On the Specific Heat of Rocks and the Velocity of Elastic Wave within the Outer Layer of the Earth's Crust

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Abstract

The authors measured the change in specific heat of the granite and andesite for the temperature ranging from the room temperature to about 800°C. In the case of these rocks, the specific heat is most influenced by silica contained in the samples and shows the anomalous change at certain temperatures corresponding to the inversion points of silica.

Using the theoretical relation, the elastic wave velocity was estimated from the specific heat. According to the results obtained from the specific heat of silica, the velocity changes with temperature in similar way to that of seismic wave velocity reported by B. Gutenberg on the low velocity layers within the earth's crust.

1 Introduction

The measurements of the specific heat were carried out by many authors, but most of them were not suitable for continuous measurement during the changes of temperature. Since the method of measurement for specific heat were developed by C. Sykes and F. W. Jones [1], the changes of specific heat of metals, alloys and other crystals have been measured precisely. At present, the measurement with respect to the anomalous changes of specific heat is one of the means of investigation on the characteristics of matter. The method of Sykes and Jones is based on the following principle ; a specimen is mounted inside a closed copper and thermally insulated from it. The specimen and the copper cylinder are heated independently and controlled so as not to cause thermal difference between the specimen and the copper cylinder. Then no external heat is received by the specimen. In this way, it is able to obtain a specific heat-temperature curve which contains the effects due to any transformation superposed on the normal heat-temperature curve.

The authors measured the specific heat of granite and andesite with the Sykes and Jones method improved so as to fit for rock samples. The temperature in the experiment is changed in the range from the room temperature to about 800°C, in which all rock forming minerals except silica indicates the scarcity of transformation points. As the most part of rocks constructing the outer layer of the earth's crust is composed of silica, it may have large effect upon the various properties of the crust.

On the other hand, taking the Debye's characteristic temperature into account, it is cleared by the theory of solid that the specific heat is related to the elastic wave

velocity. The DEBYE's relation is hold generally in the case of monoatomic substances such as metal or a sort of crystal, but it has been known from many literatures that the relation is applicable to the other substances. At first, the authors attempted to estimate the velocity of elastic wave in silica from its specific heat on the basis mentioned above, then tried to discuss the velocity distribution of seismic wave in the outer layer of the earth's crust. Then, the studies were made on the assumption that the crust consists only of silica. It is well known that silica constituent seems to be predominant in the so-called granitic layer.

Fig. 1   The equipment used in maesurment.

B. Gutenberg [2] [3] reported already that the low velocity layers seemed to be caused by the phase transformation of rocks in the lithosphere and by transformation to liquid state in the asthenosphere channel. Also, the present study on the problems concerning the low velocity layers and discontinuities in the earth's crust was made from the standpoint of thermal properties of rocks.

2   Experimental Method

SYKES and JONES method was improved to be suitable for the measurement of rock samples. The equipment is shown in Figure 1. The powdered specimen stuffed in a copper vessel A was mounted inside a close copper cylinder B and thermally insulated from it. They are set up inside of an electric furnace. A Nichrome coil H was put in the specimen to make the sample be heated independently. In order to make no thermal difference between A and B, the applied voltage to electric furnace C was carefully controlled by watching the thermoelectric current of junction J_2. The temperature of sample was measured by thermojunction J_1. When the specimen is heated by Nichrome coil H and there is no thermal difference between the specimen and the copper cylinder B, the following equation is valid ;

$$mC_p + m_v C_{pv} = \frac{vi}{dT/dt} + \Delta = vi\left(\frac{dt}{dT}\right) + \Delta,\tag{1}$$

where m and m_v are the masses of the specimen and the vessel respectively, c_p and c_{pv} are the instantaneous specific heat of the sample and the vessel at the temperature T. vi the power supplied to the coil, and Δ the heat quantity lost by conduction or radiation.

Measuring about two specimens produced from the same sample but with different masses of m_1 and m_2, and using in both cases the same vessel, the following rleation
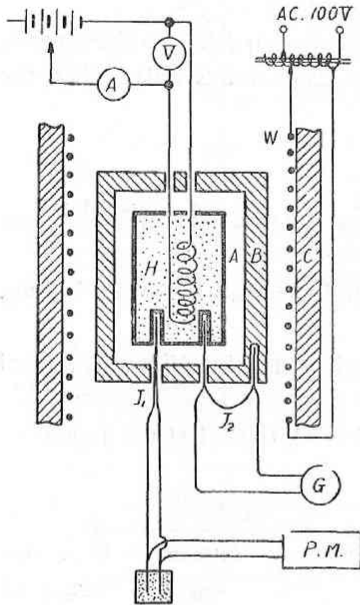
are obtained :

$$(m_1-m_2)\, C_p = v_1 i_1 \left(\frac{dt}{dT}\right)_1 - v_2 i_2 \left(\frac{dt}{dT}\right)_2 + (\varDelta_1-\varDelta_2) \ . \tag{2}$$

If the measurements are carried out in both cases under the similar condition, the term of $(\varDelta_1-\varDelta_2)$ in equation (2) is negligible. Therfore ;

$$(m_1-m_2)\, C_p = v_1 i_1 \left(\frac{dt}{dT}\right)_1 - v_2 i_2 \left(\frac{dt}{dT}\right)_2 \ . \tag{3}$$

The authors obtained the specific heat by using the equation (3). In these cases, the used values of m_1, m_2 and v_i were respectively about 25 gr and 2 watts, then the value of dT/dt becomes about $1\sim2°C/min$.

3 Results of Experiment

In measurements of the specific heat, quartz, quartz-diorite and andesite were examined. Their localities were as follows ;

granite : Tanobata, north eastern parts of Iwaizumi Town, Iwate Prefecture, Japan.

quartz-diorite : The upper stream of the Tsuchiuchi river, Hagino Village, Mogami District, Akita Prefecture, Japan.

andesite : Fumoto, Nishi-monai Town, Hiraga District, Akita Prefecture, Japan.

Table. 1. Chemical composition and Norm. of the samples. 1)

Conatituent	Granite	Quartz-Diorite	Andesite*
SiO_2	73.74	61.01	58.24
Al_2O_3	10.83	14.41	16.59
Fe_2O_3	2.46	4.39	3.68
FeO	1.50	3.23	3.99
MgO	1.38	3.16	2.27
CaO	2.82	3.82	5.80
Na_2O	3.72	3.28	3.97
K_2O	3.02	2.66	1.50
H_2O_+	0.30	2.48	0.22
H_2O_-	0.18	0.18	0.98
TiO_2	0.22	0.84	1.50
P_2O_5	0.02	0.19	0.57
MnO	0.07	0.10	0.11
Total	100.26	100.75	99.42
Quartz	34.44	18.00	14.82
Orthoclase	17.79	15.57	8.90
Albite	31.44	27.77	34.60
Anorthite	3.89	16.68	22.80
Corundam	—	—	
Diopside	7.88	5.03	0.68
Hypersthene	0.30	6.59	7.25
Magnetite	3 71	6.50	5.34
Ilmenite	0.46	1.52	2.89
Hematite	—	—	—
Ap	—	—	1.24
Normative Plagioclase	Ab_{81}–An_{19}	Ab_{62}–$An_{:8}$	Ab_{31}–An_{69}

1) Analyst ; Yoshio Ueda   * Iwao Kato

Their chemical and mineral compositions are shown in table 1.

The results of experiments for these samples are shown in Figures 2, 3 and 4.

Fig. 2. The relation between the specific heat and tmperature of Granite.
The broken line shows the value calculated from the WINKELMANN's formula.

Fig. 3. The relation between the specific heat and temperature of Quartz
Diorit. The broken line shows the value calculated from the WINKELMANN's formula.
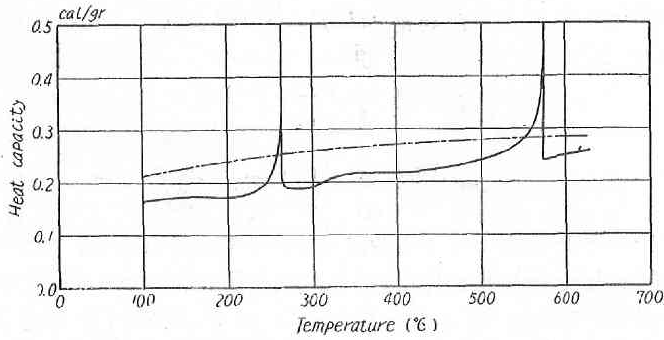

Fig. 4 The relation between the specific heat and temperature of Andesite.
The broken line shows the value calculated from the WINKELMANN's formula.
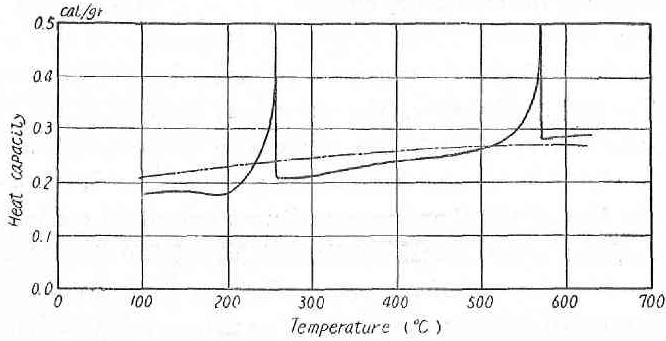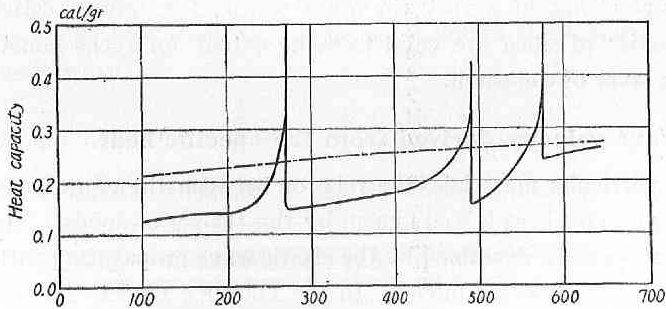
On the other hand, according to the study of A. WINKELMANN [4], the specific heat of a matter is calculated from that of respective constituents composing the matter.

It is as follows :

$$C_p = \frac{\Sigma k_i p_i}{\Sigma p_i},$$

(4)

where k_i and p_i are respectively the specific heat increments and the weight percentages of a constituents.

Now, in general,

$$k_i = a_i + b_i T - c_i T^{-2} ,$$

therefore,

$$C_p = \frac{\Sigma (a_i + b_i T - c_i T^{-2}) p_i}{\Sigma p_i}$$

$$= \frac{\Sigma a_i p_i}{\Sigma p_i} + \frac{\Sigma b_i p_i}{\Sigma p_i} T - \frac{\Sigma c_i p_i}{\Sigma p_i} T^{-2} . \tag{5}$$

In fact, these relations are valid at normal temperatures. In this paper, the specific heat of each sample is calculated by applying the same relations to the case of higher temperature ranges by using the data of F. Birch [5] and Table 1. The calculated values for each samples are plotted in Figures 2, 3, and 4. As seen from the figures, both cases of experiment and calculation are coincident fairly with one another, except in the ranges of the anomalous change.

As shown in these figures and Table 1, it is found that the specific heat of a sample is greatly dependent on the content of SiO_2, the specific heat being proportional to the content of SiO_2. Moreover, the anomalous changes of the specific heat are observed at about 250°C and 573°C. The phenomena at about 573°C may be attributed to the well-known inversion of quartz, while the peak at about 250°C is not remarkable as compared with that at 573°C and no constituent but silical composing the samples shows marked mineralogical transformation at about 250°C. However, it should be noticed that cristobalite transforms from α state to β one around the temperature in question. All the samples are composed of so many various minerals that the variation curves of their specific heat indicate some irregular line. At any rate it is obvious from the results mentioned above that the thermal properties of silica influence significantly upon that of a rock, in other words, the results estimated from the thermal properties of silica are valid to some extent for rocks constructing the so-called granitic layer of the earth.

4 Elastic Wave velocity derived from the specific heat.

As to the particular materials, the relation between the vibration of atoms in the crystal and the specific heat is well known by the theory of solids. The vibrations of atoms in a matter can be examined by the elastic wave propagating within the matter. This is based on the DEBYE's model. In the DEBYE's model, the specific heat at a constant volume is given by the following formula :

$$C_V = 3kN \left[4D \left(\frac{\theta_D}{T} \right) - 3p \left(\frac{\theta_D}{T} \right) \right], \tag{6}$$

where θ_D is the DEBYE's characteristic temperature, and $\theta_D = h/k \cdot \nu_m$. ($\nu_m$ is maximum frequency of vibrations.)

In the case of anisotropic solids, the three waves of different polarization have different velocities for each direction of propagation. Thus, the limiting frequency ν_m is a

function of the direction of propagation. In this case, the specific heat is expressed as follows ;

$$C_V = kN \left[\sum_{j=1}^{3} \left\{ \left\{ 4D\left(\frac{\theta_j}{T}\right) - 3p\left(\frac{\theta_j}{T}\right) \right\} \frac{d\omega}{4\pi} + \sum_{j=4}^{3S} S\left(\frac{\theta_j}{T}\right) \right] , \qquad (7)$$

where

$$\theta_j = \frac{h}{k} \nu_{mj} , \quad j = 1, 2, 3 \text{ for acoustical vibrations}$$

$$\text{or } j = 4, 5, 3S \text{ for optical vibrations.}$$

K. FÖRSTERLING employed an expansion method for evaluationg the integrals in Equation (7), i.e.

$$D(x) = 1 - \frac{3}{8} x - 3 \sum_{n=1}^{\infty} \frac{(-1)^n B_n}{(2n+3)(2n)!} x^{2n} , \quad |x| < \pi$$

$$p(x) = \frac{x}{e^x - 1}$$

$$B_n : \text{ Bernoullian number}$$

Substituting

$$K_n = \frac{1}{4\pi} \int \left[\sum_{j=1}^{3} \theta_j^{2n} \right] d\omega ,$$

$$C_V = 3kN \left[1 + \sum_{n=1}^{\infty} (-1)^n \frac{B_n(2n-1)}{(2n)!(2n+3)} \frac{K_n}{T^{2n}} \right] + R \sum_{j=4}^{3S} S\left(\frac{\theta_j}{T}\right)$$

$$\simeq 3kN \left[1 - \frac{1}{20} \frac{\theta_D^2}{T^2} + \frac{1}{336} \frac{\theta_D^4}{T^4} \right] + R \sum_{j=4}^{3S} S\left(\frac{\theta_j}{T}\right) . \qquad (8)$$

In equation (8), the first term of right hand is the DEBYE's term due to acoustic vibration and the second term is the EINSTEIN's term. The DEBYE's characteristic temperature θ_D is obtained from the frequency of sound wave which is related to the velocity of elastic wave,

$$\theta_D = \frac{h}{k} \nu_m = \frac{h}{k} \left(\frac{3N}{4\pi V}\right)^{1/3} v , \qquad (9)$$

where h is the PLANKS's constant, k the BOLTZMAN's constant, N the Loschmidt number, V the molecular volume and v the mean velocity of elastic wave.

If the EINSTEIN's term in equation (8) is negligible, the velocity of elastic wave is expressed as follows ;

$$v = A \cdot \left(1 - \frac{C_V}{3kN}\right)^{1/2} V^{1/3} T , \qquad (10)$$

where

$$A = \sqrt{20} \sqrt[3]{\frac{4\pi}{3N}} \frac{k}{h} ,$$

and

$$\frac{3}{v^3} = \frac{1}{v_l^3} + \frac{1}{v_t^3} ,$$

where v_l and v_t are the velocities of the longitudinal and the transverse wave respectively.

Now, taking the consideration of the fact mentioned in chapter 2 and the suitableness of theoretical relation, we intend to estimate the velocity distribution in the crust of silica model by the relation (10). R. WIETZEL [6] had already obtained the atomic heat of quartz and cristobalite as shown in Figure 5. As any satisfactory observation for tridymite have not ever been made, we tried to discuss only the phenomena with respect to equartz and cristobalite.

Fig. 5. The discontinuities of the average atomic heat (calories per 20.1 grams) of quartz and cristobalite (after R. WIETZEL).

The molecular volumes of silica are 22.6 cm³/mole for quartz and 26.1 cm³/mole for cristobalite, their atomic volume being 7.5 cm³/atom and 8.6 cm³/atom respectively. In the present case, as we consider silica as a model constructed by continuous arrangement of monoatomic moleculars, the velocity is calculated by using the atomic heat capacity as shown in Figure 5. The results obtained by calculation are illustrated in Figure 6. As seen in Figure 6, the velocity decreases rapidly and its distribution is considerably discontinuous at the peak of the specific heat.
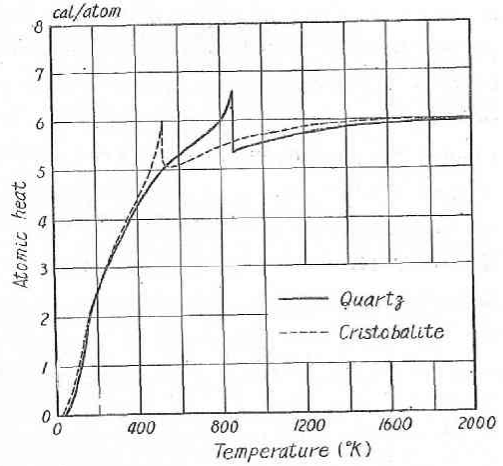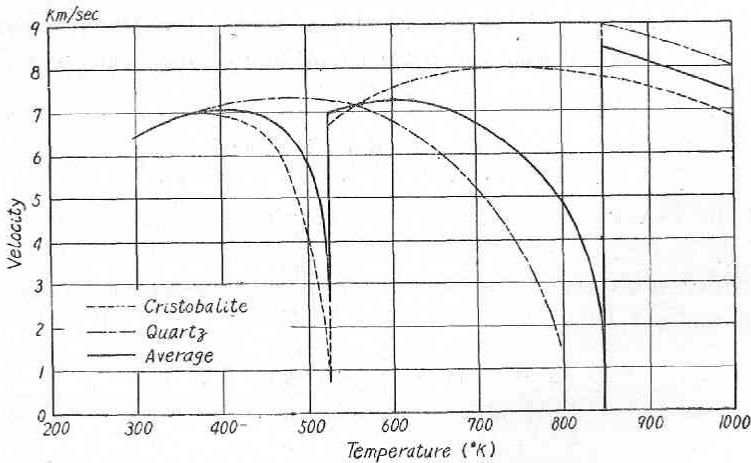

Fig. 6. The velocity distribution with temperature estimated from the specific heat.

Subsequently, the influence of the pressure upon the specific heat was estimated.

From the study of P.N.BRIDGEMAN [7], it is known that the specific heat decreases
in proportion to the pressure, however, the rate is very low for solids and liquids.   For
example, in the case of mercury, the specific heat decreases only by less than 0.2
percent with the pressure increase of 7×10^9 dynes/cm² [8] [9].   In addition, the change
of the specific heat of silica seems to attain to about 0.5 percent at most, at the bottom
of the crust, therefore the influence of pressure upon the specific heat needs not be
taken into consideration so far as the present discussion is limitted to the outer layers
of the earth's crust.   It should be also considered that the transformation temperatures
are influenced by pressure.   According to the equation of CLAUSIUS-CLAPEYRON, the
following relation is valid for the transformation from α to β quartz [10] ;

$$dT \,/\, dp = + \, 0.0215°C \,/\, atm \,.$$

Then, with the aid of the well-known relation between depth and pressure, 573°C
at the surface corresponds to about 788°C at the depth of 33 km (Fig. 7).   Taking the
same procedure as to cristobalite, the inversion point at 250°C will become 394°C at
the depth of 22 km.
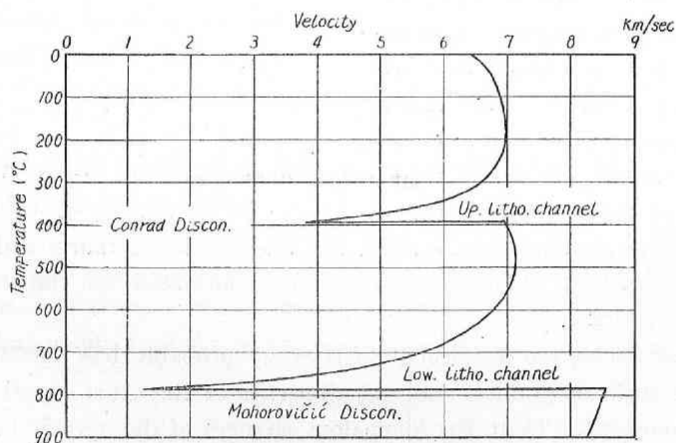
Fig. 7.   The velocity distribution with temperature case of taking the
consideration of the influence of pressure.

Furthermore, these transformations have generally a hysteresis range of 30°C and
6.°C, respectively [11].   In the case of the earth's interior, it is considered that the
transformation temperatures of the rocks in the earth's crust have the range of about
50°C on the average in view of the influence of pressure.

The anomalous changes at lower temperatures were discussed above in connection
with the properties of cristobalite.   It is a fact, however at any rate, that the
anomalous peak at 250°C of rocks used in the present experiment and that of
cristobalite are very similar to each other.   Therefore, it is expected to some extent
that a similar phenomena to that estimated by cristobalite occurs in the earth's crust.
From the considerations mentioned above and the experimental results for the specific
heat of granite and the other rocks, it may be said that the two marked low velocity

layers exist in the outer layer of the earth's crust.

On the other hand, B. GUTENBERG [12] determined the velocity distribution of seismic waves in Southern California by using the seismograms, and the results are shown in Figure 8. As shown in this figure, the two discontinuities correspond respectively to the so-called CONRAD and MOHOROVIČIĆ discontinuities.

Comparing the results estimated from specific heat with that by B. GUTENBERG, it is noticed that the both cases are in their behabiours coincident with each other. However, the difficulty is that the velocity distribution of seismic waves is given with depth, while that obtained from thermal property is concerned with temperature. Therefore, these two cases can not be compared directly, unless the temperature distribution in the region concerned is determined. The temperature distribution in the crust can not be estimated in detail,

Fig. 8. The velocity of transverse wave as a function of the depth. (after B. Gutenberg).

but the temperatures, 394°C and 788°C, of anomalous changes of the specific heat are considered to be that at the depthes where the discontinuities of seismic waves are observed. If these assumptions are valid, the velocity discontinuity and low velocity layers pointed out by B.GUTENBERG can be illustrated as the cause of the trnsformation of rocks.

In the basic rocks, the physical properties are probably less influenced by silica than in such a rocks as granite, and the properties of the other constituents except silica are predominant. Then, the anomalous changes of the specific heat as seen in the present experiment are not expected in the case of basic rocks and it may be considered that the low velocity or discontinuous layers are not distinctly observed in the regions composed of basic rocks such as those at the bottom of ocean. This estimation also conincides with the results of seismic waves.

5 Discussion and Conclusion

In calculation of the velocities of elastic waves from the data of specific heat, we used the DEBYE's model and neglected the EINSTEIN's term, although this would not be valid in the exact calculation. One of the space frequencies of normal oscillations of silica molecules is 483 cm⁻¹ [13], and many other opitical vibrations are considered. With respect to this subject, a study was made by B.D.SAKSENA [14]. These various vibrations, of course, should be taken into consideration in the case of furtherance of this discussion. Moreover, the DEBYE's model is derived from the monoatomic
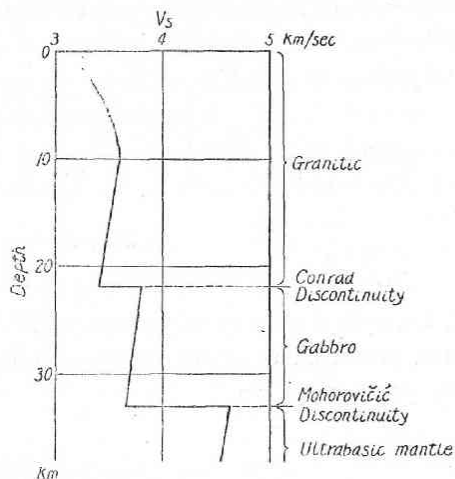
molecules, and it is not always sufficient for a substance which consists of polyatomic molecules. The maximum frequency ν_m of acoustic vibrations are so roughly approximated that the real distribution of ν_m may be different from that in the present case. While, the velocity derived from the specific heat shows different values in accordance with the change of frequency of atomic vibration. On account of various difficulties as mentioned above, only the relative distribution of velocities could be discussed from the data of specific heat.

At any rate, according to the present investigation, the following conclusions may be given.

(1) Granite, quartz-diorite and andesite show the anomalous changes in specific heat at 250°C and 573°C under the standard pressure. These phenomena are caused mainly by silica contained within the rock, and the marked change at 573°C is well coincident with the transformation point of quartz. The reason for the peak at 250°C is not clear, however, the behaviours correspond considerably to that of cristobalite at the same temperature.

(2) The distribution of elastic wave velocity estimated by using DEBYE's relation between the velocity and the specific heat shows the two low velocity regions, corresponding to the so-called CONRAD discontinuity and MOHOROVIČIĆ discontinuity within the earth's crust. Therefore, the temperatures at these depthes of the discontinuities are not resulted from the difference of materials but probably from the physical changes of the same material.

(3) In the region composed of basic rocks, such anomalous changes of velocity as in granitic layer are not expected.

In concluding this paper, the authors wish to experss their thanks to Prof. Y. KATO, for his supervision and encouragement for the present study. Their thanks are also due to Dr. I. KATO and Assist. Prof. Y. UEDA for their valuable suggestions from the petrological point of view.

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