

Thermal stability of dissolved humic acid as revealed by *in-situ* UV spectroscopy

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Humic substances (HS) are considered to be carriers of environmental pollutants such as heavy metals and some organics. However, little is known on their long-term stability in the geochemical environments.

Of many influential factors on the stability of HS, we focused on the thermal stability of aqueous humic acid (HA). In order to determine precise kinetic parameters, we developed an *in-situ* heating system combined with UV spectrometer. The time-course of the reaction was monitored at 254 nm, which is considered to represent HA concentration, every 2.5 minutes at 80 to 160 °C.

The decrease in absorbance at 254 nm for reagent HAs (Wako, Aldrich) was successfully fitted by the combination of 2 first order reactions and the activation energies were about 26 and 23 kJ/mol, respectively. These *in-situ* transformation rates are compared with those determined in batch experiments. The *in-situ* method was able to determine initial processes which could not be detected by the batch method. Moreover, the presence of more than one single reaction was discovered in our *in-situ* study.

These kinetic parameters for standard HA were also compared with some natural HA from groundwaters. Despite the differences in origin and character of HA, the transformation rates and activation energies were similar among them. This result suggests some common thermal transformation behaviors of certain functional groups. Therefore, similar experiments will be presented on model compounds such as carboxylic acids, cellulose and lignin and transformation mechanisms will be discussed.

Properties of aqueous fluids up to 200 °C by ATR-IR spectroscopy

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In order to study physicochemical properties of hydrothermal and metamorphic fluids, attenuated total reflection (ATR) infrared spectroscopy of aqueous solutions were conducted from room temperature up to 200 °C. NaCl and Na₂CO₃ had opposing effects on water structure based on our previous model of 4 water molecular cluster components in IR OH stretching bands (Masuda et al., 2003). The competing effects of NaCl (longer hydrogen bond "loose" structure) and Na₂CO₃ (shorter hydrogen bond "tight" structure) could be represented quantitatively by the relative percentages of IR band components for the mixed solutions of 1M NaCl and 1M Na₂CO₃. The contrasted effect was also evaluated for the heated synthetic solutions up to 200 °C and compared with our data by *in-situ* IR microspectroscopy on heated natural fluid inclusions containing NaCl and CO₂ (Famin et al., 2003). The difference in "loose" vs. "tight" natures of these fluids became more pronounced at higher temperatures, suggesting their distinct wetting characteristics and permeability.

References

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