Abiotic organic synthesis in clays

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Hydrothermal experiments (Au-capsules in cold seal vessels) were conducted to evaluate the role of clay minerals in the abiotic synthesis of organic molecules. Clays are common hydrothermal alteration products of volcanic glass and as nanominerals, they provide extensive and variably charged surfaces that interact with aqueous organic species. In seafloor volcanic vents, H_2 and CO_2 react with magnetite producing methanol, a single C molecule. Therefore, our organic synthesis experiments started with dilute methanol in sub-crustal seafloor hydrothermal vent conditions (300°C, 100 MPa), and examined the products of reactions with common clay minerals found in those environments.

A di-octahedral smectite (SWy-1) reacts to ~60% illite over 6 weeks, while tri-octahedral saponite and illite remain mineralogically stable. Organic products were extracted with dichloromethane from the clay samples taken at intervals during reaction progress. Gases were also collected upon quenching. A variety of complex organic molecules formed including: alkanes, alkyl-benzenes, alkyl-naphthalenes, alkyl-phenols, alkyl-naphthols, alkyl-anthrols, methoxy and alkyl-methoxy-phenols, methoxy and alkyl-methoxy-naphthols, and long-chain methyl esters. Experiments with the non-expandable illite yielded only traces of alkanes and alkyl-benzene after 6 weeks.

The largest variety and quantity of organic products are formed with di-octahedral smectite where the layer charge changes with progressive illitization. Only small quantities of alkane products are observed. We propose that the O-sites on basal interlayer surfaces of smectites provide a hexagonal crystallographic template with similar dimensions to the aromatic hydrocarbons, and may direct the synthesis of polycyclic aromatic hydrocarbons. Without clay minerals, methanol decomposes to CH_4, CO_2, H_2, and dimethyl ether.

The observed production of polyaromatic products requires the presence of an expandable clay, which points to a key role for clay minerals in the synthesis of organic compounds in seafloor hydrothermal systems. The small alkane yield suggests that either the alkanes are reactants in the synthesis of aromatic products, or they are released from the protective interlayer of the smectite as illite forms and decompose in the exterior hot water. This suggests that smectites incubate organic compounds and protect them from thermal destruction. It is not clear whether this occurs because the layer-charge in the smectite mediates the reactions and stabilizes ionic intermediates, or if dehydration within the interlayer changes the aqueous-phase chemistry to stabilize particular organic products. Future experiments will focus on the role of Fe in smectites and its influence on organic reaction pathways.

Global atmospheric budget of mercury including oxidation of Hg(0) by bromine atoms

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Atmospheric mercury models typically assume OH and O_3 to be the major oxidants of Hg (0) globally, but recent kinetic studies suggests they are unimportant under atmospheric conditions. Bromine atoms oxidize Hg (0) in the marine boundary layer and may play an important role in the free troposphere. We test the viability of Hg (0) oxidation solely by Br in a global chemistry and transport model (CTM) and evaluate the simulated distributions of mercury against global observations of concentration and deposition. We compare the results to a CTM simulation with oxidation by OH and O_3, and also test whether atmospheric Hg (II) reduction is necessary given the range of uncertainty in oxidation rate coefficients. We show that the alternative Br and OH/O_3 oxidation mechanisms can both explain the Hg (0) seasonal cycle and interhemispheric gradient. Aircraft measurements over North America also provide constraints on the vertical distribution of oxidants and Hg (0) lifetime. Wintertime wet deposition across Europe and North America constrain the scavenging efficiency of rain and snow. Analysis of event-based precipitation samples in the eastern U.S. shows that thunderstorms increase mercury deposition versus non-thunderstorm rain. Cloud heights and trace element correlations during these rain events point to a significant Hg (II) reservoir in the free troposphere. Major differences between alternative oxidation mechanisms appear in the tropics, so measurements targeted there could further clarify mercury redox chemistry.