# Thermal Diffusivity Measurement of Rock-Forming Minerals from 300° to 1100°K

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Measurement of thermal diffusivity,  $\kappa$ , of fused silica, quartz, olivine, periclase, jadeite, garnet, spinel, corundum and alkali feldspar was made at 1-atm pressure and over the temperature range from 300° to 1100°K. All the samples are of gem quality but of millimeter size. The Ångström method was slightly modified to be applicable to small samples. For all the minerals except feldspar  $1/\kappa$  increases almost linearly with temperature up to 700°K, as expected from the theory of lattice conduction. Tightly packed minerals, such as periclase, spinel, and corundum, have a diffusivity 3 to 10 times as large as that of other minerals. At temperatures higher than 700°K,  $1/\kappa$  decreases with temperature for some minerals. This decrease can be interpreted as being due to radiative heat transfer within the crystals, if the opacity of the minerals is in the range 6 to 20 cm<sup>-1</sup>. High-temperature optical data are essential for a detailed discussion of the radiation effect.

#### Introduction

Among the essential factors involved in geothermal studies are the thermal conductivities of rocks and rock-forming minerals and their dependence on temperature and pressure. A pioneer work by Birch and Clark [1940a, b] on a variety of rocks and minerals has greatly contributed to this field. Their measurement covered the temperature range up to 400°C. Recently, Kawada [1964] determined the temperature dependence of thermal conductivity of several rocks up to 600°C. The temperature limit set in these works might be partly due to experimental difficulties, but, even if those difficulties are overcome, the measurement at temperatures exceeding 600°C on rocks at normal pressures would have little significance. When a rock sample is heated, the differential thermal expansion of the constituent minerals causes a mechanical misfit between the grains and results in an irreversible change of physical properties [Ide, 1937]. Since the properties of rocks must ultimately be related to the properties of the constituent minerals, it is undoubtedly useful to have knowledge of the properties of the constituent minerals.

This study investigates the temperature dependence of thermal diffusivity, a quantity closely related to thermal conductivity, of various rock-forming minerals over the temperature range of 300° to 1100°K.

Because of the difficulty of obtaining flawless crystals of large size for measurements of this kind, an attempt is made to develop a technique that is applicable to small samples.

#### Метнор

To ensure the reliability of data at high temperatures, samples should be carefully selected. Since large samples of rock-forming minerals of geophysical interest are not usually available, we used the Angström method [Carslaw and Jaeger, 1959, p. 136], modified according to Nii [1960], and shown schematically in Figure 1. The sample was first cut in the shape of a cylinder, 3 to 5 mm long and 10 mm<sup>2</sup> in cross section. This cylinder is pasted at one end to a nickel base with silver coating material in between. The other end of the cylinder is also coated with a thin film of silver on which a chromel-alumel thermocouple is fixed. The nickel base is heated by a heating wire wound on the stem to which 5- to 20-sec period square wave electric current is supplied. The mean power is 1 to 5 watts. Since higher harmonics are quickly attenuated, the temperature wave at the base of the sample becomes almost sinusoidal when the size and the shape of the nickel base are properly designed. The departure from a purely sinusoidal wave is less than 2% in terms of the distortion factor at

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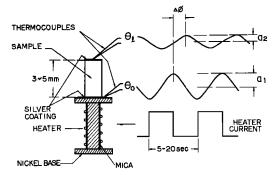


Fig. 1. Schematic illustration of the modified Angström method for measurements of thermal diffusivity. Amplitude ratio  $a_2/a_1$ , and phase shift  $\Delta \phi$  of temperatures  $\theta_i$  and  $\theta_0$  at both ends of the sample are measured to determine diffusivity.

the base of the sample. The whole assembly is placed in an electric furnace, and the measurement is made in argon at 1 atmosphere. The phase lag and the amplitude decay of the temperature wave during the transmission along the sample are measured to determine the thermal diffusivity.

The basic equation of heat conduction in a cylindrical sample extending in the x direction can be written as

$$\frac{K}{C_{\pi}\rho}\frac{\partial^2\theta(x,t)}{\partial x^2} = \frac{\partial\theta(x,t)}{\partial t} + \mu\theta(x,t)$$
 (1)

where  $\theta(x, t)$  is the temperature in the sample as a function of position and time and K,  $C_p$ ,  $\rho$ , and  $\mu$  denote, respectively, the thermal conductivity, specific heat, density, and a constant indicating a heat loss from the side of the sample.

In the case of an infinitely long rod, the boundary conditions are

$$\theta(0, t) = A_0 + A_1 \cos(2\pi t/T)$$
 (2)

$$\theta(\infty, t) = 0 \tag{3}$$

where T is the period of the temperature wave and  $A_0$  and  $A_1$  are the mean temperature and the amplitude of the temperature wave, respectively. The solution of (1) with the boundary conditions (2) and (3) is

$$\theta(x, t) = A_0 \exp(-\alpha_0 x)$$

$$+ A_1 \exp(-\alpha_1 x) \cos(2\pi t/T - \beta_1 x) \qquad (4)$$

where

$$\alpha_0 = (\mu/\kappa)^{1/2}$$

$$\alpha_1 = \{ [(\mu^2 + 4\pi^2/T^2)^{1/2} + \mu]/2\kappa \}^{1/2}$$

$$\beta_1 = \{ [(\mu^2 + 4\pi^2/T^2)^{1/2} - \mu]/2\kappa \}^{1/2}$$
and

$$\kappa = K/C_{n}\rho$$

is the thermal diffusivity. In the case of a rod with a finite length l, the boundary condition (3) must be replaced by

$$K \, \partial \theta(l, t) / \partial x = 0 \tag{3'}$$

The solution of equation 1 with the boundary conditions (2) and (3') cannot be given in a simple form. However, when the sample length l is large enough to make exp  $(-2\alpha_1 l)$  negligibly small compared with unity, an approximate solution

$$\theta(x, t) = A_0 \exp(-\alpha_0 x)/[1 + \exp(-2\alpha_0 l)]$$

$$+ A_1 \exp(-\alpha_1 x) \cos(2\pi t/T - \beta_1 x)$$

$$+ A_0 \exp[-\alpha_0 (2l - x)]/[1 + \exp(-2\alpha_0 l)]$$

$$+ A_1 \exp[-\alpha_1 (2l - x)]$$

$$\cdot \cos[2\pi t/T - \beta_1 (2l - x)]$$
(6)

can be derived by the superposition of (4) and its back reflection at x = l. The condition

(6)

$$\exp\left(-2\alpha_1l\right)\ll 1$$

can easily be met by shortening the period of the temperature wave and, thus, making  $\alpha_1$ large. Most of the measurements were taken with

$$\exp\left(-2\alpha_1l\right) < 0.05$$

The time varying part of the temperature at one end is, from (6),

$$\theta(0, t) = A_1 \cos(2\pi t/T) \tag{7}$$

and at the other end is

$$\theta(l, t) = 2A_1 \exp(-\alpha_1 l) \cos(2\pi t/T - \beta_1 l)$$
(8)

The ratio of the amplitude 2 exp  $(-\alpha_1 l)$  and the phase difference  $\beta_1 l$  are read on a stripchart recorder that is connected to the thermocouples through a dc amplifier. We then cal-

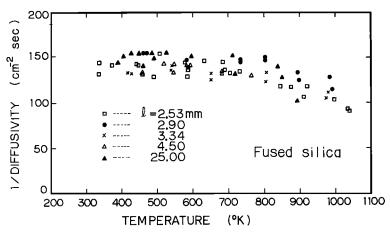


Fig. 2. Reciprocal of thermal diffusivity of fused silica.

culate the thermal diffusivity  $\kappa$  and constant  $\mu$  by (5), using  $\alpha_1$  and  $\beta_1$  thus determined.

$$\kappa = \pi/\alpha_1\beta_1 T 
\mu = \pi(\alpha_1^2 - \beta_1^2)/\alpha_1\beta_1 T$$
(9)

The ambient temperature is varied as follows. The temperature is first raised stepwise, 100°C at a time, up to 500°C, and then it is

lowered to 300°C in the same way. At every 100°C a measurement is taken. This procedure is repeated, shifting the upper limit temperature by 100° to 150°C until the maximum temperature 850°C is reached. In lowering the temperature, the procedure is reversed. Thus, we can obtain a number of determinations while constantly checking the reversibility of the measurement. The result may depend on the

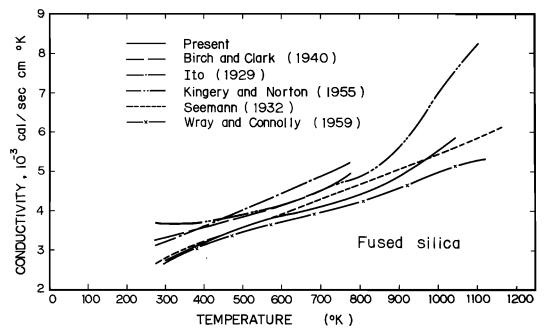


Fig. 3. Comparison of thermal conductivity measurements of fused silica. References are Clark [1966] (for the data by Birch and Clark, Ito, and Seemann), Goldsmith et al. [1961] (for the data by Kingery and Norton), and Wray and Connolly [1959].

TABLE 1. List of Samples

Material	Cell Parameter, A	Density, g/cm <sup>8</sup>	Refractive Index	Locality
Quartz		(2.65)*		Minas Gerais, Brazil
Olivine		3.45†		Miyake-jima, Japan
Periclase		(3.58)*		Synthetic
Jadeite		3.4		Burma
Garnet 1	$11.509 \pm 0.001$	3.82‡	$1.759 \pm 0.002$	Green's Creek, Delaware, Pennsylvania
Garnet 2	$11.547 \pm 0.002$	3.90‡	$1.770 \pm 0.003$	Adirondack, New York
Spinel	$8.088 \pm 0.002$	$3.55^{+}$	$1.718 \pm 0.002$	Mogok, Burma
Corundum		(3.99)*		Mogok, Burma
Alkali feldspar		$(2.6)^*$		Korea

<sup>\*</sup> Estimated from Robie et al. [1966].

method of mounting the sample on the nickel base and also of attaching the thermocouples to the sample. As it is difficult to estimate a priori the uncertainty originating therefrom, we repeated several runs, taking the sample and thermocouples completely apart from the nickel base each time and putting them together again.

The details of the experimental technique are given in a separate paper [Kanamori et al., 1968].

# COMPARISON WITH OTHER METHODS

Two assumptions are made implicitly in (1) and (3'). In equation 1, the escaping energy is represented by a single term  $\mu\theta$ . The actual energy loss, however, takes place by radiation. conduction, or convection. Since these are different physical processes, they cannot be expressed by a single term. As discussed by Carslaw and Jaeger [1959, p. 17], however, when the temperature difference between the sample and the surroundings is small, the effect of radiation and conduction can be expressed by a linear function of temperature, and the effect of convection is proportional to 5/4 power of it. In addition, since the total escaping energy in the present case is very small compared with the energy transmitted through the sample, we assumed the form  $\mu\theta$  for the energy escaping in various manners.

The boundary condition (3') specifies the condition that no heat energy escapes from the end surface. This condition is not strictly

satisfied, because a part of the energy reaching the end will escape therefrom into the surroundings by conduction and, at higher temperatures, by radiation. This incomplete boundary condition affects slightly the solution (6). but the effect is limited mainly to the boundary x = l. Since the thermal diffusivity is determined by measuring the accumulated phase change and amplitude reduction of the temperature wave in the course of transmission along the sample, the boundary effect becomes relatively unimportant if the period of the temperature wave is so adjusted as to make the phase change and the amplitude reduction sufficiently large. The period of the temperature wave is actually adjusted so that the amplitude

TABLE 2. Chemical Composition of Olivine and Jadeite

	Olivine,* % Miyake-jima, Japan	Jadeite, % Burma
SiO <sub>2</sub>	38.82	57.86
$Al_2O_3$	0.20	23.90
$Fe_2O_3$	1.65	0.75
FeO	14.93	
MgO	42.51	1.23
CaO	0.40	1.24
$Na_2O$		13.85
$K_2O$		0.11
MnO	0.23	

<sup>\*</sup> N. Isshiki (personal communication).

<sup>†</sup> Estimated from chemical data given in Table 2.

<sup>‡</sup> Estimated from cell parameter and refractive index.

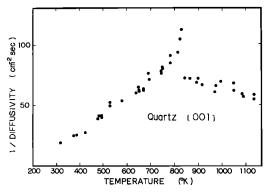


Fig. 4. Reciprocal of thermal diffusivity of quartz in [001] direction.

is well attenuated to less than 1/5, and the associated phase change is  $\pi/3$  to  $\pi/2$ .

Although the errors arising from these simplifications are probably small, it is essential, on the introduction of a new method, to compare the new result with results determined by well-established methods. The comparison was made for fused silica, whose thermal conductivity has been determined by various techniques.

Five samples having the lengths 2.53, 2.90, 3.34, 4.50, and 25.00 mm were prepared. The longest sample (l=25.00 mm) can be regarded as an infinite rod, and the ordinary Ångström method is applicable. The temperature wave was detected at two arbitrary points 3 mm apart along the axis of the sample. In this case we can use the boundary condition (3) and

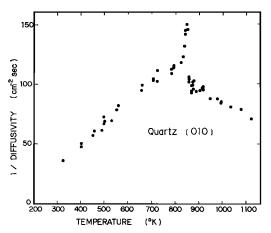


Fig. 5. Reciprocal of thermal diffusivity of quartz in [010] direction. The two points indicated by asterisks are the values under a reduced pressure of 10<sup>-2</sup> mm Hg.

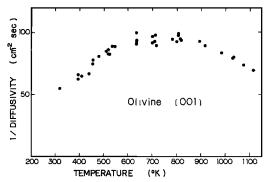


Fig. 6. Reciprocal of thermal diffusivity of olivine in [001] direction. The two points indicated by asterisks are the data obtained under a reduced pressure of 10<sup>-2</sup> mm Hg.

eliminate the incomplete boundary condition (3'). For the other samples we used the modified Angström method, and the temperature was measured at both ends of the sample. If the incomplete representation  $\mu\theta$  for the escaping energy and the boundary condition (3') seriously disturbs the measurement, we would obtain different results for samples of different lengths. The results are shown in Figure 2. No appreciable difference can be seen among samples of different lengths. This may be regarded as an experimental verification of the assumption made in (1) and (3'). To compare these data with the pre-existing thermal conductivity data, we calculated the thermal conductivity from the measured diffusivity, using the specific heat data given by Goranson [1942] and the density  $\rho = 2.21$  g/cm<sup>3</sup>. The results are given in Table 3. Figure 3 shows the comparison with the pre-existing data. The present result is consistent with other results within a reasonable range.

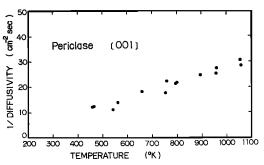


Fig. 7. Reciprocal of thermal diffusivity of periclase in [001] direction.

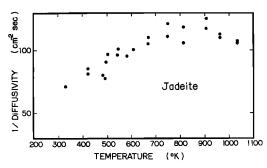


Fig. 8. Reciprocal of thermal diffusivity of jadeite.

#### SAMPLES

All the samples studied here are listed in Table 1. Table 2 gives the results of chemical analyses of olivine and jadeite. The olivine is 82% forsterite and 18% fayalite. Densities of jadeite and olivine are estimated from the chemical data. For spinel, garnet 1, and garnet 2, the cell parameter and the refractive index are measured: from these measurements we estimate the densities [Deer et al., 1964, 1965]. Garnet 1 is 60% pyrope and 40% almandite, and garnet 2 is 50% pyrope and 50% almandite. The feldspar sample used here was supplied from the mineral collection of the Geological Institute, University of Tokyo. The sample is labeled as 'moonstone; locality unknown, probably from Korea.' It is highly probable that this specimen is from the same locality as the moonstone (iridescent sanidine) described by Kozu and Endo [1921] and Kozu and Suzuki [1921]. According to these authors, it is clear that it consists of a submicroscopic intergrowth of Na-rich and K-rich feldspars, formed by unmixing of an originally homogeneous sanidine phenocryst in rhyolite. Inferred chemical composition is Ore1 Ab24 An5

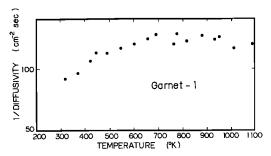


Fig. 9. Reciprocal of thermal diffusivity of garnet 1.

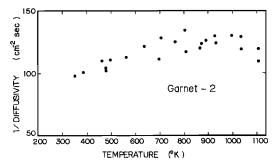


Fig. 10. Reciprocal of thermal diffusivity of garnet 2.

(mol) [Kozu and Suzuki, 1921]. Except jadeite, all the samples are single crystals. For quartz, two samples cut in the [001] and [010] directions were prepared. Olivine and periclase were oriented in the [001] direction. Garnet 2 was oriented in the [111] direction. Because of the limited size, it was not possible to cut the samples in specific directions for other minerals, but we determined the direction in which the measurements were made. The axis of measurement for garnet 1 was inclined at 15° to the [001] axis in a plane that makes an angle of 12° with the (010) plane. For corundum, the measurement was made in the direction inclined at 15° to the [0001] axis in a plane that makes an angle of  $7^{\circ}$ with the  $(10\overline{1}0)$  plane. For the moonstone (monoclinic; b = Y,  $a \land c = 65^{\circ}$ ,  $c \land Z$  in acute angle beta = 20°), the angles between the axis of measurement and a, b, and c axes are 17°, 99°, and 81°, respectively.

#### RESULTS

Figures 4 to 13 show the reciprocal of the measured values of the thermal diffusivity plotted against the absolute temperature. All the measurements obtained by using different periods and through different runs are plotted together, so that the scattering of the points can

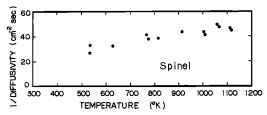


Fig. 11. Reciprocal of thermal diffusivity of spinel.

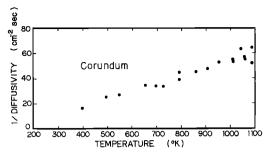


Fig. 12. Reciprocal of thermal diffusivity of corundum.

be regarded as a measure of the over-all reliability of the present method. For the convenience of other applications, smooth curves are fitted to the points and values are read therefrom at 100°K intervals. We then calculate from the smoothed diffusivity curves thermal conductivities of quartz, olivine, and periclase, using available data of the specific heat. The results are given in Table 3. The thermal resistivity, reciprocal of conductivity, is shown in Figure 14.

Quartz. The thermal resistivity increases almost linearly with temperature below 800°K. This is the result expected from the theoretical consideration of thermal conduction at moderately high temperatures, where heat energy is supposed to be transferred mainly by phonons. A number of theories [see Kingery and McQuarrie, 1954] predict this linear dependence of thermal resistivity on temperature. The values obtained here are in close agreement with the values obtained by Birch and Clark [1940a] up to 650°K (Figure 4). Their detailed discussion of the result up to this temperature also applies to the present work. A sharp peak in

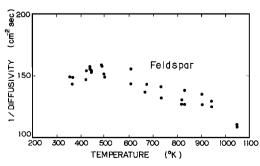


Fig. 13. Reciprocal of thermal diffusivity of alkali feldspar.

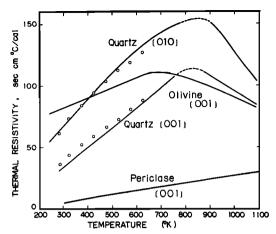


Fig. 14. Thermal resistivities of quartz, olivine and periclase. Open circles are from data by *Birch and Clark* [1940b].

both Figure 4 and Figure 5 around 850°K indicates the phase transition from  $\alpha$  to  $\beta$  quartz. Above the transition temperature, the thermal resistivity decreases with temperature. A recent work by Kawada [1966] also suggests a similar behavior of quartz.

Birch and Clark [1940b] suggested that the crystal anisotropy appears to decrease at higher temperatures. The ratio of the conductivities of quartz in the directions perpendicular and parallel to the optic axis, based on Table 3, is plotted in Figure 15, as compared with the data given by Birch and Clark. The anisotropy further decreases at temperatures higher than that covered by Birch and Clark.

To check the effect of the argon gas, two measurements were made under a reduced pressure of  $10^{-3}$  mm Hg. Although the values of  $\alpha_1$  and  $\beta_1$  changed drastically, no appreciable difference in diffusivity was observed (Figure 5).

Olivine. The thermal resistivity increases linearly with temperature below 700°K, but it decreases above 800°K.

Two measurements under a reduced pressure agree with measurements under 1 atmosphere in argon.

Periclase. The thermal conductivity of periclase is larger than that of olivine or quartz by one order of magnitude at low temperatures and about three to five times as large at higher temperatures. In general, crystals with greater

TABLE 3. Results of Thermal Diffusivity Measurements

		Temperature, °K								
Material		300	400	500	600	700	800	900	1000	1100
Fused silica (* (10	O <sup>-8</sup> cm <sup>2</sup> /sec)	7.25	7 15	7 05	7.00	7.15	7.41	8.00	8.85	
$ρ = 2.21 \text{ g/cm}^3 \left\{ C_n \right\}$	cal/g°C)*	0.172	0.205	0 231	0.250	0.262	0.272	0.280	0.285	
	10 <sup>-3</sup> cal/cm sec °C)	2 74	3.22	3.58	3.85	4.12	4.43	4.92	5.55	
Quartz [001]	K	71.4	35.7	23.8	16.9	13.7	11.4	14.1	15.4	16.4
$\rho = 2.65 \text{ g/cm}^3$	κ C <sub>p</sub> * K	0.176	0.208	0.238	0.258	0.272	0.282	0.248	0.268	0.284
	K	33.3	19.6	14.9	11.5	9.35	8.50	9.25	10.9	12.3
Quartz [010]	K	33.3	20.0	14.5	11.5	9.62	8.93	10.0	11.4	12.8
$\rho = 2.65  \text{g/cm}^3$	 C <sub>p</sub> * K	0.176	0.208	0.238	0.258	0.272	0.282	0.248	0.268	0.284
	K	15.5	11.0	9.14	7.86	6.93	6.67	6.56	8.10	9.62
Olivine [001]	κ	18.5	14.9	12.2	10.8	10.3	10.4	10.9	12.0	13.5
$\rho = 3.45 \mathrm{g/cm^3}$	$C_{m p}\dagger \ K$	0.190	0.220	0.240	0.250	0.260	0.265	0.270	0.275	0.280
l	ĸ	12.1	11.3	10.1	9.30	9.23	9.50	10.1	11.4	13.0
Periclase [001]	K		125	87.0	66.7	<b>55.6</b>	46.5	40.0	35.7	32.3
$\rho = 3.58  \text{g/cm}^{\bullet}$	$C_{p}^{*}$ $K$		0.245	0.262	0.272	0.278	0.282	0.286	0.292	0.296
l	K		110	81.5	65	55.4	46.9	40.9	37.3	34.2
Jadeite	κ	15.4	12.8	11.1	9.71	8.77	8.40	8.33	8.85	9.62
Garnet 1	K	11.1	9.9	8.93	8.33	7.94	7.94	8.00	8.13	8.33
Garnet 2	K	10.9	10.0	9.26	8.70	8.26	8.00	8.00	8.00	8.33
Spinel	K			34.5	31.3	28.6	25.6	24.4	22.5	21.3
Corundum	K		60.6	45.5	34.5	28.6	25.0	21.3	18.5	16.4
Alkali feldspar	K	7.09	6.67	6.49	6.71	6.99	7.30	7.81	8.33	8.93

<sup>\*</sup> From Goranson [1942].

symmetry in structure and less chemical impurities may have less interaction in the lattice wave transmission and, consequently, may have a higher thermal conductivity [Kingery and McQuarrie, 1954]. Since periclase belongs to the cubic system and the sample used here is synthetic and free from significant impurities, the present result is consistent with the theory.

Unlike olivine and quartz, no appreciable change of gradient is seen in the curve for periclase.

Jadeite, garnet, spinel, corundum, feldspar. The reciprocal of the thermal diffusivity of

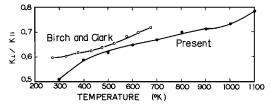


Fig. 15. The ratio of the thermal conductivities of quartz in the direction perpendicular and parallel to the optic axis. Open circles are data by *Birch and Clark* [1940b].

jadeite, given in Figure 8, also shows a linear dependence on temperature at lower temperatures. The values are approximately the same as those for olivine. Since both density and specific heat are probably about the same for jadeite and olivine, their thermal conductivities would take about the same value at temperatures lower than 700°K.

Although a slight increase of the thermal diffusivity is also seen in jadeite at temperatures higher than 850°K, the increase is small compared with that of olivine or quartz.

Two samples of garnet with a slightly different chemical composition show almost identical dependence on temperature. The diffusivities are much less compared with values for olivine, pyroxene, and quartz. This low value for garnet appears to be reflected in the low conductivity of eclogite found by *Kawada* [1964]. Although an increase of thermal diffusivity is seen at higher temperatures, the increase is far smaller than that found for olivine or quartz.

The thermal diffusivities of spinel and corundum are about three times as large as that of olivine for the temperature range up to

<sup>†</sup> From Verhoogen [1955].

700°K. They decrease monotonically up to 1100°K, indicating conduction by lattice waves. It can be said that, for the temperature range covered here, the heat conduction by the lattice waves in tightly packed minerals, such as periclase, spinel and corundum, is much more effective than that in ordinary crystals. This observation strongly suggests that the phase change of olivine to spinel, which has been experimentally verified by Ringwood [1959], Dachille and Roy [1960], and Akimoto et al. [1965], may have a significant effect on the change of the thermal conductivity and hence on the temperature distribution within the earth's mantle.

A peculiar variation of the thermal diffusivity with temperature was found for feldspar, as shown in Figure 13. The feldspar shows an increase of the thermal diffusivity with increasing temperature. This is difficult to understand in view of the ordinary theory of thermal conduction. It is noteworthy, however, that the same tendency was also found by Birch and Clark [1940a] for feldspars. They tentatively attributed this tendency to the fine imperfections of crystals. The feldspar sample used here has micro twin structure and tends to produce fine imperfections. The interpretation by Birch and Clark may also apply to the present result. The relatively low diffusivity of feldspar should also be noted.

# EFFECT OF RADIATION

The increase with temperature of the conductivities, particularly of olivine and quartz, at temperatures higher than 800°K could be interpreted in terms of radiative heat transfer. It is not possible, however, by the present method to separate the effect of radiation from that of conduction. Further, radiative transfer depends not only on the physical properties of the material but also on the size and shape of the sample [Lee and Kingery, 1960]. To examine these, it is essential to have a detailed knowledge of high-temperature absorption spectrums of minerals, which are not available. Under these circumstances, only a brief discussion will be given.

According to *Clark* [1957], when the sample size is large compared with the mean free path of the radiation, the radiative energy is transferred by an absorption-reradiation process

within materials. The effective thermal conductivity, K, of the material at temperature T is then given by

$$K = K_c + K_r$$

where  $K_o$  is the lattice conductivity and

$$K_r = 16n^2 \sigma T^3 / 3\epsilon \tag{10}$$

where n,  $\sigma$ , and  $\epsilon$  are the refractive index, the Stefan-Boltzmann constant, and opacity, respectively. The opacity at temperature T is given by

$$\epsilon = \epsilon_0 + \epsilon_A$$

where

$$\epsilon_{\bullet} = \frac{120\pi\sigma_0}{n} \exp\left(-E/2kT\right)$$

where  $\sigma_0$ , E, and k are the high-temperature limit of electrical conductivity in mho cm<sup>-1</sup>, the activation energy in electron volts, and the Boltzmann constant, respectively. To estimate the temperature effect, we measured the electrical conductivity of most of the samples used here over the same temperature range as that covered by the thermal diffusivity measurement. A detailed description of the measurement is given elsewhere [Mizutani and Kanamori, 1967], but the activation energy E and  $\sigma_0$  are summarized in Table 4 together with the values of  $\epsilon_o$  calculated therefrom at 1000°K. Table 4 shows that the temperature effect on  $\epsilon$  through electronic processes is very small over the temperature range considered here.

If we assume that the variation of lattice resistivity  $1/K_o$  is linear with temperature and that the bend of the observed 1/K curves is entirely due to radiation effect, we can estimate the radiative contribution  $K_r$  by taking the difference between  $1/K_c$  extrapolated linearly from low-temperature data and the actually measured 1/K. The values thus estimated at T = 1000°K are given in Table 5. If this radiative contribution is entirely through the absorption-reradiation process we can estimate the 'gray' opacities by (10), as shown in Table 5. These values are consistent with the results obtained by Clark [1957], who reported the value of 10 cm<sup>-1</sup> for fresh dunites. It should be noted, however, that, since the linear dimension of the samples used here is 3 to 5 mm, the validity of (10) is marginal for  $\epsilon \approx 10$  cm<sup>-1</sup>.

TABLE 4. Electrical Properties of Minerals

Material	E, ev	$\sigma_0$ , mho cm <sup>-1</sup>	$\epsilon_e$ , cm $^{-1}$
Quartz [010]	1.6	0.63	1.3 × 10 <sup>-2</sup>
Olivine [001]	1.7	0.29	$3.3 \times 10^{-8}$
Garnet 1	2.2	1.2	$7.9 \times 10^{-4}$
Jadeite	1.5	1.3	$4.4 \times 10^{-2}$

Another possible interpretation is that the material is relatively transparent ( $\epsilon \leq 5$  cm<sup>-1</sup>) and boundary-to-boundary transfer [Lee and Kingery, 1960] is predominant. In that case, the observed conductivity at high temperatures is no longer a material constant, but the radiative conductivity would be even more pronounced in large samples than that indicated here.

Measurements of high-temperature absorption coefficient for rock-forming minerals are highly desirable for supplementing the high-temperature conductivity measurement.

# Conclusion

The method developed here is useful for small samples of millimeter size to which the ordinary method of thermal conductivity measurement cannot be applied. At temperatures below 800°K, where the lattice conduction is dominant, the results are reliable within ±5%. However, when the sample is relatively transparent, the interpretation of the results becomes difficult at temperatures higher than 800°K, where the radiative heat transfer couples with the conduction transfer. It could be said, however, that, if the opacity of minerals is about 10 cm<sup>-1</sup>,

TABLE 5. Estimated Radiative Conductivities and Gray Opacities of Minerals

Material	K, at 1000°K, cal/cm sec °C	ε, cm <sup>−1</sup>
Quartz [001]*	0.0038	6
Quartz [010]*	0.0022	10
Olivine [001]*	0.0037	6
Jadeite†	0.0019	12
Garnet 1†	0.0017	13
Garnet 2†	0.0011	20

<sup>\*</sup> Estimated from curves in Figure 15.

the radiative heat transfer becomes comparable to the conduction transfer at temperatures around 1000°K. In the earth's mantle, where minerals exist as an aggregate, forming a variety of rocks, the radiative heat transfer will be limited by the boundary effect of the constituent minerals. The crystal size and the grain boundary density will therefore have an important bearing on the heat transfer in the earth's mantle.

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# REFERENCES

Akimoto, S., H. Fujisawa, and T. Katsura, The olivine-spinel transition in Fe<sub>2</sub>SiO<sub>4</sub> and Ni<sub>2</sub>SiO<sub>4</sub>, J. Geophys. Res., 20, 1969, 1965.

Birch, F., and H. Clark, The thermal conductivity of rocks and its dependence upon temperature and composition, Am. J. Sci., 238, 529, 1940a. Birch, F., and H. Clark, The thermal conductivity of rocks and its dependence upon temperature

and composition, 2, Am. J. Sci., 238, 613, 1940b. Carslaw, H. S., and J. C. Jaeger, Conduction of Heat in Solids, 2nd edition, pp. 1-161, Oxford

University Press, London, 1959. Clark, S. P., Radiative transfer in the earth's mantle, *Trans. Am. Geophys. Union*, 38, 931, 1957.

Clark, S. P., Thermal conductivity, in *Handbook* of *Physical Constants*, edited by S. P. Clark, pp. 459-482, Geological Society of America, New York, 1966.

Dachille, F., and R. Roy, High pressure studies of the system Mg<sub>2</sub>GeO<sub>4</sub>-Mg<sub>2</sub>SiO<sub>4</sub> with special reference to the olivine-spinel transition, Am. J. Sci., 258, 225, 1960.

Deer, W. A., R. A. Howie, and J. Zussman, Rock-Forming Minerals, vol. 5, pp. 56-88, Longmans, London, 1964.

Deer, W. A., R. A. Howie, and J. Zussman, *Rock-Forming Minerals*, vol. 1, pp. 77-112, Longmans, London, 1965.

Goldsmith, A., T. E. Waterman, and H. J. Hirschborn, *Handbook of Thermophysical Properties of Solid Materials*, vol. 3, pp. 895-896, Macmillan, New York, 1961.

Goranson, R. W., Heat capacity, heat of fusion, in Handbook of Physical Constants, edited by F. Birch, J. F. Schairer, and H. C. Spicer, pp. 223-242, Geological Society of America, New York, 1942.

<sup>†</sup> Estimated from curves in Figures 8, 9, and 10 with  $\rho$  listed in Table 1 and  $C_p = 0.28$  cal/g °C.

- Ide, J. M., The velocity of sound in rocks and glasses as a function of temperature, J. Geol., 45, 689, 1937.
- Kanamori, H., H. Mizutani, and N. Fujii, Method of thermal diffusivity measurement, J. Phys. Earth, 16, (in preparation), 1968.
- Kawada, K., Studies of the thermal state of the earth, 15, Variation of thermal conductivity of rocks, 1, Bull. Earthquake Res. Inst. Tokyo Univ., 42, 631, 1964.
- Kawada, K., Variation of thermal conductivity of rocks, 2, Bull. Earthquake Res. Inst. Tokyo Univ., 44, 1071, 1966.
- Kingery, W. D. and M. C. McQuarrie, Thermal conductivity, 1, Concepts of measurement and factors affecting thermal conductivity of ceramic materials, J. Am., Ceram. Soc., 37, 67, 1954.
- Kozu, S., and Y. Endo, X-ray analysis of adularia and moonstone, and the influence of temperature on the atomic arrangement of these minerals, Sci. Rept. Tohoku Univ., Ser. 3, 1, 1-18, 1921
- Kozu, S., and M. Suzuki, Optical, chemical and thermal properties of moonstone from Korea, Sci. Rept. Tohoku Univ., Ser. 3, 1, 19, 1921.
- Lee, D. W., and W. D. Kingery, Radiation energy transfer and thermal conductivity of ceramic oxides, J. Am. Ceram. Soc., 43, 594, 1960.

- Mizutani, H., and H. Kanamori, Electrical conductivities of rock-forming minerals at high temperatures, J. Phys. Earth, 15, (in preparation), 1967.
- Nii, R., Measuring method of thermal conductivity of semiconductors (in Japanese), Elec. Commun. Lab. Tech. J., 9, 817, 1960.
- Ringwood, A. E., Constitution of the mantle, 2, Further data on the olivine-spinel transition, Geochim. Cosmochim. Acta, 15, 18, 1959.
- Robie, R. A., P. M. Bethke, M. S. Toulmin, and J. L. Edwards, X-ray crystallographic data, densities, and molar volumes of minerals, in Handbook of Physical Constants, edited by S. P. Clark, pp. 27-73, Geological Society of America, New York, 1966.
- Verhoogen, J., Thermal expansion of solids and the temperature at the boundary of the earth's core, Trans. Am. Geophys. Union, 36, 866, 1955.
- Wray, K. L., and T. J. Connolly, Thermal conductivity of clear fused silica at high temperatures, J. Appl. Phys., 30, 1702, 1959.

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