Carbon isotope composition of organo-clay nanocomposites in overmature Devonian Marcellus Shale

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A strong correlation has long been observed between organic carbon (OC) and clay minerals in soils and marine sediments, which persists through partial illitization in thermally-immature black shale. Proposed mechanisms to explain this observation include intercalation of organic molecules within the clay interlayer, sorption to mineral surfaces and edges, and physical shielding through aggregation. Here we examine three thermally overmature Devonian Marcellus Shale samples ($\%R_0$ >2.0; total OC range: 2.0- 9.4 wt.%) to study the effect of thermal maturation on the isotope composition of OC associated with clay minerals. Transmission electron microscopy reveals the widespread presence of organo-clay nanocomposites. Clay minerals associated with OC display d-spacings (16 ± 1 Å) much wider than those of non-OC associated illite in the sample (10 ± 1 Å) and chlorite (14 Å), suggesting intercalation of OC into the interlayer. In order to investigate the carbon content and isotope composition of the nanocomposites, we designed a new apparatus to progressively bleach powdered black shale. This apparatus allows us to a) continuously measure the concentration of the evolved CO_2 and b) collect the CO_2 in glass vials over ~20 minute intervals; the latter is used to measure the isotope composition (ThermoFinnigan GasBench II). During oxidation of the organic fraction, we find the CO_2 evolves as two distinct peaks over ~10 hours. An increase in aluminium released, concurrent with the onset of the second carbon peak, suggests that this carbon is intimately associated with clay minerals as nanocomposites. A calcium saturation to expand the interlayer does not change the total amount of OC removed. The $\delta^{13}C$ values vary over bleaching which suggests mixing of various carbon reservoirs. Following calcium exchange, the rock releases isotopically heavier carbon that is protected by clay minerals. These observations suggest that thermal maturation generates organo-clay nanocomposites that are enriched in ^{13}C over the more accesible OC in the rock.