Investigation of three oil shales with unusual heteroatom contents using advanced ^{13}C solid-state NMR

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The quantity and quality of synthetic crude oil generated from oil shales vary based on their distinct elemental compositions and organic moiety distributions. Kinetics of oil shale retorting are also impacted by kerogen heteroatom content, particularly sulfur. Three oil shales with unusual concentrations of heteroatoms (NSO) relative to other more extensively studied oil shales (e.g., Green River Formation, New Albany Shale) were investigated to assess kerogen structural properties in cases of extreme heteroatom content. Estonian kukersite (Ordovician), Jordanian Ghareb marinite (Upper Cretaceous), and Australian Glen Davis torbanite (Permian) were selected for this study due to the high oxygen, high sulfur, and low overall heteroatom content, respectively, in their kerogens. The shales were characterized using advanced ^{13}C solid-state multiple cross-polarization magic angle spinning (multiCP/MAS), multiCP/MAS with dipolar dephasing, two-dimensional ^{1}H-^{13}C heteronuclear correlation NMR (2D HETCOR), and 2D HETCOR with ^{1}H spin diffusion. Oxygen in kukersite shale contributed to its aromatic C-O structures and also to O-alkyls. The Ghareb shale contained the highest aromaticity and most diverse alkyl structures among the three shales, though particular features related to the high organic sulfur content were not resolved. The low-heteroatom Glen Davis shale had the simplest structural features, mainly in the form of long-chain aliphatic structures, and the lowest aromaticity. 2D HETCOR with ^{1}H spin diffusion indicated that the heterogeneity of Glen Davis shale was less than 1 nm. Results from this and previous advanced solid-state NMR studies demonstrate a diversity of structural properties not necessarily indicated by kerogen typing based on elemental ratios (H/C, O/C) and provide deeper insights into the diversity of oil shale properties with contrasting elemental compositions.