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Title	Studies on the Behavior of Unfrozen Interlamellar Water in Frozen Soil.
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Citation	Contributions from the Institute of Low Temperature Science, A28, 55-78
Issue Date	1979-03-14
Doc URL	<a href="https://hdl.handle.net/2115/20241">https://hdl.handle.net/2115/20241</a>
Type	departmental bulletin paper
File Information	A28_p55-78.pdf



# Studies on the Behavior of Unfrozen Interlamellar Water in Frozen Soil\*

by

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Received January 1979

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## Abstract

Phase transformation of water in clay minerals was looked into in a temperature range from a few degrees C above zero to  $-110^{\circ}\text{C}$  by observing discontinuities in linear expansion coefficients of wet bentonite, illite and kaoline all varying in water content, with the support of the observation by the results obtained by DSC(differential scanning calorimetry) and X-ray diffraction analysis. In case of bentonite, which is marked by the large internal surface of its particle, the linear expansion coefficient showed a peculiar behavior that depends on the water content ; namely, when it was larger than 41%, the coefficient started showing discontinuities first around  $0^{\circ}\text{C}$ , and secondly around  $-9^{\circ}\text{C}$  and thirdly around  $-33^{\circ}\text{C}$ , whereas, as it decreased, the first discontinuity disappeared at the water content of 41%, the second at 38% and the third at 26%. Let water contents of 26% (or 0.26 g of water per gram of dry bentonite), 12% (38% minus 26%), 3% (41% minus 38%) and any percent in excess of 41% (26% plus 12% plus 3%) be designated as constituting Water III, II, I, and 0. It follows from the foregoing disappearance of the discontinuities that Water III was responsible for none of them, Water II only for the third discontinuity, Water I for the second and Water 0 for the first. In case of illite, which is also marked by the internal surface, it displayed a similar peculiar behavior, while in case of kaoline, which lacks the internal surface, showed only a discontinuity around  $0^{\circ}\text{C}$  irrespective of the water content. Consequently, Water I, II and III were considered interlamellar water. Results of DSC of bentonite of various water contents ranging in temperature from  $-15^{\circ}\text{C}$  to  $10^{\circ}\text{C}$  verified that at  $-9^{\circ}\text{C}$  Water I, II and III were not frozen and that the latent heat of fusion of Water 0 was about 70 cal/g. Results of DSC at temperature varying from  $-15^{\circ}\text{C}$  to  $-55^{\circ}\text{C}$  revealed some exothermal reaction. If this is considered as the phase transformation of Water II from water to ice, the latent heat on freezing of Water II is estimated to be a few calories per gram.

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\* Contribution No.1993 from the Institute of Low Temperature Science.

北海道大学審査学位論文

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## I. Introduction

Since BOUYOUCOS (1917) demonstrated, using a pycnometer, the fact that volumetric change of frozen soil due to conversion of water to ice occurs in a wide range of sub-zero temperatures, the presence of a continuous unfrozen water film in frozen soil has been established by abundant evidence, whereby it has been generally accepted that such an unfrozen film may play an important role in frost heave phenomena, especially in the so-called secondary heave in which ice lenses grow in already frozen soil.

As for quantitative measurements of the amount of unfrozen water, a calorimetric method has been mainly employed. WILLIAMS (1963, 1964) used an adiabatic calorimeter to compile phase composition data of various soils. According to his data, the amount of unfrozen water in a frozen soil at a given temperature depends greatly on grain size of the soil being larger for finer-grained soil. KOLAIAN and LOW (1963) showed, using frozen montmorillonite (bentonite), that 0.55 g and 0.45 g of water remained unfrozen per gram of dry mass respectively at  $-5^{\circ}\text{C}$  and  $-15^{\circ}\text{C}$ .

As unfrozen water is supposed to be adsorbed on the surface of soil particles, ANDERSON and TICE (1972) proposed an empirical equation in a temperature range from  $0^{\circ}\text{C}$  to  $-5^{\circ}\text{C}$  relating the amount of unfrozen water to the specific surface area of soil and to the temperature, whereby they used both an adiabatic and isothermal calorimeter to obtain the data from which the equation was derived.

As pointed out by ANDERSON and TICE (1973), the calorimetric method to determine the amount of ice at the beginning temperature is based on the assumption that the latent heat of melting ice at sub-zero temperatures in frozen soil is 79.8 cal/g and that no endothermal or exothermal reaction other than melting of ice occurs in frozen soil during the course of warming. The assumption seems to be acceptable in a temperature range down to several degrees C below zero.

Behavior of unfrozen water in soil at colder temperatures has hitherto been studied rather with an academic interest than with a practical need, resulting in a few qualitative works on it. Namely, KATO (1959), who made a cryogenic differential thermal analysis of a bentonite-water system, found two exotherms (by cooling) around  $-10^{\circ}\text{C}$  and  $-24^{\circ}\text{C}$ , while ANDERSON and TICE (1971) made a similar analysis, reporting exotherms at  $-36^{\circ}\text{C}$  and  $-45^{\circ}\text{C}$ .

A practical need has come to the fore in the recent years, however, of studying frozen soil at considerably low temperatures to treat such questions as arise in construction of subsurface tanks for storing LNG (liquefied natural gas;  $-160^{\circ}\text{C}$ ) and in strengthening of weak ground by an artificial freezing technique to facilitate civil engineering work, the former easily lowering the temperature of a nearby ground to  $-50^{\circ}\text{C}$  or below it, while the latter to around  $-20^{\circ}\text{C}$ . The extrapolation of the equation of ANDERSON and TICE to these low temperatures suggests the existence of a considerable amount of unfrozen water if the specific surface area of soil is large.

Even if a soil has a small specific surface area on the average, it may contain such constituents as montmorillonite and illite that have large specific surface areas in which case a high concentration of unfrozen water localized around them may play an important role in frost heave phenomena. Hence, it is important to study behaviors of unfrozen water in frozen materials which have large specific surface areas at low temperatures.

In the course of working with linear dilatometry of various frozen materials down to  $-110^{\circ}\text{C}$  (Horiguchi, 1973, 1978), the author noticed that this technique would provide a method to determine the amount of unfrozen water in frozen specimens with large specific surface areas. Section II of this paper gives a general interpretation of clays and a brief description of characteristics of studied clays. Section III presents results of linear dilatometry of various materials and gives estimation of the amount of unfrozen water in frozen bentonite and illite at low temperatures. Section IV deals with the dependence of the  $d(001)$  spacing on temperature. Section V gives an account of the result of DSC (differential scanning calorimetry) of bentonite from  $-10^{\circ}\text{C}$  to  $10^{\circ}\text{C}$ , the results being again in fair accordance with the previous one as well as confirming that the latent heat of melting ice in this temperature range was about 70 cal/g. Also this section gives estimation of the latent heat of melting ice in a temperature range from  $-15^{\circ}\text{C}$  to  $-55^{\circ}\text{C}$ , which turns out to be only a few calories per gram, from the result of DSC in the same temperature range together with the possible amount of ice formation in the same temperature range deduced from the results obtained in Sections III and IV. Thus, the use of calorimetry to determine the amount of unfrozen water below  $-20^{\circ}\text{C}$  is shown hardly acceptable.

## II. Selection of samples and their characteristics

### II. 1. *Clay and clay minerals*

As mentioned in Section I, among constituents of soil, those with large specific surface areas are important for the study of unfrozen water at lower temperatures. Clays have such large specific surface areas and are so widely found in various soils that typical clays call for a thorough investigation.

Clay consists of clay minerals which represent in structure a stack of unit layers. According to the construction of their unit layers, clay minerals are classified into the two-layer type and the three-layer type. As to the former, as shown in Fig. 1, one silica sheet (two-dimensional arrays of Si (or Al)-O tetrahedral) and one octahedral sheet (two-dimensional arrays of Al (or Mg)-O-OH) combine to make a unit layer.

As to the latter, as also shown in Fig. 1, two silica sheets sandwich one octahedral sheet in a unit layer; in some clay minerals (talc; phyllosilicate) exchangeable ions like  $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{K}^+$  designated as M in Fig. 1 are found between the two adjacent unit layers and in other clay

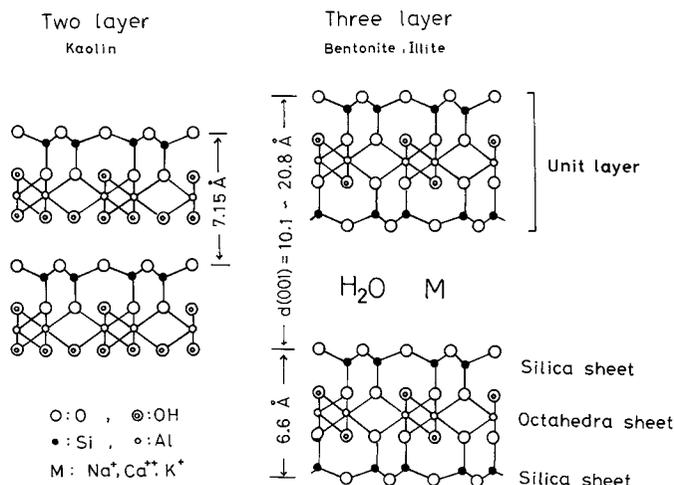


Fig. 1 Structures of clay minerals.

minerals (montmorillonite ; illite) water is found in addition to the cations, such water being called interlamellar water. While the four foregoing minerals are of the three-layer type, kaolinite is a typical clay mineral of the two-layer type. Montmorillonite shows swelling. Namely, when water molecules or organic matters having an ionic or polar character are brought into contact with it, they penetrate into the space between the two adjacent unit layers, resulting in expansion of the space. Pyrophyrite, talc, and kaolinite show no such swelling. Illite has a complicated nature in that it does not show swelling but has interlamellar water.

Chosen in this investigation as the representatives of these three modes of interaction with water are montmorillonite, illite and kaolinite, which are respectively bentonite, illite and kaoline in terms of clay. The first two were obtained from Ware's Natural Science Establishment, Inc., and kaoline from WAKO Pure Chemical Industries, Ltd.

## II. 2. Specific surface area

Because of a high correlation between retention ability and surface area of a clay, physical and chemical properties of a clay may be greatly influenced by the extent of its surface area. Clays show a great deal of difference in specific surface area ; namely, non-swelling clays like kaoline have the surface area limited only to the external surface, whereas swelling clays like bentonite have a large amount of surface area internal as well as external. Therefore, both total and external surface areas were measured of bentonite, illite and kaoline.

For the measurement of total surface area, the ethylene glycol retention method was used. It is based on the empirical fact that the negatively charged surface of a clay mineral attracts a polar molecule like ethylene glycol by an electrical force. Clay weighing about 0.2 g was poured into about 50 ml of 2% solution of ethylene glycol and was permitted to stand for about

48 hours. Then, it was dried at 110°C in an oven in which the vapour of ethylene glycol was supplied ; it was weighed twice a day until its weight became constant ; in this stage, ethylene glycol was retained in two layers in the space between the two adjacent unit layers replacing water and in one layer on the external surface. According to DYAL and HENDRICKS (1950), 0.00031 g of ethylene glycol in weight forms a monolayer on each square meter of the clay surface. The total specific surface area  $S$  in  $\text{m}^2$  per g was calculated by the equation,  $S = W_e / (W_s \times 0.00031)$ , where  $W_e$  is the weight in gram of ethyleneglycol retained by a sample, and  $W_s$  is the weight in gram of the sample when dried.

The external surface area of the clays was measured by a method, which was derived by BRUNAUER, EMMETT and TELLER (1938) using non-polar nitrogen gas. Because a weakly adsorbed nitrogen molecule dose not penetrate into the space between the unit layers in place of interlamellar water, the measurement obtained represents only that of the external surface. Used in this experiment was the surface area measurement apparatus p-600 made by SHIBATA Chemical Co., Ltd.

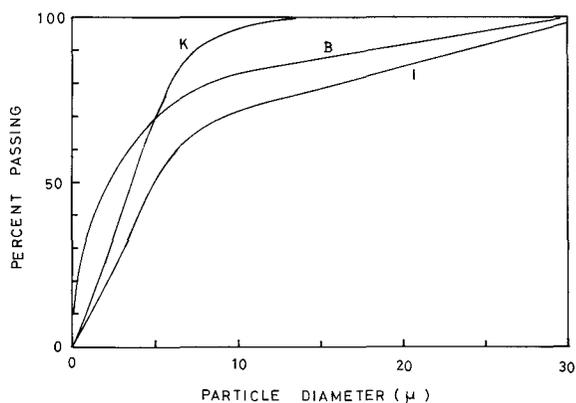
Measurements were made of specific surface area using three samples of each clay. The average of each measurement is shown in Table 1, together with the average of internal surface area calculated from the difference between the total and the external surface area of 99.5 and 700  $\text{m}^2/\text{g}$  respectively and illite 58.7 and 128  $\text{m}^2/\text{g}$ , while kaoline had the external, namely, total surface area of 4.5  $\text{m}^2/\text{g}$ .

**Table 1** Specific surface area of clays ( $\text{m}^2/\text{g}$ )

	Total	External	Internal
Bentonite	799.5	99.5	700.0
Illite	186.7	58.7	128.0
Kaoline	4.5	4.5	0.0

### II. 3. Particle size distribution

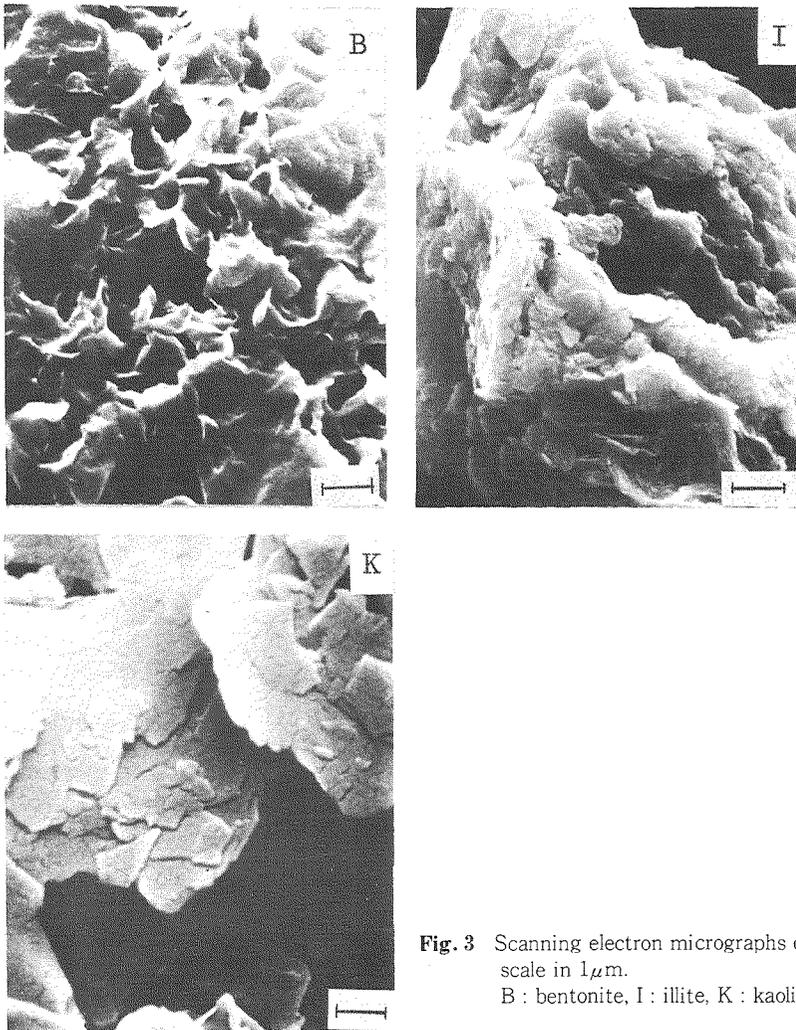
Particle size distribution being one of the stablest characteristics of clay, particle size analysis was conducted of each sample, using a microphotograph analyzer made by SEISHIN Enterprise Co., Ltd. The principle of the analyzer is based on the settling theory, which allows indirect calculation of the particle size from a screened amount of penetrating light through particles suspended in liquid. The following dispersion method was used at 25°C ; namely, a



**Fig. 2** Grain size accumulation curves.  
B : bentonite, I : illite, K : kaoline

sample of clay was put in a 2% solution of sodium metaphosphate ; then a supersonic wave was applied to it for three minutes. The results of analysis of bentonite, illite and kaoline are shown by grain size accumulation curves B, I and K, respectively in Fig. 2. The ordinate represents the percentage of accumulated weight of particles not larger than a specific diameter in  $\mu\text{m}$  against the total weight, while the abscissa represents the size of a particle in  $\mu\text{m}$ .

In spite of the similarity of three curves, the external specific surface areas of bentonite, illite and kaoline differ considerably from one another, as shown in Table 1. The difference is understood from SEM (scanning electron microscope) photographs in Fig. 3. While kaoline has a smooth surface, there exist many small crystals on the surface of illite due to weathering and



**Fig. 3** Scanning electron micrographs of clay minerals (x10,000), scale in  $1\mu\text{m}$ .  
 B : bentonite, I : illite, K : kaoline

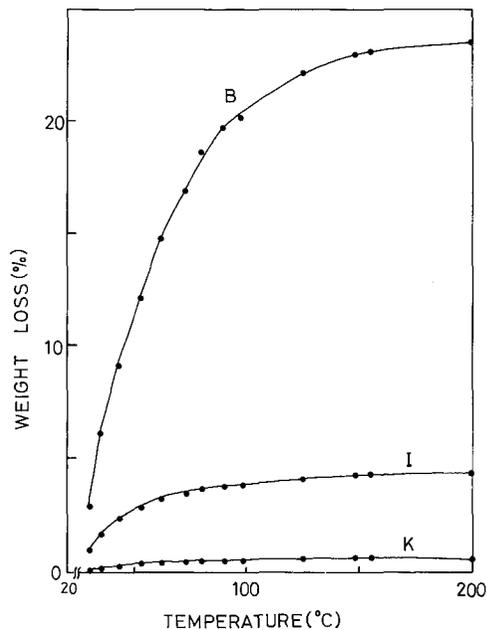
bentonite is marked by a strong development of cusp-like crystals which are characteristic of montmorillonite as pointed out by BORST et al. (1969)

#### II. 4. *Drying of clay by heating*

At ordinary temperatures, clay adsorbs a considerable amount of water, which can be almost completely removed at a temperature below 200°C. Since part of unfrozen water in clay at negative temperatures is supposed also to be adsorbed water, a process of removing adsorbed water by heating is by itself interesting for the study of unfrozen water. The loss of adsorbed water by heating was measured from changes in weight in the following procedure ; an air-dried sample weighing bottle whose accurate weight was measured ; the bottle was placed in a drying oven at a given temperature for one day ; then the weight of the bottle was measured after cooling in a desiccator for 10 minutes. Measurements were made at temperatures in incremental sequence up to 200°C.

The result is shown by weight loss curves of bentonite, illite and kaoline in Fig. 4. The ordinate represents the weight loss in percent of the weight of a clay dried at 200°C, while the abscissa represents the temperature of the drying oven. It is seen from the figure that bentonite, illite and kaoline have about 23.6%, 4.5% and 0.6% of adsorbed water respectively at 20°C.

The water content of soil is defined by the ratio of the weight of water against that of soil dried at a standard temperature. In civil engineering and agronomy, 105°C is used as standard. However, as seen from Fig. 4, bentonite has several percent of adsorbed water at this temperature relative to the 200°C-dried bentonite, so the present work used 200°C as the standard drying temperature.



**Fig. 4** Weight loss curves of adsorbed water of clay minerals.  
B : bentonite, I : illite, K : kaoline

### III. Dilatometry of frozen specimens

#### III. 1. Procedures

A specimen of a comparatively large water content (larger than 80% for bentonite, 20% for illite and 10% for kaoline) was prepared as follows : A necessary amount of distilled water and that of dried clay were thoroughly mixed. The mixture was then put into a soft plastic tube 15 to 20 mm in length and 5 mm in inner diameter and both the ends of the tube were sealed using a plastic adhesive tape to prevent water from evaporation. After the sealed tube was left for 24 hours or longer in a warm room in order that water was distributed as homogeneously as possible, it was brought into a cold room at about  $-15^{\circ}\text{C}$ . When the mixture was frozen, it was taken out from the tube and put into a liquid nitrogen bath in order that no supercooling water was left in it. Then, both the ends of the cylindrical frozen mixture was shaped perpendicular to its axis and the finished length was measured with a vernier caliper.

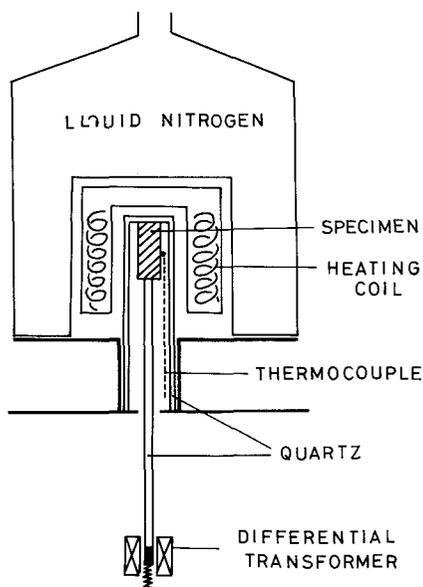


Fig. 5 Schematic diagram of the holder of a specimen.

A specimen of a less water content was prepared in the other way since thorough mixing of water and clay was difficult in this case. A specimen of a large water content frozen at  $-15^{\circ}\text{C}$  as mentioned above was dried in an oven at about  $70^{\circ}\text{C}$  to reduce its water content (see Fig. 4) and then was left in a desiccator of an appropriate vapor pressure ; specimens with different water contents were obtained by changing the vapor pressure and/or the duration of time in the desiccator. The specimen taken out from the desiccator was then brought into a cold room and frozen, and then treated as mentioned before.

Dilatometry was applied in a cold room with a thermo-dilatometer (Type DL-1500L, made by SHINKU-RIKO Co., Ltd.), whose main part is schematically shown in Fig. 5. The shaped frozen specimen was put in a cylindrical container of thin copper (not shown in the figure) 13 mm in length and 7 mm in diameter and set in the specimen chamber of the

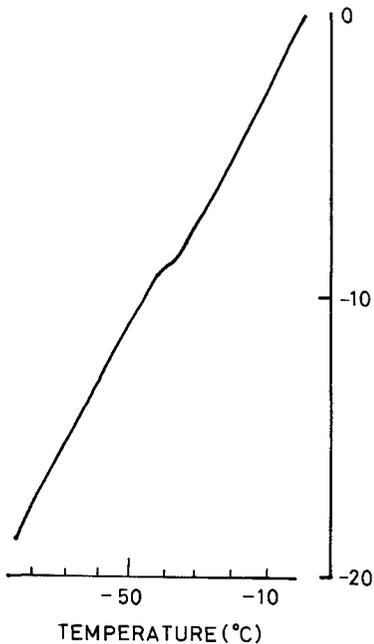
dilatometer as shown in the figure. Temperature of the chamber was controlled by a heating coil wound around the chamber, and was measured with a thermocouple kept in contact with the copper container. (The temperature was regarded as the temperature of the specimen and used as such hereafter. As for a possible lag of the latter to the former, see Fig. 14). After

setting of the specimen the temperature was raised to and kept at a few degrees C below zero until the specimen ceased to change its length. Then the temperature was lowered at a constant rate of  $0.5^{\circ}\text{C}/\text{min}$  unless stated otherwise, while the output of the differential transformer was recorded. After cooled down to a desired temperature, the specimen was warmed up to a few degrees C above zero to see the change of length around  $0^{\circ}\text{C}$ .

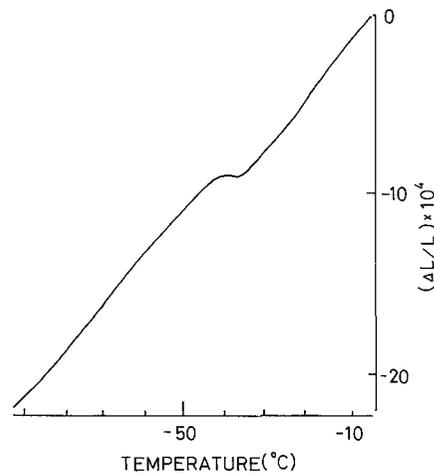
After the measurement, the water content of the specimen was determined by weighing it before and after being dried at  $200^{\circ}\text{C}$  for 24 hours.

### III. 2. Results

Examples of the results of measurements were shown in Figs. 6-11 and 13, in which Figs. 6 and 7 represent two kinds of natural soils : silty soil (water content : 42.9% ; external and internal specific surface areas :  $60\text{ m}^2/\text{g}$  and  $48\text{ m}^2/\text{g}$ , respectively) and clayey soil (water content : 79%, external and internal specific surface areas :  $40\text{ m}^2/\text{g}$  and  $80\text{ m}^2/\text{g}$ , respectively). The curves of the former and latter are anomalous between  $-33^{\circ}\text{C}$  and  $-43^{\circ}\text{C}$  and between  $-35^{\circ}\text{C}$  and  $-43^{\circ}\text{C}$ , respectively. The fact that the curves for titanium oxide (particle size :  $0.2\ \mu\text{m}$  ; specific surface area :  $6.7\text{ m}^2/\text{g}$ ),  $\alpha$ -alumina ( $0.5\ \mu\text{m}$  ;  $10.3\text{ m}^2/\text{g}$ ) and carborundum ( $4\ \mu\text{m}$  ;  $2.4\text{ m}^2/\text{g}$ ) showed no such an anomaly suggested that the anomaly might be due to the large



**Fig. 6** Change in length of a silt-water system (w : 42.9%) on cooling.



**Fig. 7** Change in length of a clay-water system (w : 79%) on cooling.

values of specific surface area.

Reproducibility of such an anomaly was tested for a specimen of illite of a water content of 40.2%, with the result shown in Fig.8. The specimen was cooled from  $-2^{\circ}\text{C}$  to  $-110^{\circ}\text{C}$ , then warmed up to  $-2^{\circ}\text{C}$  and again cooled down. To save time, the cooling or the warming rate was  $1^{\circ}\text{C}/\text{min}$  in this measurement. The curves for two cooling processes were quite similar with the anomalous part between  $-15^{\circ}\text{C}$  and  $-42^{\circ}\text{C}$  while the anomalous part in a warming process was between  $-23^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$ . The discrepancy between  $-42^{\circ}\text{C}$  and  $-23^{\circ}\text{C}$  might suggest some phase transformation of water which caused a large lag of the true temperature

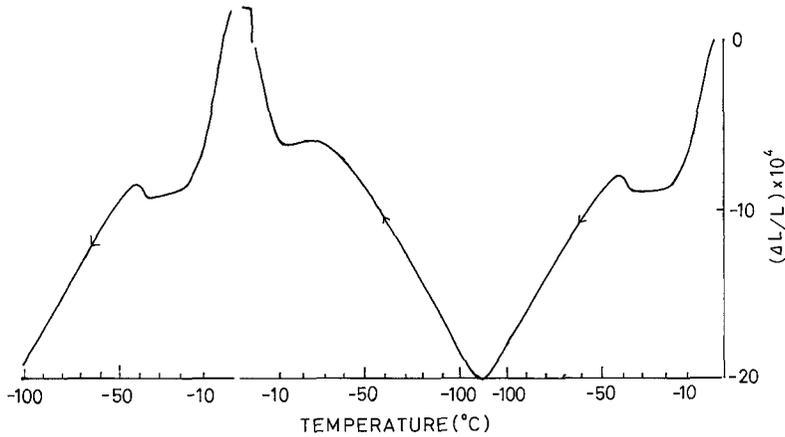


Fig. 8 Change in length of an illite-water system ( $w : 40.2\%$ ) on cooling and heating.

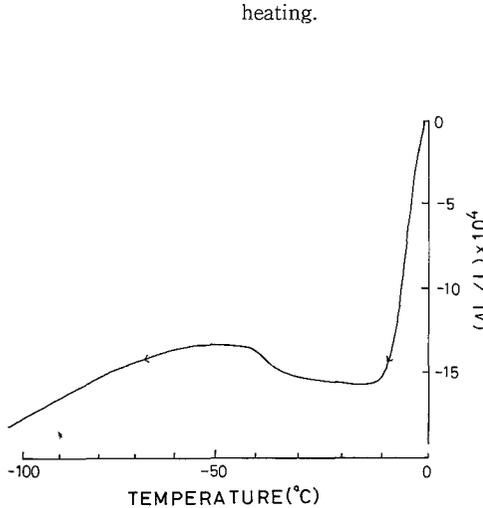


Fig. 9 Change in length of a bentonite-water system ( $w : 81.2\%$ ) on cooling.

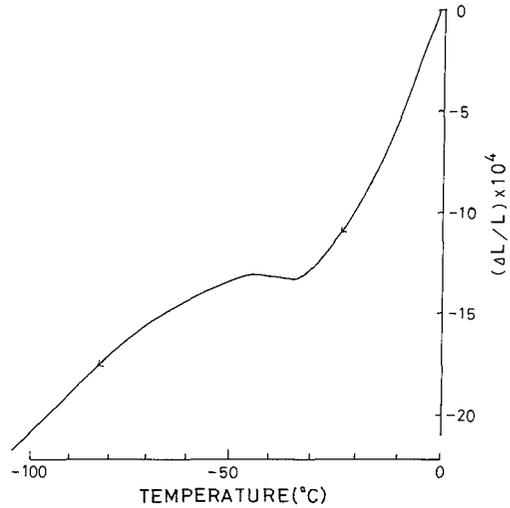
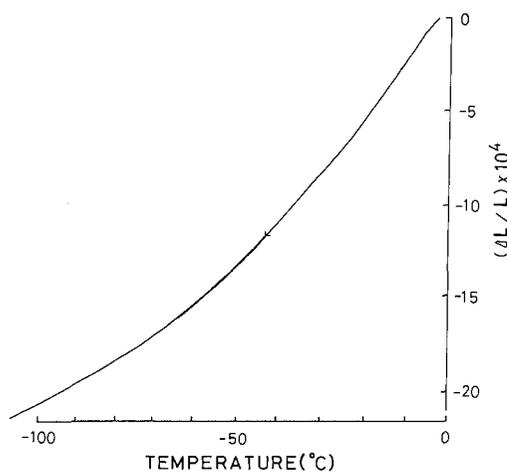
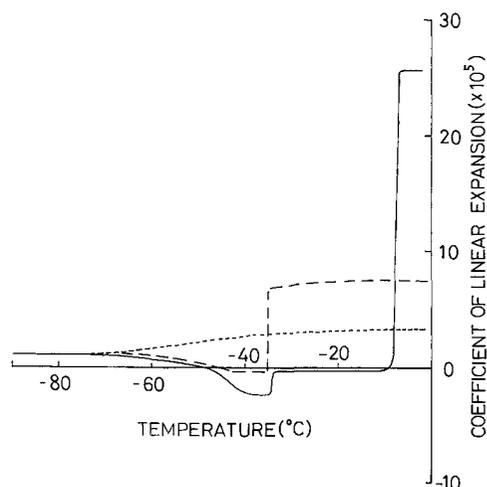


Fig. 10 Change in length of a bentonite-water system ( $w : 29.5\%$ ) on cooling.



**Fig. 11** Change in length of a bentonite-water system ( $w : 15.6\%$ ) on cooling.



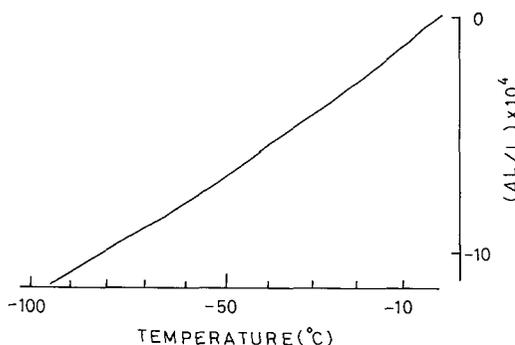
**Fig. 12** Relation between coefficient of linear expansion and temperature of bentonite.  
 — :  $w = 81.2\%$ , - - :  $w = 29.5\%$   
 ···· :  $w = 15.6\%$

of the specimen behind the measured temperature.

Figures 9, 10 and 11 show the results of change per unit length of bentonite specimen with water contents of 81.4%, 29.5% and 15.6%, respectively. The curves in Figs. 9 and 10 have anomalous parts between  $-10^{\circ}\text{C}$  and  $-50^{\circ}\text{C}$  and between  $-35^{\circ}\text{C}$  and  $-45^{\circ}\text{C}$ , respectively. But the shapes of the curves between these ranges are dissimilar. The difference is more clearly seen if the curves are compared with each other in terms of linear expansion coefficients, as is shown in Fig. 12, where the linear expansion coefficients obtained from Figs. 9, 10 and 11 are against temperature. The linear expansion curve for 81.2%-wet bentonite has two clear discontinuities at around  $-10^{\circ}\text{C}$  and  $-34^{\circ}\text{C}$ , while that for 29.5%-wet bentonite has only one discontinuity at around  $-35^{\circ}\text{C}$ . The temperature at which a discontinuity of linear expansion coefficient occurs will be hereafter called a transition temperature, which will play an important role in III. 3. Changes in length around  $0^{\circ}\text{C}$  were measured as mentioned in III. 1, though not shown in this section, and sometimes resulted in a discontinuity of linear expansion coefficient at around  $0^{\circ}\text{C}$  and other times not. It must be noted that all transition temperatures are such that, as the temperature passes any of them while being cooled, an expansion mechanism begins to occur, which is in all likelihood the transformation of unfrozen water to ice.

Irrespective of its water content, kaoline has a transition temperature at  $0^{\circ}\text{C}$  but nowhere also. One example of the result of the dilatometry of kaoline is shown in Fig. 13.

Finally, some justification of choosing a cooling rate of  $0.5^{\circ}\text{C}/\text{min}$  in the present dilatometry is shown as follows: The measured transition temperature of bentonite of a water content of 85.5% were plotted against the cooling rate in Fig. 14, where black dots represent the



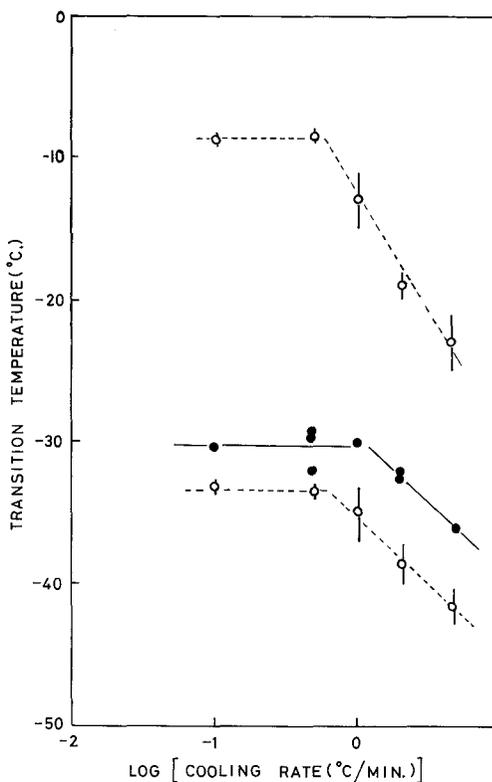
**Fig. 13** Change in length of a kaoline-water system (w : 37.5%) on cooling.

transition temperature of ammonium chloride measured in the same way. This temperature should be  $-30.5^{\circ}\text{C}$  because the discontinuity of the linear expansion coefficient of ammonium chloride is due to its  $\lambda$ -transition at  $-30.5^{\circ}\text{C}$ . From Fig. 14, it is seen that a cooling rate of  $0.5^{\circ}\text{C}/\text{min}$  is acceptable for the determination of the transition temperature.

### III. 3. Water content and transition temperature

As shown in Fig. 12, the number of transition temperatures of bentonite was dependent on water contents. To investigate the dependence in detail, more dilatometric measurements down to  $-110^{\circ}\text{C}$  were made of bentonite specimens of various water contents. The results are compiled in Fig. 15, where black dots represent temperatures at which transition occurs. The coordinate of the figure goes down only to  $-40^{\circ}\text{C}$  because no transition temperatures were found below it. It is noticed that the values of transition temperature were grouped into three, the first around  $-33^{\circ}\text{C}$ , the second around  $-9^{\circ}\text{C}$  in which one at  $-17^{\circ}\text{C}$  may be included, and the third at  $0^{\circ}\text{C}$ .

Now, four dotted lines in the figure show that specimens of water contents of 6%, 16%, 23% and 26% had no transition temperatures. Six specimens of water contents from 28% to 38% had one transition temperature in the first group. Two specimens of water contents of



**Fig. 14** Relation between cooling rate and temperature at which a phase transition of water begins.  
 ○ : bentonite, ● : ammonium chloride

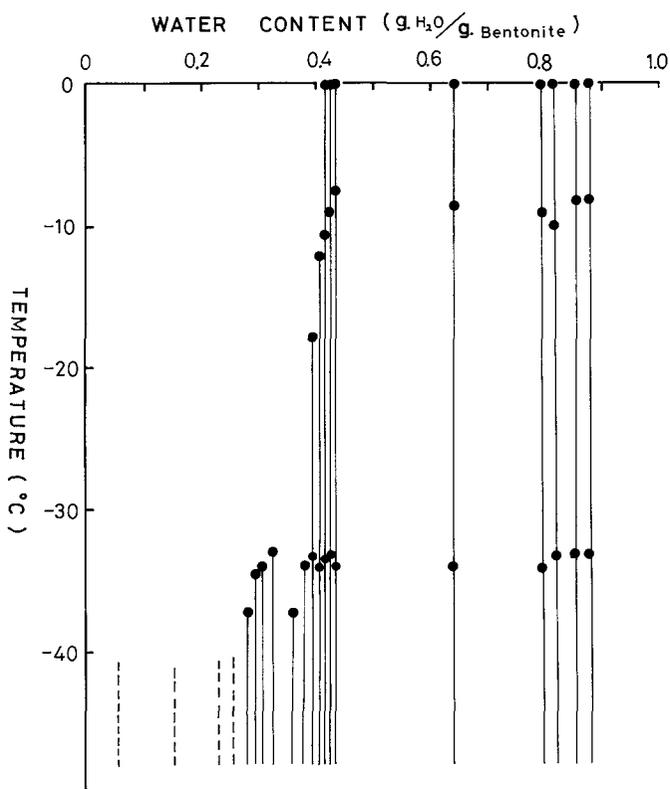
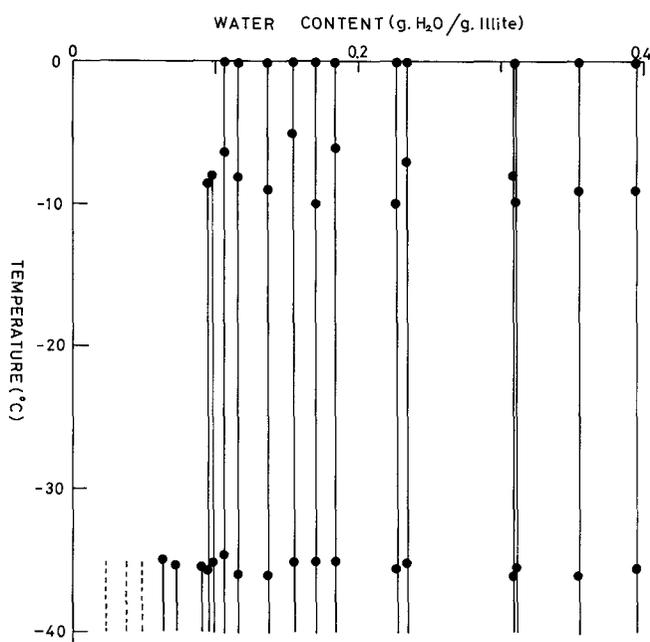


Fig. 15 Relation between water content of bentonite and temperature at which a phase transition of water begins.

39% and 41% had two transition temperatures, one in the first and the other in the second group. Specimens of water contents larger than 41% had a transition temperature in every group. As a natural consequence of the foregoing results, the amount of water added to one gram of dried bentonite in four sequences constitutes four different types designated as Water III, II, I and 0, corresponding respectively to the first addition of 0.26 g (making the water content 26%), the second addition of 0.12 g (bringing the water content to 41%) and the further addition in excess of 0.41 g. As noticed in III. 2., it is very likely that the phase transformation of water starts at the corresponding transitional temperature. Hence, one may say that Water III does not freeze down to  $-110^{\circ}\text{C}$ , while Water II, I and 0 start freezing around  $-33^{\circ}\text{C}$ ,  $-9^{\circ}\text{C}$ , and  $0^{\circ}\text{C}$ , respectively.

It will be later shown in V. 2 that Water 0 is ordinary water and that 0.41 g of water per gram of dried bentonite remains actually unfrozen at  $-9^{\circ}\text{C}$ .

The result of a similar analysis made of illite specimens shown in Fig. 16 determines that



**Fig. 16** Relation between water content of illite and temperature at which a phase transition of water begins.

0.05 g, 0.02 g and 0.03 g of water added to one gram of dried illite account for Water III, II and I, respectively.

Assuming that Water III is uniformly adsorbed on the surfaces of bentonite or illite particles and that the specific gravity of Water III is unity, the thickness of a Water III film can be calculated from the specific surface area of bentonite or illite given in Table 1. The thickness turns out to be 3.25 Å for bentonite and 3.2 Å for illite, both close to the dimension of the water molecule. In other words, the Water III film seems to be adsorbed as a monolayer on the surfaces of bentonite or illite particles. CLIFFORD (1972) showed that a water monolayer adsorbed on to a porous silica did not freeze down to  $-50^{\circ}\text{C}$ . The present work may be said to have extended the temperature range in verification of the presence of such a water monolayer.

### III. 4. Water content and linear expansion coefficient between $-2^{\circ}\text{C}$ and $-9^{\circ}\text{C}$

As seen in Fig. 12, the linear expansion coefficient of a specimen is rather constant between  $-2^{\circ}\text{C}$  and  $-9^{\circ}\text{C}$  but depends greatly on the water content of the specimen. The values of averaged linear expansion coefficient  $\bar{\alpha}$  between  $-2^{\circ}\text{C}$  and  $-9^{\circ}\text{C}$  are plotted in Fig. 17 for bentonite and in Fig. 18 for illite. Note the difference in scale, especially of the coordinate in both the figures. In Fig. 17, black dots represent the results for ordinary bentonite while two open circles those for bentonite-organic compounds. For ordinary bentonite,  $\bar{\alpha}$  sharply

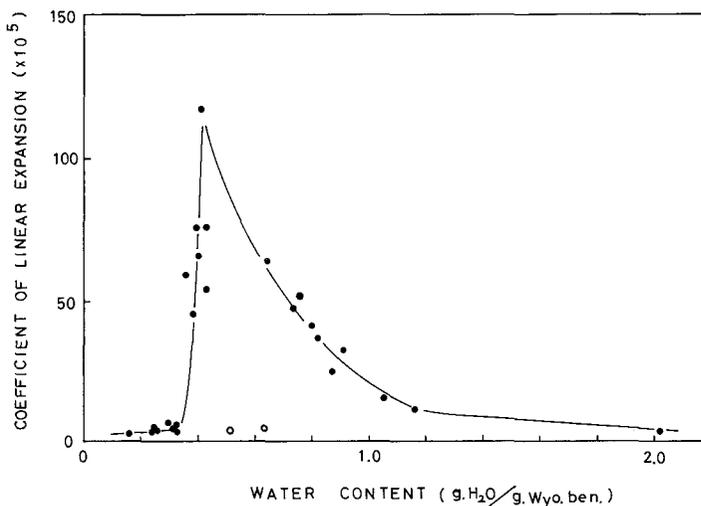


Fig. 17 Relation between water content and coefficient of linear expansion in temperature region from  $-2^{\circ}\text{C}$  to  $-9^{\circ}\text{C}$ .

● : bentonite, ○ : bentonite-organic compound

increases from  $6 \times 10^{-5}$  at the water content of 33% to  $1.3 \times 10^{-3}$  at 41% and then with increase in water content  $\bar{\alpha}$  gradually decreases to  $5 \times 10^{-5}$  at 204%.

On the assumption that the  $d(001)$  spacing of bentonite contracts with decreasing temperature by expulsion of its interlamellar water (the reverse process of swelling can be understood as the behavior of  $\bar{\alpha}$ , though qualitatively : At  $-2^{\circ}\text{C}$  Water 0 has frozen out and available water for swelling bentonite is Water I, II and III. Since water added in excess of 41% is Water 0, at  $-2^{\circ}\text{C}$  bentonite of a water content of 41% has the maximum amount of water available for swelling. At this temperature, the ice matrix made from Water 0 becomes stronger with increase in the water content of bentonite in excess of 41% and effect of a large microscopic contraction of the bentonite particle (montmorillonite) becomes less and less evident.

Now, an explanation of the sharp drop of  $\bar{\alpha}$  is given by introducing the notation  $L(w, -t)$ , which represent the length of  $d(001)$  of bentonite of a water content of  $w\%$  at  $t^{\circ}\text{C}$ . The difference in available amount of water for swelling makes  $L(41, -2)$  larger than  $L(33, -2)$ . Because of the assumed contraction in cooling,  $L(41, -9)$  is smaller than  $L(41, -2)$ . Let  $L(41, -9)$  be equal to  $L(33, -2)$ . This means that during the cooling process bentonite of a water content of 41% dispels water in excess of 33% from the interlamellar space. Then,  $L(33, -9)$  should be equal to  $L(33, -2)$  because bentonite of a water content of 33% has no water to be dispelled when it is being cooled down to  $-9^{\circ}\text{C}$ . Thus, while the length of  $d(001)$  of bentonite of a water content of 41% contracts, that of 33% shows no contraction. The dispelled water will not contribute to dilatation because it may fill pore spaces.

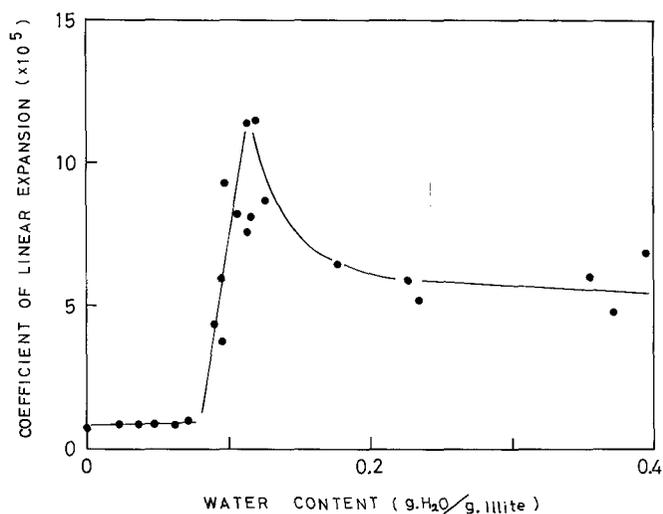


Fig. 18 Relation between water content and coefficient of linear expansion of illite in temperature region from  $-2^{\circ}\text{C}$  to  $-9^{\circ}\text{C}$ .

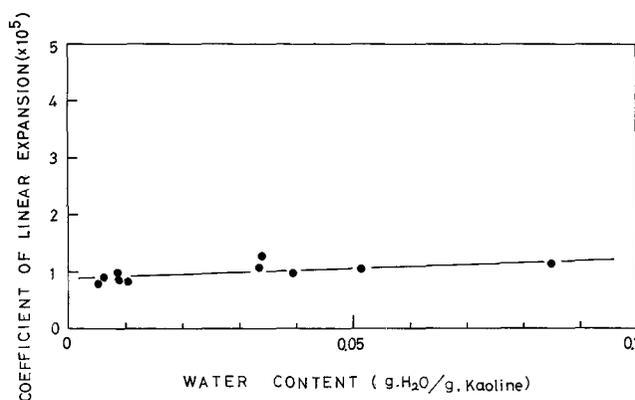


Fig. 19 Relation between water content and coefficient of linear expansion of kaoline in temperature region from  $-2^{\circ}\text{C}$  to  $-9^{\circ}\text{C}$ .

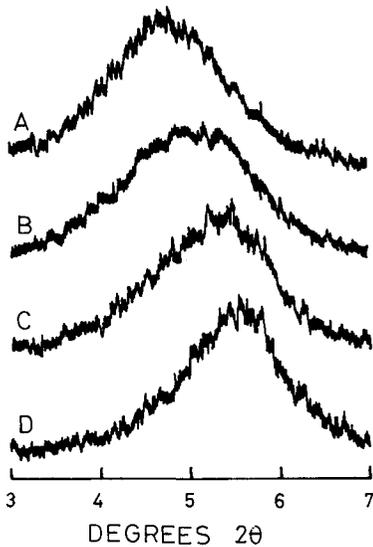
The verification of such a speculation by measuring  $L(w, -t)$  with an X-ray diffractometer will be given in IV, but a direct verification of the effect of swelling on  $\bar{\alpha}$  is supplied by the open circles in Fig. 17. The organic compound used was prepared by immersing 1 g of bentonite in 50 ml of solution of benzyltriethylammonium chloride  $\text{C}_{13}\text{H}_{22}\text{NC1}$  for about ten days and then dried at  $110^{\circ}\text{C}$  until the weight became constant. The treated bentonite showed no swelling because of organic cations adsorbed on the negatively charged surface of bentonite particles. The values of  $\bar{\alpha}$  of treated bentonite specimens of water contents of 51.5% and 60.2% were  $3.9 \times 10^{-5}$  and  $6.5 \times 10^{-5}$  respectively against  $\bar{\alpha}$  of  $8 \times 10^{-4}$  and  $7 \times 10^{-4}$  expected of

untreated bentonite specimens of respective water contents.

The result of illite in Fig. 18 showed a similar tendency to that of bentonite. Since illite is considered non-swelling, this similarity is puzzling. But the maximum value of  $\bar{\alpha}$  of illite is about one tenth of that of bentonite. Slight swelling may be accounted for it. The result of kaoline in Fig. 19 shows a very normal behavior as is expected.

#### IV. Basal spacing of frozen bentonite

In the previous section, the dependency of the basal spacing of frozen bentonite on its water content and temperature,  $L(w, t)$ , was used to explain the dependency of  $\bar{\alpha}$  on the water content. Direct evidence to support considerations in the previous section will be given below.



**Fig. 20** X-ray diffraction patterns of first order basal spacing  $d(001)$  of frozen bentonite at different temperatures.  
A :  $-3.0^{\circ}\text{C}$ , B :  $-7.8^{\circ}\text{C}$ ,  
C :  $-15.5^{\circ}\text{C}$ , D :  $-50.0^{\circ}\text{C}$

A cryogenic X-ray diffractometer made by Rigakudenki Co., Ltd., was used to measure the basal spacing of bentonite in a temperature range from  $-3^{\circ}\text{C}$  to  $-50^{\circ}\text{C}$ . The working condition for the diffractometer was as follows : target : Cu ; filter : Ni ; voltage : 32 kv ; current : 15 mA ; detector : scintillation counter. The water content of the measured specimen was 138 %. The temperature was measured with a thermocouple placed on a boundary between the holder and the specimen. After the specimen was placed on the holder, the temperature was lowered to  $-40^{\circ}\text{C}$  with an aim to prevent soil water from supercooling. After the freezing of soil water was confirmed, the temperature was raised to  $-3^{\circ}\text{C}$  and kept there for two hours to attain a thermal equilibrium in the holder. Then, the diffraction angle  $2\theta$  was measured from  $3^{\circ}$  to  $7^{\circ}$  so that the first-order basal spacing  $d(001)$  was obtained. When one measurement was finished, the temperature was lowered by about  $2^{\circ}\text{C}$  and kept for one hour before the start of the next measurement.

One of the original recording charts was reproduced in Fig. 20, where curves A, B, C and D were taken at  $-3.0^{\circ}\text{C}$ ,  $-7.8^{\circ}\text{C}$ ,  $-15.5^{\circ}\text{C}$  and  $-50.0^{\circ}\text{C}$  respectively. It is seen from the figure that with lowering temperature the peak of diffraction moved toward a large value in  $2\theta$ , showing a decrease in the  $d(001)$  spacing.

The results are summed up in Fig. 21, where solid and open circles show the measurements made in the cooling and the warming process, respectively. It must be noted that the length of

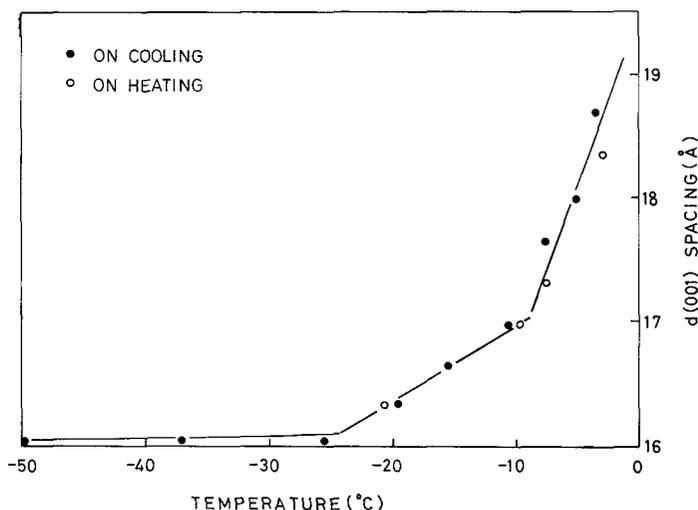


Fig. 21 Relation between basal spacing  $d(001)$  and temperature of bentonite.

$d(001)$  obtained in the course of cooling was in good coincidence with that obtained in the course of warming. The interlamellar water dispelled in the course of cooling was well recovered in the course of warming. The rapid decrease of the  $d(001)$  spacing from  $19.5 \text{ \AA}$  at  $0^\circ\text{C}$  (extrapolated) to  $17 \text{ \AA}$  at  $-9^\circ\text{C}$  is in good accordance with the previous considerations. Below  $-25^\circ\text{C}$ , the length of the  $d(001)$  was almost constant. It seems that below this temperature interlamellar water is exclusively Water III.

According to AHLRICHS *et al.* (1962), the  $d(001)$  spacing of a bentonite–water paste was about  $21 \text{ \AA}$  at room temperature, decreasing to  $16 \text{ \AA}$  or  $17 \text{ \AA}$  at  $-196^\circ\text{C}$ . ANDERSON *et al.* (1965), who measured the  $d(001)$  spacing of the same paste from  $3^\circ\text{C}$  to about  $-12^\circ\text{C}$ , reported that the paste always underwent supercooling down to about  $-6^\circ\text{C}$  where ice was formed and the  $d(001)$  spacing decreased abruptly. Such an abrupt change was not found in the present measurements, in which Water 0 was never in a supercooled condition.

## V. Analysis by differential scanning calorimeter

### V. 1. Differential scanning calorimeter

Water in wet bentonite and illite was classified into Water 0, I, II and III in Section III. The classification was based on evidences suggesting that Water 0, I and II begin to freeze at  $0^\circ\text{C}$ ,  $-9^\circ\text{C}$  and  $-33^\circ\text{C}$ , respectively, while Water III remains unfrozen down to  $-110^\circ\text{C}$ , below which

the present work is in no position to tell of its phase transformation. Now the existence of phase transformation such as freezing of water is most directly revealed with a differential scanning calorimeter.

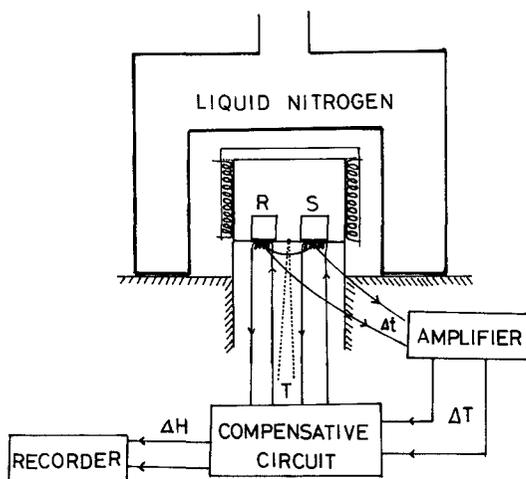


Fig. 22 Schematic diagram of DSC apparatus.

shows no phase transformation in the temperature range to be tested, is put in the cell R (the reference cell). As the chamber temperature is changed at a constant rate, the temperatures of the two cells change, but the temperature difference  $\Delta T$  of the two cells is kept nearly zero by such a feedback mechanism that the difference amplified by an amplifier causes a power supply to the heater of the colder cell. The chamber temperature and the power supply are recorded as a function of time. Because of the difference of the specific heat of the two materials, there is some power supply (background) even if the test material shows no phase transformation. However, the background of the power supply must be a smooth function of time because the specific heat of a material is a smooth function of temperature except at a temperature (or a temperature range) where phase transformation occurs. During an endothermal phase transformation such as melting of ice either the power supply to the measuring cell increases or that to the reference cell decreases and during an exothermal phase transition such as freezing of water the power supply changes reversely. This change of power supply is clearly distinguished from the background as seen below.

#### V. 2. Amount of water freezing near $0^{\circ}\text{C}$

Differential scanning calorimetry was first applied to see phase transformation near  $0^{\circ}\text{C}$  of bentonite, illite and kaoline of various water contents. Specimens were prepared similarly to the preparation of specimens for dilatometry. In case of specimen of a comparatively large water content, it was prepared by the mixing of dried clay and distilled water, putting several

Figure 22 shows a schematic diagram of a differential scanning calorimeter used (DSC 1500, made by SHINKU RIKO Co., Ltd.). Two cells of the same construction, R and S, are placed in a chamber in such a symmetrical position that an exactly similar effect is given on them by the change in chamber temperature, which is measured with the thermocouple T. The chamber temperature is controlled by a heater around the chamber, while two small heaters supply heat to the cells independently.

A specimen of a material to be tested is put in the cell S (the measuring cell) and a bit of a reference material, which

milligrams of the mixture in the measuring cell and sealing it hermetically to prevent water evaporation. Meanwhile, in case of specimen of a smaller water content, it was prepared by placing the measuring cell containing several milligrams of dried clay in a desiccator, taking the cell from the desiccator after the lapse of appropriate time, and sealing it hermetically, whereupon the sealed cell was kept at room temperature for 24 hours or more for homogeneous distribution of water before measurement.

All the measurements were made with air as the reference material; namely, the reference cell was empty. To avoid any supercooling of water, the chamber temperature was first lowered to  $-40^{\circ}\text{C}$  and then warmed up at a rate of about  $5^{\circ}\text{C}/\text{min}$ . One of the records of the supplied power was reproduced in Fig. 23, where the abscissa scaled by the temperature of the chamber was originally linearly-scaled time and the coordinate represents an algebraic difference equal to the power supply to the reference cell minus the power supply to the measuring cell (either of the supplies was zero) in an arbitrary linear scale. The occurrence of an endothermal phase transformation is evident from this figure. The two dot-dash lines show the estimated background levels before and after the transition. The transition is considered to have

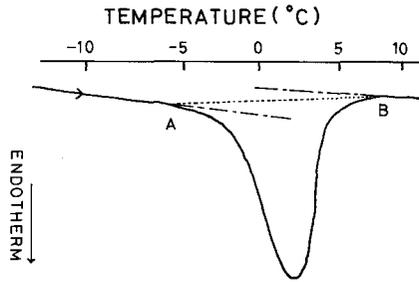


Fig. 23 DSC curve of bentonite (w : 77%).

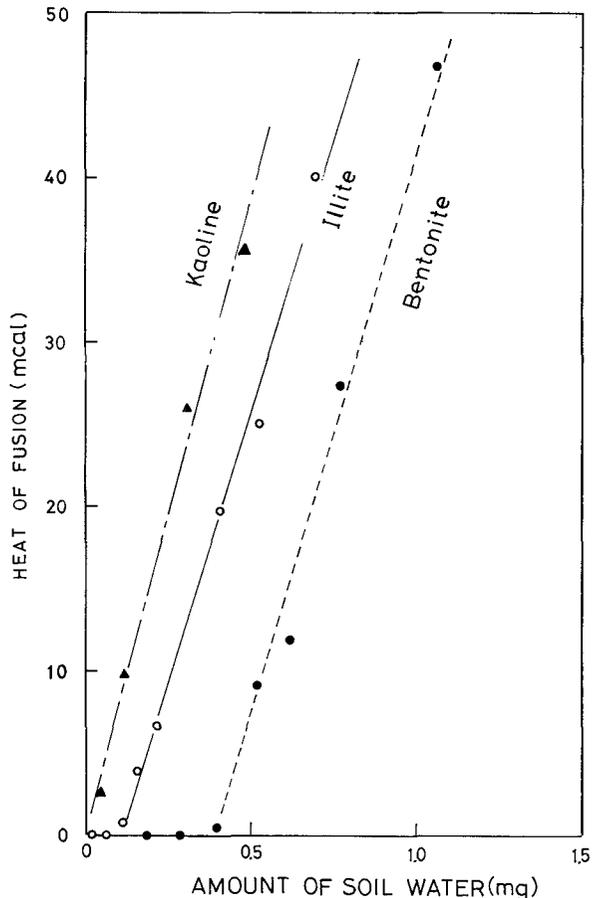


Fig. 24 Relation between heat of fusion and amount of soil water of clay minerals.

started at A and ended at B. The specimen temperature naturally lags behind the chamber temperature. The lag is especially large during the phase transformation. The specimen temperature at B was probably  $0^{\circ}\text{C}$ , while that at A was certainly below  $-5^{\circ}\text{C}$ . Now, the part bounded by the dotted line and the curve was considered due to the phase transformation. The area of the part was measured with a planimeter. Since all the measurements were recorded with the same chart speed and the same scale of power supply, the ratio of the area to the amount of absorbed heat in each measurement was constant. The ratio was determined from the results of several measurements of various known amounts of pure ice.

All the results are compiled in Fig. 24, where both the water content and the absorbed heat are represented per gram of dried clay. The three lines intersect the abscissa at 0 mg (kaoline), 0.11 mg (illite) and 0.41 mg (bentonite), showing that all water in kaoline froze near  $0^{\circ}\text{C}$  while only water in excess of 11 % in illite and in excess of 41 % in bentonite froze near  $0^{\circ}\text{C}$ . The values agreed with the amount of Water 0 estimated in III. 3. The latent heat estimated from the gradient of each line is 78 cal/g for kaoline and 69 cal/g for bentonite and illite. Though the latent heat was a little smaller than that of ordinary water, Water 0 in bentonite and in illite may be considered as ordinary water while all water in kaoline is certainly ordinary water.

### V. 3. Latent heat of Water II

Phase transitions around  $-9^{\circ}\text{C}$  and  $-33^{\circ}\text{C}$  deduced from the discontinuities of linear expansion coefficients were not detected in the measurements described in V. 2. The reason considered was that the amount of heat related to these transitions is too small to be detected by the record with the used scale of power supply, so measurements with a much more amplified scale of power supply were tried. A few records showing a transition around  $-33^{\circ}\text{C}$  were obtained, of which one for a mixture of 8.4 mg of dried bentonite and 7.8 mg of water, namely for bentonite of a water content of 93 %, was reproduced in Fig. 25, where for comparison a record of dilatometry for bentonite of a similar water content is also shown. The ratio of the area to the heat amount was determined by measurements for ammonium chloride, which shows a phase transition at  $-30.5^{\circ}\text{C}$  with a heat of transition of 3.74 cal/g. From this ratio, the heat amount released in the case of Fig. 25 was estimated about 5 mcal. It may assumed that this release was due to the freezing of Water II. The amount of Water II in this specimen would be  $8.4 \text{ mg} \times 0.12$  according to III. 3. This gives the latent heat of 5 cal/g of Water II.

The phase transition around  $-9^{\circ}\text{C}$  was never found in the present differential scanning calorimetry. This is probably due to the small amount of Water I (0.03 mg per milligram of dried bentonite) and a possible small value of its latent heat (less than 10 cal/g).

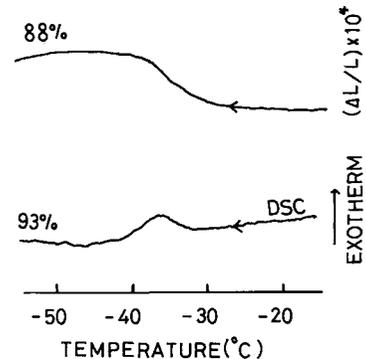


Fig. 25 DSC and dimensional change curves of bentonite ; soil water content in percentage.

## VI. Concluding remarks

The linear expansion coefficient of bentonite showed three discontinuities around 0°C, -9°C and -33°C, when its water content was sufficiently large. As the water content decreased, the discontinuities disappeared one by one in the above order, from which water contained in bentonite was classified into four types. They are Water 0, I and II, which are responsible for each of the discontinuities at 0°C, -9°C and -33°C respectively, and Water III, which is irresponsible for any discontinuity. It was determined that the first 0.26 g of water added to 1 g of dried bentonite constituted Water III, the second addition of 0.12 g Water II, the third addition of 0.03 g Water I, and any further addition in excess of the total amount of water added so far, i. e. 0.41 g Water 0. Since all the discontinuities suggested the occurrence of expansion mechanisms which lasted in lower temperatures, it was considered that Water 0, I and II began to freeze at 0°C, -9°C and -33°C respectively. The linear expansion coefficient of illite having showed a similar behavior, it was determined that per gram of dried illite, Water III, II, I and 0 were represented respectively the first addition of 0.05 g of water, the second addition of 0.02 g, the third addition of 0.03 g and any further addition in excess of 0.1 g. The linear expansion coefficient of kaoline had only one discontinuity at 0°C; namely, all water in kaoline was Water 0. Since bentonite and illite have the internal surface while kaoline has not, Water I, II and III were considered interlamellar water.

The average linear expansion coefficient of bentonite between -2°C and -9°C showed an abrupt increase as the water content increased from 33% to 41% and then a gradual decrease as the water content continued to increase. This dependency was qualitatively explained by the swelling of bentonite by Water I and II during a warming process from -9°C to -2°C and reverse shrinkage during a cooling process from -2°C to -9°C. The measurements of the d(001) spacing from -3°C down to -50°C by an X-ray diffraction analysis ascertained the occurrence of such reversible swelling down to -25°C. At -25°C, almost all of the interlamellar water was supposed to be Water III, because the d(001) spacing remained constant below this temperature. In other words, Water II was completely expelled from the interlayer space before it froze around -33°C.

Differential scanning calorimetry showed that the amount of water freezing above -5°C or so, or Water 0, was in excess of 41% for water in bentonite, in excess of 11% for water in illite and all water in kaoline. This result is surprisingly coincident with the previous estimation. The latent heat of Water 0 was estimated 78 cal/g for kaoline and 69 cal/g for bentonite and illite. The supposed phase transformation at -33°C was ascertained by differential scanning calorimetry, which gave a latent heat of several calories per gram of Water II. Another supposed phase transformation at -9°C was not revealed by the present differential scanning calorimetry, though it suggested that the latent heat of Water I was less than 10 cal/g.

## Acknowledgments

This work was carried out at the Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan. The author would like to express his sincere gratitude to Dr. D. Kuroiwa and Dr. G. Wakahama of I. L. T. S. for their useful comments on this investigation, and Dr. S. Kinoshita and Dr. Y. Suzuki of I. L. T. S. for every encouragement and valuable advice accorded in preparation for this paper. He also is indebted to Ms. Y. Mizuno for her assistance in measuring the basal spacing  $d(001)$  and Mr. M. Asada for his assistance in taking SEM photographs.

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