Elucidating the structure of gilsonite bitumen by advanced Nuclear Magnetic Resonance Spectroscopy

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Gilsonite, a naturally occurring asphaltite bitumen, consists of a complex mixture of organic compounds. Advanced one- and two- dimensional solid-state and solution nuclear magnetic resonance (NMR) techniques were used to investigate its chemical structure in detail. The solid-state NMR techniques employed in this study included quantitative direct polarization/magic angle spinning (DP/MAS) at a high spinning speed of 14 kHz, cross polarization/total sideband suppression (CP/TOSS), dipolar dephasing, CH, CH_2, and CH_n selection, ^{13}C chemical shift anisotropy (CSA) filtering [1, 2], ^{1}H-^{13}C recoupled long-range dipolar dephasing [3], two-dimensional (2D) ^{1}H-^{13}C heteronuclear correlation NMR (HETCOR) [4, 5], ^{15}N cross polarization/magic angle spinning (CP/MAS) and ^{15}N CP/MAS with dipolar dephasing. The solution NMR techniques applied were ^{1}H NMR with spin-spin relaxation time (T_2) filter, ^{1}H-^{1}H correlation spectroscopy (COSY), ^{1}H-^{1}H total correlation spectroscopy (TOCSY), and ^{1}H-^{13}C heteronuclear multiple quantum coherence (HMQC) NMR. Spectral-editing techniques clearly identified specific functional groups such as CCH_3, CCH_2, and $C{=}CH_2$ (exomethylene); ^{1}H-^{13}C recoupled long-range dipolar dephasing indicated that aromatic moieties in gilsonite were primarily of single rings; and two dimensional NMR experiments showed the detailed connectivties of different specific functional groups. ^{15}N NMR indicated that the majority of nitrogen in gilsonite was in the form of pyrrolic N. Based on the detailed NMR data, we proposed a structural model for gilsonite which was primarily a mixture of five-membered pyrrolic and six-membered aromatic rings with mobile aliphatic chains.

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Distribution and carbon isotopes of PLFAs in soil profile and its implications

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Recent studies showed that old-growth forest can result in carbon sink, and in contrast with the traditional theory [1, 2]. The finding should make a great influence on prediction and management of the global carbon cycle and ultimately the behavior of Earth’s climate system. However, the mechanisms on carbon accumulation in old-growth forest are still not clear. In this study, membrane phospholipids (PLFAs) from one such typical soil profile were analyzed and try to probe the ecological community and their metabolic processes in belowground, which finally affect carbon cycling.

Soil profile was collected from the Dinghushan Biosphere Reserve in GuangDong Province, China. As indicated by PLFAs distribution in soil profile, heterotrophs play an important role in upper 12cm soil layer, wherea the ecological community is predominated by autotrophs from 12cm to 28cm, showing an anoxia environment. Both heterotrophs and autotrophs are less active below 28cm. Compound-specific stable carbon isotopic compositions demonstrated that $\delta^{13}C$ values of heterotroph-derived PLFAs ranged from -23‰ to -32‰, approaching the mean $\delta^{13}C$ value of microbes which feed on terrestrial C3 plant [3], implying that heterotrophs in shallow depth of soil profile use C3-derived carbon as source rather than microbes-derived carbon. However, with an increase of buried depth, anoxia environment from 12cm to 28cm results in a decrease of heterotrophs and greatly slow the degradation of soil organic matter, meanwhile the biomass of autotrophs balance the respiration. This process probably plays a key role for carbon accumulation in old-growth forest and the extent of the accumulation strongly depends on the depth of anoxia layer.

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