Ordering of Opal-CT in diagenesis

KAZUHIKO KANO

Geological Survey of Japan, Higashi 1-1-3, Yatabe-cho, Ibaraki-ken 305, Japan

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Opal-CT in sediments is formed from opal-A and is converted to quartz during diagenesis. In that process, opal-CT becomes progressively ordered as is distinctly indicated by the decrease in $d(101)$ spacing.

Based on a kinetic equation experimentally found by KANO (1979) and KANO and TAGUCHI (1982), the decreasing rate of $d(101)$ spacing has been calculated from previously reported $d(101)$ spacings (MITSUI, 1975) and thermal history of sediments in a borehole, MITI Hamayuchi. The calculated rate makes a subtle difference between the reported and calculated $d(101)$ spacings, suggesting the availability of the equation applied. However, even if compared at the same temperature, the rate is much slower than that in hydrothermal alkaline conditions. Thus, the ordering process of opal-CT is more or less chemically controlled.

Taking the thermal history of sediments into account, a model based on the kinetic equation well fits the previously reported relationship between the $d(101)$ spacing of Neogene siliceous sediments and the maximum temperature to which the sediments have been subjected (IIJIMA and TADA, 1981), suggesting that the ordering process of opal-CT in diagenetic conditions is controlled mainly by temperature. The features of distribution of $d(101)$ spacing in sediment piles have been discussed by using the model.

INTRODUCTION

Opal-CT (JONES and SEGNET, 1971), a cristobalitic silica is a main constituent in siliceous sediments. It is commonly formed from amorphous silica (opal-A; JONES and SEGNET, 1971) and is converted to quartz in the early stage of diagenesis (MIZUTANI, 1966; 1967; RIECH and VON RAD, 1979). In that process, opal-CT changes its internal structure to an ordering state. The change is distinctly indicated by the shift of $d(101)$ spacing of cristobalite.

MURATA and NAKATA (1974), MITSUI and TAGUCHI (1974, 1977 in MITSUI, 1975) and many other workers reported that the $d(101)$ spacing decreases progressively from 4.12 to 4.04 Å in sediment piles. Heating by intrusive bodies also causes the decrease in $d(101)$ spacing (MURATA *et al.*, 1979). The $d(101)$ spacing of Neogene siliceous sediments is correlated closely with the maximum temperature to which the sediments have been subjected (IIJIMA and TADA, 1981). On the other hand, the decreasing

rate of $d(101)$ spacing is experimentally found to be remarkably dependent on the reaction temperature (MIZUTANI, 1977; KANO, 1979; KANO and TAGUCHI, 1982).

These results can offer a basis to correlate the $d(101)$ spacing and the thermal history of sediments in the early stage of diagenesis. However, before going to study the probable relation, it is necessary to establish the kinetics of the ordering of opal-CT under diagenetic conditions (MIZUTANI, 1978).

Recently, KANO (1979) and KANO and TAGUCHI (1982) attempted to clarify the kinetic process of the ordering of opal-CT through the inspection of their own and previously reported experiments, and showed experimentally a kinetic equation to express the decreasing rate of $d(101)$ spacing. In this paper, based on the kinetic equation, the kinetic process is examined in relation to geology and mineralogy of sedimentary rocks in nature, especially the decreasing rate of $d(101)$ spacing under diagenetic conditions and the features of the distribu-

tion of $d(101)$ spacing in sediment piles.

ORDERING OF OPAL-CT

Opal-CT is interpreted as low-cristobalite disordered by stacking of randomly interstratified tridymite layers (FLÖRKE, 1955; JONES and SEGNET, 1971; FLÖRKE *et al.*, 1975, 1976). According to JONES and SEGNET (1971), the ordering of opal-CT occurs at the expense of tridymite layers. The mechanism of the ordering however, remains still unsolved (KANO and TAGUCHI, 1982).

Based on the experiments under dry and hydrothermal conditions (JONES and SEGNET, 1971; MIZUTANI, 1977; KANO, 1979; KANO and TAGUCHI, 1982), the decreasing rate of $d(101)$ spacing was formulated by KANO (1979) and KANO and TAGUCHI (1982) as an empirical equation:

$$dS/dt = -kS \quad (1)$$

where S represents the difference of the $d(101)$ spacing from that of ideal cristobalite, t is the reaction time and k is the rate constant. The rate constant is expressed by Arrhenius equation,

$$k = A \exp(-E/RT) \quad (2)$$

where A , E , R , and T are the frequency factor, apparent activation energy, gas constant and absolute temperature, respectively. Eq. (1) is available under dry and hydrothermal conditions, and probably under diagenetic conditions. The activation energy (E) under hydrothermal conditions is about 20kcal/mol and much lower than that under dry conditions, about 170kcal/mol. In addition, the frequency factor (A) varies in response to change of chemical conditions. Therefore, the rate constant (k) under diagenetic conditions can only be estimated from geological evidences even if Eq. (1) is available under the conditions.

Taking the thermal history of sediments into account, we can calculate the decreasing

rate of $d(101)$ spacing under diagenetic conditions from the observed $d(101)$ spacings of the sediments by using Eqs. (1) and (2). Then, we could examine the applicability of the equations to the diagenetic ordering of opal-CT according to the difference between the observed and calculated $d(101)$ spacings and that between experimentally found and calculated initial S value. Let us examine actual samples in sediments of MITI Hamayuchi, a borehole in the Tempoku district, western Hokkaido, Japan.

The detailed geology and silica mineral diagenesis of MITI Hamayuchi have been reported by MITSUI (1975), MITSUI and TAGUCHI (1977) and IJIMA and TADA (1981). These results are briefly summarized in Table 1 and Fig. 1. Opal-CT dominates in siliceous sediments of the Late Miocene Wakkanai Formation. The $d(101)$ spacing decreases progressively, but a distinct discontinuity found at the unconformity between the Wakkanai and Masuporo Formations. Therefore, the $d(101)$

Fig. 1. Silica mineral diagenesis in MITI Hamayuchi, summarized from MITSUI's paper.

Table 1. Stratigraphy of MITI Hamayuchi

Geologic Age	Formation	Thickness	Lithofacies
Pleistocene	Sarabetsu F. Yuchi F.	Eroded 350-400m	
Pliocene	Koetoi F.	625 m	Diatomaceous mudst.
Late Miocene	Wakkanai F.	770 m	Siliceous hard shale
Early Middle to	Masuporo F.	2,600 m	Mudst., Sandst., Cgl.
Early Miocene	Onishibetsu F.	530 m	Mudst., Sandst.

spacings of the Masuporo Formation are not used in the following calculation.

MITI Hamayuchi is located on an anticline and some sediments above the level of the borehole have been eroded off during uplifting. According to the geologic investigation carried out around the borehole (MITANI *et al.*, 1965), maximum thickness of eroded sediments is estimated at 350 to 400 m. On the other hand, the age and depth of sediments younger than the

Masuporo Formation are nearly in a linear relationship in the borehole (Fig. 2). When the curve in Fig. 2 is extrapolated to time zero, it reaches 300 to 400 m above the level of the borehole at zero (Fig. 2). Therefore the thickness of eroded sediments is estimated to be about 300 to 400 m from the sediments presently found in the borehole. From these values, the rate of deposition can be calculated as 187 m/10⁶ year, though the effect of compaction is neglected in this case. Then the following equation may explain probable thermal history of sediments younger than the Masuporo Formation,

$$T(^{\circ}\text{K}) = T_0 + \theta wt \quad (3)$$

where T_0 , θ , w and t are the surface temperature of a sediment pile, geothermal gradient, rate of deposition and time, respectively. T_0 is assumed to be 4 $^{\circ}\text{C}$ which represents a common temperature at the sea-bottom, and θ is assumed to be 2.3 $^{\circ}\text{C}/100\text{m}$ which is the actually observed geothermal gradient of MITI Hamayuchi (MITSUI, 1975). In the above equation, the temperature changes caused by uplifting since last 0.1-0.2 Ma are not considered. However, according to a tentative calculation, this does not affect the calculated result for the decreasing rate of $d(101)$ spacing. An integration of Eq. (1) gives

$$\ln S/S_0 = - \int_0^t k dt \quad (4)$$

where S_0 is S at $t=0$. Substituting Eqs. (2) and (3) into this equation, we obtain

$$\ln S/S_0 = -A \int_0^t \exp(-E/R(T_0 + \theta wt)) dt \quad (5)$$

Fig. 2. Depth-age relation of sediments in MITI Hamayuchi. The ages at points (open circle) are estimated from the chronological data for the Japanese Neogene edited by TSUCHI (1979).

Table 2. The activation energy E and frequency factor A in the rate constant k , and $S_0(A)$ estimated from the decrease of $d(101)$ spacing in MITI Hamayuchi

$E(\text{kcal/mol})$	$A(10^7/\text{year})$	$S_0(A)$
20	2.62	0.082

When the activation energy is estimated at $E=20\text{kcal/mol}$ and the $d(101)$ spacings of MITI Hamayuchi (Fig. 1; MITSUI, 1975) are put into Eq. (5), the unknown constants (A and S_0) can be calculated through a least-squares method. Table 2 shows the result of calculation. The result is good enough to reveal the applicability of equations (1) and (2) to the ordering of opal-CT under diagenetic conditions; S_0 is very close to the experimentally found value of $0.09 \pm 0.01A$ (KANO, 1979). The maximum difference between the observed and calculated $d(101)$ spacings is $0.007A$, that is evidently smaller than the measurement error of $d(101)$ spacing of $\pm 0.01A$ reported by MITSUI (1975). The result also indicates that the activation energy for the ordering of opal-CT under diagenetic conditions is on the same order as that measured under hydrothermal conditions.

When we put the estimated values into Eq. (4), the $d(101)$ spacing at a given temperature is expressed in terms of time as illustrated in Fig. 3. The calculated decreasing rate is much slower than that under hydrothermal alkaline conditions. This implies that the ordering rate of opal-CT is controlled not only by the reaction temperature but also by the chemical conditions. Because the diagenetic ordering occurs in nearly neutral conditions, higher alkalinity or higher pH condition presumably raises the rate of the ordering.

THERMAL HISTORY AND ORDERING OF OPAL-CT

The preceding consideration enables us to discuss the variation of $d(101)$ spacing in sediment piles. When chemical conditions are kept constant during the ordering of opal-CT, the reaction temperature is the only factor controlling the rate of the ordering. If the thermal

history of sediments is known, we can predict the $d(101)$ spacing of the sediments by using equation (4) with estimated rate constant (k).

One of the simplest models of thermal history found in sediment piles is a case when temperature increases at a constant rate. Figure 4 shows the isopleths of $d(101)$ spacing in relation to the age and the maximum temperature of the sediments. The $d(101)$ spacings in Fig. 4 are calculated by using equation (4) and the rate constant shown in Table 2 for the sediments which were deposited at 4°C and have experienced a thermal history in which temperature has increased at a given rate. Figure 4 indicates that the $d(101)$ spacing markedly changes depending on the age and temperature of sediments. KANO (1979) reported similar relationship for the ordering of opal-CT in the Neogene argillaceous sediments from Akita oil field, Japan, though the Neogene sediments have experienced thermal histories in which temperature increases continuously but not at constant rate. Likewise, the distribution of diagenetic silica minerals is remarkably dependent on the age and temperature (or depth) of sediments (VON RAD and RÖSCH, 1974; KANO, 1978; RIECH and VON RAD, 1979). Such relationship among the age, temperature (or depth) and diagenetic minerals as shown in Fig. 4 probably shows that the rate of the reaction related to diagenetic minerals is controlled mainly by the

Fig. 3. Temperature dependence of the decreasing rate of $d(101)$ spacing in sediments.

reaction temperature.

Figure 5, another expression of Fig. 4, illustrates the variation of the $d(101)$ spacing in a sediment pile, where the surface temperature is 4°C and the rate of temperature increase during deposition at each place takes a certain constant value. In Fig. 5, we can find that the isopleths of $d(101)$ spacing cut the time lines of sediments, in other words, cut the stratigraphic boundaries, and the temperature intervals among isopleths of $d(101)$ spacing are larger at the place where the rate of temperature increase is greater, though the difference of the temperature intervals is rather small.

Recently, IJIMA and TADA (1981) reported that the $d(101)$ spacing of Pliocene to Middle Miocene siliceous sediments is correlated closely with the maximum temperature to which the sediments have been subjected; the higher the temperature, the smaller the $d(101)$ spacing. On the other hand, Fig. 4 implies that the temperature at a certain $d(101)$ spacing varies with the age of sediments. However, as suggested above and shown in Fig. 5, the temperature interval between a given $d(101)$ spacing and another one in one sediment column (e.g., space between isopleths of 4.09 and 4.07 Å) seems not to vary significantly in different places and ages. There-

fore, it is expected that the $d(101)$ spacings observed for the sediments in a limited range of age are apparently correlated solely with the maximum temperature, but if the range of age difference of sediments concerned are wider, the relationship significantly shifts toward the field of higher or lower temperatures. Figure 6 shows the relationship between the $d(101)$ spacing and temperature of sediments in a range of age from 5 to 15 Ma, that are taken out from the diagram of Fig. 4. In Fig. 6, the temperature holds a good correlation with the $d(101)$ spacing. The range of temperatures for a given $d(101)$ spacing is generally narrow, ± 5 to 8°C from the mean value. Moreover, the calculated relationship is compatible with that for the Pliocene to Middle Miocene siliceous sediments reported by IJIMA and TADA (1981) (Fig. 6). Consequently, the $d(101)$ spacing of opal-CT in natural sediments can be explained from a kinetic viewpoint by taking the thermal history into account.

DISCUSSION

From the above consideration, it is certain that the ordering of opal-CT in sediments is largely affected by the thermal history under

Fig. 4. Relationship among the $d(101)$ spacing, temperature and age of sediments. A result from computation.

Fig. 5. Distribution of $d(101)$ spacing in a geologic section. A result from computation.

diagenetic conditions where temperature is much lower than that under hydrothermal or metamorphic conditions. However, the rate of the ordering is controlled undoubtedly by many other factors, especially by the chemical conditions as was stated in the preceding part. Hydrostatic pressure or stress acting on solid materials affects the crystallization or dissolution of silica (CARR and FYFE, 1958; SIEVER, 1962; ERNST and BLATT, 1964). Similar effect may play a role in the ordering process of opal-CT directly or indirectly. MURATA and LARSON (1975) reported that the $d(101)$ spacing of porcellanite is 0.004 to 0.015 Å smaller than that of more siliceous rock, chert associated at any given positions in a geological sequence,

generally. This would exemplify that the ordering rate in associated chert is not much different from that in porcellanite but the other processes such as dissolution of silica have resulted in the difference of the $d(101)$ spacing by lithology. When a significant amount of silica is added to porcellaneous sediments in the early stage of diagenesis, they become more siliceous sediments, namely cherty sediments (KANO, 1979; IJIMA and TADA, 1981). And lately added silica would have the $d(101)$ spacing larger than that of initially contained silica at any time after the silica addition. This effect generally makes the $d(101)$ spacing of cherty sediments larger than that of associated porcellaneous sediments as was discussed by IJIMA and TADA (1981). Probably, the factors other than temperature are of minor importance under diagenetic conditions.

Fig. 6. Relationship between the $d(101)$ spacing and temperature of the Pliocene to Middle Miocene siliceous sediments (IJIMA and TADA, 1981) and that of the sediments in a range from 5 to 15Ma (taken out from Fig. 5).

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REFERENCES

- CARR, R. M. and FYFE, W. S. (1958) Some observations on the crystallization of amorphous silica. *Am. Mineral.* **43**, 908–916.
- ERNST, W. G. and BLATT, H. (1964) Experimental study of quartz overgrowths and synthetic quartzite. *J. Geol.* **72**, 461–470.
- FLÖRKE, O. W. (1955) Zur Frage des "Hoch"-Cristobalit in Opalen, Bentoniten und Gläsern. *Neues Jahrb. Mineral. Mh.* Heft **10**, 217–223.
- FLÖRKE, O. W., JONES, J. B. and SEGNI, E. R. (1975) Opal-CT crystals. *Neues Jahrb. Mineral. Mh.* Heft **8**, 367–377.
- FLÖRKE, O. W., HOLLMANN, R., VON RAD, U. and RÖSCH, H. (1976) Intergrowth and twinning in opal-CT lepispheres. *Contrib. Mineral. Petrol.* **58**, 235–242.
- IJIMA, A. and TADA, R. (1981) Silica diagenesis of Neogene diatomaceous and volcanoclastic sediments in northern Japan. *Sedimentology* **28**, 185–200.
- JONES, J. B. and SEGNI, E. R. (1971) The nature of

- opal. I. Nomenclature and constituent phases. *J. Geol. Soc. Australia* 18, 57–68.
- KANO, K. (1978) Kinetic consideration on the genesis of zeolites and silica minerals in Akita oil field. *Mem. Geol. Soc. Japan* 15, 119–133 (in Japanese).
- KANO, K. (1979) Deposition and diagenesis of siliceous sediments of the Onnagawa Formation. *Sci. Rep. Tohoku Univ.*, Ser. 3, 14, 135–189.
- KANO, K. and TAGUCHI, K. (1982) Experimental study on the ordering of opal-CT. *Geochem. J.* 16, 33–41.
- MITANI, K., UOZUMI, S. and FUJIE, T. (1965) Explanatory text of geological map (scale 1:50,000), Bakki, Hokkaido Development Agency (in Japanese).
- MITSUI, K. (1975) Diagenetic alteration of some minerals in argillaceous sediments in western Hokkaido, Japan. *Sci. Rep. Tohoku Univ.*, Ser. 3, 13, 13–65.
- MITSUI, K. and TAGUCHI, K. (1974) On the diagenetic alteration of silica minerals. *J. Japan Assoc. Mineral. Petrol. Econ. Geol.* 69, 164 (Abstract).
- MITSUI, K. and TAGUCHI, K. (1977) Silica mineral diagenesis in Neogene Tertiary shales in the Tempoku district, Hokkaido, Japan. *J. Sediment. Petrol.* 47, 158–167.
- MIZUTANI, S. (1966) Transformation of silica under hydrothermal conditions. *J. Earth Sci., Nagoya Univ.* 14, 56–88.
- MIZUTANI, S. (1967) Kinetic aspects of diagenesis of silica in sediments. *J. Earth Sci., Nagoya Univ.* 15, 99–111.
- MIZUTANI, S. (1977) Progressive ordering of cristobalitic silica in the early stage of diagenesis. *Contrib. Mineral. Petrol.* 61, 129–140.
- MIZUTANI, S. (1978) Silica minerals in the early stage of diagenesis of siliceous sediments. *Mem. Geol. Soc. Japan* 15, 81–90 (in Japanese).
- MURATA, K. J., DIBBLEE, T. W., JR. and DRINKWATER, J. L. (1979) Thermal effects of large bodies of intrusive serpentinite on overlying Monterey Shale, southern Diablo Range, Cholame Area, California. *USGS Prof. Paper* 1082, 8pp.
- MURATA, K. J. and LARSON, R. R. (1975) Diagenesis of Miocene siliceous shales, Temblor Range, California. *J. Res. USGS* 3, 553–566.
- MURATA, K. J. and NAKATA, J. K. (1974) Cristobalite stage in the diagenesis of diatomaceous shale. *Science* 184, 567–568.
- RIECH, V. and VON RAD, U. (1979) Silica diagenesis in the Atlantic Ocean: diagenetic potential and transformations. In M. TALWANI *et al.* (eds.), *M. EWING Series 3, Deep Sea Drilling results in the Atlantic ocean: Continental margin and paleo-environment*. Am. Geophys. Union, Washington, D.C., 1979, 315–340.
- SIEVER, R. (1962) Silica solubility, 0–200°C, and the diagenesis of siliceous sediments. *J. Geol.* 70, 127–250.
- TSUCHI, R. (ed.) (1979) *Fundamental data on Japanese Neogene Bio- and Chronostratigraphy*. IGCP 114, National Working Group of Japan.
- VON RAD, U. and RÖSCH, H. (1974) Petrography and diagenesis of deep-sea cherts from the central Atlantic. In K. J. HSÜ and H. C. JENKINS (eds.), *Pelagic sediments on land and under the sea*, Spec. Publs. Int. Assoc. Sediment. 1, 327–347.