A Chemical, XRD, and ^{27}Al MAS NMR Investigation of Miocene Gulf Coast Shales with Application to Understanding Illite/Smectite Crystal-Chemistry

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Abstract: This study assesses the distribution of Al and Fe in mixed-layer illite/smectites (I/S) in shales undergoing burial diagenetic changes, using evidence from ^{27}Al NMR, XRD, and chemical analyses. Samples studied include a sequence of mixed-layer I/S (ranging from 40% to 68% illite layers) in shales from a well located in the Caillou Island Oil Field, Terrebonne Parish, Louisiana, as well as synthetic mica-montmorillonite (Syn-1), Silver Hill illite (IMt-1), K-benonite (ISMt-1), an Fe-bearing muscovite, phengitic muscovite, and a randomly interstratified mixed-layer I/S with 50% illite layers. Using a simplified model, where Fe^{3+} isomorphously substitutes randomly for $^{[6]}$Al in the dioctahedral 2:1 structure, the ^{27}Al NMR signal intensities are examined with regard to the paramagnetic deshielding effect of the Fe^{3+}. The rapid decrease in paramagnetic deshielding with distance allows for a spherical "wipeout" model with a radius of 6 Å, over which there is complete effective paramagnetic line broadening (i.e., Al within the sphere is not "seen"). Using the average dimensions of a dioctahedral mica, the expected relative intensities of the octahedral and tetrahedral Al signal are determined as a function of Fe_2O_3 content.

Observed ^{27}Al signals, normalized per unit weight of Al_2O_3 and relative to the lowest Fe-bearing phase, show a clear trend of decreasing intensity with increasing Fe_2O_3 content. Normative fitting of oxide data to structural formulae reveals a similar trend of decreasing ^{27}Al intensity with increasing fraction of dioctahedral site occupied by Fe^{3+}. Agreement between the observed ^{27}Al intensities of low Fe-bearing 2:1 phyllosilicates and ^{27}Al intensities predicted using the wipeout model indicate regular ordering of Fe and Al within the low Fe-bearing phases. However, observed ^{27}Al intensities for the I/S specimens fall into a region where the amount of Al seen is in excess for the given X_{Fe}, thus indicating segregation of Al and Fe domains.

The second order quadrupole effect for the $^{[6]}$Al site in the I/S fraction of shales decreases very slightly with increasing depth and percent of illite in the I/S, but not enough to effect site quantitation. Quantitative apportionment of elements into the I/S phase of the <0.2 μm fraction using NMR constraints shows directly a trend of increasing number of $^{[4]}$Al sites and no change in the number of $^{[6]}$Al sites with increasing degree of illitization for samples from the Gulf Coast diagenetic environment. Stoichiometry indicates an approximate 1:1 substitution of tetrahedral Al for Si over the 40 – 68% range of illite in I/S examined.

Key Words: Burial diagenesis • Gulf Coast • Illite/smectite • Miocene • NMR

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