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THE ELASTIC CONSTANTS OF $\mathrm{Mn_2SiO_4}$, $\mathrm{Fe_2SiO_4}$ and $\mathrm{Co_2SiO_4}$, AND THE ELASTIC PROPERTIES OF OLIVINE GROUP MINERALS AT HIGH TEMPERATURE

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Abstract

Elastic constants of single-crystal $\mathrm{Mn_2SiO_4}$, $\mathrm{Fe_2SiO_4}$ and $\mathrm{Co_2SiO_4}$ olivine are measured by the rectangular parallelepiped resonance (RPR) method at temperatures between 20° and 400 °C. Elastic constants $\mathrm{C_{ij}}$ (Mbar) and their temperature derivatives $\mathrm{\partial C_{ij}}/\mathrm{\partial T}$ (kbar/deg) are:

ij	*	11	22	33	23	31	12	44	55	66
C _{ij} (25°C)	Mn ₂ SiO ₄	2.584	1.656	2.068	0.917	0.952	0.871	0.453	0.556	0.578
5	Fe ₂ SiO ₄	2.670	1.736	2.392	0.979	0.987	0.952	0.324	0.467	0.573
	Co ₂ SiO ₄	3.078	1.947	2.342	1.032	1.050	1.016	0.467	0.639	0.648
∂c _{ij} /∂T	Mn ₂ SiO ₄ , Fe ₂ SiO ₄ , Fe ₂ SiO ₄ , Co ₂ SiO ₄ ,	-0.409 -0.396	-0.347 -0.379	-0.459 -0.480	-0.054 -0.090	-0.086 -0.100	-0.168 -0.194	-0.052 +0.009	-0.048 -0.011	-0.176 -0.144

- a) mean value between 30° and 400 °C; b) mean value between 25° and 200 °C;
- c) mean value between 220° and 400 °C.

The isotropic properties, density ρ , adiabatic bulk modulus Ks, rigidity μ , the Poisson's ratio σ , and their temperature derivatives calculated by the Voigt-Reuss-Hill scheme are :

	ρ (g/cm³)	Ks (Mbar)	μ (Mbar)	σ	$\partial Ks/\partial T$ $\partial \mu/\partial T$ $\partial \sigma/\partial T$ (kb/deg) (kb/deg) (×10 ⁻⁵ deg ⁻¹)
Mn ₂ SiO ₄	4.129	1.288	0.546	0.314	-0.195 ^{a>} -0.104 ^{a>} 0.64 ^{a>}
Fe ₂ SiO ₄	4.400	1.379	0.509	0.336	-0.205 by -0.108 by 0.93 by
					-0.230 ° -0.075 ° -0.26 °
Co ₂ SiO ₄	4.706	1.482	0.620	0.316	-0.195^{α} -0.077^{α} -0.12^{α}

a), b), and c): the same as above.

By combining the present results with the previous data on a magnesium rich olivine, the effect of cation substitution on the elastic properties of olivine group minerals is discussed and the elastic constants of olivine at high temperature in the earth's mantle are clarified.

Introduction

The olivine is one of the major constituents in the upper mantle of the earth, and an accurate determination of its elastic constants is of basic importance in the interpretation of structure of the upper mantle. In nature olivine occurs mostly as the solid solution of forsterite Mg₂SiO₄ and fayalite Fe₂SiO₄. The six-coordinated cations (Mg and Fe) are substituted by small amount of Ca, Mn, Co and Ni. The known end members of olivine solid solution are tephroite Mn₂SiO₄, Co-olivine Co₂SiO₄, and Ni-olivine Ni₂SiO₄ in addition to forsterite and fayalite.

The elastic constants of forsterite Mg_2SiO_4 have been determined with fairly good accuracy by Kumazawa and Anderson (1969), Graham and Barsch (1969), and Sumino et al. (1977) by using single crystalline samples. The olivine specimens for which a set of nine elastic constants has been reported so far are natural peridot (Fe/Mg+Fe = 0.072 - 0.083) (Verma, 1960; Kumazawa and Anderson, 1969; Ohno, 1976).

On the other hand, a set of elastic constants of single crystal fayalite Fe₂SiO₄ has not been reported yet. The reported elastic properties of fayalite are limited to three dilatational wave velocities along the <u>a</u>, <u>b</u> and <u>c</u> axes of imperfect fayalite crystal (Furuhashi, see Suwa, 1964; Mizutani et al., 1970), the ultrasonic velocities in polycrystalline sample (Mizutani et al., 1970; Chung, 1970, 1971; Akimoto, 1972: revised data of Mizutani et al. 1970), and the compressibilities determined by a volumetric technique (Adams, 1931), and an X-ray diffraction technique (Takahashi, 1970; Yagi et al., 1975). The elastic properties of other olivine type silicate minerals have never been reported.

In this paper, the elastic constants of fayalite, tephroite $\mathrm{Mn_2SiO_4}$, and Co-olivine $\mathrm{Co_2SiO_4}$, which are analogue of forsterite and fayalite, are determined at temperatures between 20° and 400 °C by means of the RPR method (rectangular

parallelepiped resonance method). By combining the present results with previous results of forsterite, the elastic parameters of olivine group minerals are summarized and the elasticity systematics relating to cation substitution is discussed. The temperature variation of seismic wave velocities of olivine at high temperature in the earth's mantle is investigated.

2, Specimen

The single crystal specimens of Mn₂SiO₄, Fe₂SiO₄ and Co₂SiO₄ olivine were provided as a loan from Prof. H. Takei of Tohoku University, who grew them for his own work (Takei, 1976, 1978). Several pieces of single crystalline Co₂SiO₄ olivine were provided by Prof. S. Naka, Dr. H. Furuhashi, and Prof. T. Noda of Nagoya University (Naka et al., 1968).

Mn₂SiO₄ olivine: Single crystal of Mn₂SiO₄ was grown by the Czochralski pulling technique, and the specimen for the present purpose was the same one as sample T-6 of Takei (1976). The as-grown boule of this crystal was brownish dark under a room light. The polished thin section was clearly transparent to visible light and looked bluish gray. It does not contain any inclusion and any flaw (see the photograph of T-6 specimen in Takei, 1976).

The boule was cut along $\{100\}$ plane to yield a rectangular parallelepiped specimen (designated sample $\text{Mn}_2\text{SiO}_4(T)$). The prescribed orientations were determined within 0.5° using a Laue back-reflection X-ray camera. The surface of the specimen was polished by abrasive powder # 3000.

 Fe_2SiO_4 olivine: Single crystal of Fe_2SiO_4 was grown by the floating-zone method, and the specimen for the present purpose was sample number Fa-15 (Takei, 1978). Although as-grown boule of this crystal was opaque under a room light, the polished thin section was clearly transparent (brown in transmitted light) to

visible light. From an original boule, two rectangular parallelepiped specimens were prepared in the same way as $\mathrm{Mn_2SiO_4}$ (designated sample $\mathrm{Fe_2SiO_4}(\mathrm{TA})$ and $\mathrm{Fe_2SiO_4}(\mathrm{TB})$). The sample $\mathrm{Fe_2SiO_4}(\mathrm{TA})$ was perfect, but in the case of sample $\mathrm{Fe_2SiO_4}(\mathrm{TB})$, a few minute cracks ($\approx 10^{-2}\mathrm{mm}$) had developed at edge of specimen along (010) plane during the preparation.

 ${\it Co}_2{\it SiO}_4$ olivine: Single crystal of ${\it Co}_2{\it SiO}_4$ obtained from Takei (unpublished) was grown by the floating-zone method. The as-grown boule of this crystal was opaque under a room light, and the polished thin section was transparent to visible light. The color of the thin section was pale purple in transmitted light. From the original boule, a specimen was cut out and designated ${\it Co}_2{\it SiO}_4$ (T).

Single crystals of Co₂SiO₄ obtained from Naka et al. (1968) were grown by the Bridgman technique, and the specimen used for the present purpose was the sample E-I-3 described in Naka et al.(1968). From the original boule, a specimen was cut and designated Co₂SiO₄(F). The color of the thin secion, lattice constants, and refractive index of this crystal Co₂SiO₄(F) are the same as those of Co₂SiO₄(T) as listed in Table 1. However, bulk density of Co₂SiO₄(F) was larger than that of Co₂SiO₄(T) and of X-ray density by 0.9 %, probably as a result of deviation from Co₂SiO₄ stoichiometry. The single crystal Co₂SiO₄(F) was directly grown from the composition with an excess CoO (1.4 mole %) to stoichiometric Co₂SiO₄(Naka et al., 1968). The presence of small amount of CoO phase in single crystal Co₂SiO₄(F) was recognized by X-ray diffraction, and also it could be detected by E.P.M.A. analysis as a inclusion (less than a few microns length). When the Co₂SiO₄(F) is regarded as the mixture of CoO and Co₂SiO₄, the amount of CoO included in Co₂SiO₄(F) is calculated to be 2.3 mole % from comparison of bulk densities.

Table 1 shows the basic descriptions of specimen; the three edge lengths of specimen, density, lattice constants, mean atomic weight, molar volume, refractive index, and chemical composition. The bulk density of each specimen is in good agreement with the X-ray density with an exception of $\text{Co}_2\text{SiO}_4(F)$. The measurements for elastic constants were carried out on the five specimens described above.

3. Measurement and result

(3.1) Thermal expansion

Thermal expansivity data of the specimen are necessary for reducing the temperature derivatives of elastic constants from measured temperature variation of resonance frequencies. The coefficients of linear thermal expansion of $\mathrm{Mn_2SiO_4}$ have been reported by Okajima et al.(1978), and those of $\mathrm{Fe_2SiO_4}$ by Suwa (1964), Suzuki et al.(1977) and Takei (1978) by using a diatometric method. All the expansivity data of $\mathrm{Fe_2SiO_4}$ are consistent with 10 % one another. In the present data analysis of $\mathrm{Mn_2SiO_4}$ and $\mathrm{Fe_2SiO_4}$, the values reported by Okajima et al.(1978) for $\mathrm{Mn_2SiO_4}$ and those of Suzuki et al.(1977) for $\mathrm{Fe_2SiO_4}$ were employed, since the specimens measured by Okajima et al. and Suzuki et al. were the same ones as used in the present work.

Although the linear thermal expansivity of $\mathrm{Co_2SiO_4}$ has been determined by Sato (1970) at temperatures between 20° and 400 °C by using the X-ray diffractometer, the data are presumed to be not reliable. Since the volume expansivities of olivine group minerals are almost the same within 10 % (Suzuki, 1975; Suzuki et al., 1977; Okajima et al., 1978), the size corrections with temperature for the determination of elastic constants of $\mathrm{Co_2SiO_4}$ were made by using the thermal expansivity data of $\mathrm{Mn_2SiO_4}$. It is noted that this procedure is justified because the thermal expansion affects the temperature derivatives of elastic constants only several percent (Sumino et al., 1977).

(3.2) Elastic constants

The elastic constants were determined by an RPR method. Theory and its technical details of this method have been reported by Ohno (1976), Sumino et al. (1976), and the details of measuring the temperature variation of elastic constants were described in Sumino et al. (1977).

Measurement of resonance frequencies was made at the temperatures between room temperature and 410 °C on the lower ca. 30 vibrational modes for each specimen as listed in Table 2(A, B and C). In this table, type nomenclature of the modes follows those of Ohno (1976), and the observed values of resonance frequencies, calculated values of them, and their relative deviations are presented. At high temperatures up to 410 °C, the resonance frequencies were measured at irregular temperature interval. Several examples of temperature variation of resonance frequency are shown in Fig.1(A, B, C, and D) for each specimen. As seen in Fig.1, the data of resonance frequency at high temperature showed scattering (up to 2 %) in several modes, presumably due to the changes in the mechanical coupling between the specimen and transducers.

In the present data analysis, the nine independent elastic constants K_1 , K_2 , K_3 , Cs_1 , Cs_2 , Cs_3 , C_{44} , C_{55} , and C_{66} $[K_i = (C_{i1} + C_{i2} + C_{i3})/3$ and $Cs_i = (C_{jj} + C_{kk} - 2C_{jk})/4]$ were derived first. Elastic constants C_{11} , C_{22} , C_{33} , C_{23} , C_{31} , and C_{12} were computed from K_i and Cs_i (i = 1,2,3). All the data of elastic constants and their temperature derivatives for each olivine are listed in Table 4(A and B). In this table, the stated errors of elastic constants are the root mean square deviations calculated by the least square method. The isotropic properties calculated by the Voigt, Reuss, and Hill scheme are also summerized in Table 4 and are illustrated in Fig. 2.

 Mn_2SiO_4 olivine: Measurement of resonance frequencies was made on the lower 32 vibrational modes at the temperatures between 30° and 400 °C. From Fig.1B, the temperature variation of resonance frequencies were found to be almost linear

for all modes. Therefore, the temperature variation of resonance frequencies for $\mathrm{Mn_2SiO_4}$ were fitted by straight lines and the elastic constants were reduced at 30° and 400 °C by using 32 free vibrational modes listed in Table 2A. The relative deviations |0-C| lie wihtin 0.2 % except for EV-1 mode (0.6 % at 30 °C and 0.7 % at 400 °C) and EX-5 mode (-0.5 % at 30 °C and -0.7 % at 400 °C). The results of elastic constants and their temperature derivatives, analyzed by these 32 resonance modes, are listed in Table 4(A and B).

Fe₂SiO₄ olivine: Measurement of resonance frequencies was made at room temperature on the lower 30 vibrational modes for two specimens $Fe_2SiO_4(TA)$ and $Fe_2SiO_4(TB)$. The higher temperature measurement up to 410 °C was made on the lower 28 vibrational modes for $Fe_2SiO_4(TA)$ only. The data of resonance frequencies are listed in Table 2B. The relative deviations |0 - C| are almost within 0.2 % in the whole range of temperature. As seen from Fig.1A, the temperature variation of resonance frequencies for Fe_2SiO_4 was found to be non-linear in this temperature range, particularly for the 0X-1 mode which is identified as a C_{44} -dominated mode. Therefore, the data reduction was made at every 20 degree of temperature by using 28 resonance modes for $Fe_2SiO_4(TA)$, and all the data were 1sited in Table 3. The results of elastic constants and their temperature derivatives are listed in Table 4(A and B).

The elastic constants of two specimens $\operatorname{Fe_2SiO_4(TA)}$ and $\operatorname{Fe_2SiO_4(TB)}$ are in good agreement with one another within 0.3 % except for the constants $\operatorname{C_{22}}$, $\operatorname{C_{23}}$ and $\operatorname{K_2}$ (linear incompressibility), which are relating to the dilation in parallele to crystallographic b axis of olivine. The $\operatorname{C_{22}}$, $\operatorname{C_{23}}$ and $\operatorname{K_2}$ of $\operatorname{Fe_2SiO_4(TB)}$ are smaller than those of $\operatorname{Fe_2SiO_4(TA)}$ by 1.1 %, 1.9 % and 1.2 %, respectively. The difference of these constants in the two specimens is presumed to be due to the minute cracks (or cleavage) developed along (010) plane in $\operatorname{Fe_2SiO_4(TB)}$ as noted previously. Therefore, the recommended values of elastic constants for $\operatorname{Fe_2SiO_4}$ olivine are those of specimen $\operatorname{Fe_2SiO_4(TA)}$.

 ${\it Co}_9{\it SiO}_A$ olivine: Measurement of resonance frequencies was made at room temperature on the lower 32 vibrational modes for a specimen $Co_2SiO_L(T)$ (pure cobalt olivine) and 31 vibrational modes for a specimen $\text{Co}_2\text{SiO}_4(F)$ (cobalt olivine + 2.3 mole % CoO). The higher temperature measurement was made up to 400 °C on the selected 25 modes for $\text{Co}_2\text{SiO}_4(T)$ and selected 28 modes for $\text{Co}_2\text{SiO}_4(F)$. The results of resonance frequencies were listed in Table 2C. The temperature variation of resonance frequencies was almost linear for all modes with an exception of OX-1, which is the same C_{44} -dominated mode as in Fe₂SiO₄. The non-linearity of OX-1 mode is quite gentle both in $\text{Co}_2\text{SiO}_4(\text{T})$ and $\text{Co}_2\text{SiO}_4(\text{F})$ when compared with that of Fe_2SiO_4 as observed in Fig.1(A, C and D). Therefore, the temperature variation of resonance frequencies for Co_2SiO_4 was fitted by straight line except for the OX-1 mode, and the elastic constants were reduced at 30 °C and 400 °C by using the modes listed in Table 2C. The relative deviations $\left| \text{O} - \text{C} \right|$ in both specimens lie almost within 0.2 % for $\mathrm{Co_2SiO_4(T)}$ and within 0.3 % for $\mathrm{Co_2SiO_4(F)}$ at the temperatures 30 °C and 400 °C. The results of elastic constants and their temperature derivatives are listed in Table 4(A and B).

When the elastic constants of $\mathrm{Co_2SiO_4(T)}$ and of $\mathrm{Co_2SiO_4(F)}$ are compared, we can note the following features. First, the $\mathrm{K_1}$ (i = 1,2,3) of $\mathrm{Co_2SiO_4(T)}$ are systematically higher than those of $\mathrm{Co_2SiO_4(F)}$ up to 4 %, although the six independent shear constants $\mathrm{C_{11}}$ (i = 4,5,6) and $\mathrm{Cs_1}$ (i = 1,2,3) are almost the same within 1.2 % (mean deviation is 0.6 %). Second, the degree of anisotropy of several elastic constants in $\mathrm{Co_2SiO_4(F)}$ is smaller than that of $\mathrm{Co_2SiO_4(T)}$. For example, the ratios $\mathrm{C_{44}/C_{66}}$ (= 0.743) and $\mathrm{Cs_1/Cs_3(=0.750)}$ of $\mathrm{Co_2SiO_4(F)}$ are larger than $\mathrm{C_{44}/C_{66}}$ (= 0.721) and $\mathrm{Cs_1/Cs_3(=0.743)}$ of $\mathrm{Co_2SiO_4(T)}$ by 1.8 % and 0.9 %, respectively. These differences between two specimens $\mathrm{Co_2SiO_4(T)}$ and $\mathrm{Co_2SiO_4(F)}$ are originated possibly from the inclusion of 2.3 mole % Coo in $\mathrm{Co_2SiO_4(F)}$. Therefore, the recommended values of elastic constants for $\mathrm{Co_2SiO_4(T)}$ olivine is those of specimen $\mathrm{Co_2SiO_4(T)}$.

4. Discussion

linearly with temperature.

(4.1) Anomalous temperature variation of rigidity for Fe₂SiO₄ and Co₂SiO₄

The elastic constants are usually approximated by linear function of temperature particularly above Debye temperature. The deviation from the linearity is small for ordinary silicates and oxides even at room temperature, and the elastic wave velocities as well as resonance frequencies of these minerals also vary almost

However, a large deviation from linear temperature variation of resonance frequencies is found in all modes of ${\rm Fe_2SiO_4}$ olivine (Fig.1A). A small deviation is also found in OX-1 mode alone of ${\rm Co_2SiO_4}$ olivine (both T and F specimens), although the resonance frequencies in ${\rm Mn_2SiO_4}$ and ${\rm Mg_2SiO_4}$ (Sumino et al., 1977) vary almost linearly with temperature. The most abnormal mode is an OX-1 mode (${\rm G_{44}}$ -dominated mode) in both ${\rm Fe_2SiO_4}$ and ${\rm Co_2SiO_4}$ as illustrated in Fig.1. This anomaly is directly related to the anomalous temperature variation of shear constants ${\rm C_{44}}$, ${\rm C_{55}}$ and ${\rm C_{66}}$ for ${\rm Fe_2SiO_4}$, and ${\rm C_{44}}$ for ${\rm Co_2SiO_4}$. The behavior of elastic constants of olivine group minerals are summarized in Table 5, and also those of related rock salt oxides are summarized in the same table for comparison.

As shown in Table 5, type of anomalous temperature dependence of elastic constant in olivine group is similar to those of rock salt oxide in that the bulk modulus of both olivine group and rock salt oxide group show normal variation for temperature while the shear constant C_{44} (or Cs for CoO) are anomalous. Further, anomalous behavior does not occur in magnesium compounds. This implies that the anomaly is related to the divalent transition metal ions; Fe, Mn and Co. In those transition metal oxides, shear constant C_{44} (or Cs for CoO) shows a drastic change at and around Néel temperature and the non-linear temperature dependence take place even at temperatures 200 degrees above Néel point, while another shear constant Cs (or C_{44} for CoO) changes almost linearly with temperature even in the vicinity of the Néel point (Sumino et al., 1978).

In olivine group minerals, the temperature of antiferromagnetic-paramagnetic phase transition (Nomura et al., 1964, and Santoro et al., 1966) is around 50 K, which is considerably lower than those of the rock salt oxides as listed in Table 5. However, it is likely that the magnetic transition has an influence upon the elastic constants up to high temperature, and that non-linear temperature variation of shear constants for Fe_2SiO_4 and Co_2SiO_4 is caused by the second-order transition mentioned above, although the shear constants of Mn_2SiO_4 did not show any anomalous temperature dependence of detectable degree in the present measurement.

(4.2) Summary of elastic constants of olivine group minerals (4.2.1) The relation between elastic constants and Fe/Mg ratio

The effect of Mg-Fe substitution on acoustic velocities of the olivine solid-solution system has been investigated by Chung (1970 and 1971), by using polycrystalline samples. With the refined data of elastic properties of olivine by single-crystal measurement, this effect of Mg-Fe substitution on elastic properties is discussed here again. The complete set of elastic constants of single crystal Mg-Fe olivine has been reported by Kumazawa and Anderson (abbreviated to KA)(1969), Graham and Barsch (GB)(1969), and Sumino et al.(SE)(1977) for pure end-member Mg₂SiO₄, and by Verma (VE)(1960), Kumazawa and Anderson (1969), and Ohno (OH) for natural peridot with a ratio Fe/Mg+Fe between 7.2 % and 8.3 %.

The measured values of elastic parameters of peridot are compared with the calculated values by the weighted average of corresponding elastic parameter by mole fraction of two end-members; ${\rm Mg_2SiO_4}$ and ${\rm Fe_2SiO_4}$. The values of end-member ${\rm Mg_2SiO_4}$ are given by averaging the data of KA, GB and SE, with an exclusion of KA's ${\rm C_{44}}$ and ${\rm C_{12}}$, which are slightly deviated from the other data (Sumino et al., 1977). The actual deviations of the observed value in peridot from the calculated value obtained from the molar average of two end-members are illustrated in Fig. 3(A and B) for independent nine elastic constants (compliance ${\rm S_{ij}}$ and stiffness ${\rm C_{ij}}$), and two isotropic parameters: Ks and ${\rm \mu}$.

In Fig.3B, the measured value of deviations $(C_{ij}^{obs} - C_{ij}^{cal})/C_{ij}^{cal}$ for diagonal terms $C_{ii}(i=1,...,6)$ is 0.2 % for data of KA, 1.3 % and 0.8 % for two peridot data of OH, and 2.2 % for VE, and also that of C_{23} , C_{31} and C_{12} is 0.7 % for KA (with a exception of C_{12} , 3.6 %), 9.2 % and 4.4 % for OH, and 10.2 % for VE. These results show that the deviations $|C_{ij}^{obs} - C_{ij}^{cal}|$ of KA's data are notably smaller than those of the others. For comparison, the deviation $(S_{ij}^{obs} - S_{ij}^{cal})/S_{ij}^{cal}$ for nine elastic compliance constants S_{ij} is also shown in Fig.3A. The addition law of elastic constants in olivine solid-solution appears to be better for elastic stiffness rather than elastic compliance for rigidity, although there is not much difference for bulk modulus and other anisotropic parameters.

In Fig.4(A and B), several examples of relation between elastic parameters and chemical composition (or density) are shown. The elastic constants of KA are plotted well on the straight line between Mg2SiO4 and Fe2SiO4, although the value of C12 alone in both Mg2SiO4 and peridot of KA is systematically lower than the straight line by 4 % as illustrated in Fig.4A. In this figure, it is pointed out that the bulk modulus seems to increase linearly with increase of Fe-content in the olivine as in Mg-Fe aluminate spinel (Wang and Simmons, 1972; Chang and Barsch, 1973), pyrope-almandine garnet (Babuška et al., 1978) and MgO-FeO (Jackson et al., 1978; Sumino et al., 1978). The variational trend of bulk modulus with Mg-Fe substitution reported by Chung (1970) is opposite. From the four data set of the above solid-solution series, we concluded that a general rule in the Mg-Fe solid solution is that the bulk modulus increases with Fe-content.

The elastic wave velocities of peridot lie almost on a straight line connecting the end-members as shown in Fig.4B. However, when we carefully observe, the elastic wave velocities of peridot appear systematically lower than the straight line and lie close to the broken line indicating the linear addition law of elastic constants. Although this difference is small, it is significant as is also clearly indicated in Fig.4A. This fact implies that the addition law for the elastic wave velocities seems to be a poor choice than that for elastic constant.

(4.2.2) The effects of pressure, temperature and cation substitution on the elastic constants

For an interpretation of the seismic data and a better understanding of physical state in the earth's interior, it is important to find how the elastic constants depend upon pressure, temperature, structural and atomic parameters. The effects of pressure, temperature and cation substitution on the elastic constants in olivine group minerals are discussed in terms of the quantity w (= $\partial \ln C_{ij}/\partial \ln V$). These effects on the elastic constants are essentially expressed by three parameters;

$$w_{\rm T} = - \left(\frac{\partial \ln C_{ij}}{\partial \ln V} \right)_{\rm P,M} = - \left(\frac{\partial C_{ij}}{\partial P} \right) / \alpha C_{ij}$$
(2)

$$w_{M} = - (\partial \ln C_{ij} / \partial \ln V)_{P,T} = - \ln [C_{ij} (M_{p}) / C_{ij} (M_{q})] / \ln [V(M_{p}) / V(M_{q})] \dots (3)$$

where P, T and M represent pressure, temperature and composition (cation species $M_D = Mg$, Co, Fe and Mn), respectively, and K_T is isothermal bulk modulus.

The parameters $w_{\rm p}$, $w_{\rm T}$ and $w_{\rm M}$ are calculated by using the present elastic data combined with the data of ${\rm Mg_2SiO_4}$ reported by Kumazawa and Anderson (1969), Graham and Barsch (1969), and Sumino et al.(1977), and the results are listed in Table 6. The several examples of the quantity w and of the relation between elastic constant and molar volume are also illustrated in Fig.5 (A and B).

From Fig.5 and Table 6, we can point out the empirical rules described below.

- (1) <u>General trends</u> The quantities $w_{\rm p}$, $w_{\rm T}$ and $w_{\rm M}$ in olivine group minerals for every <u>elastic constant</u>) have generally the same order of magnitude, scarcely depending upon the parameters of pressure, temperature and cation-substitution, and their values lie usually between 1 and 8. Especially, in the case of constant C_{11} the values of $w_{\rm p}$, $w_{\rm T}$ and $w_{\rm M}$ are mostly confined in the narrow range between 3 and 5. However, there are several exceptions; (1) The $w_{\rm M}$ relating to the substitution between magnesium and transition metals are much diversed from 20 to 20, and (2) the $w_{\rm T}$ related to the shear constants of Fe₂SiO₄ influenced by magnetic transition are largely deviated from the common values of $w_{\rm p}$, $w_{\rm T}$ and $w_{\rm M}$.
- (2) $\underline{w_{\mathrm{T}}}$ -value The w_{T} in olivine group minerals is virtually constant at 5.5 \pm 1.5, being independent on the respective elastic constants and the divalent cation. An exception is w_{T} related to the shear constants of Fe₂SiO₄ as noted above.
- (3) \underline{w}_{M} -value Among Mn₂SiO₄, Fe₂SiO₄ and Co₂SiO₄, the w_{M} of the elastic constants relating to dilation [C_{ii} and K_i (i = 1,2,3), and C_{ij} (ij = 23,31,12)] are virtually constant at 1.6 \pm 0.9.

However, those $w_{\rm M}$ -values between ${\rm Mg_2Si0_4}$ and the other olivine are scattered

between - 20 and 3. Further the w_{M} related to the shear constants $[C_{ij}]$ (i = 4,5,6) and Cs_i (i = 1,2,3)] are largely scattered between - 5 and 20. all the w_{M} -values for shear constants change almost linearly with volume ; the variation of $w_{\rm M}$ -value with volume is shown as an example for ${\rm C_{44}}$ in Fig.5A. (4) w_{p} , w_{T} and w_{M} values of isotropic parameters Ks and μ The $w_{\rm p}$ and $w_{\rm T}$ values of Ks are virtually constant at 5.0 ± 0.5 for all olivines, being independent of pressure and temperature as illustrated in Fig.5B. This value 5.0 is close to those of ordinary oxide compounds, since the value of $w_{
m p}$ and $w_{
m m}$ are usually between 4 and 6 for oxide compounds, regardless of their crystalline structure and chemical component (e.g., Anderson et al., 1968). The $w_{\rm M}$ -value of Ks among ${\rm Co_2SiO_4}$, ${\rm Fe_2SiO_4}$ and ${\rm Mn_2SiO_4}$, or between ${\rm Mg_2SiO_4}$ and ${\rm Mn_2SiO_4}$ lies between 0 and 2 or $w_{\rm M}$ = 1 ± 1, which is close to the value 4/3 obtained from the assumption that the major bonding force is provided by electrostatic energy (Anderson and Nafe, 1965). The $w_{\rm M}$ -value is \approx 1 for alkali halides and flourides; the typical inonic compounds (Anderson and Nafe, 1965), and the empirical relationship K+V = constant ($w_{\rm M}$ = 1) also hold very well for many oxides (Anderson and Anderson, 1970). However, the w_{M} -values of Ks between ${\rm Mg}_2{\rm SiO}_4$ and the other olivine with transition metal ions ${\rm Co}^{2+}$ and Fe²⁺, which have a crystal field effect, are largely deviated from the ordinary value $w_{\rm M} \stackrel{\simeq}{=} 1$ as listed in Table 6. Therefore, the large deviation of $w_{\!\scriptscriptstyle M}$ -value appears to be originated from the contribution of crystal field stabilization energy (CFSE) of Co²⁺ and Fe²⁺.

The effects of CFSE of Fe²⁺, Co²⁺ and Ni²⁺ ions on bulk modulus K of divalent monoxides were investigated by Ohnishi and Mizutani (1978). They showed that the deviation of bulk modulus from the "K·V = constant "law in rock salt oxides is well explained by considering the CFSE. The variational pattern of Ks and V in olivine group minerals is quite similar to that in rock salt oxides. The same pattern is also observed in garnets (Babuška et al., 1978).

Therefore, the contribution of CFSE to the elasticity of olivines and garnets is definitely important. The discussions on these problems will be reported in the forthcoming paper. It is, however, pointed out that large deviation of bulk modulus of olivines with transition metal ions from that of ${\rm Mg_2SiO_4}$ may be too large to be accounted for by CFSE.

Rigidity The $w_{\rm T}$ for rigidity of olivine group minerals are virtually constant 6 ± 1, of which value is largely deviated from the value $w_{\rm p}$ and is almost one half of $w_{\rm p}$, although the values $w_{\rm p}$ and $w_{\rm T}$ for bulk modulus are almost the same. The $w_{\rm M}$ -values for rigidity vary almost linearly with volume as in Fig. 5B. However, they are considerably scattered generally. In other words, variation of rigidity with pressure, temperature and cation-substitution does not follow any conceivable systematics. This is an important difference between bulk modulus and rigidity.

(4.2.3) The estimated values of pressure derivatives of isotropic properties in $\mathrm{Fe_2Si0_4}$

The pressure derivatives of isotropic parameters in $\mathrm{Fe_2SiO_4}$ are discussed by using some empirical relation obtained in the previous section and the relation of elastic parameters to Grüneisen constant proposed by Suzuki and Kumazawa (1978).

The pressure derivative of bulk modulus in ${\rm Fe_2SiO_4}$ was determined by the measurement of ultrasonic velocities in polycrystalline sample up to 7.5 kbar by Chung (1971). He reported $\partial {\rm Ks}/\partial {\rm P}=5.92$ for ${\rm Fe_2SiO_4}$. The bulk modulus and its pressure derivative of ${\rm Fe_2SiO_4}$ was also investigated by Takahashi (1970) up to 150 kbar, and Yagi et al. (1975) up to 70 kbar by means of X-ray diffraction technique. The reported values of ${\rm Fe_2SiO_4}$ are ${\rm K_T}=1.35\pm0.15$ on the assumption of $\partial {\rm K_T}/\partial {\rm P}=4.5$ (Takahashi), and ${\rm K_T}=1.24\pm0.02$ on the assumption of $\partial {\rm K_T}/\partial {\rm P}=5$ (Yagi et al.). Their values of ${\rm K_T}$ (= 1.35 - 1.25) are in good agreement with the present data of ${\rm K_T}=1.37$ within 9 %. Therefore, $\partial {\rm K_T}/\partial {\rm P}$ is presumed to be around 5. Then, $\partial {\rm Ks}/\partial {\rm P}$ is also the same value, since the difference between $\partial {\rm K_T}/\partial {\rm P}$ and $\partial {\rm Ks}/\partial {\rm P}$ is usually within 1 % in oxide compounds.

On the other hand, the $\partial Ks/\partial P$ (\cong value of w_P for Ks in eq.(1)) is usually close to the w_T -value of Ks in eq.(2) and these values lie between 4 and 6 as mentioned in a previous section. For example, w_P is 5.14 - 5.08 for Ks of Mg₂SiO₄ and peridot, whereas w_T is 4.2 - 4.8. Since w_T = 5.3 for Fe₂SiO₄, $\partial Ks/\partial P$ is supposed to be around 5. Combining all the information above, we may conclude that the value of $\partial Ks/\partial P$ in Fe₂SiO₄ must be around 5, or $\partial Ks/\partial P$ = 5.0 ± 1.0, which is quite normal for ordinary solids.

The pressure derivatives of rigidity in ${\rm Fe_2SiO_4}$ is also predicted from the relation between Grüneisen constant and pressure derivatives of elastic parameters, proposed by Suzuki and Kumazawa (1978). Based on this relation, the value $\partial\mu/\partial P$ of ${\rm Fe_2SiO_4}$ is estimated to be $\partial\mu/\partial P=0.7\pm0.2$ (personal communication from Kumazawa), which is close to $\partial\mu/\partial P=0.62$ for polycrystalline ${\rm Fe_2SiO_4}$ (Chung, 1971)

and is quite different from the value $\partial\mu/\partial P=1.79-1.82$ of ${\rm Mg_2SiO_4}$ and peridot (Kumazawa and Anderson, 1969, and Graham and Barsch, 1969). The marked difference of $\partial\mu/\partial P$ in ${\rm Mg_2SiO_4}$ and ${\rm Fe_2SiO_4}$ may be related to the large difference in the value of Poisson's ratio (0.336 for ${\rm Fe_2SiO_4}$ and 0.240 for ${\rm Mg_2SiO_4}$). However, Poisson's ratio of ${\rm Fe_2SiO_4}$ tends to decrease with temperature and thus the value of $\partial\mu/\partial P$ would not be so low at high temperature.

The pressure derivatives of isotropic seismic wave velocities $\partial V_p/\partial P$, $\partial V_s/\partial P$ and $\partial V_{\Phi}/\partial P$ are calculated by using the predicted values of $\partial K_s/\partial P$ and $\partial \mu/\partial P$. All the pressure derivatives of isotropic parameters in Fe_2Sio_4 are listed in Table 7, in comparison of the data of Chung (1971).

(4.3) Elastic parameters of $\mathrm{Mn_2SiO_4}$, $\mathrm{Fe_2SiO_4}$ and $\mathrm{Co_2SiO_4}$ at high temperature. The numerical values of elastic parameters for $\mathrm{Mn_2SiO_4}$, $\mathrm{Fe_2SiO_4}$ and $\mathrm{Co_2SiO_4}$ olivine are calculated up to very high temperature by using some empirical methods based on the theory of Mie-Grüneisen equation of state.

The Grüneisen constant γ and the Grüneisen-Anderson parameter δ_s are defined by $\gamma = \alpha V K s / C p \qquad(4)$ $\delta_s = - \left(\partial \ln K s / \partial T \right) / \alpha \qquad(5)$

where Cp is the specific heat at constant pressure, V is the specific volume, and α is the coefficient of volume thermal expansion. Constancy of the quantities γ and δ_s with respect to temperature was theoretically given by Grüneisen (1926) and Anderson (1966), and was experimentally supported by many investigators [e.g., Soga and Anderson (1967) for MgO and Al₂O₃, and Sumino et al. (1977) for Mg₂SiO₄]. As far as the experimental data are concerned, constancy for δ_s was supposed to be better assumption than that for γ at high temperature (Sumino et al., 1977). Then, the calculation of the elastic parameters of Mn, Fe, and Co-olivine

up to high temperature is made by assuming the constancy of $\delta_{\mathbf{c}}$.

The values of γ and δ_s listed in Table 8 were calculated by eqs (4) and (5) from the present elasticity data combined with α reported by Okajima et al.(1978) and Cp by Jeffes et al.(1954) for $\mathrm{Mn_2SiO_4}$, and α of Suzuki et al.(1977) and Cp of Orr (1953) for $\mathrm{Fe_2SiO_4}$. In the case of $\mathrm{Co_2SiO_4}$, the computation of γ and δ_s were made by using Cp reported by Watanabe and Kawada (1978) and α of $\mathrm{Mn_2SiO_4}$. The γ is virtually constant γ = 1.1 ± 0.1 for all olivine group minerals studied here, while the value of δ_s for $\mathrm{Mn_2SiO_4}$, $\mathrm{Fe_2SiO_4}$ and $\mathrm{Co_2SiO_4}$ is 4.7 - 5.6, which is higher than that of $\mathrm{Mg_2SiO_4}$ by 20 - 30 %.

From eq.(5), the bulk modulus Ks at temperature T is given by

$$Ks(T) = Ks_{\circ}[V_{\circ}/V(T)]^{\delta_{S}} \qquad \dots (6)$$

where the subscript ($_{\circ}$) indicates the quantity at reference temperature T $_{\circ}$ (Sumino et al., 1977). The values of Ks at high temperatures are calculated by eq.(6) and listed in Table 9(A, B and C). Since the constancy of $\delta_{\rm S}$ is expected to be good at high temperature, the adopted reference temperature is 500 K, which is in the vicinity of acoustic Debye temperature $\theta_{\rm D} = 549$ K for Mn₂SiO₄, 526 K for Fe₂SiO₄, and 559 K for Co₂SiO₄ as listed in Table 8. The conversion of Ks to isothermal bulk modulus K_T is made by using $\gamma = 1.1$ for three olivine minerals.

The values of rigidity μ at high temperatures are calculated by the following equation (Sumino et al., 1977) :

$$\mu(T) = (3/2)[(1 - 2\sigma(T))/(1 + \sigma(T))]Ks(T)$$
(7) where

$$\sigma(T) = \sigma_o + (\partial \sigma/\partial T)(T - T_o) \qquad \dots (8)$$

Eq.(7) combined with eq.(8) is of good approximation at high temperature because of the weak dependence of Poisson's ratio $\sigma(T)$ on temperature.

In the case of ${\rm Fe_2SiO_4}$, however, it is obvious that even in the limited temperature range of this experiment ${\partial\sigma/\partial T}$ is not a constant as influenced by magnetic transition. Therefore, the extrapolation of σ to high temperature in

Fe $_2$ SiO $_4$ is made by using the two different ways. One is the linear extrapolation of σ to high temperature by using the lower temperature data of σ and $\partial\sigma/\partial T$. The adopted value $\partial\sigma/\partial T$ is $0.93 \times 10^{-5} \ deg^{-1}$, which is the mean value at 300 - 500 K and is close to the value of Mg $_2$ SiO $_4$ [$\partial\sigma/\partial T = 0.63 - 0.91 \times 10^{-5} \ deg^{-1}$, Kumazawa and Anderson (1969), Graham and Barsch (1969), and Sumino et al. (1977)] and is also close to $\partial\sigma/\partial T = 0.64 \times 10^{-5}$ of Mn $_2$ SiO $_4$. Another way is the linear extrapolation of σ by using the higher temperature data of σ and $\partial\sigma/\partial T$. The adopted value is $\partial\sigma/\partial T = -0.26 \times 10^{-5} \ deg^{-1}$, which is the mean value at 500 - 700 K and is close to $\partial\sigma/\partial T = -0.12 \times 10^{-5}$ of $\operatorname{Co}_2\operatorname{SiO}_4$. The rigidity of Fe $_2\operatorname{SiO}_4$ at high temperature is calculated by using these two different values of $\partial\sigma/\partial T$, and the results are compared in Table 9B. The actual value of rigidity at high temperature for Fe $_2\operatorname{SiO}_4$ is presumed to lie between the two or higher than them, since σ shows a tendency to decrease more with temperature. At the melting temperature, the difference of rigidity amounts to 8%.

The calculated values of adiabatic and isothermal bulk modulus, Ks and K_T , rigidity μ and other isotropic elastic parameters are summarized for Mn_2SiO_4 in Table 9A, for Fe_2SiO_4 in Table 9B, and for Co_2SiO_4 in Table 9C. Any elastic parameter of natural olivine, which is a solid solution between Mg_2SiO_4 and Fe_2SiO_4 with a trace of Mn_2SiO_4 , is given by the average of the corresponding parameters by mole fractions of these end-members; Mg_2SiO_4 (Sumino et al., 1977), Fe_2SiO_4 and Mn_2SiO_4 .

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Figure captions

- Fig. 1 Resonance frequencies plotted against temperature for ${\rm Fe_2SiO_4}$, ${\rm Mn_2SiO_4}$ and ${\rm Co_2SiO_4}$. The frequencies were normalized to the values at 25 °C. A: ${\rm Fe_2SiO_4(TA)}$, B: ${\rm Mn_2SiO_4(T)}$, C: ${\rm Co_2SiO_4(F)}$, and D: ${\rm Co_2SiO_4(T)}$. Type nomenclature of the modes is the same as in Table 2.
- Fig. 2 Temperature variation of elastic parameters in olivine group minerals. Lower: A and B are adiabatic bulk modulus and rigidity computed by the Voigt-Reuss-Hill scheme, respectively. The values of Mg₂SiO₄ are from Sumino et al. (1977). Upper: Values of $\partial Ks/\partial T$ and $\partial \mu/\partial T$ as calculated from the indicated data.
 - Fig. 3 The deviation of the observed elastic constant from the calculated value of peridot. The calculated value is obtained by a molar average of corresponding parameters of two end-members ${\rm Mg_2SiO_4}$ and ${\rm Fe_2SiO_4}$. A: Elastic compliance constants. Isotropic parameters ${\rm Ks}^{-1}$ and ${\rm \mu}^{-1}$ are given by the Reuss value. B: Elastic stiffness constants. Ks and ${\rm \mu}$ are by the Voigt value.
- Fig. 4 Several examples of relation between elastic parameters and density or atomic ratio in Mg₂SiO₄-Fe₂SiO₄ system. The solid-line is a straight line connecting two end-members. A: Elastic constants C₁₁ and C₁₂, and isotropic parameters Ks and μ, given by the Hill value. Broken line is calculated on the assumption that both elastic wave velocities and and density are expressed by a molar average of the corresponding parameters of two end-members Mg₂SiO₄ and Fe₂SiO₄. The dotted line shows the Ks of Chung (1970). B: Dilatational wave velocity Vp, shear wave velocity Vs, and bulk sound velocity Vφ. Broken line is calculated on the assumption that both elastic constants and density are expressed by a molar average of those of two end-members.

Figure captions (continuned)

Fig. 5 Several examples of relation between elastic constants and molar volume on logarithimic scales. $w_{\rm p},\,w_{\rm T}$ and $w_{\rm M}$ show those of eqs (1), (2) and (3), respectively. The value of molar volume for plotting $w_{\rm M}$ is the mean value between those of two end-members and is blanketed on the horizontal axis. A: Elastic constants C_{11} and C_{44} . Solid line shows the observed data and broken line shows the linear extrapolation of elastic constants to melting temperature. B: Isotropic parameters Ks and μ . Solid line is the same as above and broken line shows the calculated values listed in Table 9 (A, B and C).

Table 1. Basic description of olivne $\mathrm{Mn_2SiO_4}$, $\mathrm{Fe_2SiO_4}$ and $\mathrm{Co_2SiO_4}$

Specimen	Mn ₂ SiO ₄ (T)	Fe ₂ SiO ₄ (TA) (Fe ₂ SiO ₄ (TB))	Co ₂ SiO ₄ (T)	Co ₂ SiO ₄ (F)
Edge length (mm)				
L ₁ (a-axis)	2.5432 ± 0.0017	2.3036 ± 0.0041 (2.2879 ± 0.0029)	2.2703 ± 0.0007	2.4294 ± 0.0016
L ₂ (b-axis)	2.0025 ± 0.0008	1.9294 ± 0.0006 (1.7436 ± 0.0008)	1.7640 ± 0.0008	1.9107 ± 0.0010
L ₃ (c-axis)	2.1941 ± 0.0011	1.9745 ± 0.0016 (1.9934 ± 0.0032)	1.9787 ± 0.0005	2.0674 ± 0.0066
Density (g/cm^3)	•	•		
X-ray	4.127	4.397	4.702	4.705
Bu1k	4.129	4.400 ± 0.009	4.706 ± 0.009	4.747 ± 0.014
Lattice constants (Å)			•	
а	4.9042	4.821 ± 0.001	4.787 ± 0.001	4.786 ± 0.001
Ъ	10.5670	10.484 ± 0.002	10.313 ± 0.002	10.310 ± 0.002
С	6,254 ₅	6.089 ± 0.001	6.007 ± 0.001	6.006 ± 0.001
Mean atomic weight	28.85	29.11	29.99	29.99
Molar volume (cm ³)	48.80	46.34	44.65	44.62
Refractive index 6)				
α	1.781 ± 0.002	1.824 ± 0.002	1.840 ± 0.003	1.841 ± 0.002
β	1.812 ± 0.003	1.864 ± 0.004	1.874 ± 0.004	1.875 ± 0.003
Υ .	1.829 ± 0.003	1.877 ± 0.003	1.889 ± 0.004	1.898 ± 0.003
Chemical composition (wt%	(;)	•		
sio_2	29.5	28.62	28.33	28.48 (28.48)
MO (MnO, FeO, or CoO)	70.54	69.7	70.86	71.3 ₈ (71.52)
M ₂ O ₃	0.059			— (—)
Total	100.16	98.3	99.1 ₉	99.8 ₆ (100.00)
Molar ratio MO/SiO ₂	2.02	2.037	2.006	2.01 ₀ (2.014)

a) The same specimen as specimen T-6 of Takei (1976).

b) Immersion method by Agata.

c) E.P.M.A. analysis by Suzuki, and total metal ion reduced for $M^{2+}0$.

d) Chemical composition of the starting material by Naka et al. (1968).

Table 2A Comparison of observed and calculated RPR frequencies in $Mn_2SiO_4(T)$ at 30 °C and 400 °C

Specimen	1	· ·	Mn ₂ S	i04(T)		
Temp.		30 °C			400 °C	
Mode	F _{obs} (MHz)	F cal (MHz)	ΔF (%)	Fobs (MHz)	F cal (MHz)	ΔF (%)
EV-1	0.6588	0.6549	0.6	0.6338	0.6291	0.7
EV-2	0.8058	0.8042	0.2	0.7751	0.7725	0.3
EY-1	0.9742	0.9747	-0.1	0.9475	0.9481	-0.1
OY-1	0.9803	0.9781	0.2	0.9428	0.9407	0.2
OX-1	0.9928	0.9935	-0.1	0.9557	0.9566	-0.1
EZ-1	0.9941	0.9942	-0.0	0.9673	0.9684	-0.1
EX-1	1.0420	1.0409	0.1	1.0051	1.0052	-0.0
OZ-1	1.0466	1.0462	0.0	1.0014	1.0025	-0.1
EY-2	1.1135	1.1109	0.2	1.0793	1.0757	0.3
OD-1	1.1396	1.1376	0.2	1.0990	1.0991	-0.0
EZ-2	1.1699	1.1692	0.1	1.1297	1.1280	0.2
OD-2	1.1807	1.1788	0.2	1.1476	1.1469	0.1
OX-2	1.2272	1.2273	-0.0	1.1937	1.1928	0.1
OD-3	1.2310	1.2274	0.3	1.2060	1.2038	0.2
OY-2	1.2467	1.2472	-0.0	1.2030	1.2043	-0.1
OZ-2	1.2502	1.2486	0.1	1.2089	1.2073	0.1
OX-3	1.3241	1.3220	0.2	1.2759	1.2718	0.3
EX-2	1.3270	1.3297	-0.2	1.2857	1.2879	-0.2
OD-4	1.3959	1.3955	0.0	1.3511	1.3512	-0.0
EV-3	1.4195	1.4189	0.0	1.3633	1.3632	0.0
OZ-3	1.4433	1.4422	0.1	1.3905	1.3898	0.1
EX-3	1.4593	1.4603	-0.1	1.4159	1.4135	0.2
EZ-3	1.4748	1.4756	-0.1	1.4333	1.4305	0.2
OD-5	1.5080	1.5095	-0.1	1.4711	1.4747	-0.2
OY-3	1.5145	1.5170	-0.2	1.4573	1.4604	-0.2
EY-3	1.5274	1.5304	-0.2	1.4884	1.4857	0.2
EZ-4	1.5974	1.5993	-0.1	1.5420	1.5455	-0.2
EX-4	1.6078	1.6161	-0.5	1.5499	1.5613	-0.7
EY-4	1.6216	1.6194	0.1	1.5643	1.5631	0.1
EZ-5	1.6931	1.6923	0.1	1.6399	1.6391	0.1
EY-5	1.7215	1.7244	-0.2	1.6661	1.6703	-0.3
EX-5	1.7518	1.7475	0.2	1.7047	1.6993	0.3
 Standard	deviation		0.14			

Table 2B Comparison of observed and calculated RPR frequencies in Fe $_2$ SiO $_4$ (TA) and Fe $_2$ SiO $_4$ (TB) at 24 °C and 400 °C

Specimen			Fe ₂ S10 ₄	(TA)					Fe ₂ SiO ₄	(TB)		
Temp.		24 °C		· · · · · · · · · · · · · · · · · · ·	400 °C				24 °C			
Mode	Fobs	F cal (MHz)	ΔF (%)	Fobs (MHz)	F cal (MHz)	ΔF (%)	1 + y - y - y - y - y - y - y - y - y - y	Mode	Fobs (MHz)	Fcal (MHz)	ΔF (%)	
EV-1 EV-2 OX-1	0.6658 0.7268 0.8781	0.6645 0.7244 0.8766	0.2 0.3 0.2	 0.8679	0.6516 0.7059 0.8657	0.3		EV-1 EV-2 OX-1	0.6433 0.8011 0.9235	0.6419 0.7986 0.9211	0.2 0.3 0.3	
OX-1 OY-1 EZ-1	0.9648	0.9642 0.9963	0.1 -0.0	0.9527 0.9724	0.9523	0.0		OY-1 EY-1	0.9654 1.0419	0.9661 1.0433	-0.1 -0.1	
EY-1 OZ-1	1.0684 1.0767	1.0688 1.0754	-0.0 0.1	1.0293 1.0211	1.0307 1.0200	-0.1 0.1		EZ-1 EY-2	1.0470 1.1382	1.0482 1.1373	-0.1 0.1	
EX-1 EZ-2	1.1109 1.1392	1.1096 1.1388	0.1 0.0	1.0504 1.1102	1.0498	0.1		OZ-1 EX-1	1.1457 1.1790 1.2425	1.1450 1.1771 1.2411	0.1 0.2 0.1	
EY-2 OD-1	1.1628 1.2072	1.1614 1.2039	0.1	1.1291	1.1280	0.1		EZ-2 OX-2	1.2551	1.2555	-0.0	
OY-2 OX-2 OD-2	1.2350 1.2412 1.2739	1.2361 1.2409 1.2725	-0.1 0.0 0.1	1.1958 1.2152 1.2143	1.1938 1.2146 1.2126	0.2 0.1 0.1	į	OZ-2 OD-1 OD-2	1.2844 1.2928 1.3309	1.2822 1.2905 1.3272	0.2 0.2 0.3	
0Z-2	1.3105	1.3098	0.1	1.2757	1.2767	-0.1		OY-2	1.3509	1.3527	-0.1	
OX-3 EX-2 OD-3	1.3425 1.3654 1.3836	1.3426 1.3658 1.3800	-0.0 -0.0 0.3	1.3023 1.3272 1.3240	1.3004 1.3286 1.3205	0.2 -0.1 0.3		OX-3 OD-3 EX-2	1.3668 1.3861 1.4281	1.3652 1.3845 1.4271	0.1 0.1 0.1	
EV-3 OY-3	1.3867 1.4326	1.3857 1.4316	0.1 0.1	1.3450 1.3866	1.3445 1.3869	0.0		EV-3 0Z-3	1.4415 1.5151	1.4416 1.5139	-0.0 0.1	
OZ-3 OD-4	1.4814 1.4978	1.4780 1.4957	0.2	1.4173 1.4329	1.4145 1.4297	0.2 0.2		OY-3 OD-4	1.5658 1.5752	1.5622 1.5758	0.2 -0.0	
EZ-3 EZ-4	1.5224 1.5452	1.5252 1.5446	-0.2 0.0	1.4709 1.5010	1.4747 1.4991	-0.3 0.1		EZ-3 EZ-4	1.6001 1.6234	1.6004 1.6270	-0.0 -0.2	
EX-3 EY-3	1.5685 1.6311	1.5702 1.6348	-0.1 -0.2	1.4983 1.5652	1.5008 1.5653	-0.2 -0.0		EX-3 OD-5	1.6292 1.6968	1.6310 1.6938	-0.1 0.2	
OD-5	1.6599	1.6598	0.0	1.5943	1.5944	-0.0		EY-4	1.7149	1.7158	-0.1 -0.5	
EX-4	1.6874	1.6925	-0.3 -0.1	1.6148 1.7358	1.6204 1.7386	-0.4 -0.2		OX-4 EZ-5	1.8191 1.8352	1.8230 1.8364	-0.2 -0.1	
OD-5 EY-4	1.6599 1.6791 1.6874 1.7746	1.6598 1.6817 1.6925 1.7766	0.0 -0.2 -0.3	1.5943 1.6081 1.6148	1.5944 1.6117 1.6204	-0.0 -0.2 -0.4		EY-4 EX-4 OX-4	1.7149 1.7505 1.8191	1.7158 1.7585 1.8230		

Table 2C Comparison of observed and calculated RPR frequencies in $Co_2SiO_4(T)$ and $Co_2SiO_4(F)$ at 30 °C and 400 °C

Specime	n		Co ₂ SiO ₄	, (T)				Co ₂ SiO ₄ (F)						
Temp.		30 °C			400 °C				30 °C			400 °C		
Mode	Fobs (MHz)	Fcal (MHz)	ΔF (%)	Fobs (MHz)	F _{cal} (MHz)	ΔF (%)	Mode	Fobs (MHz)	Fcal (MHz)	ΔF (%)	Fobs (MHz)	F _{cal}	ΔF (%)	
EV-1 EV-2 OX-1 EY-1 OY-1	0.7262 0.8798 1.0626 1.0924 1.0929	0.7245 0.8751 1.0621 1.0918 1.0917	0.2 0.5 0.0 0.1	1.0460 1.0708 1.0633	0.7053 0.8563 1.0425 1.0685 1.0619	0.3 0.2 0.1	EV-1 EV-2 OX-1 EY-1 OY-1	0.6827 0.8125 0.9954 1.0237 1.0289	0.6810 0.8115 0.9959 1.0274 1.0288	0.2 0.1 -0.1 -0.4 0.0	0.9780 1.0023 1.0016	0.6638 0.7933 0.9760 1.0048 1.0025	0.2 -0.3 -0.1	
EZ-1 OZ-1 EX-1 EY-2 OD-1	1.1334 1.1709 1.1789 1.2183 1.2975	1.1351 1.1705 1.1792 1.2173 1.2965	-0.2 0.0 -0.0 0.1 0.1	1.1189 1.1396 1.1512 1.1947 1.2692	1.1190 1.1389 1.1525 1.1928 1.2703	-0.0 0.1 -0.1 0.2 -0.1	EZ-1 OZ-1 EX-1 EY-2 OD-1	1.0467 1.0802 1.1094 1.1528 1.2152	1.0438 1.0761 1.1095 1.1499 1.2152	0.3 0.4 -0.0 0.3 0.0	1.0304 1.0514 1.0832 1.1280 1.1893	1.0261 1.0476 1.0856 1.1266 1.1912	0.4 0.4 -0.2 0.1 -0.2	
EZ-2 OD-2 OX-2 OZ-2 OD-3	1.3311 1.3506 1.3667 1.3746 1.4110	1.3306 1.3486 1.3673 1.3754 1.4093	0.0 0.2 -0.0 -0.1 0.1	1.3281 1.3434 1.3397 1.3898	1.3025 1.3265 1.3443 1.3412 1.3882	0.1 -0.1 -0.1 0.1	EZ-2 OD-2 OX-2 OZ-2 OD-3	1.2225 1.2558 1.2724 1.2952 1.3179	1.2215 1.2583 1.2745 1.3020 1.3127	0.1 -0.2 -0.2 -0.5 0.4	1.1989 1.2347 1.2465 1.2667 1.2946	1.1959 1.2355 1.2499 1.2717 1.2889	0.3 -0.1 -0.3 -0.4 0.4	
OY-2 OX-3 EX-2 EV-3 OZ-3	1.4301 1.4853 1.4999 1.5659	1.4289 1.4810 1.5011 1.5662 1.5801	0.1 0.3 -0.1 -0.0 0.1	1.4469 1.4679 1.5272 1.5446	1.4034 1.4438 1.4687 1.5272 1.5440	0.2 -0.1 -0.0 0.0	OY-2 OX-3 EX-2 EV-3 OD-4	1.3275 1.3698 1.3987 1.4611 1.4814	1.3210 1.3689 1.4002 1.4593 1.4811	0.5 0.1 -0.1 0.1	1.3019 1.3358 1.3677 1.4280 1.4557	1.2965 1.3352 1.3708 1.4237 1.4524	0.4 0.1 -0.2 0.3	
OD-4 EX-3 OY-3 EZ-3 OD-5	1.5896 1.6560 1.6782 1.6827 1.7193	1.5892 1.6574 1.6790 1.6825 1.7189	0.0 -0.1 -0.0 0.0	1.5602 1.6221 1.6438	1.5574 1.6229 1.6431 1.6544 1.6885	0.2 -0.1 0.0	OZ-3 EX-3 OY-3 EZ-3 OD-5	1.4982 1.5480 1.5503 1.5630 1.5955	1.4956 1.5488 1.5547 1.5676 1.5972	0.2 -0.1 -0.3 -0.3	1.4651 1.5154 1.5338 1.5645	1.4621 1.5174 1.5204 1.5389 1.5673	0.2 -0.3 -0.3 -0.2	
EY-3 EZ-4 EY-4 EX-4 EZ-5	1.7225 1.7685 1.7875 1.8146 1.9178	1.7225 1.7710 1.7858 1.8186 1.9189	-0.0 -0.1 0.1 -0.2 -0.1	1.6876 1.7365 1.7459 1.7723 1.8711	1.6864 1.7387 1.7458 1.7742 1.8735	0.1 -0.1 0.0 -0.1 -0.1	EY-3 EZ-4 EY-4 EX-4 EZ-5	1.6152 1.6532 1.6809 1.6924 1.7962	1.6062 1.6561 1.6766 1.6981 1.7963	0.6 -0.2 0.3 -0.3	1.5806 1.6224 1.6421 1.6535 1.7529	1.5722 1.6241 1.6395 1.6578 1.7543	0.5 -0.1 0.2 -0.3 -0.1	
EY-5 EX-5	1.9489 1.9867	1.9495 1.9865	-0.0 0.0	1.9487	1.9056 1.9504	-0.1	EY-5	1.7975	1.8005	-0.2	1.7621	1.7656	-0.2	
Standaı	d deviatio	n	0.10			0.09				0.18			0.19	

Table 3 Temperature variation of elastic constants of Fe_2Sio_4 (TA) (units in Mbar).

	and the second distance	,					Ι	e ₂ Si04	(TA)										
T(°C)	د 11	c ₂₂	c ₃₃	c ₂₃	c ₃₁	C ₁₂	C ₄₄	^C 55	^C 66	K ₁ *	K ₂ *	к ₃ *	C * S1	C *	c _s ;	$\kappa^{\Lambda}_{\downarrow}$	K _R †	μ_{V}^{\dagger}	μ_R^+
25	1	1.736 ±.011	2.392 ±.014	0.979 ±.012	0.987 ±.016	0.952 ±.015	0.324 ±.001	0.467 ±.001	0.573 ±.001	1.536 ±.016	±.012	1.453 ±.013	0.543 ±.001	0.772 ±.002	0.625 ±.002	1.404 ±.014	1.356 ±.014	0.531 ±.001	0.487 ±.001
40	2.663	1.731	2.386	0.978	0.986	0.950	0.322	0.466	0.570	1.533	1.220	1.450	0.540	0.769	0.624	1.401	1.353	0.529	0.485
60	2.654	5.724	2.377	0.977	0.984	0.947	0.321	0.464	0.566	1.528	1.216	1.446	0.537	0.766	0.621	1.397	1.349	0.527	0.482
80	2,543	1.717	2.369	0.977	0.982	0.943	0.319	0.462	0.562	1.523	1.212	1.443	0.533	0.762	0.619	1.392	1.344	0.524	0.480
100	2.633	1.709	2.359	0.975	0.979	0.938	0.318	0.461	0.558	1.517	1.207,	1.438	0.530	0.759	0.617	1.387	1.339	0.521	0.477
120	2.625	1.703	2.351	0.974	0.978	0.934	0.317	0.460	0.555	1.512	1.204	1.434	0.526	0.755	0.615	1.383	1.335	0.519	0.475
140	2.618	1.696	2.341	0.973	0.976	0.932	0.316	0.459	0.551	1.509	1.201	1.430	0.523	0.752	0.613	1.380	1.331	0.517	0.474
160	2.612	1.690	2.332	0.973	0.976	0.930	0.315	0.459	0.548	1.506	1.198	1.427	0.519	0.748	0.611	1.377	1.328	0.515	0.472
180	2.606	1.683	2.322	0.971	0.975	0.928	0.314	0.458	0.545	1.503	1.194	1.423	0.516	0.745	0.609	1.373	1.325	0.513	0.470
200	2.599 ±.020	1.676 ±.012	2.312 ±.014	0.970 ±.012	0.973 ±.016		0.314 ±.001	0.458 ±.001	0.542 ±.001	1	1.190 ±.012	1.418 ±.013	0.512 ±.001		0.607 ±.002	1.369 ±.014	1.320 ±.014	0.511 ±.001	0.469 ±.001
220	2.590	1.668	2.303	0.969	0.971	0.919	0.314	0.458	0.538	1.493	1.185	1.414	0.508	0.738	0.605	1.364	1.315	0.509	0.467
240	2.582	1.661	2.293	0.967	0.968	0.916	0.314	0.457	0.535	1.489	1.181	1.410	0.505	0.735	0.603	1.360	1.311	0.507	0.466
260	2.576	1.655	2.283	0.966	0.967	0.914	0.314	0.457	0.532	1.486	1.178	1.406	0.501	0.731	0.601	1.357	1.307	0.505	0.465
280	2.569	1.648	2.274	0.965	0.966	0.910	0.314	0.457	0.529	1.481	1.174	1.401	0.498	0.728	0.599	1.352	1.303	0.503	0.463
300	2.562	1.640	2.264	0.963	0.964	0.906	0.314	0.457	0.526	1.477	1.170	1.397	0.495	0.724	0.597	1.348	1.298	0.502	0.462
320	2.552	1.631	2.254	0.960	0.961	0.901	0.315	0.456	0.524	1.471	1.164	1.392	0.491	0.721	0.595	1.343	1.293	0.500	0.461
340	2.545	1.623	2.245	0.958	0.960	0.898	0.315	0.456	0.521	1.468	1.160	1.388	0.488	0.718	0.593	1.338	1.288	0.498	0.460
360	2.537	1.616	2.235	0.956	0.958	0.894	0.315	0.456	0.518	1.463	1.155	1.383	0.485	0.714	0.591	1.334	1.283	0.497	0.459
380	2.526	1.608	2.226	0.954	0.954	0.888	0.315	0.456	0.516	1.456	1.150	1.378	0.481	0.711	0.589	1.328	1.278	0.495	0.458
400	2.520 ±.022	1.600 ±.013	2.217 ±.016	0.952 ±.013	0.953 ±.018	0.885 ±.017	0.316 ±.001	0.456 ±.001	0.513 ±.002	1.453 ±.018		1.374 ±.015	0.478 ±.001	0.708 ±.002	0.588 ±.002	1.324 ±.015	1.273 ±.015	0.493 ±.001	0.456 ±.001

^{* :} $K_{i} = (C_{i1} + C_{i2} + C_{i3})/3$, and $C_{Si} = (C_{jj} + C_{kk} - 2 \cdot C_{jk})/4$.

^{†:} V (Voigt), and R (Reuss)

Table 4A Elastic parameters in Mn₂SiO₄, Fe₂SiO₄ and Co₂SiO₄ at 25 °C. ρ : density in g/cm³, C_{ij} : elastic constants in Mbar, σ : Poisson's ratio, Vp, Vs and V $_{\Phi}$: dilatational, shear and bulk sound velocity in km/sec.

	Mn ₂ SiO ₄ (T)	Fe ₂ SiO ₄ (TA) ⁰⁾	Fe ₂ S ₁₀ 4 (TB)	Co ₂ SiO ₄ (T) ^{b)}	Co ₂ SiO ₄ (F)	
ρ	4.129	4.400	4.400	4.706	4.747	
c ₁₁	2.584 ± 0.019	2.670 ± 0.019	2.681 ± 0.017	3.078 ± 0.012	2.984 ± 0.027	
c ₂₂	1.656 ± 0.010	1.736 ± 0.011	1.717 ± 0.010	1.947 ± 0.007	1.935 ± 0.016	
C ₃₃	2.068 ± 0.013	2.392 ± 0.014	2.384 ± 0.016	2.342 ± 0.009	2.271 ± 0.020	
c ₂₃	0.917 ± 0.010	0.979 ± 0.012	0.960 ± 0.012	1.032 ± 0.007	0.987 ± 0.017	
c ₃₁	0.952 ± 0.015	0.987 ± 0.016	0.987 ± 0.017	1.050 ± 0.010	0.979 ± 0.022	
c ₁₂	0.871 ± 0.013	0.952 ± 0.015	0.948 ± 0.013	1.016 ± 0.008	0.971 ± 0.020	
C ₄₄	0.453 ± 0.001	0.324 ± 0.001	0.323 ± 0.001	0.467 ± 0.001	0.470 ± 0.002	
c ₅₅	0.556 ± 0.002	0.467 ± 0.001	0.469 ± 0.001	0.639 ± 0.001	0.638 ± 0.002	
C ₆₆	0.578 ± 0.002	0.573 ± 0.001	0.574 ± 0.002	0.648 ± 0.001	0.640 ± 0.003	
K ₁	1.469 ± 0.015	1.536 ± 0.016	1.539 ± 0.015	1.715 ± 0.010	1.645 ± 0.022	
κ_2^-	1.148 ± 0.011	1.222 ± 0.012	1.208 ± 0.011	1.332 ± 0.007	1.298 ± 0.017	
к3	1.312 ± 0.012	1.453 ± 0.013	1.444 ± 0.014	1.475 ± 0.008	1.413 ± 0.019	
Cs.	0.473 ± 0.001	0.543 ± 0.001	0.545 ± 0.001	0.556 ± 0.001	0.558 ± 0.001	
Cs ₂	0.687 ± 0.002	0.772 ± 0.002	0.773 ± 0.002	0.830 ± 0.001	0.825 ± 0.003	,
Cs ₃	0.625 ± 0.002	0.625 ± 0.002	0.626 ± 0.002	0.748 ± 0.001	0.744 ± 0.003	
Kv	1.310 ± 0.013	1.404 ± 0.014	1.397 ± 0.014	1.507 ± 0.008	1.452 ± 0.019	
к _н	1.288 ± 0.013	1.379 ± 0.014	1.371 ± 0.014	1.482 ± 0.008	1.432 ± 0.019	
KR	1.266 ± 0.013	1.356 ± 0.014	1.345 ± 0.014	1.458 ± 0.008	1.411 ± 0.019	
$\mu_{f V}$	0.555 ± 0.001	0.531 ± 0.001	0.532 ± 0.001	0.635 ± 0.001	0.633 ± 0.002	
$\mu_{ m H}$	0.546 ± 0.001	0.509 ± 0.001	0.510 ± 0.001	0.620 ± 0.001	0.619 ± 0.002	
$\mu_{ m R}$	0.537 ± 0.001	0.487 ± 0.001	0.487 ± 0.001	0.605 ± 0.001	0.605 ± 0.002	
σ	0.314 ± 0.001	0.336 ± 0.001	0.335 ± 0.001	0.316 ± 0.001	0.311 ± 0.002	
۷p	6.987 ± 0.025	6.839 ± 0.025	6.827 ± 0.025	7.004 ± 0.014	6.896 ± 0.033	
Vs	3.636 ± 0.005	3.401 ± 0.004	3.405 ± 0.004	3.630 ± 0.003	3.611 ± 0.006	
\mathtt{v}_{Φ}	5.585 ± 0.027	5.598 ± 0.027	5.582 ± 0.027	5.612 ± 0.016	5.492 ± 0.036	

a) Recommended values of $\operatorname{Fe}_2\operatorname{SiO}_4$ olivine.

b) Recommended values of Co_2SiO_4 olivine.

Table 4B Temperature derivatives of elastic parameters in Mn₂SiO₄, Fe₂SiO₄ and Co₂SiO₄ at the temperatures between 25° and 400 °C. The notation of elastic parameters is the same as that of Table 4A. The dimension of each parameter is $\partial \rho / \partial T$ in \times 10⁻³g/cm³·deg, $\partial C_{ij} / \partial T$ in kbar/deg, $\partial \sigma / \partial T$ in \times 10⁻⁵1/deg, $\partial V \rho / \partial T$, and $\partial V_{\Phi} / \partial T$ in \times 10⁻³ km/sec·deg.

4				1.5	
	$Mn_2SiO_4(T)$	Fe_2SiO_4 $(TA_1)^{a}$	Fe ₂ SiO ₄ (TA ₂) as	Co ₂ SiO ₄ (T) b)	Co ₂ SiO ₄ (F)
 Τ6\q6	-0.114	-0.124	-0.137	(-0.137) ^{c)}	(-0.137) ^{c)}
ЭС ₁₁ /ЭТ	-0.350 ± 0.037	-0.409 ± 0.039	-0.396 ± 0.039	-0.331 ± 0.031	-0.345 ± 0.031
∂C ₂₂ /∂T	-0.283 ± 0.019	-0.347 ± 0.023	-0.379 ± 0.023	-0.212 ± 0.023	-0.196 ± 0.018
22 ∂С33/ЭТ	-0.285 ± 0.026	-0.459 ± 0.028	-0.480 ± 0.028	-0.337 ± 0.026	-0.275 ± 0.023
° ас ₂₃ /ат	-0.112 ± 0.021	-0.054 ± 0.024	-0.090 ± 0.024	-0.136 ± 0.022	-0.104 ± 0.019
ЭС ₃₁ /ЭТ	-0.144 ± 0.029	-0.086 ± 0.032	-0.100 ± 0.032	-0.136 ± 0.026	-0.102 ± 0.025
ЭС ₁₂ /ЭТ	-0.163 ± 0.025	-0.168 ± 0.030	-0.194 ± 0.030	-0.183 ± 0.025	-0.145 ± 0.023
ЭС <mark>44</mark> /ЭТ	-0.094 ± 0.002	-0.052 ± 0.001	$+0.009 \pm 0.001$	-0.049 ± 0.002	-0.055 ± 0.002
ЭС ₅₅ /ЭТ	-0.121 ± 0.003	-0.048 ± 0.002	-0.011 ± 0.002	-0.102 ± 0.002	-0.095 ± 0.003
ЭС ₆₆ /ЭТ	-0.136 ± 0.003	-0.176 ± 0.003	-0.144 ± 0.003	-0.101 ± 0.003	-0.098 ± 0.003
∂К ₁ /∂Т	-0.219 ± 0.029	-0.221 ± 0.033	-0.230 ± 0.033	-0.217 ± 0.026	-0.198 ± 0.025
∂К2/ЭТ	-0.186 ± 0.021	-0.190 ± 0.024	-0.222 ± 0.024	-0.177 ± 0.022	-0.148 ± 0.019
ЭК <mark>3</mark> /ЭТ	-0.180 ± 0.024	-0.200 ± 0.026	-0.224 ± 0.026	-0.203 ± 0.024	-0.160 ± 0.022
∂Cs ₁ /∂T	-0.086 ± 0.002	-0.175 ± 0.003	-0.170 ± 0.003	-0.069 ± 0.001	-0.066 ± 0.002
∂Cs ₂ /∂T	-0.087 ± 0.003	-0.174 ± 0.003	-0.169 ± 0.003	-0.099 ± 0.003	-0.104 ± 0.003
∂Cs ₃ /∂T	-0.077 ± 0.003	-0.104 ± 0.004	-0.097 ± 0.004	-0.044 ± 0.003	-0.063 ± 0.003
ЭК _V /ЭТ	-0.195 ± 0.025	-0.203 ± 0.028	-0.225 ± 0.028	-0.199 ± 0.024	-0.169 ± 0.022
ЭК _Н /ЭТ	-0.195 ± 0.025	-0.205 ± 0.028	-0.230 ± 0.028	-0.195 ± 0.024	-0.165 ± 0.022
ЭК _R /ЭТ	-0.194 ± 0.025	-0.207 ± 0.028	-0.234 ± 0.028	-0.191 ± 0.024	-0.161 ± 0.022
$_{ m T6}\sqrt{_{ m V}}$ 46	-0.104 ± 0.003	-0.116 ± 0.003	-0.087 ± 0.003	-0.079 ± 0.002	-0.081 ± 0.003
ομ _μ /3Τ	-0.104 ± 0.003	-0.108 ± 0.003	-0.075 ± 0.003	-0.077 ± 0.002	-0.078 ± 0.003
эμ _R /эт	-0.105 ± 0.003	-0.100 ± 0.003	-0.062 ± 0.003	-0.075 ± 0.002	-0.076 ± 0.003
∂σ/∂T	$+0.64 \pm 0.24$	$+0.93 \pm 0.27$	-0.26 ± 0.27	-0.12 ± 0.26	$+0.19 \pm 0.22$
76\qV6	-0.489 ± 0.042	-0.483 ± 0.044	-0.454 ± 0.044	-0.358 ± 0.032	-0.317 ± 0.030
T6\aV6	-0.304 ± 0.008	-0.313 ± 0.009	-0.205 ± 0.009	-0.177 ± 0.004	-0.180 ± 0.006
$_{\Phi}$ V $_{\Phi}$ V6	-0.349 ± 0.044	-0.338 ± 0.057	-0.380 ± 0.057	-0.294 ± 0.036	-0.241 ± 0.032

a) Temperature derivatives given as mean value between 25° and 200 °C for $Fe_2SiO_4(TA_1)$, and those between 220° and 400 °C for $Fe_2SiO_4(TA_2)$.

b) Recommended values of Co2SiO4 olivine.

C) The value of Mn_2SiO_4 is adopted.

Table 5. Anomaly of temperature derivatives of elastic constants for olivine group minerals at the temperature between 20 ° and 400 °C, and for simple oxides at the temperature between the Néel temperature and room temperature. \times : normal or linear temperature variation, S: small degree of anomaly, L: large degree of anomaly, and T_N : Néel temperature (paramagnetic-antiferromagnetic phase transition).

divalent ions	OLIVINE	K _i (1=1,2,3)	Cs _i)(i=1,2,3	C ₄₄	c ₅₅	C ₆₆	T _N (K)	ROCK SALT OXIDE	Ks	Cs	C ₄₄	T _N (K)
Mg	Mg2SiO4	×	×	· ×	×	×	<u> </u>	MgO .	×	×	×	
Со	Co ₂ SiO ₄	×	×	S	×	×	49 ± 2 19	CoO	×	L	×	291 3)
Fe	Fe ₂ SiO ₄	· ×	×	L	S	S	65 ± 2 **	Fe0	×	×	L	198 ³⁾
Mn	Mn ₂ SiO ₄	×	×	×	×	×	50 ± 5 2)	MnO	×	×	· L	116

¹⁾ Nomura et al. (1964), 2) Santoro et al. (1966), and 3) Kittel (1974).

Table 6. The variation of elastic constants with molar volume as function of temperature T, pressure P and cation substitution M. The calculated values of $\partial lnC_{ij}/\partial lnV$ are obtained from eqs (1), (2) and (3). The isotropic parameters Ks and μ are calculated by Voigt-Reuss-Hill scheme.

a	- (ðlnC _{ii} /ð1	$\text{nV)}_{\text{T,M}} (= w_{\text{P}})$	\	- $(\partial lnC_{ij}/\partial lnV)_{P,M} (= w_T)$								
$^{\mathrm{c}}_{\mathtt{i}\mathtt{j}}$	Mg ₂ SiO ₄ ¹⁾	PERIDOT ²⁾	Mg ₂ SiO ₄ ³⁾	PERIDOT		Fe ₂ SiO ₄ ⁴⁾	Fe ₂ SiO ₄ 5)	Mn ₂ SiO ₄				
c ₁₁	3.29 ± 0.03	3.16	3.9 ± 0.3	4.2	3.7 ± 0.4	5.5 ± 0.5	4.9 ± 0.5	4.9 ± 0.5				
c ₂₂	4.00 ± 0.20	4.14	4.9 ± 0.4	5.8	3.8 ± 0.4	7.1 ± 0.5	7.3 ± 0.4	6.2 ± 0.4				
C ₃₃	3.43 ± 0.05	3.48	4.0 ± 0.5	4.9	5.0 ± 0.4	6.9 ± 0.4	6.7 ± 0.4	5.0 ± 0.5				
C ₂₃	6.69 ± 0.51	6.38	2.7 ± 0.7	2.7	4.5 ± 0.7	2.0 ± 0.9	3.0 ± 0.8	4.4 ± 0.8				
C ₃₁	8.42 ± 0.57	8.03	4.6 ± 0.5	5.3	4.5 ± 0.9	3.1 ± 1.2	3.3 ± 1.1	5.5 ± 1.1				
C ₁₂	8.55 ± 0.36	9.15	5.5 ± 0.7	6.3	6.2 ± 0.9	6.3 ± 1.1	6.8 ± 1.1	6.8 ± 1.0				
C ₄₄	4.06 ± 0.00	4.21	6.6 ± 0.7	7.9	3.6 ± 0.2	5.7 ± 0.1	-0.9 ± 0.1	7.5 ± 0.2				
c ₅₅	2.62 ± 0.01	2.68	5.6 ± 0.5	6.6	5.5 ± 0.1	3.7 ± 0.2	0.8 ± 0.1	7.9 ± 0.2				
C ₆₆	3.73 ± 0.04	3.75	6.6 ± 0.5	8.0	5.4 ± 0.2	11.0 ± 0.2	8.6 ± 0.2	8.5 ± 0.2				
к ₁	4.82 ± 0.16	4.78	4.2 ± 0.3	4.7	4.4 ± 0.5	5.1 ± 0.8	5.0 ± 0.7	5.4 ± 0.7				
к2	5.48 ± 0.29	5.62	4.6 ± 0.4	5.2	4.6 ± 0.6	5.6 ± 0.7	6.0 ± 0.7	5.9 ± 0.7				
к3	4.98 ± 0.23	4.91	3.8 ± 0.3	4.5	4.8 ± 0.6	4.9 ± 0.6	5.1 ± 0.6	5.0 ± 0.7				
Cs ₁	2.17 ± 0.08	2.38	5.3 ± 0.9	6.7	4.3 ± 0.1	11.5 ± 0.2	10.7 ± 0.2	6.6 ± 0.2				
Cs ₂	1.70 ± 0.14	1.67	3.7 ± 0.3	4.2	4.1 ± 0.1	8.1 ± 0.1	7.4 ± 0.1	4.6 ± 0.2				
Cs ₃	1.85 ± 0.01	1.61	3.9 ± 0.3	4.3	2.0 ± 0.1	5.9 ± 0.2	5.2 ± 0.2	4.5 ± 0.2				
Ks	5.14 ± 0.20	5.08	4.2 ± 0.3	4.8	4.5 ± 0.6	5.3 ± 0.7	5.5 ± 0.7	5.5 ± 0.7				
μ	2.86 ± 0.02	2.90	5.5 ± 0.5	6.6	4.3 ± 0.1	7.6 ± 0.2	4.9 ± 0.2	6.9 ± 0.2				

¹⁾ mean value of the reported data by Kumazawa and Anderson (1969), and Graham and Barsch (1969).

²⁾ Kumazawa and Anderson (1969).

³⁾ mean value of the reported data by Kumazawa and Anderson (1969), Graham and Barsch (1969), and Sumino et al. (1977).

⁴⁾ mean value between 25° and 200 °C.

⁵⁾ mean value between 220° and 400 °C.

Table 6. (continued)

			(21-	oc (21=11)	(- a)	
c ij	- 1 G 6)	y 77 6)		$\frac{\text{nC}_{ij}/\partial \text{lnV})_{P,T}}{\text{Co - Fe}^{6)}}$	$\frac{(= \omega_{\rm M})}{\text{Co - Mn}^{6)}}$	Fe - Mn ⁶
	Mg - Co ⁶⁾	Mg - Fe ⁶⁾	Mg - Mn ⁶⁾	Co - Fe	Co - Mn	re - Mn
c ₁₁	3.1 ± 0.3	3.6 ± 0.1	2.2 ± 0.1	3.8 ± 0.2	2.0 ± 0.1	0.6 ± 0.2
c ₂₂	1.5 ± 0.3	2.5 ± 0.1	1.8 ± 0.1	3.1 ± 0.2	1.8 ± 0.1	0.9 ± 0.2
c ₃₃	0.3 ± 0.3	-0.3 ± 0.1	1.2 ± 0.1	-0.6 ± 0.2	1.4 ± 0.1	2.8 ± 0.2
c ₂₃	-17.3 ± 0.6	-5.1 ± 0.3	-2.1 ± 0.1	1.4 ± 0.3	1.3 ± 0.1	1.3 ± 0.3
c ₃₁	-21.0 ± 0.8	-6.3 ± 0.4	-2.9 ± 0.2	1.7 ± 0.5	1.1 ± 0.2	0.7 ± 0.4
C ₁₂	-20.6 ± 0.7	-6.1 ± 0.3	-2.4 ± 0.2	1.8 ± 0.4	1.7 ± 0.2	1.7 ± 0.4
C ₄₄	18.1 ± 0.2	12.8 ± 0.1	3.6 ± 0.0	9.9 ± 0.1	0.4 ± 0.0	-6.4 ± 0.1
C ₅₅	12.0 ± 0.2	9.7 ± 0.1	3.5 ± 0.0	8.5 ± 0.1	1.6 ± 0.1	-3.4 ± 0.1
c ₆₆	11.0 ± 0.2	6.0 ± 0.1	3.1 ± 0.0	3.3 ± 0.1	1.3 ± 0.0	-0.2 ± 0.1
ĸ ₁	-5.2 ± 0.4	0.1 ± 0.2	0.5 ± 0.1	3.0 ± 0.3	1.7 ± 0.1	0.9 ± 0.3
К2	-8.0 ± 0.3	-1.3 ± 0.2	-0.1 ± 0.1	\cdot , 2.4 ± 0.3	1.7 ± 0.1	1.2 ± 0.3
К3	-8.0 ± 0.4	-2.5 ± 0.2	-0.4 ± 0.1	0.4 ± 0.3	1.3 ± 0.1	2.0 ± 0.2
Cs ₁	13.2 ± 0.2	5.1 ± 0.1	3.9 ± 0.0	0.7 ± 0.1	1.8 ± 0.0	2.7 ± 0.1
Cs ₂	12.3 ± 0.2	5.6 ± 0.1	4.0 ± 0.0	2.0 ± 0.1	2.1 ± 0.0	2.2 ± 0.1
Cs ₃	13.7 ± 0.2	8.0 ± 0.1	4.2 ± 0.0	4.9 ± 0.1	2.0 ± 0.0	0.0 ± 0.1
Ks	-6.9 ± 0.4	-1.1 ± 0.2	0.0 ± 0.1	2.0 ± 0.3	1.6 ± 0.1	1.3 ± 0.3
μ	13.5 ± 0.2	8.2 ± 0.1	3.6 ± 0.0	5.3 ± 0.1	1.4 ± 0.0	-1.4 ± 0.1

⁶⁾ cation substitution between two different species M_p - M_q in eq.(3).

Table 7. Pressure derivatives of isotropic properties in Fe₂SiO₄

I.			
		Chung (1971) ¹⁷	Predicted
∂Ks/∂P		5.92	5.0 ± 1.0
9µ/9P		0.62	0.7 ± 0.2
9Vp/9P	$(km/s)Mbar^{-1}$	8.8	7.4 ± 2.1
∂Vs/∂P	(km/s)Mbar ⁻¹	0.6	1.1 ± 0.7
∂VΦ/∂P	(km/s)Mbar ⁻¹	10.6	8.1 ± 2.0

¹⁾ Measurement by polycrystalline sample up to 7.5 kbar.

Table 8. Grüneisen constant γ and Grüneisen-Anderson parameter δs at the temperature between 300 and 700 K, and Debye temperature of olivine group minerals

	Υ	$\delta_{\mathbf{s}}$	(K)
Mg 2SiO4b)	1.20 ± 0.02	4.0 ± 0.2	772
Co2SiO4	1.07 ± 0.02°	4.7 ± 0.6 c)	559
Fe ₂ SiO ₄	1.15 ± 0.02	5.6 ± 0.7	526
Mn 2SiO 4	1.06 ± 0.02	5.6 ± 0.7	549

a) acoustic Debye temperature calculated from the elastic wave velocities extrapolated to 0 K.

b) Sumino et al. (1977)

c) calculated by using the thermal expansion data of $\mathrm{Mn}_2\mathrm{SiO}_4$ olivine.

Table 9A Observed and calculated values of elastic parameters of Mn_2SiO_4 as a function of temperature. Ks and K_T : adiabatic and isothermal bulk modulus, μ : rigidity, σ : Poisson's ratio, ρ : density, and Vp and Vs: dilatational and shear wave velocity.

T	Ks (Mbar)		K _T μ ((Mbar) σ		ſ	ρ	v_p	Vs
(K)	obs	eq.(6)	(Mbar)	obs	eq.(7)	obs	eq.(8)	(g/cm³)	(km/s)	(km/s)
0	• • • •	1.310	1.310		0.562		0.312	4.143	7.05	3.68
100		1.307	1.306		0.559	• • • •	0.313	4.142	7.04	3.67
200		1.300	1.295		0.553		0.314	4.138	7.02	3.66
300	1.288	1.285	1.275	0.546	0.545	0.314	0.314	4.129 >>	6.98	3.63
400	1.268	1.267	1.253	0.535	0.535	0.315	0.315	4.119	6.93	3.60
500	1.249	1.249	1.230	0.525	0.525	0.316	0.316	4.108	6.89	3.58
600	1.229	1.229	1.206	0.514	0.515	0.316	0.316	4.096	6.84	3.55
700	1.210	1.209	1.181	0.504	0.504	0.317	0.317	4.084	6.79	3.51
800		1.188	1.156		0.494		0.318	4.072	6.73	3.48
900		1.167	1.131		0.483		, 0.318	4.058	6.68	3.45
1000	• • • • •	1.146	1.106	• • • •	0.472	• • • • •	0.319	4.046	6.63	3.42
1100		1.124	1.080	• • • • •	0.462	• • • • •	0.319	4.032	6.57	3.38
1200		1.103	1.054		0.451		0.320	4.018	6.51	3.35
1300		1.082	1.029		0.441		0.321	4.004	6.46	3.32
1400	• • • •	1.060	1.003		0.430		0.321	3.989	6.40	3.28
1500	• • • •	1.039	0.978	• • • •	0.420	• • • •	0.322	3.975	6.34	3.25
1600 ^{a)}	• • • •	1.017	0.952	• • • •	0.409		0.323	3.960	6.28	3.21

a) melting temperature of Mn_2SiO_4 is 1618 K.

b) Takei (1976)

Table 9B Observed and calculated values of elastic parameters of ${^{\rm Fe}2^{\rm SiO}}_4$ as a function of temperature. Ks and K $_{\rm T}$: adiabatic and isothermal bulk modulus, μ : rigidity, σ : Poisson's ratio, ρ : density, and Vp and Vs : dilatational and shear wave velocity.

T	Ks	Ks (Mbar)			μ (Mbar)			σ		ρ	۷p ^{۵)}	۷p	Vs Vs	۷s
(K)	obs	eq.(6)	(Mbar)	obs	eq. (7) a)	eq. (7)	obs	eq.(8)	ed.(8)p)	(g/cm³)	(km/s)	(km/s)	(km/s)	(km/s)
0	• • • •	1.418	1.418	• • • •	0.533	• • • • •		0.333		4.413	6.95		3.48	• • • •
100	• • • •	1.414	1.412	• • • •	0.528	• • • • •		0.334		4.411	6.93	• • • •	3.46	
200	,	1.401	1.394	• • • • •	0.520	• • • •		0.335	• • • •	4.404	6.90	• • • •	3.44	
300	1.380	1.382	1.370	0.509	0.510		0.336	0.336		4.393 d)	6.85		3.41	• • • •
400	1.360	1.362	1.345	0.498	0.499	• • • •	0.337	0.337	• • • • •	4.381	6.80	• • • •	3.38	• • • •
500	1.339	1.339	1.317	0.487	0.488	• • • • •	0.338	0.338	• • • • •	4.368	6.75	• • • •	3.34	• • • •
600	1.316	1.316	1.289	0.480	0.480	(0.476)	0.337	0.337	(0.339)	4.355	6.70	(6.69)	3.32	
7 00	1.293	1.293	1.262	0.472	0.473	(0.465)	0.337	0.337	(0.340)	4.341	6.66			(3.31)
800		1.270	1.234	••••	0.465	(0.454)	••••	0.337	(0.340)	4.327	6.61	(6.64)	3.30	(3.27)
900	• • • •	1.246	1.205	• • • • •	0.457	(0.442)		0.337	(0.341)			(6.58)	3.28	(3.24)
1000	• • • •	1.223	1.178	••••	0.450	(0.431)	• • • • •	0.336	(0.342)	4.313 4.298	6.56 6.51	(6.52) (6.47)	3.26 3.23	(3.20) (3.17)
1100	• • • • •	1.201	1.151	• • • •	0.442	(0.421)		0.336	(0.343)	4.284	6.46	(6.41)	3.21	·
1200	• • • • •	1.177	1.123		0.434	(0.410)		0.336	(0.344)	4.268				(3.13)
1300	• • • • •	1.153	1.094	• • • • •	0.426	(0.399)	• • • • •	0.336	(0.345)	4.253	6.41	(6.35)	3.19	(3.10)
1400	• • • •	1.130	1.067	• • • • •	0.418	(0.388)	• • • •	0.335	(0.346)		6.36	(6.29)	3.16	(3.06)
دی 1500 ^{د)}	• • • •	1.107	1.040	• • • • •	0.411	(0.378)	• • • • •	0.335	(0.347)	4.238 4.222	6.31 6.26	(6.23) (6.18)	3.14 3.12	(3.02) (2.99)

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values above 700 K are calculated by using $\partial \sigma/\partial T = -0.26 \times 10^{-5} \text{deg}^{-1}$. values above 700 K are calculated by using $\partial \sigma/\partial T = +0.93 \times 10^{-5} \text{deg}^{-1}$.

melting temperature of Fe₂SiO₄ is 1478 K.

Table 9C Observed and calculated values of elastic parameters of Co_2SiO_4 as a function of temperature. Ks and K_T : adiabatic and isothermal bulk modulus, μ : rigidity, σ : Poisson's ratio, ρ : density, and Vp and Vs: dilatational and shear wave velocity.

T	Ks (Mbar)		K _T	μ	(Mbar)	σ		ρ	Vp	Vs
(K)	obs	eq.(6)	(Mbar)	obs	eq.(7)	obs	eq.(8)	(g/cm³)	(km/s)	(km/s)
0		1.502	1.502		0,627		0.317	4.724	7.04	3.64
100	• • • •	1.499	1,498		0,626	• • • •	0.317	4,723	7.03	3.64
200		1.492	1,487		0.624		0.317	4.718	7.02	3.63
300	1.482	1.478	1.467	0.620	0.618	0.316	0.316	4.708 b)	6.99	3.62
400	1.463	1.461	1.445	0.612	0.612	0.316	0.316	4,696	6.96	3.61
500	1.443	1.443	1.421	0.605	0.604	0.316	0.316	4.684	6.93	3.59
600	1.424	1.423	1.396	0.597	0.597	0.316	0.316	4.671	6.89	3.58
700	1.404	1.404	1.372	0.589	0.589	0.316	0.316	4.657	6.86	3.56
800		1.384	1.347		0.581		0.316	4.643	6.82	3.54
900		1.363	1,321		0.573	• • • •	0.316	4.627	6.78	3.52
1000	• • • • •	1.343	1.296		0.565	• • • •	0.316	4.613	6.74	3.50
1100	• • • •	1.321	1.269		0.556	• • • • •	0.315	4.597	6.70	3.48
1200		1.300	1.243	• • • •	0.548		0.315	4.582	6.66	3.46
1300		1.279	1,217	• • • • •	0.539		0.315	4.566	6.61	3.44
1400		1,257	1.190		0.530		0.315	4.549	6.57	3.41
1500	• • • • •	1.237	1.165	• • • •	0.522		0.315	4.533	6.53	3.39
1600	• • • • •	1,215	1.138		0.513		0.315	4.516	6.48	3.37
1700 ⁴⁾		1.193	1.111		0.504		0.315	4.499	6.44	3.35

a) melting temperature of Co_2SiO_4 olivine is 1693 K.

b) ASTM card No. 15-865



















