Adsorption and oxidative transformation of aromatic acids by Fe(III)-montmorillonite

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Aromatic acids are involved in important soil processes, such as mobilization of microelements by plants and formation of humic components. The interactions of aromatic acids (ferulic, p-coumaric, syringic, vanillic and benzoic) with montmorillonite enriched with Fe (III) was investigated. Adsorption of the phenolic acids on Fe (III)-montmorillonite was accompanied by their oxidative transformation and formation of Fe (II). Oxidative transformation of phenolic acids was affected by their molecular structure. The order of maximal transformation at the initial acid concentration of 20 mg/L on the surface of Fe (III)-montmorillonite was: ferulic (94%), syringic (60%), p-coumaric (35%) and vanillic (25%). Benzoic acid which was used as a reference aromatic compound exhibited only 5% transformation [1]. Adsorption of benzoic acid by Fe (III)-montmorillonite increased in the presence of 5 mM $CaCl_2$. Desorption of benzoic acid from Fe (III)-Ca^{2+}-montmorillonite was greater than that from Fe (III)-montmorillonite [2]. Removal of aromatic acids from solution by Fe (III)-montmorillnite increased with decreasing pH. LC-MS analysis demonstrated the presence of dimers, trimers, and tetramers of ferulic acid on the surface of Fe (III)-montmorillonite [1]. Oxidation and transformation of ferulic acid were more intense on the surface of Fe (III)-montmorillonite as compared to Fe (III) in solution due to stronger complexation on the clay surface: 90% of the ferulic acid was transformed following by interaction with Fe (III)-montmorillonite at an initial concentration of 0.1 mM, whereas only 20% was transformed in $FeCl_3$ solution. The concentrations of Fe (II) formed in Fe (III)-montmorillonite-ferulic acid suspensions at equilibrium was 0.46 mM. In the corresponding $FeCl_3$-ferulic acid system, the concentrations of Fe (II) was 0.06 mM [1]. The results of the current study demonstrate the importance of Fe (III)-clay surfaces for the abiotic formation of humic materials and for the transformation of aromatic (phenolic) pollutants.

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Isotope fractionation between metallic Fe and Fe^{3+}- and Fe^{4+}-bearing compounds

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We determined β-factors for Fe^{3+} and Fe^{4+} ($CaFeO_3$ and $SrFeO_3$) compounds at ambient pressure from Mössbauer and inelastic nuclear resonant x-ray scattering (INRXS) spectra [1-6] using techniques developed previously [7-10]. The pressure effect on Fe β-factors were estimated from a relation between pressure and temperature derivatives of β-factors [11]. For metallic Fe, we used the pressure dependence of β-factors [12] calculated from INRXS spectra [13].

Compound	Equilibrium fractionation factor (‰)			
	2000 K		3000 K	
	ambient	24 GPa	ambient	32 GPa
Fe_2O_3	0.05 - 0.07	0.07 - 0.09	0.03 - 0.04	0.05 - 0.06
$ReFeO_3$-Pv*	0.03 - 0.09	0.05 - 0.12	0.02 - 0.06	0.03 - 0.10
$CaFeO_3$-Pv	0.12 - 0.17	0.15 - 0.21	0.06 - 0.09	0.07 - 0.12
$SrFeO_3$-Pv	0.15 - 0.25	0.19 - 0.30	0.08 - 0.13	0.10 - 0.17
(Mg, Fe)SiO_3-Pv ferric	0.04 - 0.09	0.06 - 0.11	0.02 - 0.04	0.03 - 0.05

Table 1: Equilibrium isotope fractionation factor between Fe^{3+}- and Fe^{4+}-bearing compounds and metallic Fe.
* Re is the rare earth element, except Yb.

The isotope fractionation between Fe^{3+} compounds and Fe-metal is smaller than observed isotopic shifts (~0.1‰ [14]) between Earth's basalts and those from Mars and Vesta. The putative disproportionation via Fe^{4+} species might allow one to agree estimations and observations. Addition of S, H, and C to the Fe metallic phase is also a favorable factor for the enrichment of Earth's core in light Fe isotope [15].

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