GEOTHERMOMETRY AND GEOCHRONOLOGY USING CLAY MINERALS-AN INTRODUCTION

Interest in the geothermometry and geochronometry of clay mineral assemblages was rekindled in the late 1970s by the contributions of Aronson and Hower (1976, *GSA Bull.* 87, 738-744) and Hoffman and Hower (1979, *Aspects of Diagenesis:* SEPM Spec. Pub. No. 26, 55-79). Progress was made during the 1980s on both the practical and theoretical fronts, especially in geochronologic interpretation of illite diagenesis through K-Ar dating. Also, kinetic modeling of illitization reactions assisted paleogeologic reconstruction of basin thermal history. With the scientific advances of the 1980s in the field of clay geochronometry and geothermometry, it was time for a meeting to highlight new ideas and future areas of research. Accordingly, a symposium was convened at the 1991 CMS meeting in Houston concerning geothermometry and geochronometry using clay minerals. Forty-eight papers were presented in either oral, poster, or mixed oral/poster fashion. Several of the papers are published in this issue of *Clays* & *Clay Minerals.* An additional paper will appear in a later issue of the journaL

Rich Pollastro reviews the use of basic XRD data on I/S materials from different sedimentary regimes to estimate maximum burial temperatures. He says that temperature is the dominant factor in illitization, but that several secondary controls exist, such as time. He invokes two simple time-dependent models. One, the "Hoffman and Hower" model, is applicable to longterm, burial diagenesis where the [regional] geothermal gradient is the major source of heat. The second, the "short-life geothermal" model, is applicable where the residence time at the critical reaction temperatures is less than about 3 Ma. Pollastro has examined clay mineral suites that are not simply from shales or mudstones, and has concluded that these rocks can yield temperature data based on I/S mineralogy that is comparable in utility to earlier studies based primarily on samples from shales.

Kirsten Price and Doug McDowell studied the illite/smectite in the 1.0 billion-year-old Proterozoic Nonesuch Formation in the context of regional burial, hydrocarbon maturation, copper-sulfide mineralization, and rifting/fracturing/faulting. They used I/S geothermometry to estimate maximum burial temperatures, the fossil geothermal gradient, and the maximum burial depth. In addition to monitoring changes from 80% to 0% expandability in I/S with depth, a transition from kaolinite to chlorite was detected in some drill holes. This study provides an example of useful information obtained by analysis of the I/S mineralogy of very old rocks.

David Bish and James Aronson studied altered volcanics from three boreholes in Yucca Mountain, which is one of the proposed sites for a nuclear waste repository. They correlated the observed depth-dependent changes in I/S composition, silica and zeolite mineralogy, and K-Ar ages. They derived a 3-dimensional model of hydrothermal fluid movement and concluded that the hydrothermal solution composition, particularly the silica activity, may have had as much influence on diagenesis as temperature.

Wuu-Liang Huang, John Longo, and David Pevear determined a kinetic model for illitization based on laboratory experiments with Na-saturated smectite. The result is a simple kinetic expression that can be used to model the depth and timing of diagenesis within a variety of thermal regimes. Sensitivity studies demonstrate that at "norma)" shale pore fluid $K⁺ concentrations (approximately 200 ppm), temperature is the dominant factor controlling$ illitization, indicating that variation in geothermal gradient significantly influences the depth zone associated with major changes in the percent of illite layers in I/S.

Bruce Velde and Bruno Lanson examined clays from the Salton Sea geothermal area (Cerro Prieto field) and the Paris Basin. They compare the thermal trends interpreted from the clay mineral data with vitrinite reflectance data. In the Salton Sea area, both vitrinite and clay data reflect the short-duration, high temperature regime, but in the Paris Basin only the vitrinite responded to a similar short-duration, high temperature regime. The difference in water/rock ratio in the two regimes may be the reason that the clays responded in the hydrous geothermal area but not in the [assumed anhydrous] Paris Basin.

A. E. Fallick, C. I. MacCaulay, and R. S. Haszeldine studied $\delta^{18}O$ and δD values of kaolinite and illite from the North Sea Magnus Sandstone. Although there are linear relationships between the δ^{18} O and δ D values in both kaolinite and illite, the evolution of pore waters from which these diagenetic minerals precipitated is not fully understood. Clearly, there are some aspects of rock-water exchange involving the hydrogen reservoir that require more study.

Joe Small discusses the kinetics of illite and kaolinite precipitation from diagenetic solutions. Laboratory clay mineral syntheses at elevated temperatures $(160^{\circ}-250^{\circ}C)$ in the presence of oxalate were used to estimate the rate of clay mineral precipitation at diagenetic temperatures (generally < 1 SO°C). Kaolinite precipitation is unlikely to be kinetically controlled. However, illite precipitation is predicted to occur at a much slower rate than kaolinite and to exhibit a pronounced kinetic threshold related to illite nucleation and crystal growth.

In another clay mineral synthesis study, Gene Whitney and Bruce Velde considered the external changes in illite particle morphology that are associated with the smectite-to-illite reaction. TEM studies of dispersed and sedimented reaction products revealed the presence of dissolution features on initial smectite particles. Particle thickness increases with continuing reaction, perhaps reflecting precipitation of secondary illite layers on a 2:1 layer template provided by a primary smectite particle. Highly illitic particle aggregates show a preponderance of 60° and 120° interfacial angles, which with continued crystal growth, merge into a single grain with overall euhedral form yielding single crystal electron diffraction patterns. The authors propose an illitization reaction involving four steps: smectite dissolution, epitaxial overgrowth of primary smectite by authigenic illite, formation of illite aggregates (quasicrystals), and, finally, infilling and syntaxial growth of quasicrystals to form homogeneous crystals of illite.

Patrice de Caritat and his co-workers discuss the complexities, applications, and limitations of chlorite geothermometry. They show that chlorite composition is influenced by many factors other than temperature (among these are the $fO₂$ and pH of chlorite-precipitating solutions, and the Fe/(Fe $+$ Mg) and bulk composition of the host rock). Dogmatic application of a particular thermal model on the basis of chlorite mineralogy is risky. The authors review four current methods applied to chlorite geothermometry and conclude that it should be used with caution, preferably in combination with other means of paleotemperature estimation.

Stephen Hillier presents a well-documented and detailed discussion of chlorite and corrensite genesis in relation to burial diagenetic/metamorphic processes in the Orcadian Basin of northem Scotland. Unlike the well-studied smectite-to-illite burial diagenetic reaction, the understanding of corrensite development is embryonic and Hillier's work provides a data-rich case study that should greatly assist future research in this area. The most significant change in composition of the corrensite/chlorite clay mineral assemblage is the increase in tetrahedral AI from corrensite to chlorite. Hillier suggests that the occurrence of corrensite in Mg-rich evaporites and carbonates is a reliable indicator of paleotemperatures in excess of 100°C.

Additional data on chlorite are provided in a review of poly type distribution by Jeff Walker. He cautions that the transition from type-I to type-II does not always occur at 200°C and indicates that type-II structures may form at temperatures as low as 135°C. More information on compositional and structural details of this diverse group and laboratory calibration are required before chlorite polytype transformations can be used as a reliable geothermometer.

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