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CLAYS IN THE PETROLEUM INDUSTRY

This special issue on the role of clay minerals in the petroleum industry is an outgrowth of a successful three-day symposium on the topic held at the annual meeting of The Clay Minerals Society in Baton Rouge, Louisiana, in October 1984. The symposium emphasized clay diagenesis and was attended by nearly two hundred clay scientists. The talks and ensuing discussion served as a stimulus for further research in industrial, academic, and government laboratories where efforts are being made to delineate the effects of clays on reservoir quality, mineral reactions, and hydrocarbon maturation processes.

Each session was chaired by a distinguished scientist who worked with the organizers to obtain a representative blend of invited and contributed titles on the varied applications of clay science in the petroleum industry. The list of nine session titles below demonstrates the breadth of coverage of the subject matter and identifies the chairperson of each session.

1. The Effects of Clays on Reservoir Quality: Alan Thomson
2. Clay Petrology and Paragenetic Sequences: James Boles
3. Authigenic Clay Mineral Compositions and Trends Related to Progressive Burial Metamorphism: Dennis Eberl
4. Geochemistry and Modeling of Clay Diagenesis: Carol Bruton
5. Shale and Semipermeable Membranes: Chemical and Reverse Osmosis and Other Membrane Properties: Steven Fritz
6. Isotope Methods and Results in Delineation of Time and Conditions of Clay Diagenesis: Samuel Savin
7. Clay–Organic Interactions: Richard Lahann
8. Remote Methods for Identifying Clays: Remote Sensing Techniques and Log Interpretations: David Pevear
9. Applications of Nuclear Magnetic Resonance Techniques: Sheldon Sommer

With the help of the chairperson, papers were nominated from each session. In addition, manuscripts were solicited from scientists having active research interests in related clay subjects but who did not participate in the Symposium. The result was an informative collection of papers on clay mineral diagenesis and its role in the petroleum industry.

A majority of the papers in this issue report on interpretations of the smectite-to-illite conversion during diagenesis. It is not surprising that this topic is currently receiving so much attention. Ever since the pioneering work of J. F. Burst, reported in the 1960s, the smectite reaction has been implicated as a process responsible in part for the accumulation of hydrocarbons. Smectite diagenesis occurs simultaneously in time and space with the maturation of organic matter to oil and gas. Our lack of understanding of both the reaction and its relation to organic transformations and hydrocarbon migration is the source of much debate among clay mineralogists and geochemists.

In this special issue, Ramsayer and Boles summarize important field data on the conversion rate of smectite to illite in the San Joaquin basin. They relate differences within the basin and between the Gulf of Mexico basin to the coupling effect of residence time and temperature and to diagenetic events, such as carbonate cementation. In addition, new microprobe data of smectites and smectite-rich I/S clays are presented which will prove useful in constraining thermodynamic stabilities and reaction kinetics and mechanisms, such as those suggested in several of the theoretical papers that follow.

Bethke, Vergo, and Altaner utilize junction probability diagrams to follow the conversion of smectite to illite in shales, bentonites, and hydrothermally altered tuffs. The diagrams conveniently show short-range and long-range ordered, random, and segregated interstratifications. The conversion in shales, bentonites, and tuff plots along characteristic reaction pathways on the diagrams.

The following paper by Bethke and Altaner uses a solid-state "Monte Carlo" layer-by-layer mechanism model to predict the observed layer sequences of mixed-layer clay minerals. The stoichastic model uses the presence and absence of adjacent illite layers arbitrarily to set the probability of a smectite layer converting to an illite layer. A first-order kinetic expression for smectite illitization is proposed that is independent of solution composition. The expression predicts illitization to occur at lower temperatures and shallower depths in slowly subsiding basins than in more rapidly subsiding basins.

Five of the papers discuss developments in the application of high-resolution transmission electron microscopy (HRTEM) and other microanalytical devices for observing stacking sequences, lattice dislocations, and crystal morphologies in natural and artificially prepared mixed-layer clays. In some instances, these new ob-

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servations (the two papers by Ahn and Peacor) and the recognition of interparticle X-ray diffraction effects by P. H. Nadeau and his co-workers at Aberdeen have raised questions about the models employed in predicting X-ray powder diffraction patterns of mixed-layer clays. Are X-ray powder diffraction patterns reflecting sample preparation rather than *in situ* interstratified clays? Other papers raise similar questions (Bell; Klemintidis and Mackinnon) while providing some observational evidence for the presence of interstratified illite and smectite during diagenesis. A fifth paper (Keller, Reynolds, and Inoue) follows the change in crystal morphology of the smectite-to-illite transformation. The observations reported in all of these papers are fundamental to determining if a dissolution and reprecipitation process is the dominant mechanism in the illitization of smectite. Can the transformation be treated as a reaction between separate clay minerals without including the effect of interstratification in a complex solid solution? These questions will undoubtedly be discussed in future volumes of *Clays and Clay Minerals.*

The remaining papers cover a wide range of topics. Sposito presents a refinement of Nriagu's "polymer" solid solution thermodynamic model for 2:1 clays. His polymer model uses a linear correlation equation relating the standard Gibbs free energy of the polymerization reaction to the half-cell layer charge of the clay mineral and to the valence and ionic radius of the exchangeable cation. The "calibrated" model can be used, assuming equilibrium controls reactions rather than kinetics, to predict clay mineral transformations during diagenesis as a function of solution composition, temperature, and pressure.

Herron proposes and tests a "statistical" model to estimate mineralogy from geochemical well-logging tools. The estimates are based on relating elemental concentrations of Al, Fe, and K to mineral abundances assuming constant mineral compositions and the absence of minerals other than kaolinite, illite, and K-feldspar to account for the detected variations of these three elements. The model can be expanded to handle more complex mineral suites and should prove useful in providing rapid, reliable estimates of mineralogy on a continuous basis as a function of depth.

Fritz presents an overview of osmotic processes related to the ideality of clay membranes. A computer model is used to illustrate the development of osmotic flow and pressure in ideal and nonideal systems. The high fluid pressures within the Triassic Dunbarton basin in South Carolina are used as an example of osmotically induced potentials. The importance of both osmosis and hyperfilitration (reverse omosis) in modifying reservoir fluid compositions is currently being debated among geochemists.

The final note by Bethke and Reynolds presents a new method for determining X-ray frequency factors for interstratified clay diffraction calculations. It makes use of recursive algorithms and has computational advantages over existing methods.

Many additional important topics involving clay mineral diagenesis have not been covered in this issue. Some of the most interesting research areas are those suggested by observations of reservoir petrologists, e.g., the puzzling association of chlorite rims and illite rims on quartz grains, respectively, with the apparent preservation and destruction of primary porosity. A major research effort is needed to delineate relationships between clay diagenesis and organic reactions involved in producing hydrocarbons, generating secondary porosity, and forming hydrogen sulfide. More laboratory measurements and field data are needed on the stabilities, reaction kinetics, compositions, and ages of the clays if we are ever to be able to do more than qualitatively predict their occurrences during diagenesis.

Coordinating this issue was a rewarding experience, and we thank the editor and reviewers for their time and effort. These papers represent a small part of the growing scientific dialogue between the hydrocarbon industry and academia.

Department of Earth Sciences
University of New Orleans
New Orleans, Louisiana 70148

R. K. STOESSELL

Department of Geology
Louisiana State University
Baton Rouge, Louisiana 70803

R. E. FERRELL, JR.

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