RELATIONSHIPS BETWEEN AUTHIGENIC MINERAL TRANSFORMATION AND VARIATION IN VITRINITE REFLECTANCE DURING DIAGENESIS: AN EXAMPLE FROM THE TERTIARY OF NORTHERN KYUSHU, JAPAN

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ABSTRACT: The Tertiary sequences in northern Kyushu, Japan, contain several types of zeolite and clay minerals together with carbonaceous materials. A correlation between authigenic mineral zones and vitrinite reflectance reveals the delay in mineral authigenesis relative to the increase in vitrinite reflectance compared with similar studies in other regions. This may be ascribed to causes such as high paleo-geothermal gradient, and chemical composition of pore-waters and host sediment.

Transformation of minerals and organic materials in sediments during diagenesis has recently been studied in considerable detail, particularly since the pioneering work on zeolites by Coombs (1954). During the past decade, correlation among organic and inorganic indicators of diagenesis has become a central interest of researchers (e.g. Kisch, 1969; Castañó & Sparks, 1974; Shimoyama & Iijima, 1977). The results of these studies reveal that mineral zones and coal rank classifications correspond differently with each other in respective localities.

In the northern part of the island of Kyushu, Japan, tuffaceous sediment-coal associations are well developed throughout a number of Tertiary sedimentary basins. It is, therefore, an attractive region to study the relationships between organic and inorganic diagenesis. This paper describes the distribution of zeolites and clay minerals in the Tertiary sedimentary rocks of northern Kyushu, together with the variation of vitrinite reflectance of associated carbonaceous materials. The correlation between indicators of organic and inorganic diagenesis and its related problems are discussed.

GEOLOGICAL SETTING

The Paleogene and Miocene sedimentary sequences are exposed in 13 separate basins in the northern part of Kyushu (Fig. 1). In the area studied, the Tertiary occurs at six localities: numbers 1 to 6 in Fig. 1. The sequences consist of conglomerate, sandstone and shale with frequent intercalation of coal. Tuffaceous sandstone and tuffaceous shale are also often intercalated. The sequences in area no. 3 (Tsuyazaki), which consist of coarse grained facies deposited in the marginal area of the basin, are the youngest in the area studied. The sequences in area no. 4 (Osahima) which contain a coal seam might have been deposited near the land area. The observable thickness of the sequences changes markedly from 30 m
in area no. 4 (Oshima) to nearly 1000 m in area no. 2 (Kasuya). This change in the thickness of the sequences was also recognized in other basins of Kyushu, and may be due to a difference in sedimentary conditions from basin to basin (Matsushita, 1949). The sequences, from which no animal fossils have been discovered, are the products of fluviatile to shallow marine sedimentation.

METHODS

Tuffaceous shale samples were selected for clay mineral investigation. Oriented samples of the fine fraction (<2 mm) mounted on glass slides were studied by X-ray diffraction (XRD) using Ni-filtered Cu-Kα radiation. Ethylene glycol and glycerol treatments were also performed to determine the amounts of smectite layers in illite-smectite (I-S) mixed-layer minerals using visual inspection methods (MacEwan et al., 1961) of X-ray diffractograms.

Tuffaceous shale, tuffaceous sandstone, and a small number of black shale samples were subjected to heavy-liquid separation to concentrate zeolites which were identified by XRD. Macro- and microscopic observations reveal the zeolites to exist as small spots and/or fine grains in the cement. Discrimination between heulandite and clinoptilolite, both of which show similar XRD patterns for non-treated specimens (Mumpton, 1960; and others), is based on the results of the following heating experiment (Miki & Nakamuta, 1985).

Clinoptilolite: X-ray peaks show no change after heating at 550°C for 16 h. Heulandite type 2: a peak of phase A at 9-1 Å becomes weak after heating at 550°C for 16 h, and a new peak of phase B at 8-3 Å appears after heating at ~300°C. Heulandite type 1: a peak of phase A at 9-1 Å vanishes after heating at 550°C for 16 h, and a peak of phase B at 8-3 Å appears after heating at 220-280°C. The heating response of heulandite type 2 is intermediate between heulandite type 1 and clinoptilolite.

Some selected coal and coaly shale samples were used for measurement of vitrinite reflectance with a Leitz Ortholux microscope in polarized light. During the measurement the polarizer was kept at an azimuth of 45°. The maximum reflectance values in oil were obtained by rotation of the stage for 100 vitrinite grains per sample.
RESULTS

Clay minerals

Smectite is the main clay mineral constituent except in areas 3 and 4 where I-S mixed-layer minerals predominate (Fig. 2). The amounts of smectite layers in the interstratified I-S in area no. 3 decrease from 90 to 40% (Nakamuta, 1976). Mixed-layer minerals from area

Fig. 2. Distribution of authigenic minerals and variation in vitrinite reflectance (R max %). Samples collected from respective areas are shown by the marks indicated with the numbers in each column. In each column, very thin tuffaceous layers are omitted. Each section is arranged relative to diagenetic grade from top to bottom. Solid lines connecting the various sections show the stratigraphic correlation lines. The rates of increase of reflectance with stratigraphic thickness are great in area no. 3 and small in areas 1, 2, 5 and 6.
no. 4 contain 50% smectite. Kaolin and chlorite minerals occur sporadically throughout the areas.

Zeolites

Several varieties of zeolites including clinoptilolite, heulandite type 2, heulandite type 1, analcime and laumontite can be identified in stratigraphically descending order in respective localities. This stratigraphic occurrence reflects the diagenetic transformation series of zeolites (Coombs, 1954; Iijima & Utada, 1971; and others). Throughout the areas studied, the zeolite zone boundaries cut across the stratigraphic boundaries, and zeolite diagenesis increases regionally toward the NW, independently of the geological ages of the sequences (Miki & Nakamuta, 1985). A relationship between the occurrence of the zeolite varieties and the facies types can not be recognized.

Silica minerals

Silica minerals are fully converted, for the most part, to quartz. Opal-CT has only been found in two samples from area no. 5, and is considered to be the metastable relict of other precursor silica phases.

Vitrinite reflectance

Vitrinite reflectance values increase stratigraphically downward in each locality, and regionally northwestward throughout the area. The values remain around 0.7% in area no. 2, and attain the highest reflectivity value of 1.4% in the northwesternmost area no. 4. The rates of increase in reflectance with stratigraphic thickness are small (0.08–0.5%/km) in the southeastern areas, and great (1.2%/km) in the northwestern locality.

The above data from the six localities are summarized in Fig. 2, based not on stratigraphic age, but on diagenetic grade.

DISCUSSION

During diagenesis, clay minerals follow the transformation pathway from smectite through I-S mixed-layer minerals to illite (Dunoyer de Segonzac, 1970; and others). Accompanying this transformation, zeolite assemblages change as follows: volcanic glass, clinoptilolite + mordenite, heulandite + analcime, laumontite + analcime, and albite. These assemblages correspond to the zones I, II, IIIa, IIIb and IV, respectively, of Iijima (1975). Silica minerals change from opal-A through opal-CT to quartz. The reflectance values of carbonaceous materials increase with progressive diagenesis.

The results indicate that the sequences studied belong to the clay mineral zones of smectite to the early stage of mixed-layer minerals, the zeolite zones of clinoptilolite to laumontite, and the quartz zone. Such zones correspond to the mineral zones II to IIIb of Iijima (1975) and D to G of Aoyagi & Kazama (1980).

Both the organic and inorganic indicators of diagenesis show a stratigraphically downward increase in the degrees of diagenesis in each separate basin. Comparison of the diagenetic grade among the basins proves that the diagenetic boundaries regionally intersect the stratigraphic boundaries (Fig. 3). The stratigraphically youngest sequences in
area no. 3 show the second highest degree of diagenesis in the areas. The diagenetic grade increases northwestward throughout the area studied, and the regional arrangement of zeolite zones extending in a ENE–WSW direction is clearly recognized. Judging from the litho-facies indicating the sedimentation in the marginal area of the basin, it is considered that the original sequences in areas 3 and 4 were not significantly thick. The rates of increase in reflectance with the thickness of the sequences (paleogeothermal gradients) are greater in the NW area than in the SE areas. A regional increase in the degree of diagenesis offshore has been recognized not only in the northern Kyushu region, but also in the SW and W parts of Kyushu (Miki, 1988). Although the higher coalification gradient in the NW part of the region may be explained by a different degree of coalification (e.g., Robert, 1985), the systematic increase in the degree of diagenesis offshore in combination with the higher gradient may indicate that this degree of diagenesis was attained by burial diagenesis at each locality, and by additional heat supply from a high paleotemperature zone situated NW of the investigated land areas. These results suggest the existence of a high palo-heat flow zone off the northwestern coast of Kyushu, which may be the result of the opening of the Sea of Japan since the Tertiary.

In the area studied, the boundary between the clinoptilolite zone (clinoptilolite) and the analcime zone (analcime + heulandite + laumontite) corresponds to a vitrinite reflectance of 0-65%. The first appearance of laumontite is associated with coaly samples having reflectance values of ~1-1%. The boundary between the smectite zone and the mixed-layer minerals zone should be placed at a reflectance level of ~0-9%.

Kisch (1987) reviewed the correlation between zeolite zonation and coal rank in many localities of the world. According to his results, the appearance of laumontite is associated with coals having reflectance values ranging from 0-36–1-3%.

Fig. 4 shows the relationship between vitrinite reflectance and mineral zones for five sections including the area studied. Although laumontite occurs only sporadically in the Neogene sequences in Hokkaido and northern Honshu, the lower part of the analcime zone can be correlated to the laumontite-analcime (IIIb) zone. This clearly indicates that
laumontite appears at a remarkably higher coalification rank in northern Kyushu than in the other areas. The appearance of laumontite with low reflectance values in California is ascribed to the brief duration of burial (Kisch, 1987). The different vitrinite reflectance values associated with laumontite formation in the two Californian localities is ascribed to load pressure against fluid pressure, and differences in the permeability of the rocks (Castaño & Sparks, 1974; Kisch, 1987).

The results presented indicate that laumontite appears in association with markedly different coal ranks (Fig. 4). Obviously, the factors influencing diagenesis varied in the respective areas. Vitrinite reflectance increases as a function of paleotemperature and time of heating (Bostick, 1973; and others). A higher coalification rank in northern Kyushu is attributed to high paleotemperature due to additional heat supply. Mineral transformation and neoformation may be affected by various factors other than temperature such as chemical composition of the pore-waters and host sediment, permeability of the rocks, overburden pressure, etc. (Aoyagi & Kazama, 1980; Vavra, 1989; and others). As the lithology of the sequences studied is not remarkably different in the various areas, permeability during diagenesis might not have been significantly different amongst them. Zeolites from northern Honshu are rich in Na as represented by an abundance of analcime, whereas zeolites from northern Kyushu are rich in Ca as shown by the occurrence of

![Figure 4](image-url)

**Fig. 4.** Relationships between vitrinite reflectance and mineral zones in Hokkaido (Borehole MITI “Hamayuchi”; Sasaki et al., 1982), northern Honshu (Borehole MITI “Ohbuchi”; Sasaki et al., 1982), northern Kyushu (this study), and California (Castaño & Sparks, 1974). G: volcanic glass zone; Cl: clinoptilolite-mordenite zone; An: analcime zone; Ab: albite zone; S: smectite zone; I-S: illite-smectite mixed-layer minerals zone. A circled L indicates the first appearance of laumontite. In the two columns of Hokkaido and northern Honshu, the lower parts of the analcime zone correspond to laumontite-bearing horizons in other columns. A zone bounded by two broken lines in northern Kyushu contains heulandite type 2, which is an intermediate phase between clinoptilolite and heulandite type 1. Vitrinite reflectance values are indicated by $R_\text{max}$ in the northern Kyushu column, and $R_0$ in other columns.
heulandite and laumontite. It is possible that the mineral transformation was influenced by this difference in the chemical composition of the source materials and pore-waters, and the mineral transformation was delayed in northern Kyushu.

Kisch (1987) pointed out that the conversion of smectite to I-S mixed-layer minerals with <70% smectite layers usually takes place in association with reflectance values of 0.45-0.65%. The examples from Hokkaido and northern Honshu (Fig. 4) coincide with this range. He also reported the conversion at higher reflectance values in areas with high geothermal gradients. In area no. 3 (northern Kyushu) the paleo-geothermal gradient must have been high, judging from the greater rate of increase in reflectance with the thickness of sediments. In this area, the conversion of smectite to mixed-layer minerals took place at a reflectance level of ~0.9%, in good agreement with Kisch's (1987) data. A similar conversion for zeolites may be possible.

The correlation between indicators of organic and inorganic diagenesis of the Tertiary formations in the present areas is summarized in Fig. 5 in relation to the generation of oil. In this figure, the data for highly advanced diagenesis are from the Tertiary in the Amakusa area (~150 km SW of the regions described), where I-S mixed-layer minerals and illite occur (Miki, 1978), and zeolites are rarely found. Vitrinite reflectance values are >2.0% (Miki & Tashiro, 1979). It should be noted that northern Kyushu is peculiar in that there is a delay in authigenic mineral transformation after organic diagenesis. This peculiarity is ascribed to many causes including the high paleo-geothermal gradient and a difference in the chemical composition of pore-waters and host sediment. The high paleo-geothermal gradient may be due to a high paleo-heat flow around northern Kyushu (Uyeda & Hōrai, 1964), and may relate to the opening of the Sea of Japan. The present study demonstrates that the northern Kyushu region is suitable for comparative research on organic and inorganic diagenesis of sediments.
CONCLUSIONS

A study of organic and inorganic diagenesis of the Tertiary sequences in northern Kyushu, Japan has revealed that the degree of diagenesis observed was attained by a combination of burial diagenesis in each basin and additional heat supply from a high paleotemperature zone to NW of the area. The correlation between indicators of organic and inorganic diagenesis has been established, indicating a delay after organic diagenesis before inorganic diagenesis occurred. This is unusual compared to similar studies in other areas, and is ascribed to causes such as a high paleo-geothermal gradient and a difference in chemical composition of pore-waters and host sediments. High paleo-geothermal gradient, which may be related to high heat-flow conditions in the area, is ultimately ascribed to the geological situation of the area at the continental margin.

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REFERENCES

Mineral transformation and vitrinite reflectance


