

## Study on the influence factors of oil cracking

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Oil cracking gas is an important source of deep gas. The oils generated from kerogen have three kinds of existing states: dispersive liquid hydrocarbon inside of source rocks, dispersive liquid hydrocarbon outside of source rocks and concentrated liquid hydrocarbon outside of source rocks, which is paleo-oil pool.

A comparative study on the gas generating from oil cracking and from kerogen shows that large quantities of gas are generated from oil when temperature reaches 160°C, that is the major period of gas generation from oil cracking occurs later than that from kerogen degradation, giving rise to the relay contribution of natural gas generation at different evolution stages. The above knowledge enlarges exploring field of deep gas.

The average activity energy of oil cracking methane is relevant to oil physical properties through kinetic experiments. That of light oil and heavy oil is 62.34 Kcal/mol and 68.86 Kcal/mol, respectively. Both the oil samples were selected from Lunnan area, Tarim basin in China.

In view of the overall situation, high pressure constrains the decomposition of oil to gas, but this repression is not noticeable in fast buried condition and it also has different effect at different evolution stages.

Through kinetic experiments on mixtures of oil with various minerals, using mixture with mudstone represents dispersive liquid hydrocarbon inside of source rocks while with calcareous rock and sandstone represent dispersive liquid hydrocarbon outside of source rocks, we infer that the carbonatite has the greatest influence on oil cracking and can largely reduce the activation energy of oil cracking gas, which leads to the decrease of pyrolysis temperature. The mudstone ranks the second and the sandstone the smallest. The corresponding Ro value of main gas generating period in different medium are as follows: 1.5%~3.8% with pure crude oil, 1.2%~3.2% with dispersive oil in carbonatite, 1.3%~3.4% with dispersive oil in mudstone and 1.4%~3.6% with dispersive oil in sandstone.

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## Mg isotope fractionation between aragonite and fluid

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The detectable Mg-isotope variations in biogenic aragonite (including corals, aragonitic forams and sponges) can potentially be applied as a paleoproxy. In this study, we report the result of a set of inorganic precipitation experiments to evaluate factors that could control Mg isotope fractionation between aragonites and fluid.

These 'free drift' experiments were conducted at 23.5-55 °C in freshwater by passive degassing for 1-4 weeks, with initial Ca concentration ([Ca]) spanning 400-2000 ppm and Mg/Ca molar ratio of 5.0. The solution chemistry (including pH and alkalinity) was closely-monitored over the course of the experiments. Observations using SEM after experiments demonstrate the occurrence of aragonite as major mineral phases. Magnesium from final solution and aragonite precipitates was purified by two chromatographic columns to remove Na, Ca, Sr and Ba, and pure Mg solution (in 5% HNO<sub>3</sub>) was analysed for <sup>26</sup>Mg/<sup>24</sup>Mg ratio by MC-ICP-MS (Neptune) at Yale University.

Our results show the initiation of aragonite precipitation occurred at different time for experiments having various [Ca], i.e., in an experiment initially having higher [Ca] aragonite started to precipitate earlier (e.g., a couple of hours for [Ca] = 2000ppm vs. a couple of days for [Ca] = 400 ppm), with a drop in pH and alkalinity at lower pH (e.g., pH = ~ 6.5 for [Ca]=2000ppm vs. pH = ~ 8.2 for [Ca] = 400 ppm). The Mg isotope fractionation between aragonite and final solution decreases noticeably with increasing temperatures, having a temperature sensitivity of ~0.01-0.0133‰/°C. This fractionation also depends on [Ca], i.e., Mg isotope fractionations in aragonites precipitated from solutions with higher [Ca] are smaller, and have smaller temperature sensitivity. These results can be understood by a kinetic model that can explain both Mg and O isotope fractionation in aragonites, and are consistent with our previous observations and models on the kinetic process of aragonite precipitation from seawater during CO<sub>2</sub> degassing. This temperature-dependent Mg isotope fractionation has the potential to be used as a paleo-thermometer to extract SSTs from coral skeletons, and provide constraints on biomineralization process.