

Experimental Investigation into the Role of Water During the Thermal Alteration of Aliphatic Hydrocarbons

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The generation of oil by the geological maturation of sedimentary organic matter is primarily a thermal process involving a complex mix of free radical hydrocarbon cracking reactions. The presence of water has been shown to participate in the process of oil formation. The degree to which water is involved and the precise mechanisms by which this interaction occurs are still uncertain. A series of pyrolysis experiments was conducted at 350°C and 210 bar to identify reaction pathways between water and organic compounds under high temperature hydrothermal conditions. The experiments were performed in Dickson-type flexible gold bag rocking autoclaves. GC-MS analyses were used to obtain information about the bulk properties of the mixtures and detailed information of individual components in the reacted solutions. This work was aided by the use of isotopic labeling to provide insight to help establish reaction mechanisms under the experimental conditions.

Recent reports have demonstrated how hydrogen from water is incorporated into hydrocarbons via double bond isomerization of transient alkenes. Hydration of double bonds to form alcohols readily occurs, and these alcohols can react further to form ketones, thus acting as reducing agents. This pathway can continue to generate organic acids and ultimately CO₂, along with elevated levels of H₂ relative to the dry experiments.

The presence of water inhibits the formation of the high molecular weight polycondensed aromatic hydrocarbons. The production of hydrogen gas is a less reactive reservoir of the hydrogen, but some of the reducing potential goes directly back into the hydrocarbon pool by a reaction pathway opened up by the presence of water. Hydrogen, donated from the alcohols during their conversion to ketones, ends up reacting with low molecular weight alkylaromatic molecules, interfering with the oxidative, coke-forming pathway to result in the observed decrease in high molecular weight polycyclic aromatic hydrocarbons. In essence, water appears to decrease the "reaction severity" as compared to parallel experiments with no water present.

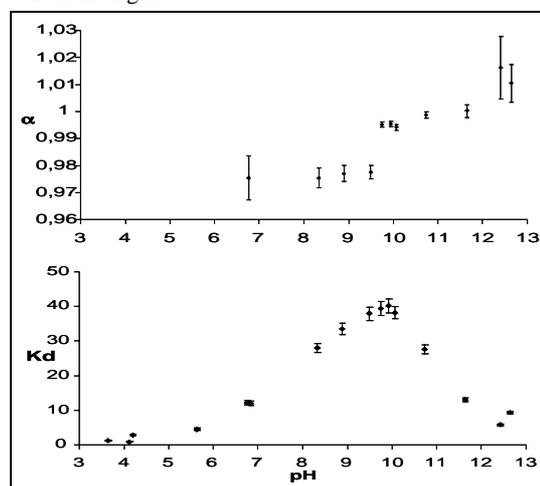
Isotopic fractionation related to boron sorption on humic acids

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For a better understanding of boron isotopes behavior during weathering processes, the isotopic effects of B sorption on humic acids have been investigated at different pH. Experiments were performed with purified commercial humic acids by adding boric acid to a 10 g/L colloidal suspension of humic acid. After solid/solution separation by ultrafiltration, boron adsorption constant and isotopic composition were measured using an improved Cesium borate PTIMS and a new chemical procedure for extracting B from organic matter (Gaillardet et al. 2001). The results of these experiments are shown on the figure.



Variations with pH of $\alpha = R_{\text{adsorbed}}/R_{\text{dissolved}}$ ($R = {}^{11}\text{B}/{}^{10}\text{B}$) and $K_d = [B]_{\text{adsorbed}}/[B]_{\text{dissolved}}$ of boron on humic acids.

Maximum B adsorption ($K_d=40$) is observed for pH=9.5-10. Moreover, this study demonstrates for the first time that boron sorption on humic acids strongly fractionates the isotopes, especially at pH<9.5, with ¹⁰B being strongly enriched in the organic phase relative to the solution ($\Delta^{11}\text{B}=-25\%$). Boron isotopic fractionation decreases when pH increases, with no or very minor fractionation of isotopes at high pH. This behavior can be modelled within a surface speciation approach with preferential sorption of tetrahedral B forming chelates on phenolic groups. This study demonstrates that boron-organic matter interactions can significantly affect the boron isotopic budget at the surface of the earth.

Gaillardet J., Lemarchand D., Göpel C., and Manhès G. (2001). "Evaporation and sublimation of boric acid: application for boron purification from organic rich solutions." *Geostandards Newsletter* **25**(1).