Characterization of raw and spent oil shale using low field NMR relaxometry

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Examination of longitudinal (T_1) and transverse (T_2) proton relaxation behavior in nuclear magnetic resonance (NMR) experiments is typically done to assess pore structure and fluid properties in porous media partially or fully saturated with water or petroleum. Recent improvements in low field (LF) NMR instrumentation has allowed for the observation of very short relaxation times ($< 10^{-4}$ sec) which makes it possible to differentiate between highly viscous or high-molecular-weight organic components beyond the range where T_1 and T_2 relaxation times diverge. We examined dry, crushed (-8 mesh) oil shale samples before and after pyrolysis to determine what organic phases can be observed using LF-NMR relaxometry by collecting T_1-T_2 correlation data. Kerogen ($T_1 >> T_2$) and bitumen ($T_1 \approx T_2$) in unpyrolyzed samples can be differentiated by their T_1 relaxation times, which can also be used to distinguish aliphatic ($T_1 \sim 10^{-2}$ s; $T_2 \sim 10^{-4}$ s) and aromatic ($T_1 \sim 1$ s; $T_2 \sim 10^{-4}$ s) kerogen moieties. Partial conversion of kerogen to bitumen and oil by incomplete pyrolysis was evident and a relationship between aliphatic kerogen and bitumen can be clearly discerned from T_1-T_2 correlation plots. As kerogen conversion was taken to completion, a range of bitumen T_2 relaxation times were observed, potentially indicating a shift in the distribution of pore sizes within the shale mineral matrix. Oil shale samples pyrolyzed by Fischer Assay showed only faint indications of residual bitumen or aliphatic kerogen, suggesting complete conversion of oil-generating moieties. Hydrous pyrolysis spent shales generated correlation plots that were more complex than those generated by other methods, which may be a result of incomplete expulsion of pyrolysis products. These results demonstrate the utility of LF-NMR for examining the chemical composition and physical distribution of viscous organic components within raw and spent oil shale and other source rocks.