

SMECTITE DIAGENESIS IN NEOGENE MARINE SANDSTONE AND MUDSTONE OF THE NIIGATA BASIN, JAPAN

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Abstract—Illitization of smectite during progressive burial diagenesis occurs differently in sandstone and mudstone, which are interbedded in the sedimentary sequence of the Niigata basin. Reaction progress of illitization of smectite via mixed-layer illite-smectite (I-S) in the mudstone is more complete than in the sandstone. In sandstone, smectite converts to (Reichweit, $R \geq 3$) I-S and illite via random ($R = 0$) I-S to ordered ($R = 1$) I-S, and authigenic chlorite and quartz form as products of the illitization of smectite.

The original composition of detrital smectite and the occurrence of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Fe^{2+} in pore fluids partly control both illitization of smectite and the resulting authigenic mineral products in the diagenetic process. In mudstone, detrital smectite is K- and Si-rich in composition, and the illitization of smectite indicates that the original composition is mostly inherited. Excess silica owing to illitization is released to produce authigenic quartz. In sandstone, smectite forms primarily by precipitation. The evolving compositions produced by early illitization form smectite, then random ($R = 0$) I-S, and then ordered ($R = 1$) I-S. These transitions are related to compositions of pore fluid. Changes in $\text{K}/(\text{K} + \text{Ca} + \text{Na})$ vs. $\text{K} + \text{Ca} + \text{Na}$ imply that the increase of interlayer cations occurs by absorption and smectite transforms to random ($R = 0$) I-S, followed by the exchange of interlayer cations to ordered ($R = 1$) I-S with increasing diagenetic grade. Late illitization from ($R = 1$) I-S to $R \geq 3$ suggests decomposition of smectite and early I-S with an increase in the number of illite layers. Dissolution experiments of host rocks with pure water and 0.01 M HCl solution reflect the differences in chemistry of the original pore fluid and authigenic carbonate in the process of diagenesis of clastic rocks. These results explain how chemical composition produces large variations in transformation temperature of smectite to illite in the diagenetic process.

Key Words—Authigenic Chlorite, Diagenesis, Illitization, Mixed-Layer Illite-Smectite, Pore Fluid, Smectite, Smectite-Illite Transformation.

INTRODUCTION

Illitization of smectite has been investigated in many sedimentary basins. For example, the percentage of smectite layers in smectite-illite interstratification is often used as an indicator of burial diagenetic grade and temperature (*e.g.*, Burst, 1959; Hower *et al.*, 1976; Lindgreen, 1991; Velde, 1995). However, because the measured differences are not simply a function of temperature alone (Howard, 1981; McCarty and Thompson, 1991), these differences may result in a misinterpretation of the geothermal history of the studied region without additional information about illitization. For example, the rates of illitization are different for mudstone and sandstone, even if both exist in the same sedimentary basin and both have similar burial temperature and pressure conditions (Boles and Franks, 1979; Bruce, 1984; Velde and Ijima, 1988; Freed and Peacor, 1992; Pollastro, 1993). Many factors affecting the transformation of smectite to illite during diagenesis have been identified, including temperature, pressure, reaction time, chemical composition of the detrital smectite, K^+ availability and content in host rocks, other active cation and anion components in strata fluid, organic materials, *etc.* (Inoue, 1991; Lind-

green, 1991). Among these, some change continuously with burial depth such as temperature, pressure, and reaction time, and these are called “continuous” factors; whereas the others have no relation with burial depth and are recognized as “discontinuous” factors, *e.g.*, chemical composition. The stable conditions for some clay minerals were specified by Weaver (1989). Disequilibrium between the original smectite and variable thermodynamic conditions, such as temperature and pressure, acts as the driving force in the transformation to illite, chlorite, or other minerals (Perry and Hower, 1972; Eberl and Hower, 1976; Pytte and Reynolds, 1989; Yoshimura, 1994). In a sedimentary sequence, however, the differences in temperature and pressure are negligible for sandstone and mudstone that coexist. Moreover, a mineral assemblage can be metastable with respect to temperature and pressure only slightly away from equilibrium conditions (Bloss, 1994). Thus, the continuous factors, such as temperature and pressure, are not the most important parameters in producing illitization in two coexisting sedimentary-rock types (Sucha *et al.*, 1993). The amount and type of the chemical components can also promote or inhibit the reactions at certain temperatures and

pressures (Hower *et al.*, 1976; Aagaard and Jahren, 1992). These chemical-composition factors can not be neglected.

We found differences in illitization from smectite in interbedded sandstone and mudstone in the Niigata basin in unpublished research, which we initially attributed to experimental error. However, further study has revealed that these differences probably result from other factors. Systematic sampling and analyses were performed to identify these factors and the present paper reports the results. We found that chemical-composition factors are especially important in the illitization process in the Niigata basin.

EXPERIMENTAL

Geologic background

The Neogene Niigata basin, which is a backarc basin, is located onshore along the Sea of Japan along the main island of Japan (Figure 1). Most of the oil and gas fields in Japan are in this basin (Kikuchi *et al.*, 1991). The basement rocks are Paleozoic metamorphic and nonmetamorphic rocks and Cretaceous granitic rocks. The largest thickness of the Neogene section probably exceeds 7000 m in this basin. The Neogene sections, ranging in age from Miocene through Pleistocene, are divided in ascending order into the Mikawa Group, the Tsugawa-Nanatani, Teradomari, Shiiya, Nishiyama and Haizume Formations, and the Uonuma Group. During the early Miocene to early middle Miocene, volcanic rocks were laid down. Some of these rocks are called "green tuffs" because of their green color, and they are covered by black or siliceous marine mudstone of the Nanatani and Teradomari Formations that were deposited in a stagnant marine environment. The source rocks for oil and gas are probably these mudstone of middle Miocene age. The Shiiya and Nishiyama Formations consist mostly of marine siliciclastic rocks, including turbidite sandstones. The Haizume Formation and Uonuma Group consist of shallow marine and fresh-water siliciclastic rocks. In the Niigata basin, major folds and associated faults have north-northeast to south-southwest trends.

Samples

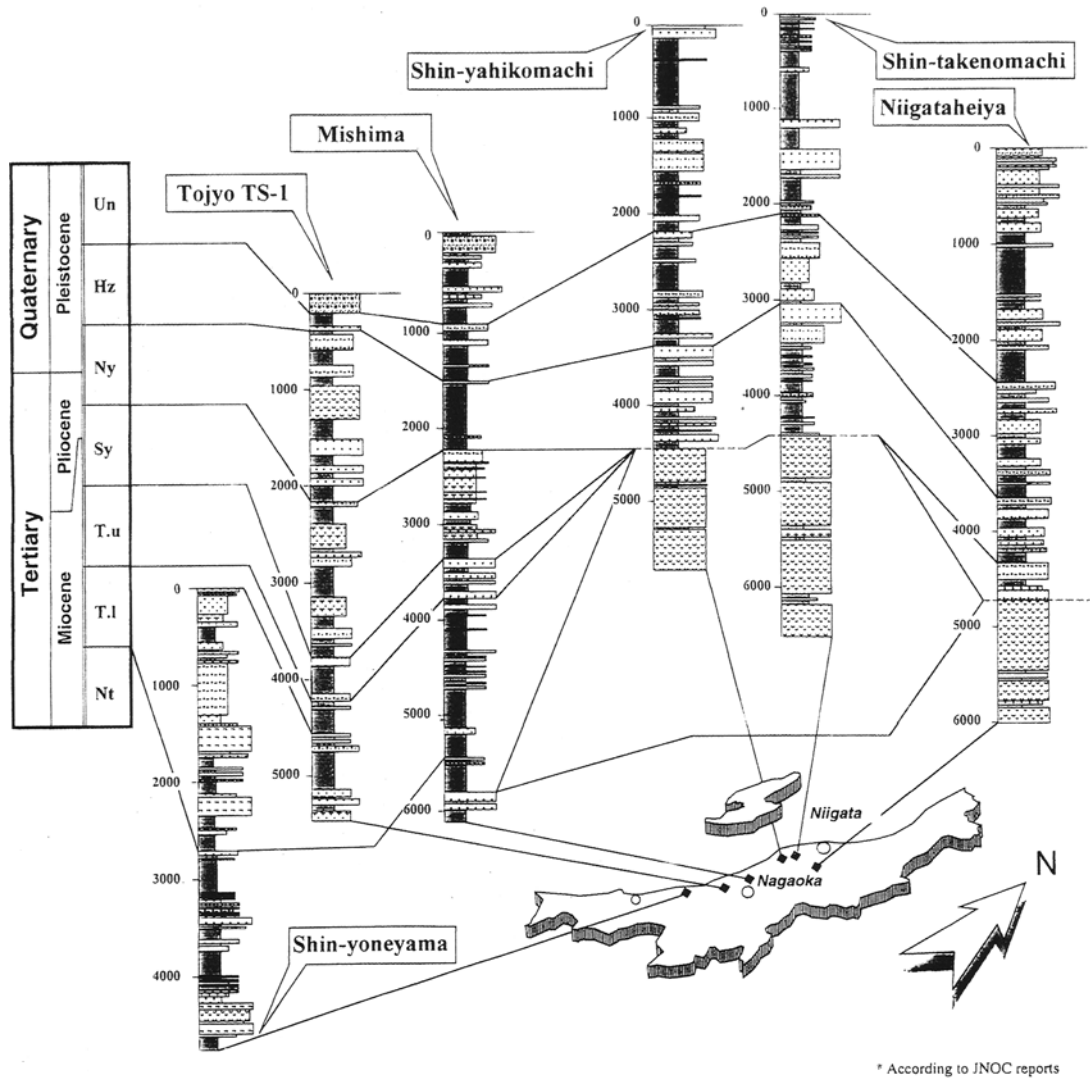
Samples were taken from the cores and cuttings of four exploration wells of Japan National Oil Corporation (JNOC) [which are also referred to as MITI (Ministry of International Trade and Industry) exploratory test wells], MITI Mishima, MITI Shin-yoneyama, MITI Niigataheiya, and MITI Shin-takenomachi wells, one well of the Teikoku Oil Co., Ltd., Shin-yahikomachi, and one well of the Japan Petroleum Resources Exploitation Co., Ltd. (JAPEX), Tojyo TS-1. Of these, the maximum depth of the exploratory wells is 6310 m at the Shin-takenomachi well. The recovered stratigraphies are from the middle Miocene Nan-

atani Formation to the Pleistocene Uonuma Group, and they are mainly interbedded mudstone and sandstone, as well as some intercalated strata of thin tuff, lava, and pyroclastic beds (Figure 1). The three wells in the northern part of the Niigata basin, Niigataheiya, Shin-yahikomachi, and Shin-takenomachi, have a thick sequence (>4000 m) of Pleistocene and upper Pliocene clastics. These wells lack upper Miocene sediment and a part of the Pliocene sediments. The average thermal gradient is 2.88–3.14°C/100 m in the Shin-yahikomachi, Shin-takenomachi, and Niigataheiya wells (Figure 2). In contrast, the three wells in the southern part of the basin, Mishima, Shin-yoneyama, and Tojyo TS-1, have Pleistocene and upper Pliocene sediments <2000 m in thickness, but a thick Miocene clastic section is present. In the Mishima, Shin-yoneyama, and Tojyo TS-1 wells, the average geothermal gradient is 3.31–3.58°C/100 m. The maximum measured temperature of 226.2°C was recorded in the Mishima well.

These samples range in geologic age from the middle Miocene Nanatani Formation to the Pleistocene Uonuma Group. Samples of sandstone and mudstone were sampled in pairs at the same depth and at similar intervals.

Methods

Samples of sandstone and mudstone were hand picked from cores and cuttings, crushed in a mortar, and then disaggregated in deionized water with an ultrasonic shaker. The <2- μm size fraction of each sample was separated by settling and centrifugation method. The <0.5- μm and <0.1- μm fractions of some samples were separated for X-ray diffraction (XRD) comparisons. Oriented clay-particle specimens were prepared by pipetting the suspension onto a glass slide and air-drying at 25°C for 24 h. At least 30 min before measuring by XRD, liquid ethylene glycol (EG) was applied directly to the oriented clay-particle specimen. The results were similar to those of an air-dried slide solvated with EG for 6 h at 60°C in a closed vessel (Reynolds and Hower, 1970). Based on the XRD patterns, the clay-mineral assemblage of the <2- μm fraction consists of illite-smectite (I-S), discrete illite, chlorite, and quartz (Figure 3). The peak profile fitting and deconvolution of XRD patterns were simulated (Figure 3d) by JADE (Materials Data, Inc., 1991). I-S interstratifications were identified by comparing the deconvolution patterns with patterns calculated using NEWMOD (Reynolds, 1985). The diagram of Watanabe (1988) was used to determine the ordering type (Reichweite, R) and the percentage of nonexpandable (illite) layers of the I-S (Figure 4). The compositions of clay minerals were also analyzed by energy dispersive spectrometry (EDS), in both a transmission electron microscope (TEM), and a scanning electron microscope (SEM).



* According to JNOC reports

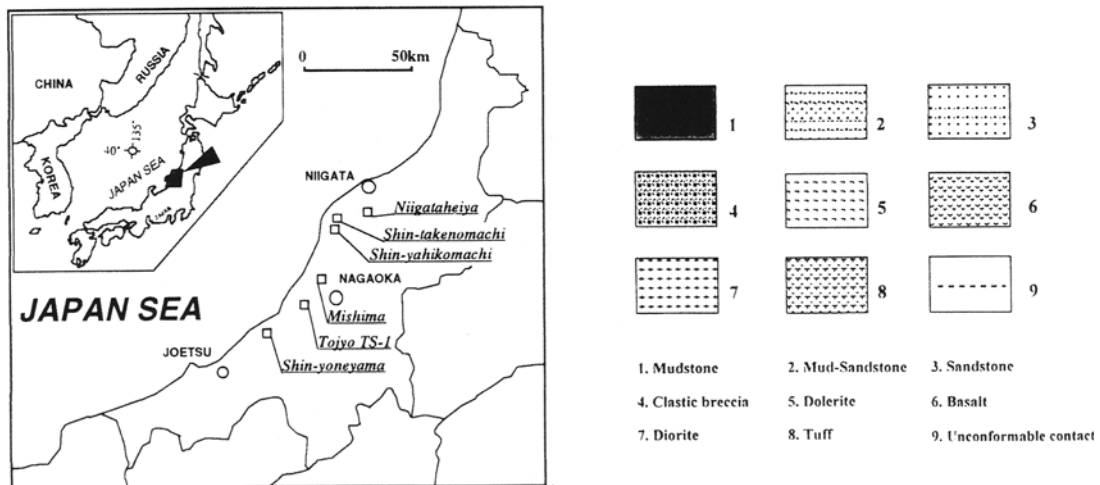


Figure 1. Location map and studied well positions: Mishima, Tojo TS-1, Shin-yoneyama, Shin-yahikomachi, Shin-takenomachi, and Niigataheiya in the Niigata basin, Japan. Shin-yahikomachi, Shin-takenomachi, and Niigataheiya wells have an unconformity, with Shiya Formation and the Upper and Lower Teradomari Formations missing. Abbreviations: Un = Uonuma Fm.; Hz = Haizime Fm.; Ny = Nishiyama Fm.; Sy = Shiya Fm.; Tu = Teradomari Upper Fm.; Tl = Teradomari Lower Fm.; and Nt = Nanatani Fm.

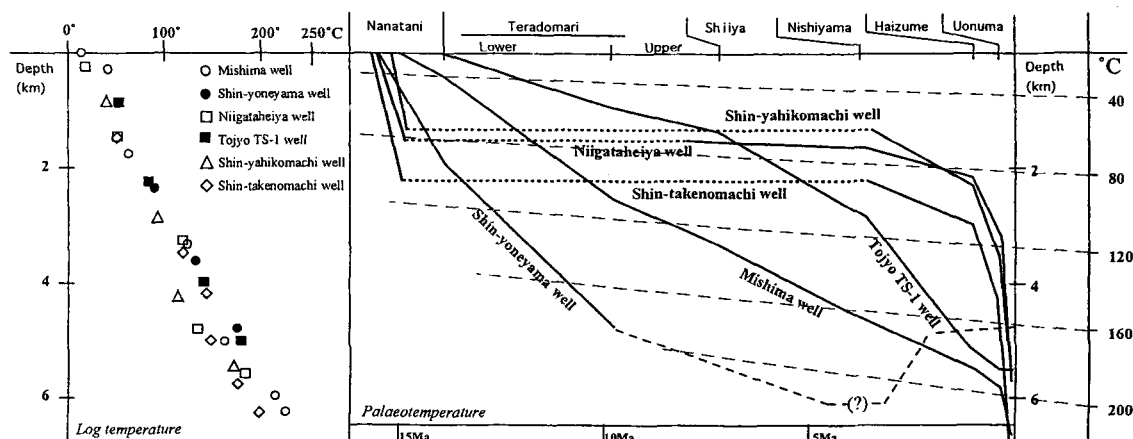


Figure 2. Superimposed plots of depth vs. observed temperature. The highest temperature is 226.3°C in the Mishima well. The relation between the geologic age vs. depth and paleotemperature of the bottom stratum of the wells is given.

Bulk chemical composition of rocks was determined by X-ray fluorescence (XRF) analysis. Samples were also analyzed for exchangeable cations and to obtain the chemistry of authigenic carbonates, since these chemistries are related to pore fluids and diagenesis. The solutions were prepared as follows: 10 g of powdered sample were suspended in 100 mL of pure water and 100 mL of 0.01 M HCl solution, then the mixture was placed in an ultrasonic shaker at 50–60°C for 24 h. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Fe^{2+} cations contained in the resultant solutions by filtering the mixture were analyzed using ion chromatography.

RESULTS

The obtained I-S ratios are given in Figures 3 and 5. As mentioned above, the sedimentary sequences to the south and north of the Niigata basin are different, so they are discussed separately.

Wells from the south area

Shin-yoneyama well. Samples were obtained from the Miocene Teradomari Formation, which is present at depths of >50 m. Illitization in sandstone reveals the following stepwise progression with depth: smectite and random ($R = 0$) I-S are found in samples from depths of <800 m; ordered ($R = 1$) I-S with 70% illite layers occurs from 800 to 1300 m; ($R \geq 3$) I-S with 85% illite occurs from 1400 m to the bottom of the well. In mudstone, the illitization of smectite is the same as that in sandstone in the portion <800 m, however, ($R \geq 3$) I-S with >80% illite layers is present in samples from depths of >800 m without the intermediate phases.

Mishima well. In the upper 3500 m portion of this well, the illitization of smectite is similar to the Shin-yonayama well. Smectite, detrital illite, and chlorite are in the Pleistocene to upper Miocene strata with the depth of <3000 m; random ($R = 0$) I-S is present from

3000 to 3500 m and within the lower Shiiya Formation. However, the illitization of smectite is different in the interbedded sandstone and mudstone in portions deeper than 3500 m. In sandstone, ordered ($R = 1$) I-S is present from depths of 3500 to 5000 m and within the upper and middle Teradomari Formation. In addition to the illitization of smectite, abundant authigenic chlorite is recognized also (Figure 6). Other secondary minerals include calcite, dolomite, glauconite, pyrite, and minor kaolinite, as identified from thin section and XRD analysis. ($R = 3$) I-S is present in samples from depths of 5000–5800 m and ($R > 3$) I-S from 5800 m to the bottom of the well in the lower Teradomari and Nanatani Formations. In mudstones, however, ($R = 1$) I-S occurs at depths ranging from 3500 to 3800 m; ($R \geq 3$) I-S occurs in samples >4100 m.

Tojyo TS-1 well. Sandstone samples contain smectite and random ($R = 0$) I-S at depths of <3800 m in the lower Shiiya Formation, ordered ($R = 1$) I-S from 4400 to 4800 m in the Teradomari Formation, and ($R \geq 3$) I-S at 5200 m near the base of the lower Teradomari Formation. In mudstones, the I-S transformation from $R = 0$ to $R > 3$ occurs between 3800–4400 m, and ($R > 3$) I-S persists to the bottom of the well.

In summary, smectite-illite interstratification in sandstone is a slow, progressive reaction from smectite to random ($R = 0$) I-S, then through ordered ($R = 1$) I-S to ($R \geq 3$) I-S. In contrast, illitization of smectite in the mudstone is a more rapid transition completed in a small interval of depth. Based on the I-S sequence, the sedimentary strata are divided into four zones: smectite, random ($R = 0$) I-S, ordered ($R = 1$) I-S, and ($R \geq 3$) I-S and illite zones.

Typical analytical data (EDS) and calculated formulae of smectite and illite are listed in Table 1, with formulae given on the basis of 11 oxygen atoms in the 2:1 layer, $(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$. The variation in I-S chemical composition of the formula unit in sandstone

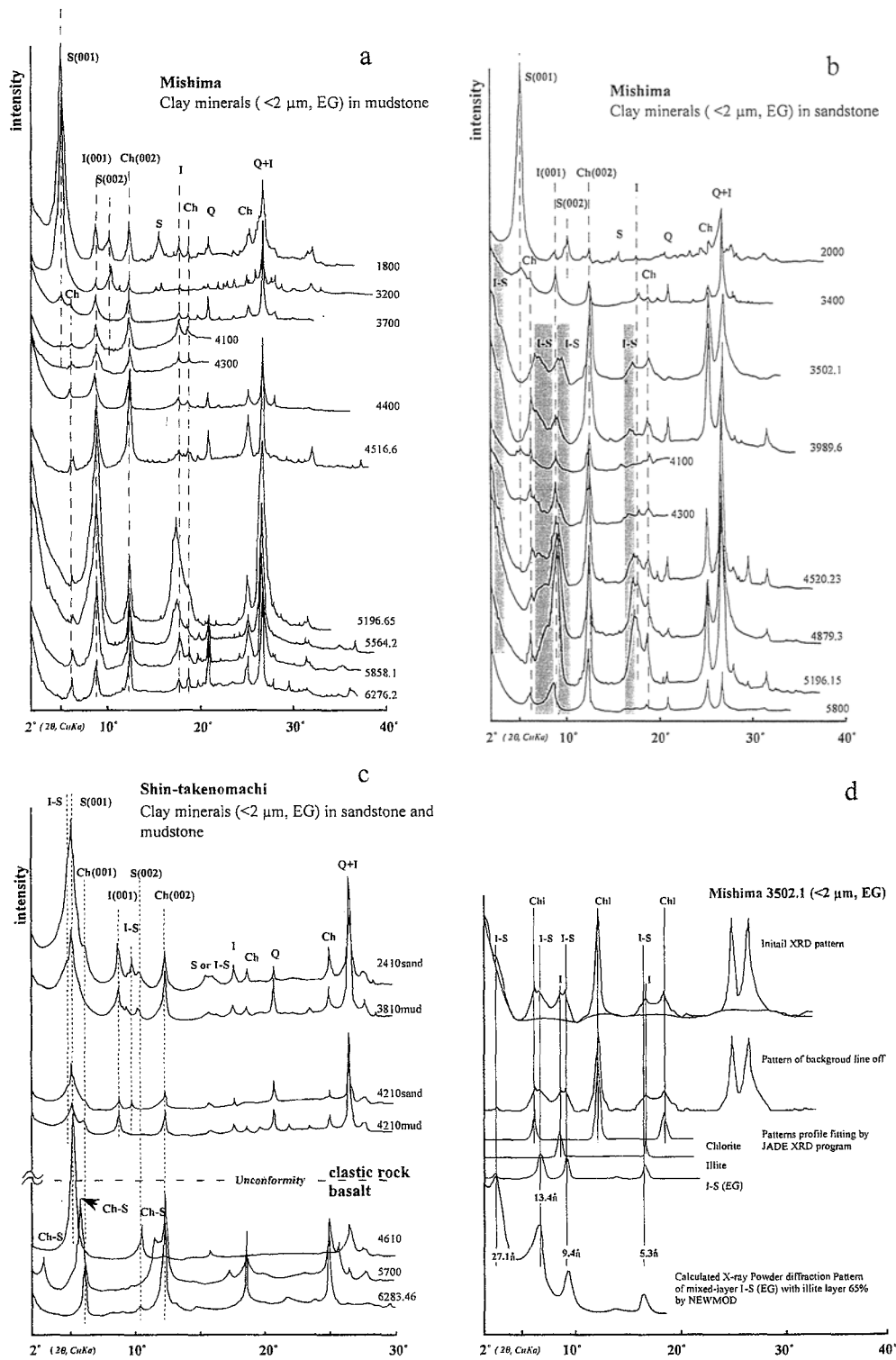


Figure 3. Powder X-ray diffractograms of EG mixed-layer clay minerals (<2- μ m size fraction) from the sandstone and mudstone in the Mishima well. (a) In the sandstone, I-S conversion requires a longer time interval from the random, $R = 0$ ($I < 20\%$) to ordered, $R = 1$ ($I = 40\text{--}65\%$) to $R = 3$ ($I > 80\%$) and much chlorite coexists at this depth. (b) In the mudstone, I-S conversion requires a shorter duration from random, $R = 0$ ($I < 20\%$) to $R = 3$, ($I > 80\%$) and there is little chlorite in this interval of depth. (c) In the Shin-takenomachi well, the clay minerals (<2 μ m) from the sandstone, mudstone, and volcanic rocks show similar features to both the sandstone and mudstone above the unconformity. Below the unconformity,

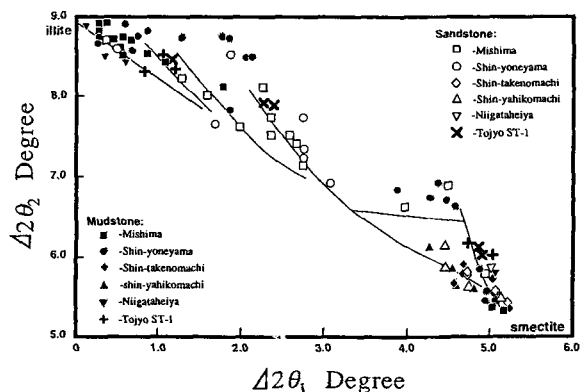


Figure 4. Plots of I-S variation in the method of Watanabe (1988). In the Niigata basin, the sandstone I-S shows $R = 1$ to $R = 3$ mixed-layer characteristics. The I-S in mudstone rarely occurs in the ordered $R = 1$ range, but usually shows $R = 0$ and ($R \geq 3$) I-S characteristics.

vs. mudstone is shown in Figures 7 and 8. In the zones of smectite and random I-S in mudstone, the composition characteristics of smectite and random I-S are similar, commonly being K-rich [$K/(Na + Ca + K) > 0.62$], with low numbers of interlayer cations [$(Na + Ca + K) < 0.55$] and low ^{IV}Al (< 0.3). The detrital illite is also K-rich [$K/(Na + Ca + K) > 0.7$], but has a greater number of interlayer cations (> 0.6), high tetrahedral Al ($^{IV}Al > 0.3$), and high octahedral Al ($^{VI}Al > 1.5$). In smectite zones, the sandstone contains two types of smectites as well as a small amount of detrital illite and chlorite. The two smectites are characterized as K-poor [$K/(Na + Ca + K) < 0.6$] and K-rich [$K/(Na + Ca + K) > 0.6$]. In the random I-S zone of sandstone, although interlayer cations ($Na + Ca + K$) and $K/(Na + Ca + K)$ content increases, the relations between ^{IV}Al vs. ^{VI}Al and Fe vs. Mg are not significantly changed. In the ordered ($R = 1$) I-S zone, the I-S of the sandstone shows a trend where $K/(Na + Ca + K)$ increases, ^{IV}Al vs. ^{VI}Al increases also, and a slight decrease occurs in Fe vs. Mg. In mudstone, I-S shows ($Na + Ca + K$), $K/(Na + Ca + K)$, and ^{IV}Al increasing; however, ^{VI}Al , Fe, and Mg are not changed significantly. In the ($R \geq 3$) I-S zone, the ($R \geq 3$) I-S in the sandstone is a K- and Al-rich type of illite [$(Na + Ca + K) > 0.58$ and $K/(Na + Ca + K) > 0.78$] to pure illite, but Fe and Mg decrease distinctly in this diagenetic stage. The ($R \geq 3$) I-S of mudstone shows a similar composition to detrital illite in the smectite zone, and a slight increase in ($Na + Ca + K$), $K/(Na + Ca + K)$, and ^{IV}Al .

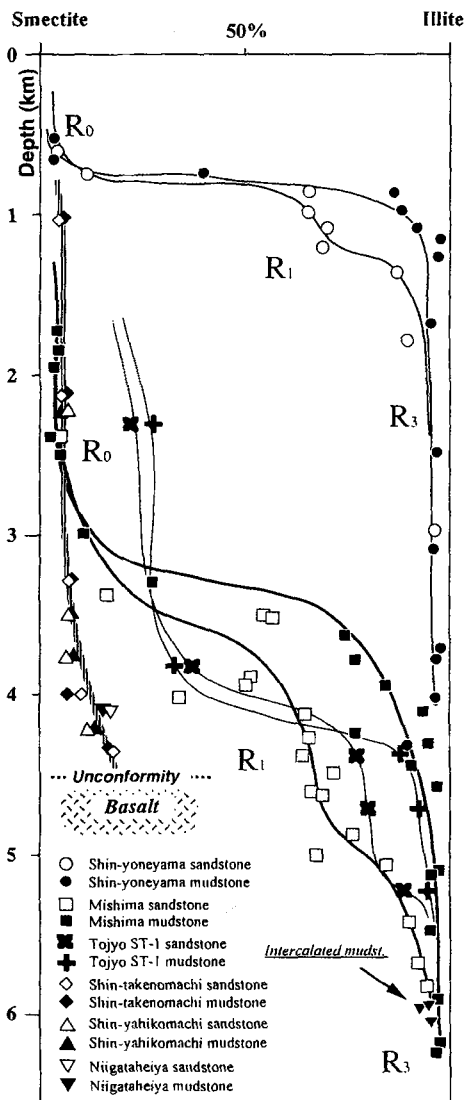


Figure 5. Relation of percent illite in I-S vs. burial depth in the studied wells.

TEM images show that the clay-size fraction ($< 2 \mu m$) of sandstone includes numerous euhedral crystals and detrital-like anhedral crystals of I-S (Figure 9). However, in the mudstone, the major crystal form of I-S is anhedral-like crystals. Morphologies from SEM images show that I-S in sandstone occurs with authigenic chlorite, smectite, and quartz, contemporaneous with the dissolution of feldspar (Figure 10). Illitization of smectite and cementation involving quartz over-

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the smectite transition to mixed-layer chlorite-smectite occurs. (d) Procedure to determine illite-layer % by use of JADE and NEWMOD simulation methods. Q, quartz; I, illite; S, smectite; Ch, chlorite; I-S, mixed-layer illite-smectite; Ch-S, mixed-layer chlorite-smectite.

Table 1. Chemical composition (EDS) and structural formula based on 11 oxygen atoms in the tetrahedral-sheet unit.

Sample names		Compositions of EDS data						
		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	FeO ¹
Illite(detrital), Mishima	1800mudstone	0.63	2.85	28.72	56.38	6.16	0.48	4.78
Smectite, Mishima	3200mudstone	0.47	2.13	26.75	63.67	2.64	0.33	4.02
Smectite, Tojyo ST-1	2400mudstone	0.66	2.20	27.16	62.64	3.18	0.48	3.68
I-S, Mishima	4000mudstone	0.53	3.88	28.13	58.09	4.64	0.25	4.48
I-S Tojyo ST-1	4200mudstone	1.12	2.94	27.88	58.23	5.71	0.36	3.78
Illite Shin-yoneyama	4000mudstone	0.48	2.91	27.97	57.51	7.32	0.28	3.53
Illite Mishima	5200mudstone	0.46	1.08	33.80	54.90	890	0.17	0.70
Smectite, Mishima	2600sandstone	0.35	7.70	22.77	56.54	0.84	0.20	11.60
Smectite, Tojyo ST-1	2400sandstone	0.62	3.03	30.20	59.84	0.56	0.68	5.06
Illite(detrital) Mishima	2000sandstone	0.35	4.66	24.57	58.87	5.09	0.32	6.15
I-S (R = 0) Mishima	4000sandstone	0.95	3.30	27.28	58.73	0.66	1.55	7.53
I-S (R = 1) Shin-yoneyama	1000sandstone	0.48	5.60	20.47	62.69	4.84	0.23	5.68
I-S (R = 1) Mishima	4600sandstone	0.40	3.46	26.17	64.12	2.33	0.37	3.15
I-S (R > 3) or illite Mishima	5200sandstone	0.43	4.47	27.83	55.70	4.88	0.16	6.53
I-S (R > 3) or illite Tojyo ST-1	5200sandstone	0.44	2.77	29.11	60.18	6.35	0.00	1.16

FeO¹ = total Fe oxide(FeO + Fe₂O₃).

growths proceeded simultaneously (Figure 11) in the mudstone. Sandstones, however, are cemented by calcite and authigenic clay minerals; quartz cement only occurs in samples from the deepest part of the well.

Table 2 shows the compositions of euhedral chlorite grains in the (R = 1) I-S zone of sandstone in the Mishima and Tojyo TS-1 wells. Chlorite in the (R = 1) I-S zone is Fe-rich and Mg-poor, near ideal clinosite in composition. Generally, the chlorite is near clinocllore in chemical composition in the (R ≥ 3) I-S zone of mudstone, although small amounts of Na⁺, Ca²⁺, and K⁺ are found in associated smectite as chlorite-smectite mixed-layer phases.

The bulk compositions of mudstone show higher amounts of K₂O, MgO, and Fe₂O₃ and lesser amounts of Na₂O and CaO than the bulk compositions of the sandstone (Figure 12). However, the water and the HCl

dissolution analyses show lower concentrations of K⁺ and Ca²⁺ and higher Mg²⁺ and Fe²⁺ in solution for the mudstone samples (Figure 13) than for the sandstone samples.

Wells from the north area

In the three wells from the north area, the Pleistocene and late Pliocene clastic sedimentary formations are very thick to depths of >4000 m. Authigenic clay minerals are smectite and random (R = 0) I-S with illite-layer contents of <20% in both sandstone and mudstone. In the Miocene basalt, trioctahedral smectite, mixed-layer chlorite-smectite (Chl-S), and chlorite are observed (Niu and Yoshimura, 1996). Powder X-ray diffraction patterns of the clay minerals are shown in Figure 3c. Some illite occurs in the thin mudstone strata of the interbedded mudstone in Miocene basalt below the depth of 4665 m in the Shin-takenomachi well.

DISCUSSION

Illitization of smectite clearly progresses more slowly in sandstone than in mudstone in the Niigata basin. The differences in the illitization of smectite between interbedded sandstone and mudstone in the same sedimentary succession is possibly caused by differences in the chemical compositions of the two different sediment types.

Illitization of smectite in mudstone

As discussed by Hower *et al.* (1976), illitization of smectite is not only dependent on initial smectite composition, but also on chemical reactions between the initial smectite and pore fluids in the diagenetic environment, which produces I-S and secondary mineral products. Many researchers (*e.g.*, Eberl and Hower, 1977; Freed and Peacor, 1989) have proposed that K⁺

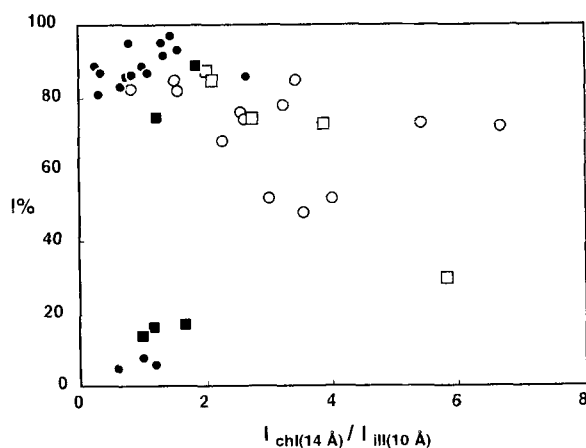


Figure 6. Relation of intensity of peaks ($I_{chl(14\text{\AA})}/I_{ill(10\text{\AA})}$) and percent illite of I-S. Black squares and circles are mudstone samples and open squares and circles are sandstone samples from the Shin-yoneyama and Mishima wells.

Table 1. Extended.

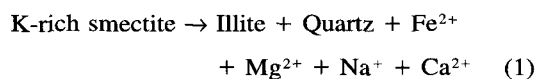
Smectite and illite formulae with (Si, Al) ₄ O ₁₀ (OH) ₂							
Na	Ca	K	^{iv} Al	Mg	Fe	Si	^{iv} Al
0.08	0.03	0.49	1.61	0.26	0.25	3.51	0.49
0.05	0.02	0.20	1.70	0.19	0.20	3.81	0.19
0.08	0.03	0.24	1.69	0.20	0.18	3.77	0.23
0.06	0.02	0.36	1.60	0.36	0.23	3.57	0.43
0.13	0.02	0.45	1.62	0.27	0.20	3.59	0.41
0.06	0.02	0.58	1.62	0.27	0.18	3.57	0.43
0.06	0.01	0.70	1.85	0.10	0.04	3.39	0.61
0.04	0.01	0.07	1.22	0.72	0.61	3.54	0.46
0.07	0.04	0.04	1.72	0.27	0.25	3.59	0.41
0.04	0.02	0.40	1.45	0.43	0.32	3.65	0.35
0.11	0.10	0.05	1.56	0.30	0.39	3.59	0.41
0.06	0.02	0.38	1.35	0.51	0.29	3.86	0.14
0.05	0.02	0.18	1.66	0.31	0.16	3.82	0.18
0.05	0.01	0.39	1.52	0.42	0.34	3.47	0.53
0.05	0.00	0.49	1.73	0.25	0.06	3.65	0.35

and Al³⁺ concentrations in the fluid phase and dissolution of detrital K-feldspar and mica have an effect on increasing the illite-layer content in I-S. Boles and Franks (1979) suggested two reactions to explain illitization during the diagenetic process: 1) illitization with active K⁺ and Al³⁺: 4.5K⁺ + 8Al³⁺ + smectite = illite + Na⁺ + 2Ca²⁺ + 2.5Fe³⁺ + 2Mg²⁺ + 3Si⁴⁺ + 10H₂O, and 2) illitization with active K⁺: 3.93K⁺ + 1.57Al³⁺ + smectite = illite + 1.57Na⁺ + 3.14Ca²⁺ + 4.87Fe³⁺ + 4.28Mg²⁺ + 24.66Si⁴⁺ + 57O²⁻ + 11.4(OH)⁻ + 15.7H₂O. They also noted that a number of deeply buried sandstones have ordered I-S with relatively high percentages of expandable layers in comparison to the I-S in interbedded shale.

The relative increase in K⁺ and the decrease in Na⁺ and Ca²⁺ in the interlayer are the most remarkable features with increasing illitization of smectite. The increase in K⁺ content and the conversion process from Na and Ca-rich montmorillonite to illite is by either absorption or ion exchange and possibly by both. Figure 14a describes the compositional relationships from smectite to illite and illustrates possible transformation models of illitization. As shown in Figure 14b, the K/(Na + Ca + K) vs. Na + Ca + K plot of smectite from mudstone, I-S, and detrital-degraded illite from different zones of illitization exhibits a trend similar to area II (Figure 14a). Thus, illitization of smectite in mudstone proceeded by both exchange with interlayer Na⁺ and Ca²⁺ and absorption of K⁺ Figure 15a shows a convergent trend of Al, Fe, and Mg components from initial smectite to I-S and finally to detrital illite in the ternary Al-Fe-Mg diagram based on the chemistry of the octahedral sheet. This result implies that the detrital illite and the smectite are from the same parent source of illite.

As shown in Figure 11, quartz overgrowth occurs closely with the progression of the transformation of smectite to illite, and thus SiO₂ is probably the result of being released from smectite during the process.

Illitization in mudstone occurs rapidly from smectite to illite, because the chemistry of the transformation product is similar to the parent. The reaction process is expressed as follows and represents diagenesis:



Observed data of this transformation show that the structural change from random to regular interstratification occurs over a narrow interval of depth. Eberl and Hower (1977) proposed that the layer charge becomes sufficiently high by the substitution of Al for Si in the tetrahedra, and the interlayer contracts irreversibly and illite layers form. According to the chemical trends (Figure 14b), the increase in ^{iv}Al and K⁺ is accompanied by simultaneous release of SiO₂, Na⁺, Ca²⁺, Fe²⁺, and Mg²⁺ from the precursor smectite. The relatively higher Fe²⁺ and Mg²⁺ concentrations in solution obtained by leaching mudstone with HCl (Figure 13b) are expected, and this result suggests a similar release of Fe²⁺ and Mg²⁺ during illitization of smectite.

Illitization of smectite in sandstone

In deeply buried sandstones, clay minerals are altered by diagenetic and low-grade metamorphic processes, and tend to become more similar to the clay minerals in the adjacent mudstone (Weaver, 1989). In the shallow zone of the Niigata basin, smectites are divided into two types based on the K/(Na + Ca + K) ratios: low vs. high ratios. The 'high' ratio type is uncommon and is interpreted as detrital smectite, similar to that of detrital smectite in mudstone. The 'low' ratio type is primarily authigenic smectite with a composition that is Fe- and Mg-rich and Al-poor. The illitization of most smectite in sandstones progresses from smectite to (R = 0) I-S to (R = 1) I-S, and then to (R ≥ 3) I-S, and the composition changes as shown in Figures 8 and 14b. The major trend is the increase in interlayer cations except K⁺ from smectite to (R = 0) I-S as illitization proceeds. As K⁺ does not show such a trend, this transformation step occurs in a K-poor environment.

In the ordered I-S zones, I-S has been recrystallized, and authigenic quartz, chlorite, and calcite crystallize in pore spaces. I-S gains K and Al from pore fluids to produce an increase in the number of illite layers. However, the sandstone is K-poor (Figure 12) and is overpressured (in the Nishiyama Formation) to produce a semi-closed system of chemical composition (Hiltabrand *et al.*, 1973), and the K₂O is supplied from the dissolution of detrital minerals. During the conversion of the (R = 0) I-S to R = 1, authigenic quartz and chlorite are also precipitated as products of the dissolution of detrital silicates (Figure 10). In contrast, Hower *et al.* (1976) suggested that burial metamor-

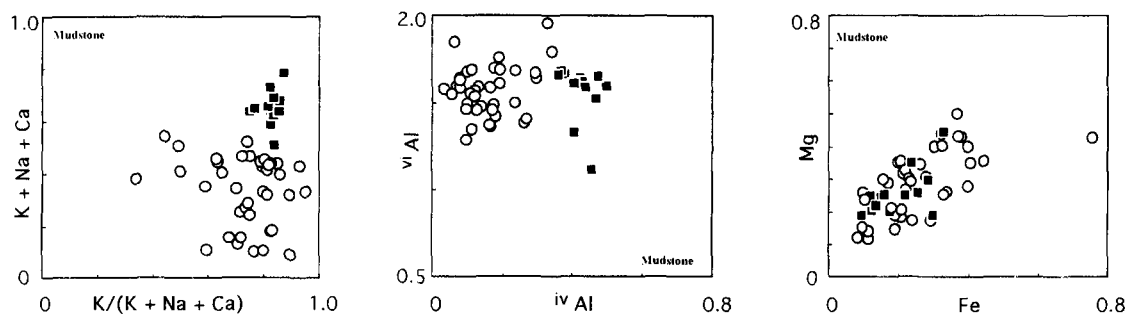
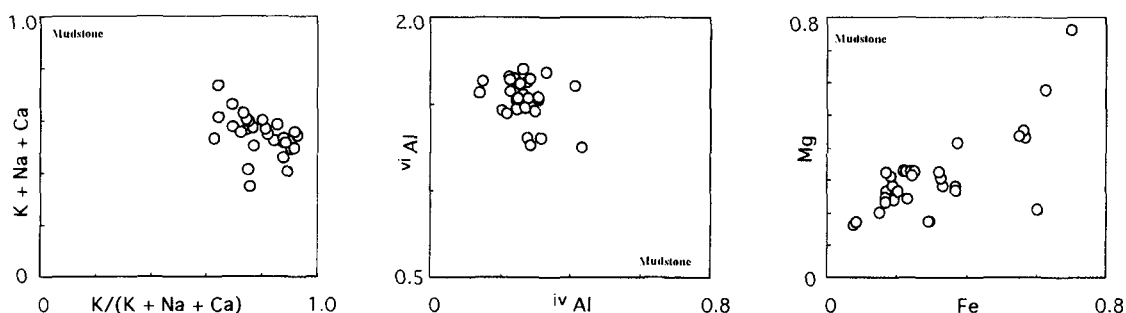
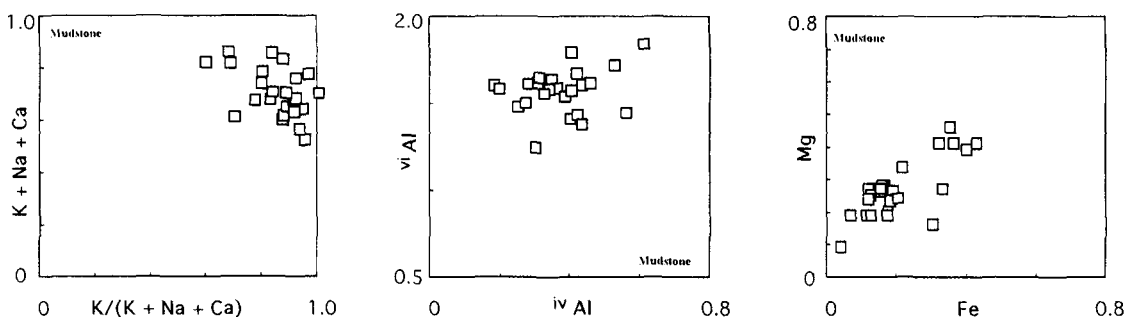
Smectite and random I-S ($R = 0$) zoneOrdered I-S ($R = 1$) zoneI-S ($R \geq 3$) zone

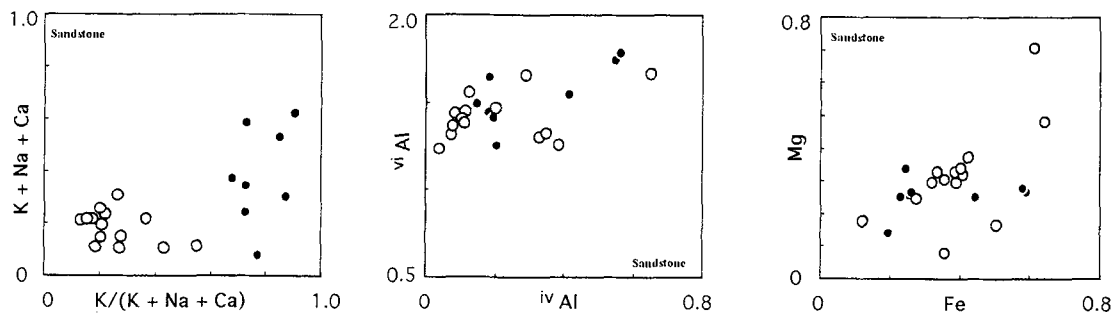
Figure 7. Compositional trends and relations of mudstone I-S (a) interlayer action $K^+ + Na^+ + Ca^{2+}$ vs. $K^+/(K^+ + Na^+ + Ca^{2+})$, (b) octahedral ^{VI}Al vs. tetrahedral ^{IV}Al , (c) Fe vs. Mg in the octahedral sheet in the different stages of transition by EDS analyses. Black squares are detrital illite in the smectite zone, open squares are illite in the I-S ($R \geq 3$) zone and open circles are smectite and I-S.

phism (diagenesis) may be significant only in the removal of CaO and CO_2 during calcite dissolution along with the loss of small amounts of Na as the cation-exchange capacity is reduced in I-S. The simultaneous authigenic-chlorite and calcite precipitation implies that cations, such as Ca^{2+} and Na^+ , in the pore fluid in the studied sequences were over-saturated, and such oversaturation would constrain illitization (Figure 13a). These factors result in slow illitization over a long period, but illitization is favorable for the formation of ordered I-S in sandstone. The process of

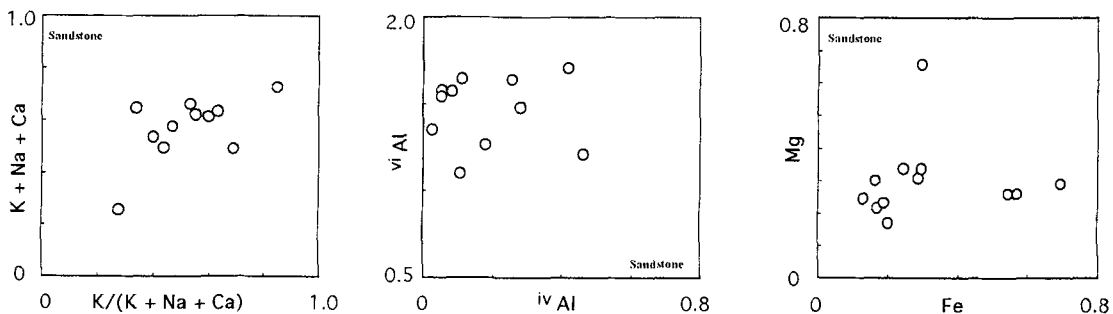
illitization exhibits a clear gradual transition from random $R = 0$ to ($R = 1$) I-S.

In the late stage of illitization, the transformation from ($R = 1$) I-S to $R \geq 3$ is different from in the early stages (Figure 15b). In sandstone, the concentrations of interlayer cations do not significantly increase the ordering process of ($R = 1$) I-S and $R \geq 3$. However, K content increases to form illite with Si , Fe , and Mg decreasing and Al increasing (Figure 15b). Structural formulae also show this trend (Figure 8). This trend indicates that the reaction at this late stage in-

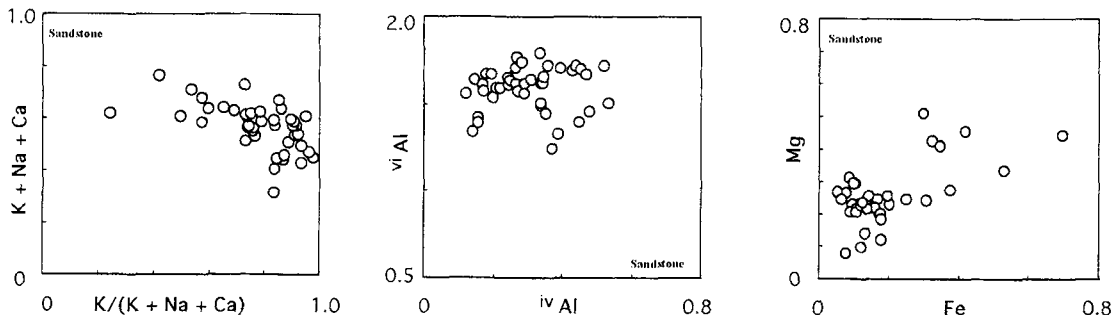
Smectite zone



Random I-S (R = 0) zone



Order I-S (R = 1) zone



I-S (R ≥ 3) zone

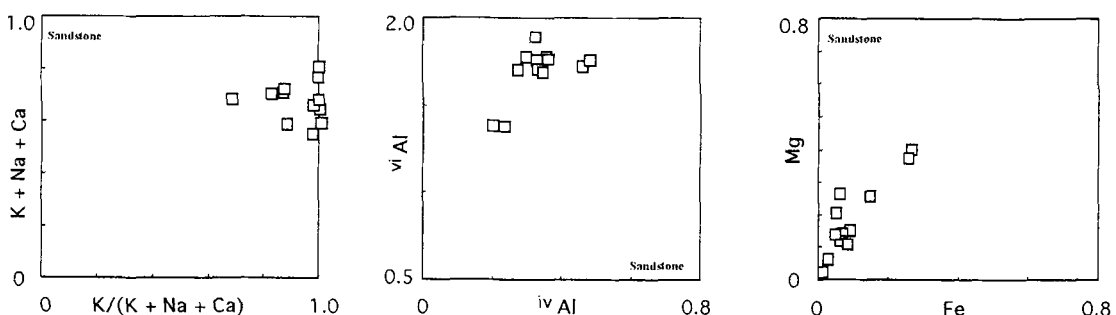


Figure 8. Compositional trends and relations of sandstone I-S (a) interlayer $K^+ + Na^+ + Ca^{2+}$ vs. $K^+/(K^+ + Na^+ + Ca^{2+})$, (b) octahedral ^{VI}Al vs. tetrahedral ^{IV}Al , (c) Fe vs. Mg in the octahedral sheet in the different transition zones by EDS analyses. Solid circles are degraded I-S, open circles are smectite and I-S, and open square is illite in I-S ($R \geq 3$) zone.

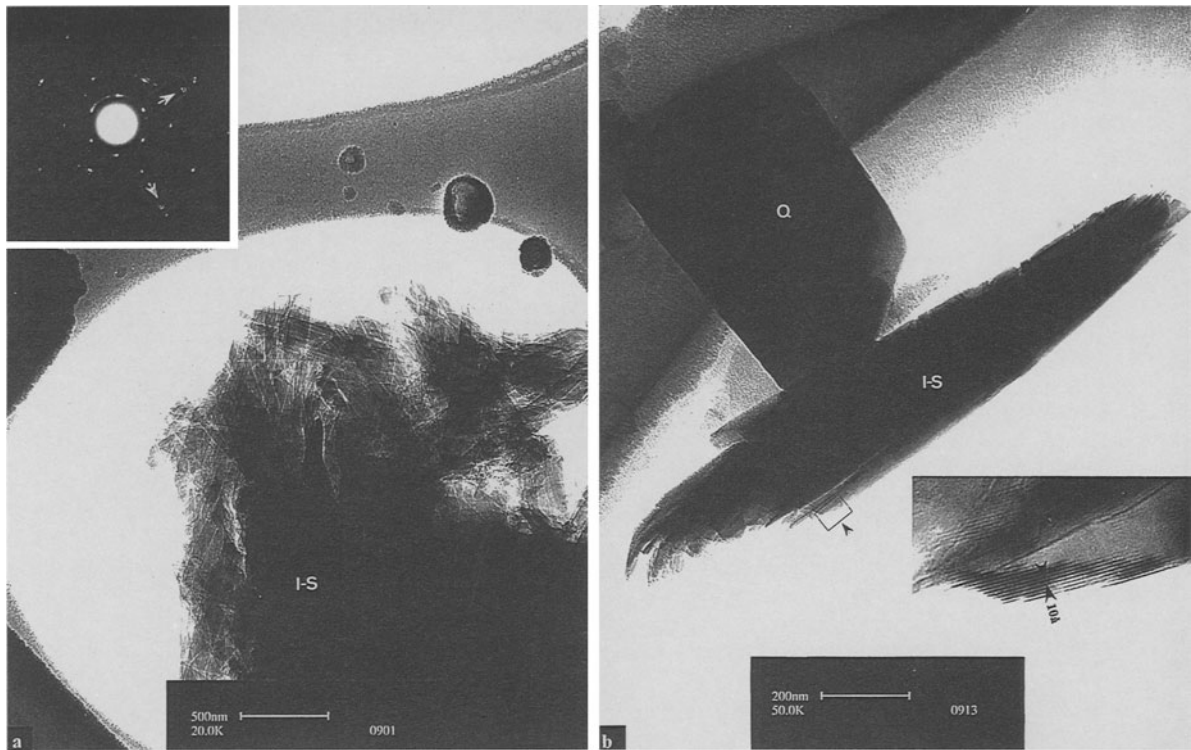


Figure 9. (a) Typical authigenic near-euhedral I-S crystal from the Tojyo TS-1 3800 m sandstone sample and corresponding selected area electron diffraction pattern on the (001) plane. (b) Detrital illite-rich I-S crystal from the Tojyo TS-1 3800-m mudstone sample. Note the lattice-fringes of the TEM image where the $d(001)$ -values are ~ 10 Å.

Table 2. Compositions of near-euhedral chlorite in ($R = 1$) I-S zone and late chlorite¹ in ($R \geq 3$) I-S zone in sandstone.

Name	In ($R = 1$) I-S Zone		In ($R \geq 3$) I-S Zone	
	Mi-3508.2	To-4400	Mi-6000	To-5000
SiO ₂	29.80	33.04	40.86	45.25
Al ₂ O ₃	22.13	20.92	21.13	18.48
MgO	8.24	8.67	15.72	12.08
FeO ²	39.83	37.37	20.33	22.32
K ₂ O	0.00	0.00	0.79	0.60
Na ₂ O	tr.	tr.	0.72	0.96
CaO	0.00	0.00	0.46	0.30
total	100.00	100.00	100.00	100.00
Structural Formulae of Chlorite [with O ₁₀ (OH) ₈]				
Si	2.89	3.14	3.55	3.92
^{IV} Al	1.11	0.86	0.45	0.08
Tetrahedral sheet	4.00	4.00	4.00	4.00
^{VI} Al	1.42	1.49	1.71	1.81
Fe	3.23	2.97	1.48	1.62
Mg	1.19	1.23	2.04	1.56
Octahedral sheet	5.84	5.69	5.23	4.99
K			0.09	0.07
Na	tr.	tr.	0.12	0.16
Ca			0.04	0.03
Interlayer	0.00	0.00	0.25	0.26

¹ Late chlorite includes few Chl-S mixed-layers.

FeO² = total Fe oxide (FeO + Fe₂O₃).

Mi = Mishima well, To = Tojyo well.

volves primarily the fixation of K in the interlayer position of I-S. Inoue (1983) showed that Al/Si ratios were affected by the decomposition of montmorillonite layers during hydrothermal treatment, and found that dissolved Al is substituted into the remaining montmorillonite layers and exchanged for Si at high pH in the experiments. In natural environments, however, Al-rich ($R > 3$) I-S and illite may recrystallize from environments with previously formed I-S and from the decomposition of other minerals, which produces excess Fe and Mg in the pore fluid.

In the sandstone, chlorite is an important paragenesis mineral during illitization. In the stage of ($R = 1$) I-S, the authigenic chlorite coexisting with I-S has a composition near that of chamosite. However, in late diagenesis, as indicated by the progression of ($R \geq 3$) I-S, the increase of K and Al of I-S, and the composition variation of the chlorite, these changes are due to the decomposition of smectite, I-S, and other minerals. The chlorite (Chl) is clinocllore with Chl-S interstratification containing source Na⁺, and Ca²⁺ cations in the interlayer (Table 2).

Heterogeneous conversion

It is clear that compositional factors affect the rate of illitization between sandstone and mudstone coexisting at the same diagenetic stage in the Niigata basin.

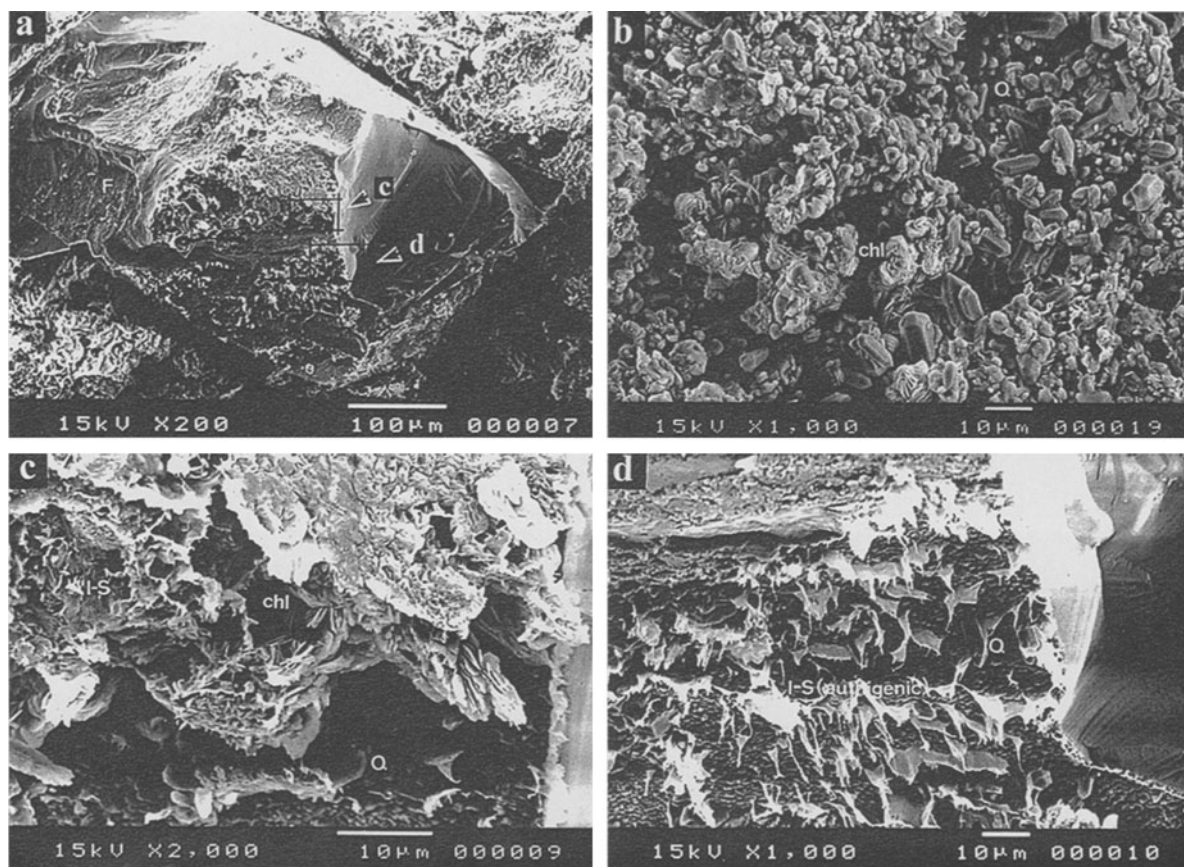


Figure 10. (a) Feldspar dissolution, authigenic clay minerals, and quartz inclusions from the Mishima well at 3989.6 m core of sandstone. (b) Precipitated euhedral quartz and rosette-shape chlorite filling pore spaces. (c) Details from (a) Quartz + chlorite + I-S paragenesis on a feldspar grain surface. (d) Authigenic thin-flake and filamentous I-S and quartz on the feldspar surface (from a).

The initial composition of the smectite is related to a specific activation energy and enthalpy of formation. Differences in composition of the smectite relate to different temperatures of transformation (or reaction) of illitization in the same environmental system. Ranson and Helgeson (1995) calculated the interlayer-dehydration equilibrium constant K (usually given as $\log K$) of various homologous homoionic solid solutions of montmorillonite at given values of specific temperature and pressure (Table 3) as follows: hydrous smectite(*hs*) = anhydrous smectite(*as*) + $n\text{H}_2\text{O}$. Thus, the equilibrium constant is:

$$K = \frac{a_{\text{as}}(a_{\text{H}_2\text{O}})^{n_c}}{a_{\text{hs}}} \quad \left(\text{or } \log K = -\frac{\Delta G_r^\circ}{2.303RT} \right) \quad (2)$$

where $a_{\text{H}_2\text{O}}$, a_{hs} and a_{as} are the activities of H_2O , hydrous, and anhydrous smectite, respectively, n_c is a count of H_2O in the reaction, ΔG_r° is Gibbs free energy of reaction at temperature and pressure, and T and R are the temperature and gas constant, respectively. The equation shows that smectite dehydration is dependent on composition and it may not be a uniform process

even under equivalent conditions. Although dehydration is not smectite illitization, Perry and Hower (1972) discussed that clay mineral dehydration must occur either before or during illitization in diagenesis. Based on this analytical data and the structural formulae, the initial smectite, the altered I-S, and the detrital illite in the mudstone show a similar trend in composition of K and Si in the Niigata basin. The Si , K -rich smectite has a lower Gibbs free energy of dehydration, and consequently mudstone will experience a more rapid illitization rate than that of Na - and Ca -rich smectites in the sandstone.

Diagenetic temperature in the Niigata basin

The temperature of illitization of smectite to ordered ($R = 1$) I-S via random ($R = 0$) I-S relates to the geologic age (*i.e.*, time) and sedimentary model in the argillaceous sediment. Pollastro (1993) summarized the approximate temperatures for the transformation of mixed-layer I-S based on the data of Hoffman and Hower (1979) and the "short-life" geothermal I-S models (*e.g.*, involving short time

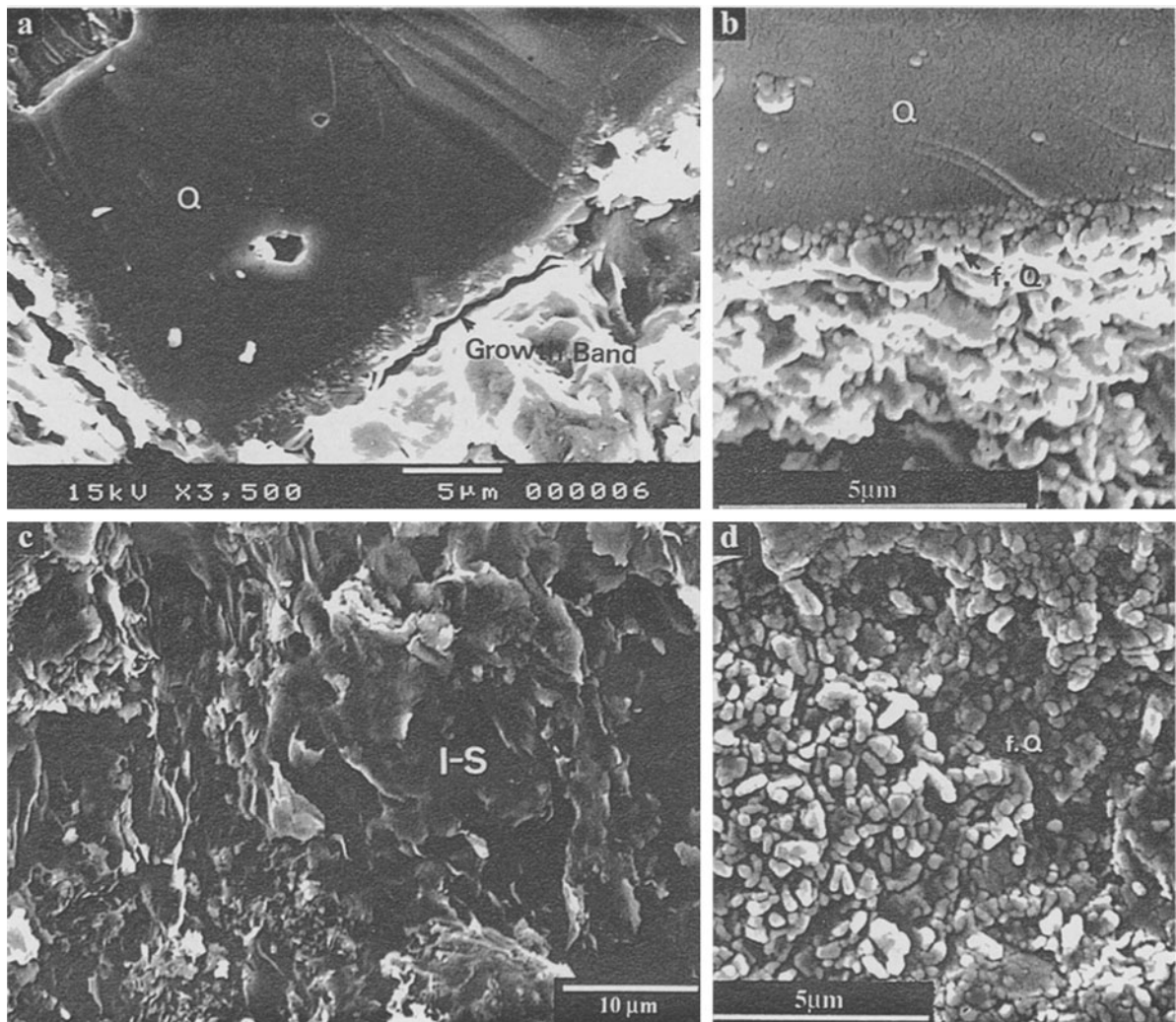


Figure 11. (a) Growth bands of quartz in the mudstone from the Mishima well at 4516.6 m depth. (b) Secondary fine quartz (f.Q) and the coarsening process. (c) Illite-rich I-S structure image in mudstone. (d) Fine quartz (f.Q) from illitization of smectite of mudstone.

intervals) developed by Jennings and Thompson (1986). In the model of Hoffman and Hower from Upper Carboniferous to Neogene (5–300 Ma), ($R = 0$) I-S appears at 50–60°C, ($R = 1$) I-S at 100–110°C, and ($R \geq 3$) I-S at 170–180°C, whereas in the “short-life” geothermal model of younger sedimentary basins (<3 Ma), ($R = 0$) I-S appears at 120–140°C and ($R > 3$) I-S at 170–180°C. In the Niigata basin, the measured temperature at the depth where ($R = 1$) I-S occurs is different from that obtained from the above models for illitization. In the northern three wells, the smectite and ($R = 0$) I-S still occur even for temperatures of 143°C at ~4235 m of the Nishiyama formation (5.1 Ma, JNOC, 1995). However, in the Mishima and Tojyo TS-1 wells, the random ($R = 0$) I-S has transformed to

ordered ($R = 1$) I-S at 122–128°C at 3200–3600 m depth of the lower Shiiya formation (<6.2 Ma, JNOC, 1994). According to the analysis of the geothermal history (Figure 2), the sluggish transformation reaction of smectite at high temperatures in the northern three wells is probably related to the short time interval (<1.6 Ma) and thus, these minerals are in a metastable state. In the interbedded succession of mudstone and sandstone in the southern area, the transition temperature from $R = 1$ to $R \geq 3$ in mudstone is measured at ~130°C, near the transition temperature from $R = 0$ to $R = 1$ in the “short-life” geothermal model. In contrast, I-S of $R = 1$ in sandstone persists even at 165°C. As noted above, this diagenetic heterogeneity is related to differences in precursor compositions. Affected by lat-

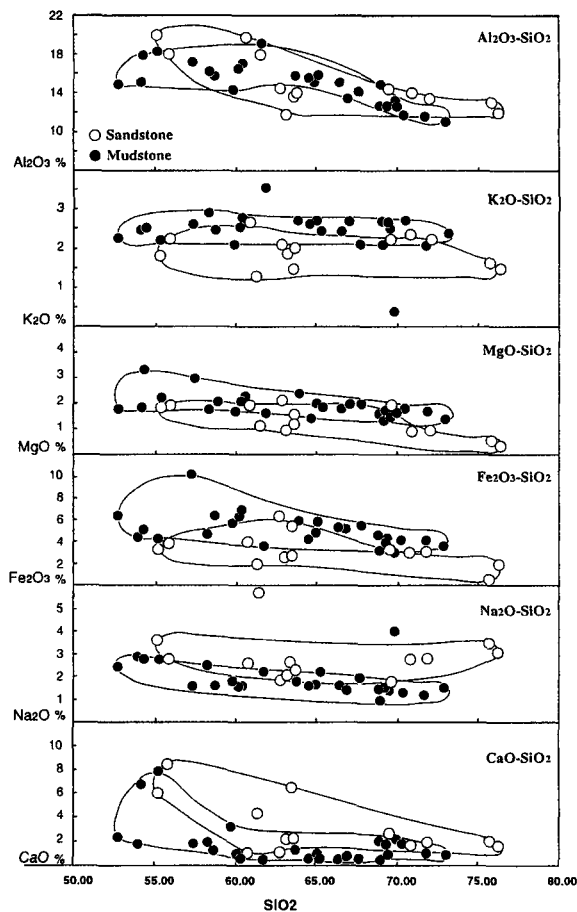


Figure 12. The relation of SiO_2 and other major-element oxides of the bulk rock. Open circles are sandstone samples and solid circles are mudstone. K_2O , MgO , and Fe_2O_3 of mudstone are higher, CaO and Na_2O are lesser than sandstone.

er tectonic activity (Figure 2), the transformation from $R = 0$ to $R \geq 3$ occurs at an extremely shallow depth in the Shin-yoneyama well compared to other wells.

CONCLUSION

The illitization of smectite in interbedded sandstone and mudstone occurs differently in the Niigata basin. In sandstone, illitization of smectite occurs at a slower rate than that in mudstone and is accompanied by chlorite precipitation and calcite cementation. In mudstone, the illitization of smectite of I-S ($R = 0$) to $R > 3$ is rapid and is associated with authigenic quartz. These differences are determined by two factors: the original detrital smectite composition and the difference in the chemistry of the pore fluid in sandstone and mudstone.

Illitization of smectites in sandstone and mudstone showed different transformation pathways. In mudstone, ordered I-S and illite have distinct features and inherited compositions from the initial smectite and detrital illite. In sandstone, I-S compositions are altered by pore-fluid components. Illitization of smectite in mudstone is recognized as a reconstruction process from the smectite structure to the illite structure, whereas illitization in sandstone involves both crystallization of authigenic smectite and recrystallization of detrital smectite. Early illitization in sandstone proceeded by absorption and exchange of cations with pore fluid, followed by Al and K increases owing to the decomposition of silicates.

The temperature of the transition from random ($R = 0$) I-S to ordered ($R = 1$) I-S in sandstone was measured at $\sim 125^\circ\text{C}$ in the southern Niigata basin, whereas random I-S occurs at temperatures $> 145^\circ\text{C}$ in the northern Niigata basin. The phenomenon of a very high illitization temperature is probably related to a high temperature that was experienced over a

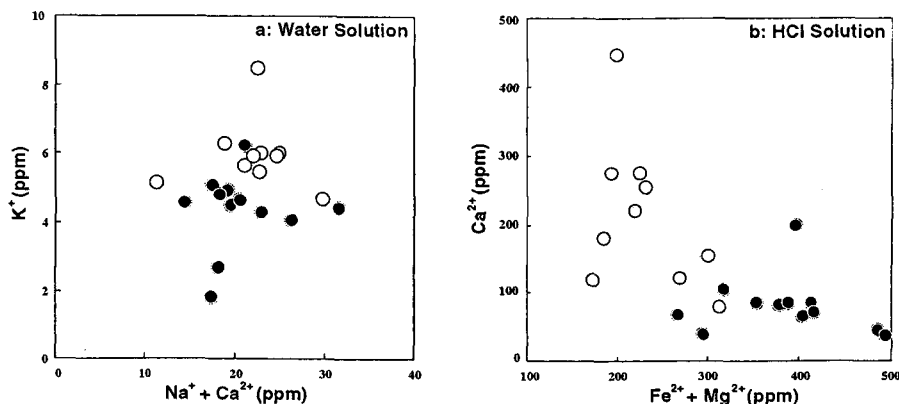


Figure 13. (a) K^+ vs. $\text{Na}^+ + \text{Ca}^{2+}$ variations of the host rock based on the dissolved rock by pure water with condition: 10 g/100 mL at 50°C and ultrasonic-vibration processing for 24 h.; (b) Ca^{2+} vs. $\text{Fe}^{2+} + \text{Mg}^{2+}$ variations of the host rock based on the dissolved rock by 0.01 M HCl conditions: 10 g/100 mL, in 50°C water and ultrasonic vibrating for 24 h. Open circles represent sandstone and solid circles-represent mudstone.

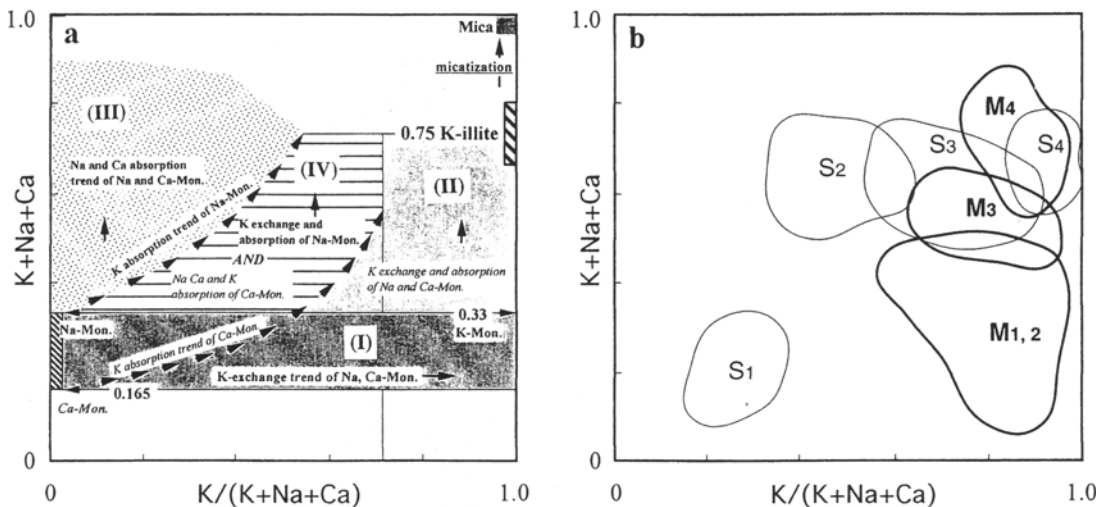


Figure 14. The relation of interlayer $K + Na + Ca$ vs. $K/(K + Na + Ca)$ of smectite and illite. (a) Ideal distribution and transformations of K , Na , and Ca -rich montmorillonite (mon.) to illite. In area I, Na and Ca -rich mon. are exchanged with K to K -rich mon.; in area II, K -rich mon. absorbs K to illite; in area III, Na - and Ca -poor mon. absorbs K , Na , and Ca to I-S and high-charge Na - and Ca -rich mon.; in area IV, Na -rich mon. absorbs K and is exchanged by K to I-S, and Ca -rich mon. absorbs K to I-S. (b) In this different S to I transformation process, the distribution and transformation involves K , Na , and Ca -rich montmorillonite to illite. In the sandstone, S_1 = smectite zone, S_2 = random I-S zone, S_3 = order I-S ($R = 1$) zone and S_4 = illite and I-S ($R \geq 3$) zone. In the mudstone, $M_{1,2}$ = smectite and random I-S zones, M_3 = order I-S ($R = 1$) zone and M_4 = illite and I-S ($R \geq 3$) zone.

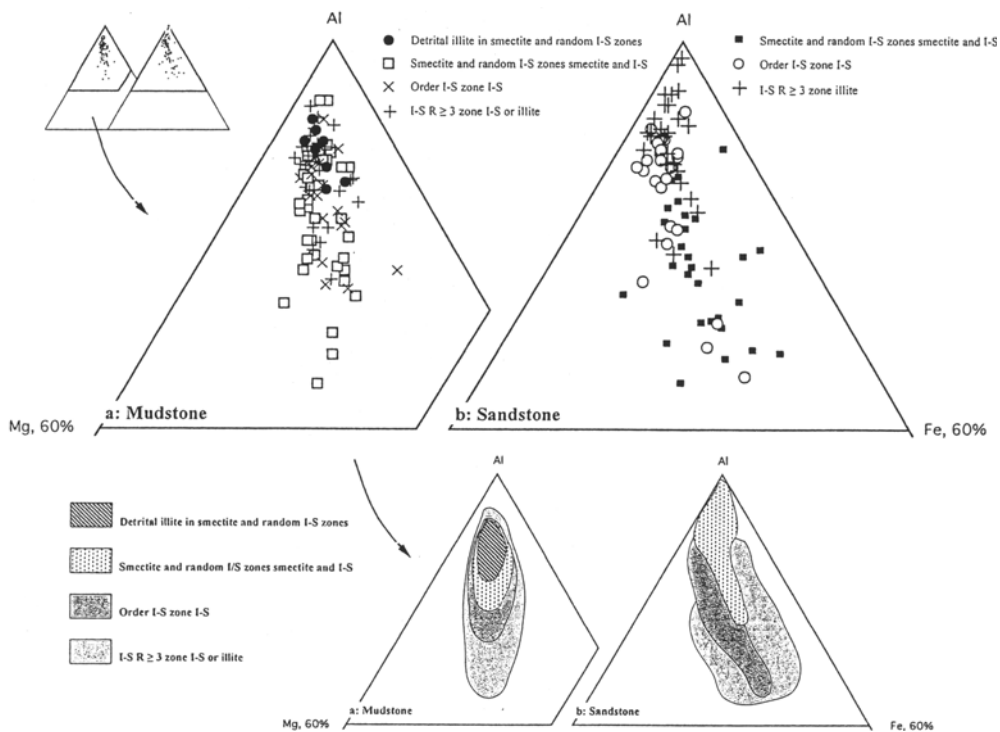


Figure 15. Ternary Al - Fe - Mg diagram for the octahedral sheet of I-S structures based on formula calculations. (a) Mudstone-deep zone I-S Al , Fe , and Mg ratio trend towards detrital illite features. (b) Sandstone I-S shows that Al increases, Fe and Mg decreases with burial depth.

Table 3. LogK (1 Kb) for dehydration as a function of temperature for select pure homoionic smectite with different interlayer cations from Ranson and Helgeson (1995).

T (°C)	LogK (1 Kb)		
	Na-rich smectite	K-rich smectite	Ca-rich smectite
50	-0.44	-0.12	-3.07
75	-0.05	0.48	-2.48
100	0.36	0.86	-1.91
125	0.78	1.24	-1.35
150	1.21	1.64	-0.8
175	1.63	2.04	-0.26

short period and the remaining smectite continues to persist. However, based on present research, these phenomena may also possibly be caused by differences in the original bulk chemistries of the sandstone and mudstone.

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