An experimental approach for studying the stability of organic compounds under simulated submarine hydrothermal conditions

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Introduction

Sub-seafloor hydrothermal systems have been proposed as likely environments for chemical evolution and the origin of life. However, a controversy exists as to whether or not amino acids and other organic compounds that are essential to life processes can be formed under hydrothermal conditions. It has been argued in the literature that at high temperatures organic compounds are highly unstable and decompose rapidly. Thermodynamic calculations on the other hand, indicate that organic substances may exist in metastable equilibrium in high temperature environments of the lithosphere. Previous stability studies of organic compounds and abiotic synthesis experiments have only been partly successful in simulating natural hydrothermal systems. This contribution describes a recently developed experimental approach for the study of the stability of amino acids under simulated deep-sea hydrothermal conditions.

Redox and pH buffering

The intention of this work is to apply hydrothermal simulation methods similar to those used in studies of alteration processes, mineral stability and metal complexing in hydrothermal environments on stability studies of organic compounds. When performing hydrothermal experiments it is necessary to constrain the experimental conditions properly. This can be achieved by the use of different mineral buffer assemblages that buffer the oxidation state, gasfugacities, pH and activities of aqueous ions to geologically plausible values. Here we have used the PPM buffer assemblages (pyrrhotite-pyrite-magnetite) for this purpose:

$$\underset{\text{pyrrhotite}}{2FeS} + \tfrac{1}{3}H_2O = \underset{\text{pyrite}}{FeS_2} + \tfrac{1}{3}\underset{\text{magnetite}}{Fe_3O_4} + \tfrac{1}{3}H_2 \quad \text{(PPM)}$$

At equilibrium the pyrrhotite-pyrite-magnetite assemblage fixes the fugacities of O_2, H_2, S_2 and the activity of H_2S.

pH of the fluid has been buffered to geologically reasonable values by using the assemblage potassium feldspar-muscovite-quartz (KMQ):

$$\underset{\text{K-feldspar}}{\tfrac{1}{2}KAlSi_3O_8} + H^+ = \tfrac{1}{2}\underset{\text{muscovite}}{KAl_2AlSi_3O_{10}(OH)_2} + 3\underset{\text{quartz}}{SiO_2} + K^+ \quad \text{(KMQ)}$$

The KMQ assemblage (K-feldspar-muscovite-quartz) is a sliding scale buffer that changes its position in response to changes in the activity of H^+ or K^+. At a specific temperature and pressure pH is fixed by the activity of potassium, a_{K^+}.

Experimental procedure

The hydrothermal technique used in this work differs from previous redox and/or pH buffered stability experiments with respect to a few important details. The buffered hydrothermal fluid is allowed to equilibrate at the experimental conditions before it is brought into contact with the organic compound that is studied. The equipment that has been used consists of two stainless steel autoclaves that are connected to each other with a steel capillary. Each autoclave has one liquid and one gas sampling valve. The experimental procedure is divided into two main steps. In the first step redox and pH buffer minerals are inserted together with a KCl-solution into one of the autoclaves. Air inside is removed by bubbling argon gas trough the solution. All valves are then closed and the autoclave is externally heated and pressurised with argon as pressure medium to the chosen experimental conditions. The time required to reach equilibrium conditions depends on factors such as temperature, grain size, solution composition and mineral reactivity. In the second step the equilibrated solution is transferred trough the capillary into the second preheated autoclave which contains the organic substance of interest. The transfer of the solution is accomplished by the

initial pressure difference. Sampling can start as soon as the transfer is complete.

The experimental method described above has so far been used to study the stability of some selected amino acids under simulated hydrothermal conditions. In such experiments a 0.03 molal KCl solution (pH adjusted to 6 with HCl) was allowed to react with the PPM (pyrrhotite-pyrite-magnetite) and the KMQ (K-feldspar-muscovite-quartz) buffer assemblages for three weeks at 200°C and 50 bar. Approximately 40 ml solution was subsequently transferred to a second preheated autoclave that contained 9×10^{-5} mole each of aspartic acid, serine, alanine and leucine. Sampling of the transferred solution was done continuously during the run. Preliminary data indicate that the experiments are carried out in or close to the stability fields of alanine and leucine.