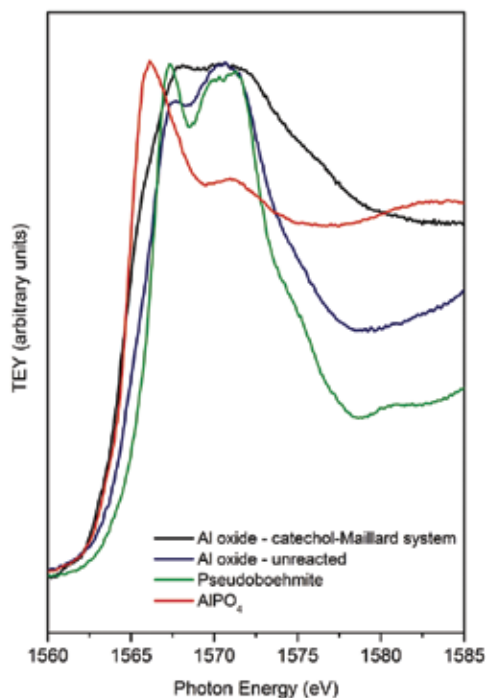


**Figure 1:** Carbon *K*-edge NEXAFS spectra of the IHSS (a) soil and (b) river humic acids, and the HA extracted from the supernatants of the integrated catechol-Maillard reaction systems: (c) Al oxide system, (d) Fe oxide system (e) Mn oxide system, and (f) HA extracted from the supernatant of the birnessite catalyzed Maillard reaction system. \*Ar = aromatic.



**Figure 2:** Carbon *K*-edge NEXAFS spectra of the solid residues (SR) from the integrated catechol-Maillard reaction systems catalyzed by (a) Al oxide, (b) Fe oxide and (c) Mn oxide (birnessite). \*Ar = aromatic.

Dissolved metals (resulting from catalysis reactions) have a higher affinity to form complexes with carboxylic groups than phenolic groups [3], therefore, humic polymers containing carboxylic groups are more likely to be co-precipitated with the metals and found in the solid residue. Furthermore, the surfaces of metal oxides also have a higher affinity to form complexes with carboxylic groups than phenolic groups. This explains why the solid residues (Figure 2) are richer in aliphatic carboxylic groups than the HA in the supernatant (Figure 1).



**Figure 3:** Aluminum *K*-edge NEXAFS spectra of the Al oxide catalyst prior to (blue) and after reaction in the integrated catechol-Maillard system (black), compared with octahedral Al-containing pseudoboehmite (green) and tetrahedral Al-containing  $\text{AlPO}_4$  (red).

The humification processes also influenced the surfaces of the oxides. Figure 3 illustrates the change that occurred in speciation of Al in the Al oxide after reaction in the catechol-Maillard system. It appears that Al oxide has a greater content of tetrahedral-Al than before reaction with the biomolecules, indicating the effect of organic humic polymers bound to the Al (either through surface complexation or by co-precipitation with dissolved Al) on Al speciation.

## Conclusions

The Al, Fe and Mn oxides have significantly different effects on the humification processes in polyphenol-Maillard pathway. Mn oxide resulted in humic substances with a more aliphatic character than the Fe or Al oxides. There were also significant differences in the effect of the humification reactions on the structural chemistry on the surface of the metal oxides. The findings obtained in this study are of fundamental significance in understanding the importance of the nature of metal oxide catalysts in influencing abiotic humification pathways and products in natural environments.

## References

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