## Rutile (II): density at $298^{\circ}$ K, $4.212 \text{ g/cm}^{3}$ (0.9% porosity); size, $1.0424 \times 0.9848 \times 0.8878 \text{ cm}$ ; 99.9% TiO<sub>2</sub> with 0.03% Pb, 0.02% Fe, and 0.01% Zn.

The measurement of sound velocities at room conditions and as a function of hydrostatic pressure to about 7 kb were made with the pulse-echo-overlap method [4] as modified by Chung et al. [5]. We used the pressure system described in detail by Brace [6] with the exceptions that we used reagent grade petroleum ether as the pressure medium, and the pressure was read directly from a precalibrated, 7500-bar Heise gauge. The readability of this gauge is better than 0.2%. X-cut and AC-cut quartz transducers with resonance frequencies of 20 MHz were used for generation of compressional (P) and shear (S) waves, respectively. The material used for acoustic bonding between specimen and transducer was a 50% (by volume) mixture of phthalic anhydride and glycerine.

The primary data determined in our ultrasonic experiments were (1) P and S velocities in each specimen at 25°C and 1 bar, and (2) pulse-repetition frequencies corresponding to these velocities as a function of pressure to about 7 kb. The first derivative of an elastic modulus with respect to pressure was calculated from

$$\begin{pmatrix} \frac{\mathrm{d}M_j}{\mathrm{d}P} \end{pmatrix}_{P=0} = \left( \frac{M_j}{3K_{\mathrm{T}}} \right)_{P=0} + \\ + \left( M_j \frac{\mathrm{d}}{\mathrm{d}P} \left( F_{jp} / F_{jo} \right)^2 \right)_{P=0}, \quad (1)$$

where  $F_{jo}$  and  $F_{jp}$  are the corrected pulse-repetition frequency at zero-pressure and at pressure *P*, respectively.  $K_{\rm T}$  is the isothermal bulk modulus calculated from the adiabatic bulk modulus  $K_{\rm S}$  by the relation  $K_{\rm T} = K_{\rm S}(1 + \alpha T \gamma)^{-1}$ , where the quantity  $(1 + \alpha T \gamma)$ is 1.0078 for quartz and 1.0116 for rutile at 300°K.  $M_j$  is an elastic modulus, and the subscript (j) refers to either the longitudinal or transverse elastic mode. From the values of  $\{dM_j/dP\}_{P=0}$  we calculated values of the first pressure derivatives of P and S velocities from

я

$$\left(\left(\frac{\partial V_j}{\partial P}\right)_{\mathrm{T}}\right)_{P=0} = \left(\frac{1}{2\rho_0 V_j} \left[\left(\frac{\partial M_j}{\partial P}\right)_{\mathrm{T}} - -\frac{\rho_0}{K_{\mathrm{T}}}(V_j)^2\right]\right)_{P=0}, \qquad (2)$$

where  $\rho_0$  is the initial density of the specimen.

The dependence of the quantity  $(F_{in}/F_{io})^2$  on pressure for both quartz and rutile was linear within experimental precision; the data are given in table 1. Variations with direction in the velocities are due probably to physical inhomogeneities in the specimens and represent the apparent anisotropy of the specimens. The anisotropies are rather small, about the same size as the experimental uncertainties in our measurement of velocities. The values of  $(F_{in}/F_{io})^2$ and their dependence on pressure vary slightly with direction in the sample, are probably real, and imply also that the specimens were slightly anisotropic. This dependence on direction of the elastic properties is attributed to the effects of residual porosity. The effects of pores and cracks on the elastic properties have been discussed by Walsh [7].

Various elastic parameters for the specimens are listed in table 2. On the basis of these parameters, the isotropic elastic properties of polycrystalline aggregates at zero-porosity were evaluated. The elastic moduli of non-porous polycrystalline aggregates can be estimated from acoustic measurements made on a porous aggregate (see Weil [8]). The shear modulus is given by the Weil-Hashin relation

$$\mu^{0} = \mu (1 + k_{1} \theta) / (1 - \theta)$$
(3)

and the adiabatic bulk modulus

$$K_{s}^{0} = K_{s}(1 + k_{2}\theta)/(1 - \theta) , \qquad (4)$$

where

$$k_1 = 2(4 - 5\sigma)/(7 - 5\sigma) ,$$
  
$$k_2 = (1 + \sigma)/2(1 - 2\sigma) ,$$

and  $\theta$  is the volume fraction of total pores,  $\sigma$  is Poisson's ratio, and the superscript (0) refers to the value at zero-porosity. From these values of  $\mu^0$  and  $K_s^0$  all the other isotropic elastic parameters are calculated and these values may be compared with the quantities obtained on the corresponding single crystals. Effects of porosity upon pressure derivatives of the elastic moduli are complicated not only by the manner in which the porosity-sensitive modulus changes with pressure but also by the change of porosity with

Material	Initial density, 00	Compressional velocity, Vp	Shear velocity, Vs	$(F_p/F_{po})^2$	$(F_{\rm s}/F_{\rm so})^2$
	(g/cm <sup>3</sup> )	(km/sec)	(km/sec)	(at 10 kb)	(at 10 kb)
Quartz	2.645	6.062 (±0.007) *	4.106 (±0.005) *	1.06480 (±0.00023) *	1.00170 (±0.00011) *
Rutile I	3.189	8.281 (±0.009) *	4.760 (±0.007) *	1.02075 (±0.00024) *	1.00302 (±0.00017) *
Rutile II	4.212	9.146 (±0.009) *	5.146 (±0.007) *	1.01984 (±0.00020) *	1.00679 (±0.00013) *

 Table 1

 Measured properties of polycrystalline quartz and rutile at 298°K

\* These uncertainties are due to observed variations in the property measured for different directions of the specimen.

Quantity	Unit	Quartz		Rutile		
		(measured)	(extrapolated)	(measured)		(extrapolated) *
		ets de Anala	14	(I)	(II)	for the does
00	g/cm <sup>3</sup>	2.645	2.649	3.189	4.212	4.250
VP	km/sec	6.062	6.066	8.281	9.146	9.193
VS	km/sec	4.106	4.110	4.760	5.102	5.122
$L_{\rm S} (= \rho_0 V_{\rm P}^2)$	10 <sup>9</sup> dyn/cm <sup>2</sup>	971.8	974.6	2186.7	3523.6	3592
$\mu (= \rho_0 V_{\rm S}^2)$	10 <sup>9</sup> dyn/cm <sup>2</sup>	446.0	447.4	722.5	1096.3	1115
Ks	10 <sup>9</sup> dyn/cm <sup>2</sup>	377.2	378.1	1223.4	2061.9	2105
KT	$10^9 dyn/cm^2$	374.3	375.2	1209.3	2038.3	2081
Js	none	0.076	0.076	0.253	0.264	0.274
$\partial V_{\rm P}/\partial P)_{\rm T}$	$10^{-3} ({\rm km/sec})/{\rm kb}$	14.2	14.2	21.0	7.6	7.7
$(\partial V_{\rm S}/\partial P)_{\rm T}$	$10^{-3} ({\rm km/sec})/{\rm kb}$	-3.3	-3.3	-0.6	0.9	0.9
$\partial L_{\rm s}/\partial P)_{\rm T}$	none	7.16	7.2	5.14	7.57	7.7
$(\partial \mu / \partial P)_{\rm T}$	none	0.47	0.5	0.42	0.91	0.9
$\partial K_{\rm s}/\partial P)_{\rm T}$	none	6.53	6.5	4.58	6.35	6.4
$\partial K_{\rm T}/\partial P)_{\rm T}$	none	6.54	6.5	4.57	6.33	6.4
$(\partial \sigma_s / \partial P)_T$	10 <sup>-3</sup> /kb	4.93	4.9	19.6	0.46	0.4

\* Extrapolation based on Rutile II data (see text).

pressure. In an earlier discussion [9] of this problem, we suggested that for porosity less than 1%

$$\frac{\mathrm{d}\,\ln M}{\mathrm{d}P} = \frac{\mathrm{d}\,\ln M^0}{\mathrm{d}P} \tag{5}$$

is a good approximation. Our data have been corrected on the basis of eq. (5) and the results are shown in table 2 under the column designated "extrapolated". The data on the highly porous rutile specimen (Rutile I) are included here to illustrate the important result that the intrinsic properties of materials *cannot* be estimated reliably from the properties of highly porous materials. Anderson et al. [10] recently pointed out this difficulty in connection with their earlier measurements of the elastic properties of a polycrystalline sample of forsterite with 6% porosity. Our present set of data on Rutile I shows not only