Clays and Clay Minerals, Vol. 36, No. 4, 337–342, 1988.

COMPARISON OF CLAY AND ZEOLITE MINERAL OCCURRENCES IN NEOGENE AGE SEDIMENTS FROM SEVERAL DEEP WELLS

B. VELDE[1] AND A. IIJIMA[2]

[1] Laboratoire de Geologie, Ecole Normale Superieure
46 rue d'Ulm, 75230 Paris Cedex, France

[2] Geological Institute, University of Tokyo
Hongo, Tokyo 113, Japan

Abstract—Clay and zeolite mineral assemblages were determined for five deep wells in volcano-clastic sediments (Japan) and for one well in mudstones (California). The clay mineral suites in these wells showed a gradual change with depth of illite/smectite (I/S) composition, which increases in smectite content in the upper portion towards a fully expandable mineral (2–3-km depth) and then decreases in smectite content with depth (2–5 km). The temperature of transformation or recrystallization to a fully expandable smectite mineral is about 60°–70°C in non-zeolite bearing rocks and 70°–90°C in zeolite-bearing rocks, with no apparent dependence on time. Comparison is made between the I/S smectite content in the lower part of the wells (i.e., below the occurrence of the fully expandable mineral) and the zeolite mineral zone boundaries. The 60% smectite composition was found at 108°–118°C maximum burial temperatures. The zeolite II/III zone boundary, i.e., the onset of the analcime zone, occurs between 85° and 95°C and may be slightly time-related in the span of 1–15 Ma. The clay and zeolite minerals can be used as temperature indicators in the range of the Neogene age.

Key Words—Analcime, Geothermal temperature, Illite, Diagenesis, Smectite, Zeolite.

INTRODUCTION

Previous studies (Iijima and Utada, 1971; Iijima, 1986) of samples from the MITI deep drill holes in Japan have shown that the zeolite facies boundaries were essentially temperature dependent. The temperature range of the alkali zeolite-analcime boundary (zones II/III) was determined to be between 80° and 95°C based on bottom-hole temperatures. The transformation of clay minerals in pelitic sediments from deep wells in the Gulf Coast of the United States (see review by Velde, 1985), a Colorado River delta geothermal well (Jennings and Thompson, 1985), and deeply buried Plio-Miocene sediments in southern California (Ramseyer and Boles, 1986) indicate that the composition of the illite/smectite mineral (I/S) is dependent on temperature and also probably on time (i.e., length of the thermal event). Most of the detailed data in the literature come from late Tertiary to Cretaceous age sediments and rocks; few attempts have been made to compare the effects of time and temperature on the I/S clay mineralogy in younger sediments and sedimentary rocks of varied mineralogy. By using the well-established zeolite zoning as a reference, the evolution of the zeolites can be compared with that of the clays and, hence, insight into the dynamics of clay mineral transformation or recrystallization can be gained.

EXPERIMENTAL

Material studied

Cuttings and core material were investigated using X-ray powder diffraction methods of identification on the fine fraction (<2 μm) of the volcanoclastic zeolite-bearing mudstones from five deep wells in Japan and from one in a non-zeolitic mudstone in the eastern portion of the Los Angeles basin, near Whittier, California. The material from the Japanese wells was previously studied by Iijima and Utada (1971), Iijima (1986), and Tada and Iijima (1983). Wells were from the Nigata basin, Honshu; and northern and southern Hokkaido. The California well cuttings were supplied by Cities Service Company. The cuttings were hand picked to avoid detrital rock fragments, which commonly contain clays or zeolites that have not reacted with the fine-grained material of the sample to form the new diagenetic clay mineral assemblage.

Temperature measurements

Temperatures were determined by extrapolating the equilibrated bottom-hole temperature to a surface value of 15°C for the wells. Temperatures measured in the Toyokoru well were corrected for a total burial depth, assuming an erosion of 700 m of sediments. Therefore, the temperatures used for this well are the maximum values to which the sediments could have exposed (Iijima, 1986), assuming the present day geothermal gradient. At the site of the Hamayuchi well, outcropping sediments are about 4 Ma old, which gives an eroded overburden of about 200 m (Tada and Iijima, 1983). Temperatures were also corrected for this initial burial. The bottom-hole temperature in the Los Angeles basin well was measured after only 7 hr; thus, this value was corrected to be more in line with the overall gradient established for the eastern part of the Los Angeles basin

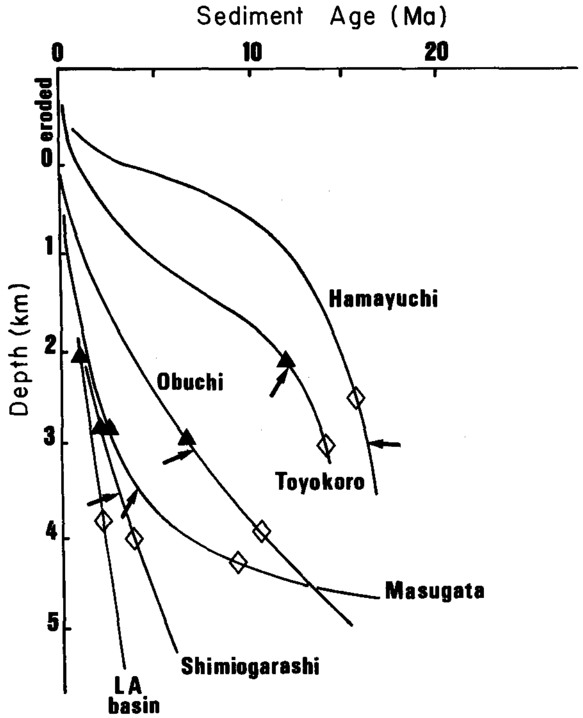

Figure 1. Representation of the sediment age and depth relations for the wells studied. Arrow = depth at which zeolite zones II/III were determined; diamonds = the depth at which illite/smectite containing 60% smectite layers was found in the lower illite/smectite mineral suites; triangles = point at which 100% smectite occurs.

(given in Philipi, 1962). This correction was made by comparing the difference in equilibrated producing and down-hole drilling temperatures given by Boles and Franks (1979) for wells in southwest Texas, where the geothermal gradient is similar. The 121°C measured temperature at 5 km depth was increased here to 140°C.

Temperatures at various points in the wells were estimated using a linear extrapolation of bottom-hole maximum temperatures to surface temperature. Some measured temperatures in mid-hole (Iijima and Utada, 1971) fall below the linear extrapolation, which suggests that the measurements at lower temperatures do not represent those of the rock, which should form a series in a slightly convex upward curve. Whatever the inaccuracies of the linear extrapolation method, they are presumably the same in all of the wells, and, thus, the temperatures used will be internally consistent and useful for comparison between the wells.

A plot of depth vs. age for the wells is given in Figure 1, and the overall gradients are reported in Table 1. The temperature for any point in the wells is estimated to be accurate within ±5°C.

Clay mineralogy

The mineralogy of the mudstones was determined for the <2-μm fraction by X-ray powder diffraction using Ni-filtered CuKα radiation. Determinations of smectite of the illite/smectite (I/S) mixed-layer mineral were made using the ratio of peak and low-angle background intensity for the 001/001 reflections of ethylene glycol-saturated samples, following the results in Reynolds (1980) for disordered, R=0 structure minerals having seven constituent layers in the crystallites. The smectite content of these minerals varied from 100 to slightly less than 40%. Duplicate preparations gave differences in estimated smectite content of as much as 7%. The R=1 ordered structure was encountered for samples having 40 to 50% smectite layers. Estimation of percent smectite was made using the method of Velde *et al.* (1986) for air-dried samples. These identification methods were used because of the low intensity of the smectite peaks at ~9A (indicating that a small number of layers is present in the crystallites) and because of the frequent interference of zeolite, mica, and quartz peaks with I/S reflections.

ZEOLITE ZONES

Estimations of zeolite zone boundaries (depth) are found in Iijima and Utada (1971), Iijima (1978, 1987, 1988) and Tada and Iijima (1983). This boundary es-

Table 1. Thermal data for seven wells in volcanoclastic sediments.

Well	Total depth (km)	Bottom-hole temperature (°C)	dt/dz[1]	dx/dt[2]
Shimoigarshi, Nigata basin, Japan	5	136	24.2	0.93
Masugata, Nigata basin, Japan	4.2	138	29.3	0.77
Obuchi, Nigata basin, Japan	5.0	150	27.0	1.3
Toyokoro, Hokkaido, Japan (corr)[3]	3.2	113	30.6	0.96
Hamayuchi, Hokkaido, Japan (corr)	4.5	128	25.1	0.60
Los Angeles basin, California (corr)	5.0	140	25.0	0.80
Colorado River delta, California				0.77

The Colorado River delta data are those reported by Jennings and Thompson (1985); depth information is not given.
[1] dt/dz = the overall thermal gradient using the linear extrapolation of the stabilized bottom-hole temperature and 15°C as the surface temperature.
[2] dx/dt = the change in smectite content (x = % smectite) as function of temperature change (°C).
[3] corr = corrected bottom-hole temperatures as discussed in the text.

sentially indicates the replacement of the alkali zeolites, predominantly sodic-potassic clinoptilolite and mordenite, by analcime and locally by heulandite. Discussions of the methods and importance of zeolite identification are found in the above papers and the studies cited therein. This zeolite zone boundary is part of the glass-to-albite transition series common in volcanoclastic materials, which gives rise to zeolites and I/S minerals. The existence of the zonal sequence depends upon the existence of glass-bearing sediments, and, thus, the sequence indicates a continuity in the abundance of such sedimentary material in the sequences penetrated by the drill holes in Japan. Boles (1971) and Iijima (1978) noted that the presence of analcime could be influenced by local variations in solution chemistry. Similarity of the temperatures at which the analcime is found in the wells suggests that such an influence is minor in the wells studied.

RESULTS

Figure 2 gives the clay and zeolite data as a function of depth in the wells and maximum temperatures to which the sediments have been exposed. The lower I/S mineral compositional sequences are delimited by trend lines which outline the data. A dashed, median trend line has been drawn to represent the over-all evolution of the clays with depth. In each series, the point is indicated at which 60% smectite I/S minerals occur. This composition has no special significance. It is used because it is the point of furthest evolution common to all of the I/S mineral sequences. Extrapolation to a 100% smectite mineral composition is made where needed, although nearly all of the sequences show a fully expandable smectite at depth.

DISCUSSION

Zeolites are present in all the Japanese wells. These minerals are due to the transformations of volcanoclastic material into the various facies or zeolite zones mentioned above. The formation of zeolites is accompanied by the crystallization and probable transformation of I/S minerals. By comparing the clay facies from these wells with those from a non-zeolitic sequence (Los Angeles basin) which has a similar age range of sediments, one can see whether or not the presence of zeolites affects the evolution of the I/S minerals.

In all wells the smectite content of the I/S minerals is variable in the upper 2–3 km. A gradual increase in the percentage of smectite layers with depth in the California well and the Japanese Obuchi and Masugata wells can be seen. In the other wells, the change in smectite content of the I/S minerals in the upper levels is more irregular. In the Japanese wells, below or near the alkali-zeolite zone boundary (2–4 km), the smectite content of the I/S decreases continuously with depth in the well. This same trend is clearly seen in the California well below 2 km depth. A similar, linear trend was also reported by Jennings and Thompson (1985) for a Pliocene well in the Colorado River delta. In this well, sediments were apparently subjected to their present thermal gradient for only a short period of time (<1 Ma).

The appearance of 100% smectite can be noted at or above the zeolite II/III zone boundary in all but one of the suites studied, but it does not coincide exactly with this boundary. In the Hamayuchi well, however, the 100% smectite stage does not seem to have been reached at all. In this well the evolution of the I/S mineral composition appears to change at about 2 km depth at an I/S composition of about 70% smectite layers. This well has penetrated essentially highly siliceous shales, which have been studied in detail by Tada and Iijima (1983). Noncrystalline or cryptocrystalline forms of silica are present in the upper part of the well, but at 1.8-km depth, the most apparent form of silica is quartz. This difference in mineralogy is probably important; the change to a quartz-rich mineralogy occurs where the clay suite begins to change, suggesting that the silica activity had an influence on the transformation of the I/S. Thus, the six wells studied are not exactly identical in their clay mineral and zeolite mineralogy, but they are similar. The clay mineralogy of the silicified shale sequence is slightly different from that in the zeolite-bearing mudstone lithologies.

Temperatures at which the I/S containing 60% smectite layers and zeolite zone II/III boundaries occur are plotted against age in Figure 3 for the various wells. Estimations of maximum temperatures to which sediments were exposed is based upon a linear extrapolation of equilibrated bottom-hole temperatures. Such a procedure does not allow for the thermal effects due to sedimentation rate, nor does it take into account the conductivity differences due to changes in sediment lithology or chemical variations due to changes in lithology.

In the wells studied here (except the Hamayuchi well) the point at which the I/S containing 60% smectite layers occurs is at nearly the same present-day temperature despite the age of the sediments in which they are found. The data scatter over a range of about 10°C, which is small considering the variability of the initial data, such as the uncertainty of the temperature estimations (±5°C) and the variation in the determination of the clay mineral composition (±7% smectite layers). The temperature range over which 60% smectite I/S occurs (10°C) is smaller than that over which the zeolite zone II/III boundary occurs (18°C). The temperature of the zeolite zone boundary is similar to that established by Iijima (1986). The differences in temperature of the zeolite zone II/III boundary in the wells do not vary significantly as a function of age; however, for the older sediments (i.e., Toyokoro and Hamayuchi wells), the zone boundary seems to be at a slightly lower tem-

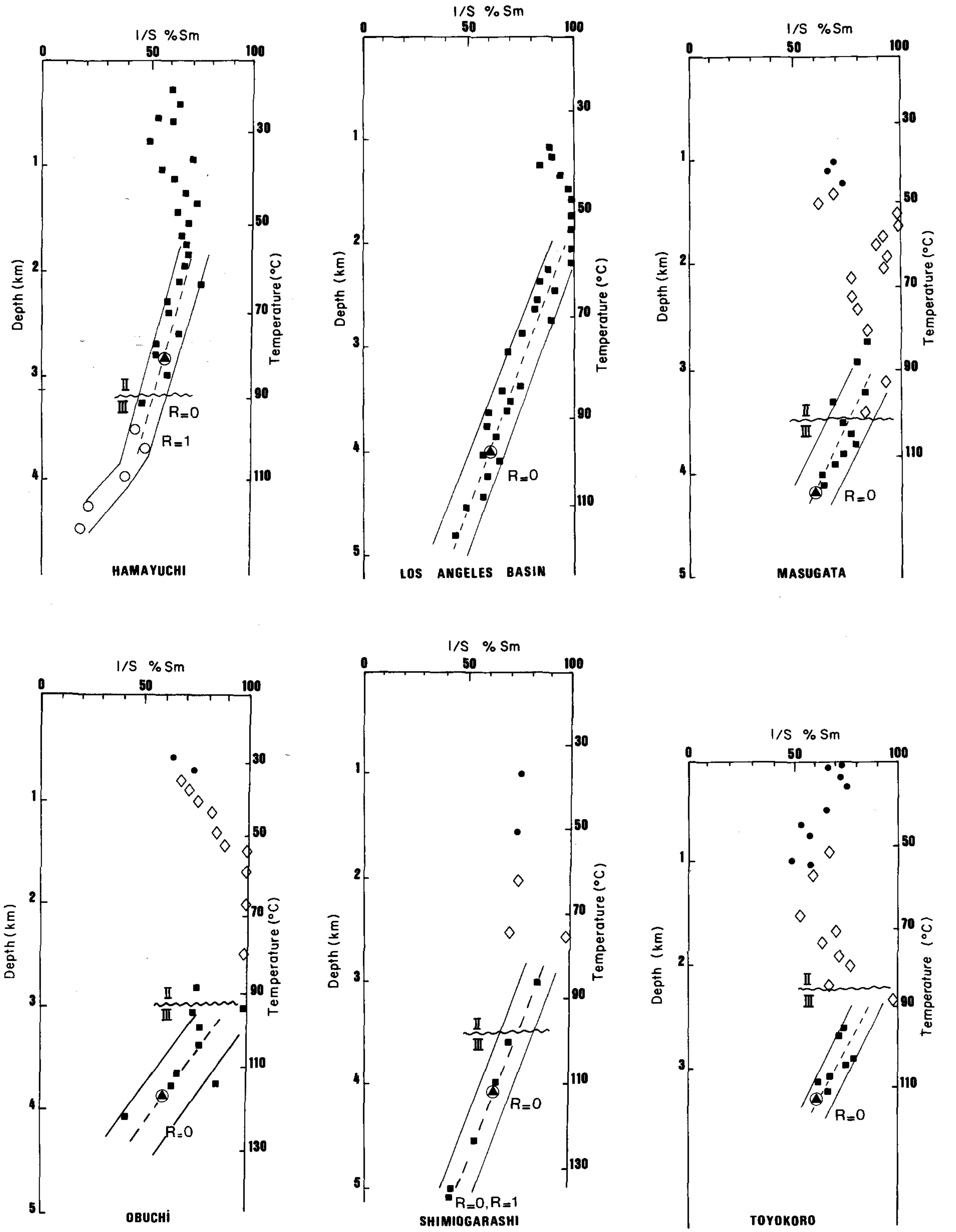

Figure 2. Plots of the smectite layer content of illite/smectite minerals and zeolite facies data. Crosses = samples containing no alkali zeolite in the 2-μm fraction of the mudstone; circles = samples with alkali zeolites; dots = samples in which glass was assumed to be present, due to a lack of zeolites in the upper levels of the wells. II/III = zeolite zone boundary as determined

https://doi.org/10.1346/CCMN.1988.0360407 Published online by Cambridge University Press

perature. The correlation of the two sets of data indicates that the smectite-layer content of I/S is dependent on temperature and independent of time in most of the wells studied. Given the possible variations in lithology (chemistry) and errors in temperature estimations, as well as the scatter in the smectite-content determinations, the evolution of the smectite-layer content of I/S and the transition in zeolite mineralogy are approximately thermally constant. Kinetics appears to have had little effect during the time scale covered in the wells studied (1–15 Ma). The temperatures at which the 100% smectite minerals were estimated to occur in mid-sequence at or above the zeolite zone II/III boundary vary from 60° to 90°C, with a slight tendency for the temperatures to be lower in the younger, deeper wells.

The change in I/S composition with depth in the upper parts of the wells to one of higher smectite content suggests that this material has recrystallized in the upper 2 km of the wells. This is important, because it is generally accepted that the smectite content of I/S decreases as a function of temperature due to the smectite-to-illite transformation (Velde, 1985). Such a sequence has been found in the lower portion of the wells studied. An explanation of the increase of I/S smectite content with temperature in the upper parts of the wells is that the initial I/S minerals are not of the same composition or type as those in the lower zones. Increasing temperature with burial changes the physical conditions, which favors a new smectite mineral that appears in mid-sequence of the drill hole. Velde and Brusewitz (1986) discussed several types of I/S mineral series in which the smectite component varies in chemical composition from one series to the other. If I/S minerals of different compositions exist in the two portions of the wells, the upper zone contains a series which is not stable at higher temperatures, and the new phases first form a 100% smectite which then transforms (smectite to illite) as temperature increases further.

The observation that the temperature at which an I/S having a specific smectite-layer content mineral forms is independent of time is important. In the Japanese, the Los Angeles basin, and the Colorado River delta wells (Jennings and Thompson, 1985), the temperature at which a given I/S mineral composition occurs is independent of time; thus no kinetic effect is apparent. Studies of the Gulf Coast sediments (see review in Velde, 1985), however, indicate that kinetics effects the transition of I/S minerals in older sediments.

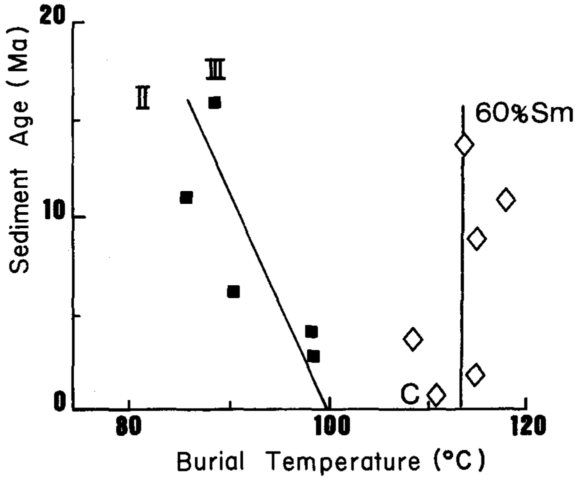

Figure 3. Plot of temperature vs. sediment age showing where illite/smectite containing 60% smectite layers was encountered (diamonds) and where the zeolite zone II/III boundary was encountered in the wells (squares). Smectite value for the Hamayuchi well is not plotted because of its anomalous position (see text). The 60% smectite layer composition point is indicated by C for the Colorado River delta well (Jennings and Thompson, 1985).

The I/S minerals found in young sediments (<15 Ma), therefore, do not behave in the same manner as those in older sediments.

CONCLUSIONS

If the estimates of the temperature of the zeolite zone boundaries are correct, a slight kinetic effect may exist in the zeolite transitions in the range 3–15 Ma. The wells containing mudstones that have ~100% smectite zone in mid-well show nearly the same temperature for the 60% smectite stage at greater depth. In the Los Angeles basin well, which has no zeolites in the clay fraction, the temperature at which I/S containing 60% smectite layers exists is the same as that in the Japanese wells below the alkali-zeolite zone. Thus, the bulk composition and/or mineralogy of the sediments do not appear to influence the authigenic I/S minerals in the absence of alkali zeolites in the fine fractions. The mineralogy of clay fraction of the siliceous shales in the Hamayuchi well, however, suggests that the very high silica activity could change the mineralogy of the I/S minerals present in a mudstone.

In summary, the smectite layer content of I/S mineral and the zeolite zone II/III boundary can probably be used as a thermal marker in young sediments (<15

←
by Iijima and Utada (1971) and Iijima (1978). See Iijima (1978) for more details on the zeolite zone determinations. Triangle = point at which average value of smectite layer content reached 60% in the lower, depth-dependent compositional series. R=0 and R=1 indicate the stacking type of the I/S minerals. Solid lines limiting the lower I/S compositions indicates limits of compositional trends and dashed line indicates the middle trend line, which is used to show the evolution of the I/S mineral composition in the lower portion of the wells.

Ma). In older sediments, the zeolites may change at lower temperatures as a function of sediment age, but the differences in temperature were less than 15°C over the age range studied. A temperature-dependent I/S mineral series forms between 60° and 90°C in the wells studied and does not appear to be related to the age of the sediment, and, thus, the time it has been subjected to temperatures higher than those during its sedimentation.

REFERENCES

Boles, J. R. (1971) Synthesis of analcime from natural heulandite and clinoptilolite: *Amer. Miner.* **56,** 1724–1734.

Boles, J. R. and Franks, S. G. (1979) Clay diagenesis in Wilcox sandstones of southwestern Texas: Implications of smectite diagenesis on sandstone cementation: *J. Sed. Petr.* **49,** 55–70.

Iijima, A. (1978) Geological occurrences of zeolite in marine environments: in *Natural Zeolites: Occurrence, Use, Properties,* L. B. Sand and F. A. Mumpton, eds., Pergamon Press, Elmsford, New York, 175–198.

Iijima, A. (1986) Volcanoclastic rocks: in *Principles and Application of Sedimentary Petrology,* K. Aoyagi, ed., Japan National Oil Corporation, Tokyo, 80–102 (in Japanese).

Iijima, A. (1987) Diagenetic transformation of minerals as exemplified by zeolites and silica minerals—A Japanese view: in *Contributions to Diagenesis,* K. H. Wolf and G. V. Chilingar, eds., Elsevier, Amsterdam (in press).

Iijima, A. (1988) Applications of zeolites to petroleum exploration: in *Zeolite: Occurrence, Properties, and Utilization of Natural Zeolites,* D. Kalló and H. S. Sherry, eds., Akadémiai Kiadó, Budapest, Hungary, 29–37.

Iijima, A. and Tada, R. (1981) Silica diagenesis of Neogene diatomaceous volcanoclastic sediments in northern Japan: *Sedimentology* **28,** 185–200.

Iijima, A. and Utada, M. (1971) Present-day zeolite diagenesis of the Neogene geosynclinal deposits in the Niigata oil field, Japan: in *Molecular Sieve Zeolites—Advances in Chemistry Series* **101,** 334–341.

Jennings, S. and Thompson, G. R. (1985) Diagenesis of Plio-Pleistocene sediments of the Colorado delta, southern California: *J. Sed. Petr.* **56,** 89–98.

Philipi, G. T. (1962) On the depth, time and mechanism of petroleum production: *Geochim. Cosmochim. Acta* **29,** 1021–1049.

Ramsayer, K. and Boles, J. R. (1986) Mixed layer illite/smectite minerals in Tertiary sandstones and shales, San Joaquim Basin, California: *Clays & Clay Minerals* **34,** 115–124.

Reynolds, R. J. (1980) Interstratified clay minerals: in *Clay Structure of Clay Minerals and Their X-ray Identification,* G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 249–303.

Tada, R. and Iijima, A. (1983) Petrology and diagenetic changes of Neogene siliceous rocks in northern Japan: *J. Sed. Petr.* **53,** 911–930.

Velde, B. (1985) *Clay Minerals: A Physico-chemical Explanation of Their Occurrence:* Elsevier, Amsterdam, 427 pp.

Velde, B. and Brusewitz, A. M. (1986) Compositional variation in component layers in natural illite/smectite: *Clays & Clay Minerals* **34,** 651–657.

Velde, B., Suzuki, T., and Nicot, E. (1986) Pressure-temperature-composition of illite/smectite mixed-layer minerals: Niger delta mudstones and other examples: *Clays & Clay Minerals* **34,** 435–441.

(Received 10 August 1987; accepted 1 February 1988; Ms. 1706)