Effect of light on birnessite catalysis of the Maillard reaction and its implication in humification

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Jokic, A., Frenkel, A. I. and Huang, P. M. 2001. **Effect of light on birnessite catalysis of the Maillard reaction and its implication in humification**. Can. J. Soil Sci. **81**: 277–283. The Maillard reaction between carbohydrates and nitrogenous compounds originally investigated in 1912 has subsequently been proposed as a possible pathway for the formation of humic substances in natural environments. However, the role of mineral catalysis of the Maillard reaction is little understood and the promoting effect of light on such catalysis is not known. Birnessite (δ-MnO_2), which is commonly present in soil environments, was investigated for its activity in promoting the Maillard reaction between glucose and glycine at a light intensity of 168 $\mu E\ s^{-1}\ m^{-2}$ or in the dark. The presence of substantial quantities of Mn(II) was detected in both the supernatant and solid phase of the glucose-glycine-birnessite systems. The spectroscopic evidence indicates that birnessite, in the presence of light, is a very effective catalyst in abiotic browning of solutions of glucose and glycine. Furthermore, birnessite significantly promoted the reaction even in the absence of light. Therefore, the abiotic heterogeneous catalytic role of soil minerals such as birnessite in polycondensation of simple sugars and amino acids merits close attention in the formation of humic substances in natural environments.

Key words: Maillard reaction, heterogeneous catalysis, light, birnessite, humic substance formation, XANES

Jokic, A., Frenkel, A. I. et Huang, P. M. 2001. **Influence de la lumière sur la catalyse de la réaction de Maillard par la birnessite et implications au niveau de l'humification**. Can. J. Soil Sci. **81**: 277–283. Après sa découverte en 1912, d'aucuns ont suggéré que la réaction de Maillard entre les glucides et les composés azotés pourrait expliquer la formation des substances humiques en milieu naturel. Toutefois, on sait peu de choses sur le rôle catalytique des minéraux dans cette réaction et on ignore si la lumière favorise la catalyse. Les auteurs ont examiné comment la birnessite (δ-MnO_2), qu'on trouve couramment dans le sol, facilite la réaction de Maillard entre le glucose et la glycine à une intensité lumineuse de 168 $\mu E\ s^{-1}\ m^{-2}$ ou dans l'obscurité. Ils ont décelé une quantité appréciable de Mn(II) dans le surnageant et dans la phase solide des systèmes glucose-glycine-birnessite. Les données spectroscopiques indiquent qu'en présence de lumière, la birnessite catalyse efficacement le brunissement abiotique des solutions de glucose et de glycine. Par ailleurs, la birnessite facilite sensiblement cette réaction, même dans l'obscurité. Le rôle de catalyseur abiotique hétérogène des minéraux comme la birnessite dans la polycondensation des sucres simples et des acides aminés mérite donc d'être examiné de plus près dans le contexte de la formation des substances humiques en milieu naturel.

Mots clés: Réaction de Maillard, catalyse hétérogène, lumière, birnessite, formation de substances humiques, XANES

The Maillard reaction was initially proposed by Maillard (1912, 1913) who investigated the formation of yellow-brown to dark-brown "pigments" or melanoidins upon refluxing solutions of glucose and lysine together. Since then, evidence has accumulated which suggests that natural humic substances may be produced by polycondensation reactions between sugars and amino acids (Hodge 1953; Ikan et al. 1996). Further support is lent by the presence of humic substances in marine environments where carbohydrates and proteins, because of their abundance, are more probable precursors of humic substances than are lignin or phenolic polymers (Nissenbaum and Kaplan 1972; Hedges and Parker 1976; Ikan et al. 1996). For example, proteins and carbohydrates are the principal constituents (up to 80% of dry cell material) of marine organisms such as algae (Harvey 1969). Marine floras such as *Spartina alterniflora* contain and release the chemical precursors of melanoidins, i.e., sugars and amino acids, which include glucose and glycine (Ikan et al. 1990).

Additional evidence for the contribution of melanoidin-type structures to humic substances was supplied by thermal (Ioselis et al. 1981) and spectroscopic studies (Rubinsztain et al. 1984). Ikan et al. (1996) found that ^{13}C-CP-MAS NMR spectra of melanoidins were remarkably similar to those of some humic acids. They suggested, therefore, that the Maillard reaction between sugars and amino acids plays a more significant role in the formation of the skeletal matrix structure of humic substances than previously thought. Evershed et al. (1997) have recently detected the presence of Maillard reaction products in decayed plant materials from an archaeological site dating from ancient Egypt.

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However, the effect of light in promoting abiotic mineral catalysis of the Maillard reaction is little understood. Further, the catalytic effect of soil minerals on the Maillard reaction remains obscure. The objective of the present study was to investigate birnessite catalysis of the Maillard reaction under conditions of darkness and exposure to mild light conditions.

Glucose and glycine were used in this study because they are present in polymers of plant and microbial origin. Structural components of plants are relatively rich in glucose (McKeague et al. 1986) and microbial carbohydrate is generally rich in glucose (Cheshire 1979). Proteinaceous material in soil originates from animals, plants, and microorganisms; proteins and peptides of plant tissues are rich in glycine among other amino acids (McKeague et al. 1986). Manganese oxides are very common mineral components of soils; birnessite, a short-range ordered tetravalent Mn oxide, is one of the most widely occurring forms (McKenzie 1989).

MATERIALS AND METHODS

Chemicals Used

Glucose and glycine were purchased from Sigma Chemical Co. (St. Louis, MO). All chemical reagents used were of ACS reagent grade or higher purity.

Preparation of Birnessite

Birnessite was synthesized according to the method recommended by McKenzie (1971). It was characterized by X-ray diffractometry and **Fourier transform infrared absorption** (**FTIR**) spectroscopy. The X-ray diffractogram exhibited peaks at 0.720 nm, 0.360 nm and 0.243 nm, which are characteristic for birnessite. The FTIR spectra had absorption bands at 3431, 1624 and 524 cm^{-1}, which are diagnostic for birnessite (Potter and Rossman 1979).

Reaction Procedure and Monitoring

Utensils, birnessite and double deionized water used in the experiment were sterilized by autoclaving. Two and a half grams of autoclaved birnessite were suspended in 85 mL of glucose:glycine (0.05 mole each) solution, which contained 0.02% wt/vol thimerosal (an antiseptic). The pH was adjusted to 7.00 by addition of 0.1 M HCl and autoclaved double-deionized water was added to total volume of 100 mL. The flasks were sealed and secured on a wrist-action shaker in an environment chamber with constant light intensity of 0 or 168 $\pm$ 2 $\mu E\ s^{-1}\ m^{-2}$. Light intensities were measured and adjusted using a LI-COR (model LI–250) light meter (Lincoln, NE). The system was allowed to react for up to 60 d at 25.5 $\pm$ 0.5°C. At the end of each reaction period, the supernatant liquid phase was separated from the solid phase by centrifugation at 25 000 $\times$ *g* for 40 min. In addition, two controls were prepared. Control 1 duplicated the above conditions, but contained no birnessite and control 2 duplicated the above conditions, but consisted of birnessite and water alone.

Examination of Microbial Activity

Samples of the reaction systems were incubated for 6 d under aerobic or anaerobic conditions on **Trypticase Soy Agar** (**TSA**) plates to test for abiotic conditions (Dandurand and Knudsen 1997). TSA is a nonselective growth medium suitable for the cultivation of a wide variety of microorganisms. Using a bent glass rod, a small portion of the suspension was spread on TSA plates at the beginning and the end of the reaction period to examine whether there had been any microbial growth in the systems.

Characterization of Final reaction Products

The supernatant was analyzed by visible absorption spectrophotometry using a Beckman DU 650 microprocessor-controlled spectrophotometer (Fullerton, CA). The supernatant was investigated by electron paramagnetic resonance spectrometry using a Bruker B-ER418S spectrometer (Bruker, Germany) operating in the field modulation mode at 100 KHz and a frequency of 9 to 10 GHz (X band) at room temperature. The microwave frequencies were measured with an EIP model 548A microwave frequency counter. The field positions were calibrated using a Bruker NMR Gaussmeter ER035M and corrections. The relative positions of the sample and the NMR probe were adjusted using 1,1-Diphenyl–2-picryl-hydrazil (DPPH) as a standard. The pH and Eh of suspensions of the systems were measured and the Mn content of the supernatants was determined at 279.5 nm by atomic absorption spectroscopy.

The solid phase of the reaction products of the glucose-glycine-birnessite systems exposed to 0 or 168 $\mu E\ s^{-1}\ m^{-2}$ were lyophilized and examined by X-ray absorption near edge structure (XANES) and FTIR spectroscopy. The results were compared with a control sample of pure birnessite and to a sample of birnessite suspended in water, which had also been exposed to 168 $\mu E\ s^{-1}\ m^{-2}$ for the same reaction period as the above systems. XANES experiments were conducted in transmission mode at the Materials Research Laboratory (MRL) University of Illinois – Lucent Technologies beam line X16-C at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York. The X-ray energy varied from 200 eV below, to 1000 eV, above the absorption K-edge of Mn (E_k = 6540 eV) using a Si 111 double-crystal monochromator.

FTIR spectra of the samples were obtained using KBr disks containing 0.5% wt/wt sample on a Biorad 3240 SPS microprocessor-controlled spectrometer (Cambridge, MA). Samples were flushed with dry N_2 gas for 10–15 min prior to analysis in order to remove atmospheric CO_2 and moisture.

RESULTS AND DISCUSSION

In all the systems studied, growth of microorganisms was not observed (Table 1), indicating that all the processes in the systems studied were abiotic in nature. Samples were studied at two different light intensities, 0 and 168 $\mu E\ s^{-1}\ m^{-2}$, in an environment chamber at 25.5 $\pm$ 0.5°C. For comparison purposes, the intensity of the midday sun is approximately 2000 $\mu E\ s^{-1}\ m^{-2}$ and the lower limit of the light intensity on a typical cloudy day is approximately 500 $\mu E\ s^{-1}\ m^{-2}$ (Sunda et al. 1983). The results after 30 d are shown in Table 2 and Fig. 1. Maillard reaction products are brown, and this was apparent in the supernatant of the glucose-glycine-birnessite systems. At 400 and 600 nm, the

Table 1 Examination of the growth of microorganisms in glucose-glycine-birnessite, glucose-glycine, and birnessite systems at 25.5 ± 0.5°C[z]

Glucose	Glycine	Birnessite	Thimerosal	Growth of micro-organisms in TSA
+[y]	+	–[x]	+	ND[w]
+	+	+	+	ND
–	–	+	+	ND

[z]Glucose-glycine and glucose-glycine-birnessite systems exposed to 168 μE s^{-1} m^{-2} were incubated for 58-d and glucose-glycine and glucose-glycine-birnessite at 0 μE s^{-1} m^{-2} and birnessite-water at 0 and 168 μE s^{-1} m^{-2} were incubated for 60-d. Growth of microorganisms in all the reaction systems at the end of the 30-d reaction period was also not observed.
[y]In the presence of.
[x]In the absence of.
[w]Not detected.

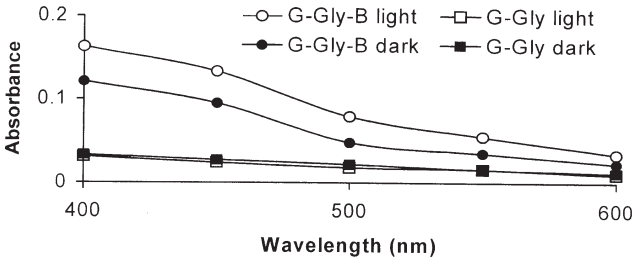

Fig. 1. Effect of birnessite on the absorbance of the glucose-glycine solution at the initial pH 7.00 and 25.5 ± 0.5°C at the end of a 30-d reaction period under light intensity of 0 (dark) and 168 (light) μE s^{-1} m^{-2}. G, glucose; Gly, glycine; and B, birnessite.

absorbance of the supernatant of the glucose-glycine-birnessite system was respectively five and three times higher than that of glucose-glycine system at light intensity of 168 μE s^{-1} m^{-2}. In the absence of light (0 μE s^{-1} m^{-2}), the absorbance of the supernatant of the glucose-glycine-birnessite system at 400 and 600 nm was four and two times higher than that of glucose-glycine system. In the absence of birnessite the effect of light at 168 μE s^{-1} m^{-2} was not evident. The data indicate that humification of glucose and glycine through their polycondensation was significantly enhanced by the presence of birnessite, especially in the presence of light.

EPR analysis confirms the presence of Mn (II) in the supernatant of the glucose-glycine-birnessite system both at 168 μE s^{-1} m^{-2} (Fig. 2) and at 0 μE s^{-1} m^{-2} (not shown).

Figure 3 shows the FTIR spectra of the solid phase of the glucose-glycine-birnessite system exposed to 0 and 168 μE s^{-1} m^{-2} and of pure birnessite exposed to 168 μE s^{-1} m^{-2} at the initial pH of 7.00 and 25.5 ± 0.5°C for 58 d. The FTIR spectrum of the birnessite exposed to light (Fig. 3A) is identical to that of a control sample of birnessite (not shown), and is very similar to that reported in the literature (Potter and Rossman 1979) indicating that light alone had no effect. The broad absorption band with maximum at 3431 cm^{-1} is caused by hydroxide ion, or water, in a specific crystallographic site, while the small band with maximum at 1624 cm^{-1} is ascribed to less ordered water. The broad band at 524 cm^{-1} is attributed to vibrations of the MnO_6 octahedral framework of birnessite.

The spectrum of the glucose-glycine-birnessite system at 0 μE s^{-1} m^{-2} still shows the presence of birnessite (broad absorption band at 506 cm^{-1}) in the system, but the appearance of new absorption bands at 3377, 2910, 1601, 1445, 1409, 1074, and 1032 cm^{-1} (Fig. 3B and Table 3) indicates the presence of organic reaction products in the solid phase. The absorption band at ca. 500 cm^{-1}, which is indicative of vibrations of MnO_6 octahedra is absent in the solid phase of the glucose-glycine-birnessite system exposed to light at 168 μE s^{-1} m^{-2} (Fig. 3C). Absorption bands at 721 and 859 cm^{-1}, probably from carbohydrate ring stretching and/or Mn–O interactions (Colthup et al. 1990), are present. Absorption bands at 3401, 2910, 1589, 1457, 1409, 1074, and 1032 cm^{-1} (Fig. 3C and Table 3) from the organic components were observed. The absence of a band at ca. 1714 cm^{-1} (undissociated carboxyl), (Fig. 3B and 3C) is consistent with the system pH being near or above 7.00 (Wang and Huang 1992) and, therefore, the carboxyl groups are present in dissociated form (absorption bands at 1409, 1589 and 1601 cm^{-1}) (Colthup et al. 1990). The FTIR spectroscopic data confirm that some reaction products were adsorbed on the solid phase. The results also indicate that the reductive dissolution of birnessite was promoted by the presence of light. This is in accord with atomic absorption spectroscopic evidence on Mn concentration in the respec-

Table 2 Effect of exposure to light (168 μE s^{-1} m^{-2}) on the glucose-glycine-birnessite system and on the control system (no birnessite) at the initial pH 7.00 at the end of the reaction period of 30-d at 25.5 ± 0.5°C

System[z]	Absorbance 400 nm	Absorbance 600 nm	Mn (mg μL^{-1})	pH (final)	Eh (mV) (final)	pE + pH (final)
Glucose + glycine + birnessite (light)	0.162 ± 0.007	0.033 ± 0.003	4254 ± 77	7.65 ± 0.08	328 ± 10	13.19 ± 0.25
Glucose + glycine (light)	0.030 ± 0.001	0.011 ± 0.001	0	6.94 ± 0.05	425 ± 13	14.12 ± 0.27
Glucose + glycine + birnessite (dark)	0.121 ± 0.006	0.023 ± 0.002	2475 ± 111	7.59 ± 0.07	364 ± 12	13.74 ± 0.27
Glucose + glycine (dark)	0.032 ± 0.001	0.012 ± 0.001	0	7.01 ± 0.06	431 ± 9	14.29 ± 0.21

[z]Control samples of birnessite and water only, exposed to 0 or 168 μE s^{-1} m^{-2} at the initial pH 7.00, had absorbances <0.01 at 400 and 600 nm and contained <0.5 μg Mn mL^{-1}.

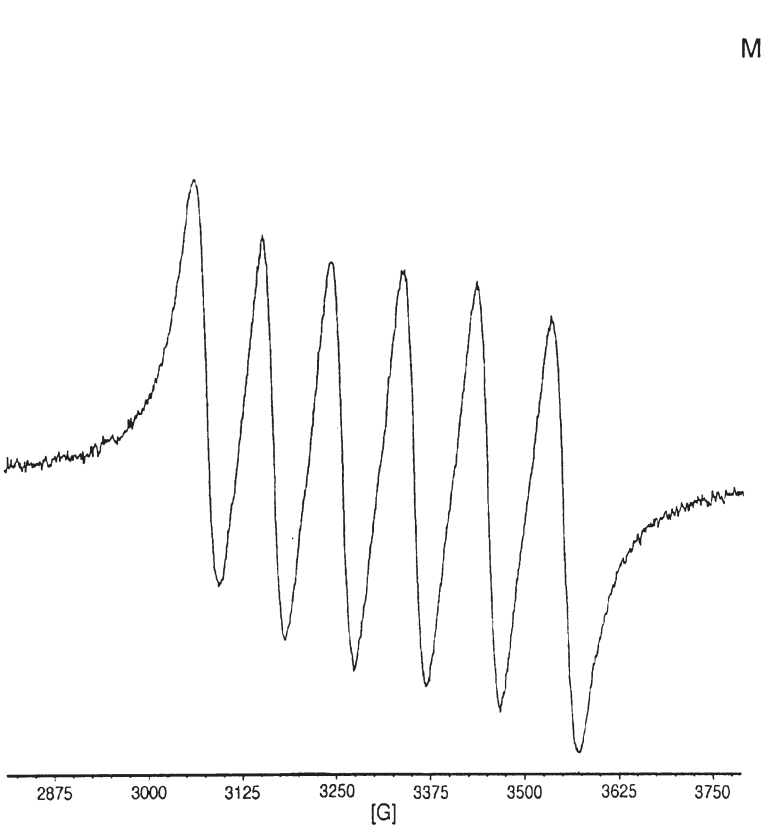

Fig. 2 The EPR spectrum of the supernatant of the glucose-glycine-birnessite system exposed to light at 168 μE s^{-1} m^{-2} at the initial pH of 7.00 and 25.5 ± 0.5°C for 30 d.

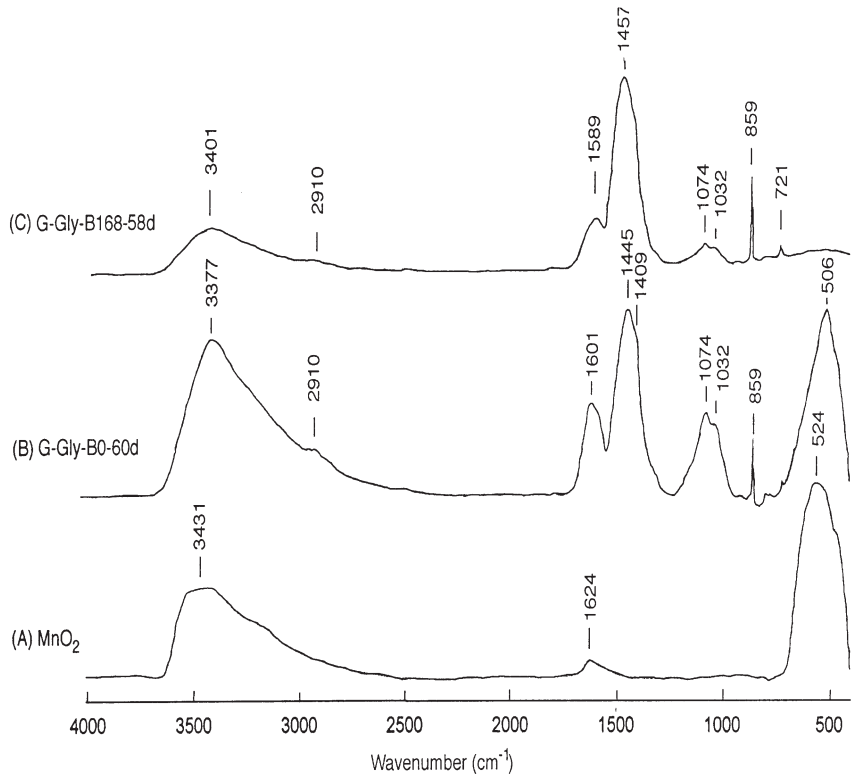

Fig. 3. FTIR spectra of (A) pure birnessite exposed to 168 μE s^{-1} m^{-2} (60 d) and of the solid phase of the glucose-glycine-birnessite system exposed to (B) 0 μE s^{-1} m^{-2} (60 d) and (C) 168 μE s^{-1} m^{-2} (58 d) at the initial pH of 7.00 and 25.5 ± 0.5°C. G, glucose; Gly, glycine; and B, birnessite; 0, 0 μE s^{-1} m^{-2} and 168, 168 μE s^{-1} m^{-2}. The FTIR spectra of birnessite whether exposed to light or not are identical.

Table 3. Assignations of FTIR absorption bands of the solid phase of the glucose-glycine-birnessite and birnessite systems as influenced by light[z]

Birnessite		Glucose +glycine + birnessite (0 μE s^{-1} m^{-2})		Glucose +glycine + birnessite (168 μE s^{-1} m^{-2})	
Wavenumber (cm^{-1})	Relative intensity	Wavenumber (cm^{-1})	Relative intensity	Wavenumber (cm^{-1})	Relative intensity
524 (vibrations of MnO_6 octahedra)	Broad, strong	506 (vibrations of MnO_6 octahedra)	Broad, strong		
				721 (Mn–O interactions) or carbohydrate ring stretch	Weak
		859 (Mn–O interactions) or carbohydrate ring stretch	Moderate, sharp	859 (Mn–O interactions) or carbohydrate ring stretch	Moderate, sharp
		1032 (–C–O– stretch for hydrated polyols and carbohydrate)	Broad, moderate	1032 (–C–O– stretch for hydrated polyols and carbohydrate)	Broad, moderate
		1074 (C–C stretch of aliphatic groups)	Broad, moderate	1074 (C–C stretch of aliphatic groups)	Broad, moderate
		1409 (sym $–COO^-$ stretch)	Strong		
		1445 (–CH bending of CH_2)	Strong	1457 (–CH bending of CH_2)	Strong
		1601 (Aromatic C=C stretch and/or asym $–COO^-$ stretch)	Strong	1589 (Aromatic C=C stretch and/or asym $–COO^-$ stretch)	Strong
1624 (less ordered water)	Broad, weak				
		2910 ($–CH_2–$ sym stretch)	Weak	2910 ($–CH_2–$ sym stretch)	Weak
3431 (–OH, H_2O adsorbed on birnessite)	Broad, strong	3377 (stretching vibration of H-bonded OH)	Broad, strong	3401 (stretching vibration of H-bonded OH)	Broad, strong

[z]The assignations are based on Colthup et al. (1990) and Wang and Huang (1992).

tive supernatants (Table 2). Except for the absence of the absorption band at 506 cm^{-1}, the FTIR spectrum of the solid phase of the glucose-glycine-birnessite system at 168 μE s^{-1} m^{-2} is qualitatively very similar to that of the glucose-glycine-birnessite system at 0 μE s^{-1} m^{-2}. The presence of Mn(II) in the supernatant and solid phase is evident from the EPR (Fig. 2) and XANES (Fig. 4) spectra, respectively. In the XANES spectra, the presence of Mn(IV) was still detected, in both systems, whether exposed to 0 or 168 μE s^{-1} m^{-2}, but Mn(IV) was still dominant in the solid phase of the glucose-glycine-birnessite system at 0 μE s^{-1} m^{-2}, whereas Mn(II) was the predominant species in the solid phase of the glucose-glycine-birnessite system at 168 μE s^{-1} m^{-2}. Moroever, in the solid phase, XANES spectroscopic evidence shows that whether exposed to light or not, Mn(IV) in birnessite was partially reduced to Mn(II) in the glucose-glycine-birnessite system.

The data indicate that light accelerated the rate at which electrons were transferred from glucose to the surface of the birnessite leading to the following reductive reaction:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

As a consequence of the consumption of H^+, the pH of the system increased, further driving the polycondensation reaction of glucose and glycine. The glucose was apparently oxidized to D-gluconic acid initially and then, probably, either further oxidized to α-dicarbonyl compounds or decarboxylated with loss of carbon dioxide. It is known that glucose can reduce transition metals forming a dicarbonyl compound (Wolff 1996). The dicarbonyl compound formed could then react with the amino acid present, undergoing the Strecker degradation reaction, which is an essential part of the Maillard reaction (Wong and Shibamoto 1996). Simultaneously or subsequently a complex polycondensation process between glucose and glycine resulted in the formation of Maillard reaction products. The Mn(II) released into solution may form complexes with intermediate Maillard reaction products and further catalyze the Maillard reaction. Other metals can exert similar effects: for example, Arfaioli et al. (1999) noted the ability of Cu(II) ion to catalyze the formation of humic-like substances in a system containing glucose and tyrosine.

Light intensity of 168 μE s^{-1} m^{-2} exerted a positive effect on the browning of the glucose-glycine-birnessite system compared with the same system which was kept in the dark. As a consequence, illumination increases the reductive dissolution of the birnessite and release of Mn (II) to the supernatant. Equally important is that even in complete darkness, birnessite catalyzed the Maillard reaction between glucose and glycine. Therefore, birnessite catalysis of the Maillard reaction can occur in soil or sediment environments at any depth, but the presence of sunlight should strongly accelerate the reaction. The oxidation and catalytic reactivity of manganese oxides results in their significant participation in environmental oxidation-reduction reactions (Oscarsson et al. 1981; Shindo and Huang 1982, 1984; Stone 1987; Wang and Huang 1992; Huang 2000). The data obtained in the present study indicate that the heterogeneous catalysis of birnessite in promoting the Maillard reaction may be an important abiotic pathway for the formation of humic substances in soil and aquatic environments.

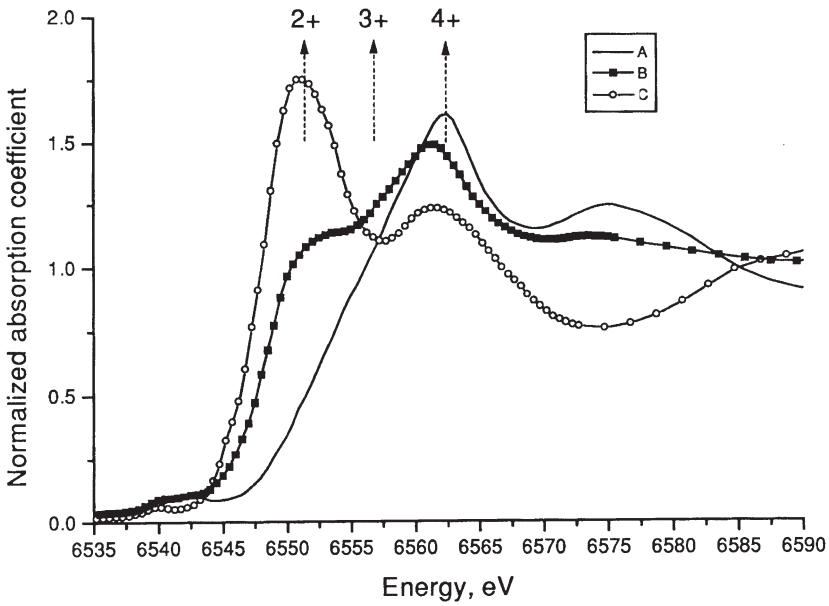

Fig. 4. XANES spectra of the sediment from (A) pure birnessite exposed to 168 μE s^{-1} m^{-2} (60 d) and of the solid phase of the glucose-glycine-birnessite system exposed to (B) 0 μE s^{-1} m^{-2} (60 d) and (C) 168 μE s^{-1} m^{-2} (58 d). The reaction systems were maintained at the initial pH of 7.00 and 25.5 ± 0.5°C. The oxidation states of Mn (2+, 3+ and 4+) at respective energy levels are indicated by arrows.

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