

The experimental evidence indicates that hydrocarbons form directly from a mineral surface-hydrogen reaction rather than from a subsequent reaction between generated gases and hydrogen. In general, the reaction rate is rapid at temperatures well below the "in air" calcination temperatures of the carbonate minerals.

An inverse relation exists between the complexity of the hydrocarbon formed and the temperature of the experiment. The lower the initial reaction temperature of the carbonate mineral-hydrogen pair, the more complex the hydrocarbon.

Equilibrium was not generally established in these experiments, although it must have been attained locally at higher temperatures at the reaction surfaces. An evaluation of the kinetic data for calcite-hydrogen shows the reaction to be pseudo-first order. For our experimental system the Arrhenius apparent activation energy is 18,000 cal/mole. The reactions between dolomite-hydrogen and siderite-hydrogen are more complex and an interpretation of the kinetics from our present data is not possible.

This study is pertinent to a number of geologic problems. It defines a simple process to produce inorganic hydrocarbons under conditions that could reasonably exist within the crust. These data indicate that the reactions are temperature rather than pressure sensitive and that the partial pressure of hydrogen is of greater importance than is the absolute pressure of hydrogen in initiating the reaction.

The process of limestone and dolomite assimilation by a magma is also germane. If the gases associated with a magma are reducing (hydrogen need only be a part of such a reducing gas) then  $\text{CO}_2$  need not develop. The water generated in the reaction: carbonate mineral+hydrogen = methane+water+metal oxide or hydroxide, would inhibit the reaction; carbon dioxide would not. This water can, of course, be effectively removed from the system by being incorporated in the rock-forming minerals. The hydrocarbons may or may not leave the system. There is limited field evidence to support such a hypothesis. Petersil'ye (1962) estimates that the rocks of the Khibina massif contain  $7 \times 10^8 \text{ m}^3$  of inorganically derived hydrocarbon gases.

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