^{43}Ca NMR spectroscopy of natural organic matter

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Ca^{2+} is thought to play a central role in the structure and behavior of natural organic matter (NOM) and in its binding to mineral surfaces. There are, however, few molecular scale experimental data about how these interactions occur. We present here the first ^{43}Ca NMR spectroscopic data for Ca-exchanged NOM: Suwanee River humic acid (HA) fulvic acid (FA). The spectra were collected at temperatures from -173K to 273K at an H_0 field of 20.0T under magic angle spinning conditions after equilibration of the sample at 100% R.H. over D_2O. For HA at 273K, there is a single, relatively narrow resonance at ~-4 ppm that at 173K resolves into two broader resonances at ~3 and -14 ppm. In contrast, for FA at 273K there is a single narrow resonance at ~2 ppm that becomes progressively broader with decreasing temperature, covers a larger chemical shift range than for HA, and remains centered at approximately the same chemical shift. For both samples, the line broadening with decreasing temperature demonstrates dynamical averaging over the Ca^{2+} sites at frequencies of the order of 100 kHz at room temperature. The chemical shifts are broadly similar to those of Ca carbonates (~20 to -25 ppm), and the -14 ppm resonance for HA is very similar to those of Ca acetate and Ca ascorbate. ^{43}Ca chemical shifts are known to correlate with Ca-O bond distances and coordination number (e.g., Singer et al., 2012), and our results suggest that its dominant interaction in NOM is with carboxylic and phenolic sites, although amine sites may also play a role. This conclusion is in agreement with previous molecular dynamics modelling (Iskrenova-Tchoukova, et al, 2010). The signal intensity for the FA is much greater than for the HA, as expected from its greater O-content.

[1] Singer, J.W., Yazaydin, A.O., Kirkpatrick, R.J., and Bowers, G.M., 2012, *Chem. Materials*, **24**, 1828-1836. [2] Iskrenova-Tchoukova, E., Kalinichev. A.G., and Kirkpatrick, R.J., 2010, *Langmuir*, **26**, 15909-15919.