

X-ray absorption study of iodine retention by organic matter

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Nuclear accidents, like the Chernobyl disaster, and disposal of spent nuclear fuel in radioactive waste repositories can result in the release of important amounts of radioactive ^{129}I (half-life 1.57×10^7 years) and ^{131}I (half-life 8.04 days) in environmental systems [1]. Under terrestrial pH and redox conditions, these isotopes are present as highly mobile I^- anions and they can endanger human health. Thus understanding the migration of iodine in subsurface environments is essential to estimate the long-term exposure of populations to radioactive iodine. Several field studies have pointed out the significant affinity of iodine for natural organic matter, such as humic substances [2, 3]. Parallel laboratory studies have confirmed that iodine can be quantitatively retained by HS [4]. However, these studies did not clarify the nature and possible diversity of the of the binding mechanism(s) between organic matter and iodine.

X-ray absorption spectroscopy (XAS) at the iodine L_{III} edge was performed over inorganic and structural references (Fig. 1). Figure 1 shows that the X-ray absorption near-edge structure (XANES) of iodine in inorganic solids is highly sensitive to the molecular and electronic properties of the X-ray absorber. Specifically, an increase in energy of the edge position with increase in the iodine oxidation degree is evident. XANES spectra for organic references in which iodine forms covalent bonds with the organic molecules were recorded (Fig. 2). This investigation showed that a shoulder at ~ 4560 eV always appears on the absorption edges (Fig. 2, arrow), a feature fairly insensitive to the molecule nature of the probed references. Finally, the main oscillations above 4565 eV markedly differ for distinct structural references, suggesting that the XANES spectra can be used to identify the binding mechanism of iodine to organic matter.

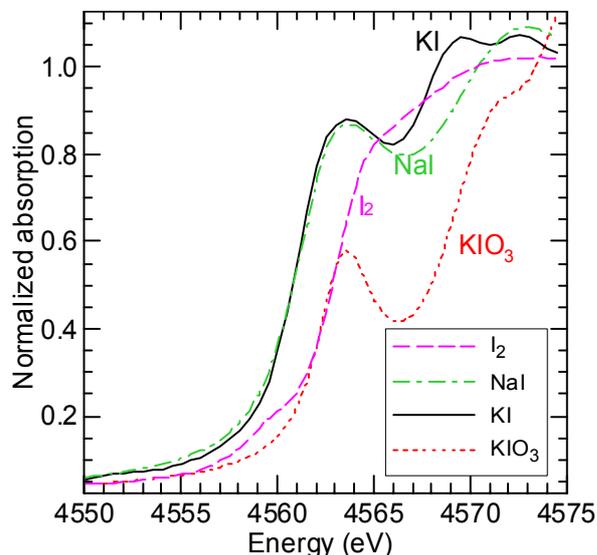


Fig. 1. Comparison of Iodine L_{III} -edge XANES spectra from inorganic compounds

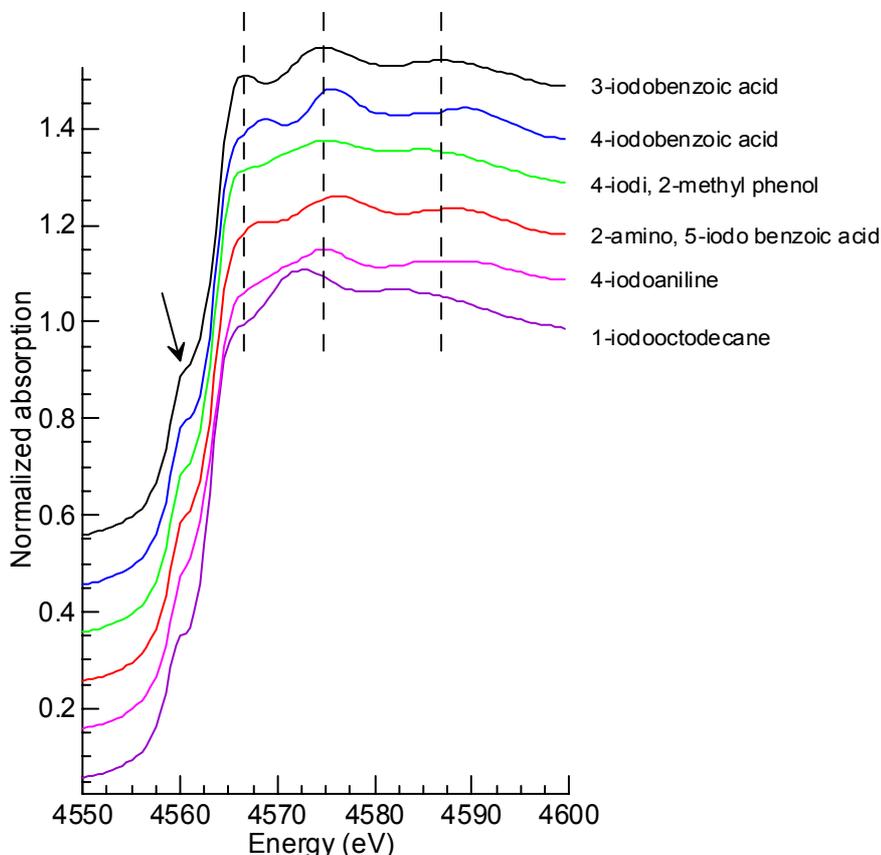


Fig. 2. Comparison of selected iodine L_{III} -edge XANES spectra for organic compounds.

Naturally iodinated humic acids (HA) and fulvic acids (FA) were then probed to clarify the mechanisms of iodine retention and their dependence on modifications of the HS **chemical and functional** composition (Fig. 3). XAS spectra were collected for a set of five samples covering a concentration range of ~5 % (FA Mobarra) down to as little as **600 ppm** (FA Fanay). For all spectra, the main absorption jump occurs near 4560 eV, a value coinciding with that for iodine covalently bonded to organic molecules. A detailed analysis further shows that the amplitude of the pre-edge shoulder varies among the samples, as do the positions and amplitudes of the XANES maxima. This indicates that iodine in these samples binds to distinct organic macromolecules, and suggests that more than one functional group is involved in iodine retention. Further insight into the nature of these groups will be obtained by modeling each sample spectrum by a linear combination of structural references. The results of these simulations will then be compared with the known structural properties of humic substances, to eventually identify high-affinity and low-affinity sites. We plan to publish these results in the forthcoming months.

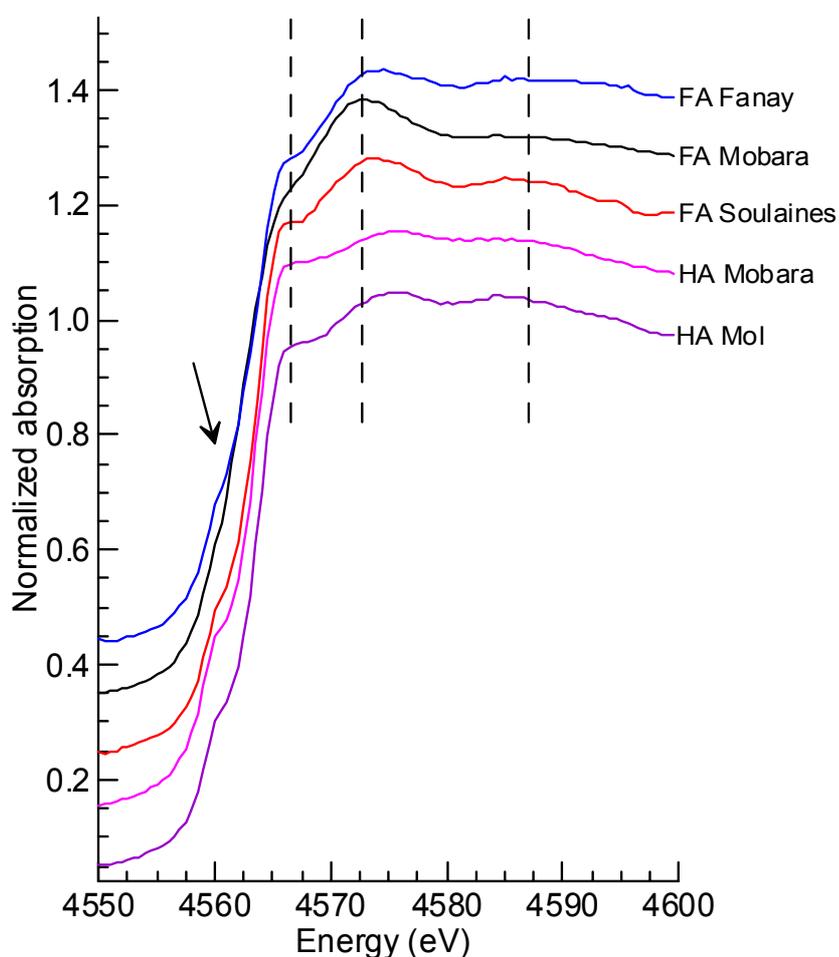


Fig. 3. Iodine LIII edge XANES spectra in humic substances. Note the disparity in amplitude of the pre-edge shoulder (arrow).

References

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