SIMS analysis of illite isotopic systems during crystal growth: Application to gas exploration

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Clay minerals, especially illite-smectite (I-S), are the predominant minerals found in hydrocarbon source rocks worldwide. The study of I-S has been very useful in understanding the thermal histories and fluid flow events in sedimentary basins hosting significant amounts of crude oil and natural gas (e.g. U.S. Gulf Coast). In the last decade, we have conducted experiments to evaluate the relationship between several light stable isotopes and diagenetic ilite. In particular, ammonium, boron and lithium are notably enriched in brines associated with hydrocarbon (HC) production. Our research has shown that N, B, and Li are released from kerogen coincident with the release of HC's, and are incorporated into illitic clays that demonstrate significant crystal growth (R1 ordering) at temperatures of HC generation. This coincidence of processes allows diagenetic illite to ideally record changes in fluid chemistry associated with the passage of HCs. Our primary analytical tool for this research is secondary ion mass spectrometry (SIMS). The solid-state analysis of trace elements and their isotopes in clay minerals by SIMS eliminates the necessity for chemical extractions that may alter the original chemistry, and elucidates chemical heterogeneity associated with crystal growth.

The distribution of HC-related trace elements and isotopic variations were studied in Ordovician – Early Devonian bentonites from the Baltic Basin. The bentonite represents a *stratigraphic* timeline, whereas the different crystal size populations of illite in the bentonite record changes in *fluid chemistry* over time. K-Ar dating of the different sized illite crystals indicates their relative age of crystallization and this range of dates can be correlated with chemical changes to derive the timing of HC migration. The data reflect a pathway of HC migration away from the Alum shale source rock in Poland toward the northeast, where gaseous HCs are found in Estonia. High N (as NH_4^+; >1500ppm) substitutes for K^+ in illites formed near the generated oil. High B (>250 ppm) substitutes for Si in clay tetrahedral sheets and is concentrated farther away from the source. Lithium, which substitutes in octahedral sites of the clay, is concentrated (>150 ppm) farthest from the source rock, apparently accumulating with the volatile HCs. The diagenetic illite in bentonite equilibrates with fluids carrying light elements (N, B, Li) and records changes in fluid chemistry analogous to a chromatograph. Whether the separation of light elements is due to preferential incorporation into illite (more illite forms near the heat/HC source), differential timing of release from kerogen, relative volatility of each element, or other geologic factors is still under investigation.

The isotopic composition of B and Li changes by tens of per mil over the 1000km distance of migration, and the potential for evaluating the temperatures and/or chemical composition of the migrating fluid is quite exciting from an exploration point of view. If we can show a distribution of the light trace elements that indicates the direction of gas movement through micropores and fractures, we may elucidate areas of gas accumulation and thereby focus exploration for HC gas in limited, but most productive regions. The goal is to use relatively simply obtained geochemical indicators to reduce the environmental impact of gas production and increase the carbon return for dollars spent in recovery.