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The origin of illite in sedimentary basins as determined by K, Si, Fe, and Mg isotope analysis: new tools for basin analysis

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(1) Research Progress

We proposed to use a multi-isotope approach to better understand the smectite-illite (S/I) transformation that is arguably the most common clay diagenetic reaction in sedimentary basins. Stable K isotopes ($^{41}K/^{39}K$, or $\delta^{41}K$) are central in our approach, because K is the key element that directly underpins the S/I reaction. Resolution of small K isotopic variations in terrestrial samples has not been possible until recent analytical advances that made high-precision stable K isotope ratio analysis possible for the first time.

Smectite-illite samples from 4 different sedimentary basins with distinct diagenetic history were selected from a large S/I collection owned by our collaborator Prof. Crawford Elliott at Georgia State University, and brought back to UW-Madison for isotope analysis. These samples were mostly extracted from bentonite layers, so potential complications in geochemical signals from detrital clays can be minimized. To date, we have completed Fe isotope analysis on samples from the Denver Basin, and K isotope analysis on samples from the Denver Basin and the Disturbed Belt. These results are in preparation for publication, and also provide useful guidance for our 2nd-year research efforts. The main findings were summarized as follows.

1.1. Fe isotope results

The measured $\delta^{56}Fe$ values for samples from the Denver Basin ranged between 0.10‰ and 1.02‰ with an average of ~0.5‰. No correlation was found between $\delta^{56}Fe$ values and the degree of illitization (I%, Fig. 1). Compared to a presumed $\delta^{56}Fe$ value of ~0% in bentonite precursors, $\delta^{56}Fe$ values in S/I samples are consistently higher. Such moderately positive values are inconsistent with Fe isotope fractionation expected between aqueous Fe(II) and structural Fe(III) in clays during microbial or abiotic reduction, and may be explained by a mixture of Fe residing in clay and oxide components in the samples. This hypothesis will be tested through quantitative XRD analysis on a selection of representative samples based on our Fe isotope data.

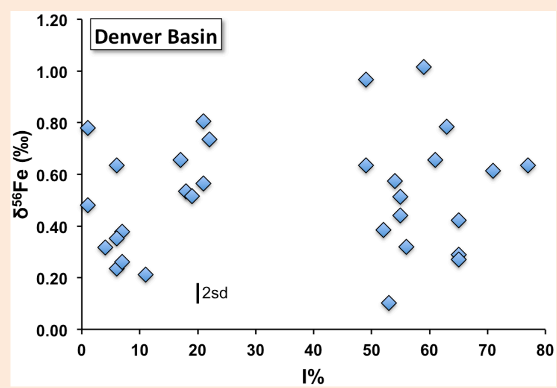

Fig. 1 *Fe isotope results of S/I samples from the Denver Basin*

1.2. K isotope results

Potassium isotope results from the Disturbed Belt and Denver Basin have revealed several exciting and potentially important features. First, a clear contrast in the measured $\delta^{41}K$ values between the two basins was observed (Fig. 2). S/I samples from the Disturbed Belt fell in a narrow range between -0.57‰ and -0.27‰, except for SD-03 samples that were collected from strata of ages substantially different from other samples from the same basin. In contrast, samples from the Denver Basin spread over a much larger range between -1.15‰ and -0.01‰. A possible explanation of this contrast lies in large K isotope fractionation between smectite and illite endmembers, but different K supply conditions during the transition; the Disturbed Belt may represent a diagenetic condition with only a limited K supply so that a full expression of smectite-illite fractionation is not possible, but the Denver Basin represents an opposite condition with a sufficient K supply during S/I transition. This is the first evidence that $\delta^{41}K$ can be a useful tracer for the S/I transition.

Second, a linear correlation was observed between $\delta^{41}K$ and reconstructed burial depths based on drill core samples from the Denver Basin (Fig. 3). Although I% generally positively correlated with burial depths, samples from the Wattenberg Gas Field (WGF) that is associated with an anomalous geothermal "hot spot" in the basin appear to be distinguishable from $\delta^{41}K$ values. This result indicates that $\delta^{41}K$ may provide useful information that is invisible from I% data on the kinetics of the S/I reaction.

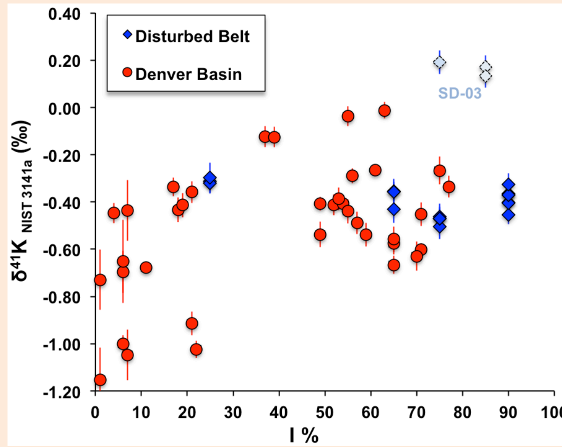

Fig. 2 *K isotope results from the Denver Basin and Disturbed Belt*

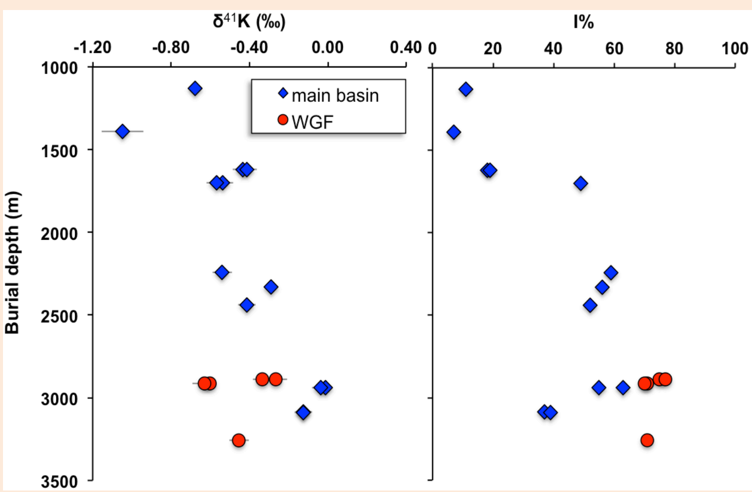

Fig. 3 *$\delta^{41}K$ and I% plotted against burial depths for drill core samples from the Denver Basin*

Our ongoing efforts are focused on exploring correlations between $\delta^{41}K$ results and other available thermal maturation indicators, such as vitrinite, and on incorporation of $\delta^{41}K$ data into existing S/I kinetic models. Also, a parallel NSF-supported study in our group that calibrates K isotope fractionation factors between aqueous K and various clay minerals in laboratory will provide a better-informed foundation for interpretation of data generated from this project.

2. Project Impact

This ACS PRF grant has enabled Johnson group to initiate a major new research direction that merges metal stable isotope geochemistry and petroleum geology. With the support from this project, 6 undergraduates, including 2 female students, have been trained with clean lab techniques that purify K, Fe, and Mg sequentially from clay samples. This PRF project also provided critical support for an early career scientist, Dr. Xinyuan Zheng who successfully landed a tenure-track assistant professor position at University of Minnesota-Twin Cities recently. The success of students and postdoc from this project manifests the necessity and success of PRF program in fostering the next generation of earth scientists in conducting cutting-edge, interdisciplinary research that drives the field of petroleum geology to advance.