

ZEOLITES FROM SEDIMENTARY ROCKS

This special issue on zeolites reaffirms the scope of *Clays and Clay Minerals* to present the latest advances in research concerning clays and other fine-grained minerals. The papers selected for the issue illustrate the diverse types of research being conducted on zeolite minerals and are representative of the theoretical, experimental, and field-laboratory approaches being taken. Intentionally excluded were articles concerning zeolites in igneous rocks and reports on potential applications of natural or synthetic zeolites. Like many fine-grained phyllosilicate minerals, zeolites have attractive cation-exchange, adsorption, hydration, and catalytic properties that make them ideal for use in numerous industrial and agricultural processes. The commercialization of natural zeolites, however, is still in its infancy.

Zeolites are among the most common authigenic silicate minerals in sedimentary rocks. They have been found in rocks of diverse age, lithology, and geologic setting and are valuable indicators of the depositional and post-depositional (diagenetic) environments of the host rocks. Geologically, zeolites have much in common with clay minerals, and all occurrences in sedimentary rocks are intimately associated with clay minerals or are interbedded with clay-rich strata in the same stratigraphic sequence. In fact, much of the early work on zeolites in sedimentary environments was accomplished by clay scientists (e.g., Sudo, 1950; Ross, 1928; Kerr, 1931; Keller, 1952). Some clay minerals have apparently formed during diagenesis from precursor zeolites, whereas others provided the chemical components from which zeolites formed later in the crystallization history of the rock.

Zeolites are especially common in tuffaceous rocks, and the early formation of authigenic smectite caused a modification of pervading pore fluids such that zeolites subsequently became the predominant phases to crystallize. In the following articles, W. E. Dibble, Jr. and W. A. Tiller propose a kinetic model to explain the formation and zonation of authigenic zeolites, clay minerals, and feldspar in tuffaceous rocks of saline, alkaline-lake deposits. Based on previous field-laboratory studies of these deposits by others and on considerations of thermodynamic and kinetic constraints, the authors indicate that kinetic factors may determine the specific types of authigenic silicate minerals that form and both the temporal and spatial parameters on the solution composition during irreversible dissolution and growth reactions in the tuffaceous rocks. D. B. Hawkins reports the results of the hydrothermal synthesis of clinoptilolite, mordenite, and phillipsite from natural rhyolitic glass in Na-K carbonate solutions. These results are most applicable to geothermal systems, and the rate constants derived from this investigation may contribute to our understanding of the dissolution of silicic, glassy rocks and to the kind and amount of zeolites and associated secondary silicate minerals that form.

T. H. McCulloh and coworkers report the discovery of well-crystallized laumontite that is precipitating at temperatures of 89°–43°C on alluvial boulders in Hot Springs Creek, Ventura County, California. This occurrence demonstrates for the first time that laumontite, a common zeolite in rocks subjected to burial diagenesis or burial metamorphism, can crystallize directly from solutions of appropriate composition. The concept of a depth zonation of zeolite minerals in burial diagenesis is, therefore, not necessarily valid with respect to laumontite, and the petrogenetic grid in terms of temperature and pressure may need revision.

N. G. Ratterman and R. C. Surdam characterize the diagenetic history of a thin rhyolitic tuff that was deposited in Eocene Lake Gosiute, Wyoming. They report significant differences in total mineralogy both at individual sample sites and areally throughout the deposit, testifying to the heterogeneous nature of the mineralizing pore solutions. Two stages of alteration were recognized: (1) hydration and solution of the glass by saline, alkaline solutions produced siliceous zeolites such as clinoptilolite, and (2) dehydration and sodium metasomatism occurred later and resulted in the formation of analcime from the early-formed zeolites. The sodium carbonate brines for the latter stage were apparently derived from dewatering of underlying evaporite deposits. M. W. Taylor and R. C. Surdam describe the authigenic minerals in a 10,000 year-old tuff at Teels Marsh, Nevada (a saline, alkaline-

lake deposit) and suggest that phillipsite formed from the glass through an aluminosilicate-gel precursor and that analcime formed later by reaction of the phillipsite with the interstitial brine. The latter reaction allowed the authors to calculate the free energy of formation of phillipsite. G. K. Moncure and coworkers describe the vertical zonation of diagenetic zeolites, clay minerals, feldspars, and silica minerals in Tertiary silicic tuffs at the Department of Energy's Nevada Test Site, a region undergoing intensive investigation as a possible disposal site for radioactive wastes. They attribute three diagenetic zones to: (1) changing pore-water chemistry in an essentially *closed* hydrologic system, (2) disequilibrium precipitation of metastable phases, and (3) a higher thermal gradient than that now present in the area. Of special interest is the evidence that mordenite postdates authigenic analcime and albite.

A. J. Gude, 3rd and R. A. Sheppard describe an unusual woolly form of erionite from Reese River Valley, Nevada. Although this erionite is identical in appearance to that found at the type locality near Durkee, Oregon, most erionites from other deposits are prismatic or acicular in habit. Neither chemical nor physical properties seem to distinguish the woolly erionites from other erionites; however, the chemistry of the host rock seems to influence the composition of all erionites. G. D. Knowlton and coworkers present thermal gravimetric evidence for three types of water in the zeolite fraction of clinoptilolite-rich tuffs from the Nevada Test Site that evolve at $\sim 75^\circ$, $\sim 170^\circ$, and $\sim 270^\circ\text{C}$. The three types are described as "external" water, "loosely bound zeolitic" water, and "tightly bound zeolitic" water, respectively, and can also be distinguished by their heats of hydration. Yasuhiro Shibue describes the exchange isotherms for Na-K and Na-Ca for a low-silica and a high-silica phillipsite. The free-energy affinity sequence is $\text{K} > \text{Na} > \text{Ca}$ for both zeolites, with the more siliceous phillipsite preferring the larger cation in the Na-K system and the smaller cation in the Na-Ca system.

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