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Influence of chemical structure on carbon isotope composition of lignite

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During the last two decades, a number of studies on carbon isotopes in terrestrial organic matter (OM) have been carried out and used to determine changes in paleoatmospheric δ13C value as well as assisting in paleoclimate analysis. Coal is abundant terrestrial OM. However, application of its δ13C value is very limited, because the understanding of changes in isotopic composition during coalification is relatively insufficient. The purpose of this study was to examine the influence of the chemical structure on the carbon isotope composition of lignite. Generally, lignite has more complex chemical structures than other higher rank coal because of the existence of various types of oxygen-containing functional groups that are eliminated at higher rank level.

A total of sixteen Lower Cretaceous lignite samples from Baganuur mine (Mongolia) were studied by ultimate, stable carbon isotope and solid-state 13C CP/MAS NMR analyses. The carbon contents of the samples increase with increase in depth, whereas oxygen content decreases continuously. This is undoubtedly due to normal coalification process and also consistent with solid state NMR results. The δ13C values of the samples range from -23.54‰ to -21.34‰ and are enriched in 13C towards the lowermost samples.

Based on the deconvolution of the NMR spectra, the ratios between carbons bonded to oxygen (60-90 ppm and 135-220 ppm) over carbons bonded to carbon and hydrogen (0-50 ppm and 90-135 ppm) were calculated for the samples. These correlate well with δ13C values (R2 0.88). The results indicate that the δ13C values of lignite are controlled by two mechanisms: (i) depletion in 13C as a result of loss of isotopically heavy oxygen-bounded carbons and (ii) enrichment in 13C caused by a loss of isotopically light methane from aliphatic and aromatic carbons. At the rank of lignite, coal is enriched in 13C because the amount of isotopically heavy CO_2 and CO, released from coal as a result of changes in the chemical structure, is less than that of isotopically light methane.

Coal is made up of complex macromolecules and this complexity influences the changes in carbon isotope composition during coalification. This study provides some information on the changes in the carbon isotope composition of lignite. However, further detailed investigation is required to reveal the relationships between δ13C value and chemical structure changes at certain levels of coal maturation.