# Geochemical characteristics of abiogenic hydrocarbons from Songliao Basin, China

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We discuss the formation of abiogenic hydrocarbons by polymerization of simple carbon-bearing molecules ($CH_4$, CO and $CO_2$), and the kinetic fractionation effect on carbon and hydrogen isotope composition and distribution in this process. The $\delta^{13}C$ values of methane from 26 commercial wells from Songliao Basin vary from -30.5‰ to -16.7‰. The δD values vary from -203‰ to -196‰. The alkane gases from these wells are characterized by a reverse distribution of $\delta^{13}C$ values and a normal trend of δD values, namely $\delta^{13}C_{CH4} > \delta^{13}C_{C2H6} > \delta^{13}C_{C3H8} > \delta^{13}C_{C4H10}$ and $\delta D_{CH4} < \delta D_{C2H6} < \delta D_{C3H8}$. The $\delta^{13}C$ value and δD value distributions are negatively correlated, showing the characteristics of abiogenic isotope composition controlled by kinetic isotope fractionation. The $R/R_A$ values of helium isotope composition of samples are between 1.05 and 2.36, shows significant contribution of helium from mantle. These samples have $^{21}Ne/^{22}Ne$-$^{20}Ne/^{22}Ne$ values between Loihi line and MORB line, and have enriched $^{129}Xe$ with respect to the atmosphere (0.15%-2.16%). The existence of mantle origin noble gases provides isotope evidence of mantle degassing in Songliao Basin. It supports the deep origin of the abiogenic hydrocarbons in Songliao basin. Our early studies [3, 4, 5] show the thermo-stability of hydrocarbons under high pressure condition in deep earth. The present study has revealed that abiogenic hydrocarbons not only exist in nature but also can make significant contribution to commercial gas reservoirs. It is estimated that the reserve volume of alkane gases with abiogenic characteristics in these 26 gas wells in Songliao basin is over $500\times10^8 m^3$. This work is supported by the NSF of China, 40572087, the NS&TRP China, 96110010602.

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# U-Th systematics in deep-sea red clays

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We followed the pioneer study by Ku [1] and applied uranium and thorium analysis on three deep-sea red clay cores from the southwestern subtropical Pacific. With high-precision multi-collector ICP-MS techniques, only a few mg of clay samples (~10 ng of U) were digested for the analysis. The precision of our analysis is ~1%, mainly limited by weighing uncertainty. Using $^{230}Th_{excess}$ profile, extraterrestrial $^3He$ flux, and Ar-Ar dating method on volcanic ash layers, we estimated a sediment mass accumulation rate of ~1-3 mm/kyr down the cores, and therefore, up to 10 million years of U and Th elemental and isotopic variations could be recovered from the ~10-meter long cores. We found that the $\delta^{234}U$ value (defined as $(^{234}U/^{238}U)$ activity – 1) * 1000‰) was close to 0‰ at the core top, rapidly decreased and then fluctuated between ~ -50‰ and -70‰ until ~7 m deep, and gradually came back to the equilibrium state in the lower portions. Our findings therefore confirmed the Ku's observations, albeit now with better precision on much advanced techniques. The negative $\delta^{234}U$ values in the main portion of the cores suggest that $^{234}U$ could be preferentially dispersed from red clay grains into marine pore water, due to the alpha-recoil effect. Such exchange of uranium between red clay and its surroundings could continue for a significant amount of time, only possibly been limited by the upward diffusion rate of $^{234}U$ with the increasing depth in the cores.

As red clay covers about half of the ocean floor, its preferential release of $^{234}U$ into pore water, and subsequently into bottom seawater could have significant contribution in the uranium isotope budget in the ocean. Quantifying this $^{234}U$ source will benefit our understanding of the history of seawater $(^{234}U/^{238}U)$ activity; therefore help to screen coral samples for a reliable sea level reconstruction using their uranium-series ages.

[1] Ku (1965) 'An evaluation of the $U^{234}/U^{238}$ method as a tool for dating pelagic sediments.' *J. Geophys. Res.* **70**, 3457–3474.