

PHYSICAL PROPERTIES OF OXIDES AND SILICATES AT HIGH PRESSURES AND TEMPERATURES*

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(ABSTRACT)

Values of 14 parameters are tabulated for 56 minerals (oxides and silicates), including density, mole weights and volumes, and elastic moduli. The elasticity is found to be very much dependent on the oxygen packing density and, to a smaller extent, on the valency, electronegativity, etc., of the cations. The entropy is correlated with the volume, while the free energy is more dependent on the properties of the cations. Some of the physical and thermodynamic parameters show additivity; the summation should be made over the volumes. The density and elastic moduli of rocks and minerals are discussed as functions of temperature and pressure. The degree of variation with pressure bears a direct relation to the oxygen density. —Author's Abstract

Detailed structural studies have been made of oxides and silicates [1 - 4], and their main physical and thermodynamic parameters have been determined [5 - 8]. The density and elastic parameters have been examined over a wide range in P [5, 9 - 14], and some fragmentary results have been reported [5, 15 - 18] on the effects of T on these. Concepts from atomic physics have been used [17, 18] to derive a theory of the equations of state for these substances, but little has been published on the relation of crystal structure to physical properties for minerals; thus, many concepts from mineralogy and chemical crystallography have been inadequately used in studying the internal structure of the Earth. In particular, more attention should be given to the close-packing concept for oxygen ions in minerals, since the crust, mantle, and (in part) the outer core consist of oxides and silicates [17, 19 - 21]. Chemical crystallography provides insight into the physical basis of the changes during differentiation of the material of the Earth [20 - 22].

This paper is a continuation of a previous one [23] and gives a quantitative description of the oxygen-ion packing density in oxides and silicates, together with a consideration of the effects on some physical and thermodynamic parameters. The effects of P and T on physical properties are also considered.

OXYGEN-ION PACKING IN OXIDES AND SILICATES

First I discuss the advantages of considering together oxides and silicates as regards oxygen-anion packing. In Povarennykh's classification [4], oxides and silicates are assigned to different classes of a major type (oxygen compounds). Binary oxides and complex oxides and complex oxides of the spinel type are assigned mainly to the subclass of coordination compounds on the basis of the principal structural pattern, i. e., to crystals with essentially ionic bonds between the atoms; but the oxides include minerals with framework (perovskite), chain (rutile, stishovite), and layer (molybdate, plumbite) structures [4]. Silicates from the chemical viewpoint resemble sulfates, phosphates, etc., and are salts of oxyacids, but the

*Trans. from *Geokhimiya*, No. 2, pp. 169 - 184, 1970.

[SiO₄] tetrahedra differ substantially in structure from [SO₄] and [PO₄] ones, where the tetrahedra are typical complex ions (acid radicals) with essentially homopolar (covalent) bonds. The [SiO₄] tetrahedron differs from [SO₄] or [PO₄] in being larger, having a higher charge, and less internal bonding [3]. The mean R - O distances (Å) in sulfates, phosphates, and silicates are respectively 1.49, 1.54, and 1.6, while the mean O - O edge lengths are 2.45, 2.49, and 2.53 [4]. The mean distance between nearest O²⁻ ions not in the same tetrahedron is 2.8 - 2.9 Å [1 - 3]. The silicate tetrahedron falls between the typical acid radicals and the tetrahedral groups in certain oxides, e.g., [MgO₄] in spinels. Sobolev states that silicates are the salts of oxyacids most similar to oxides, and they may be assigned to a special type (mesodesmic) falling between compounds with identical bond types (isodesmic) and different bond types (anisodesmic) [4].

Repeated attempts have been made in geochemistry and mineralogy to define quantitatively the structural densities for the various types of mineral [24]. The quantities of main interest to us are the mean atomic volume \bar{v} and the oxygen packing density or mean volume per oxygen atom v_0 . Much use is made of \bar{v} in geophysics, especially in relating the elastic parameters to the density [9, 23].

Table 1 gives \bar{v} and the packing-density coefficient X [3] for some minerals of interest in geophysics, X being the ratio of v_0 for a mineral with the densest packing (e.g., corundum) to v_0 for the particular mineral. An attempt has been made to calculate v_0 as the true volume per oxygen ion via allowance for the volume in the empty spaces between the spheres containing the cations. This somewhat artificial approach yields the effective radius of the spherical oxygen ions if we assume that the spheres are in contact, or nearly so.

To find v_0 (Å³) we use

$$v_0 = \frac{v_c \cdot 0.74}{z \cdot n_0}, \quad (1)$$

in which v_c is the unit-cell volume (Å³), z is the number of formula units in the cell, and n_0 is the number of oxygen ions in the chemical formula of the mineral. Here it is assumed that 74% of the volume in the structure is taken up by spherical oxygen ions, which are in contact and have a mean effective radius R.

Table 1 gives v_0 and other characteristics of the minerals. The minerals have been grouped by structure types as follows:

1) zincite type, coordination numbers k of cations and anions 4:4, 2) periclase type (NaCl-type structure), 6:6, 3) rutile type, 6:3, 4) quartz type, 4:2, 5) corundum type, 6:4, 6) spinel type, 4:6:4, 7) forsterite type, k of cations 6:4, 8) zircon, 8:4, 9) sphene, 7:4:6, 10) pyrope type (garnet group), 8:6:4, 11) kyanite type (aluminosilicates), 6:4, 12) pyroxenes, 6:4, 13) hornblende, 14) feldspars. Table 1 also gives the density ρ , molecular weight M, molecular volume v , and also the parameters l , b , K , ϕ , and d_1 , which will be considered below.

The v_0 of (1) is related to \bar{v} by

$$\bar{v} = c_1 \cdot v_0 \quad (2)$$

in which c_1 is dependent on the ratio of K (number of cations) to A (number of anions): $c_1 = 0.41$ for K/A = 1 (ZnO and MgO type), 0.54 for K/A = 0.5 (TiO₂, quartz, zircon), 0.49 for K/A = 2/3 (corundum, garnets, pyroxenes), 0.46 for K/A = 3/4 (spinel and olivine), 0.51 for K/A = 3/5 (kyanite, sphene), and 0.50 for K/A = 5/8 (feldspars). This c_1 thus varies between the narrow limits 0.41 and 0.51 as a function of K/A, so \bar{v} reflects in general v_0 . I have shown [23] that \bar{v} is closely related to the elasticity for minerals.

If (following Pauling) we take $R_0 = 1.40$ Å as the effective radius of the oxygen ion, we get $v_0 = 11.48$ Å³. Table 1 shows that such v_0 occur only for certain minerals with the closest oxygen-ion packing. This feature enables us to distinguish the following groups of minerals: 1) rutile, pyrope, and phenakite, 2) chrysoberyl and kyanite, 3) bromelite, pyrolusite, and corundum, 4) stishovite. These groups have the following R_0 (Å): 1.40, 1.37, 1.35, and 1.27. Goldschmidt gave R_0 as 1.32 Å, while Belov and Bokiy [25] give 1.36 Å. All minerals apart from the above thus show the Magnus-Goldschmidt effect, in which the cations disturb the close packing of anions [1, 2]. This expansion may be characterized via the factor (in %))

$$k_e = 100 (v_0 - v_p) / v_p,$$

in which v_p is the volume of an oxygen ion for $R = 1.40$ Å. For instance, k_e increases in the garnets from 0 to 14.8% from pyrope to andradite, while it varies from 0 to 20% in the kyanite-sillimanite-andalusite group of aluminosilicates.

Table 1

Physical Parameters of Oxides and Silicates

No.	Mineral and formula	ρ , g/cm ³	M, g/mole	$\nu = \frac{M}{\rho}$, cm ³ / mole	$\bar{M} = \frac{M}{n}$, g	$\bar{\nu} = \frac{M}{\rho n}$, cm ³	v_0 (Å) ³	$l = \frac{1}{v_0}$	b	$K \cdot 10^{-4}$, kg/cm ³	$\Phi = \frac{K}{\rho}$, (km/ sec) ²	$d_1 = \frac{1}{0.1b\omega l}$, (Å) ⁻³	x
1	Zincite ZnO (zincite)	5.67	81.38	14.36	40.68	7.15	17.6	5.7	4.2	14.3	25.2	47.9	0.59
2	Bromellite BeO	3.0	25.0	8.32	12.5	4.16	10.2	9.8	7.2	37 (?)	123	141	1.02
3	Periclase MgO	3.58	40.32	11.25	20.0	5.65	13.8	7.25	5.3	17.4	48	78	0.75
4	Wüstite FeO (ferroxite)	5.74	71.85	12.5	35.8	6.3	14.8	6.7	5.0	15.4	27	67.3	0.70
5	Lime CaO (calcoxite)	3.35	56.08	16.76	28	8.35	20.4	4.9	3.6	11.4	34	35.2	0.51
6	Manganos. MnO	5.37	70.93	13.2	35.4	6.6	16.8	6.1	4.5	14.5	27	55.7	0.64
7	Bunsenite NiO	6.81	74.69	11.0	37.3	5.5	13.5	7.4	5.5	19.8	29.2	82	0.77
8	— CoO	6.44	74.93	11.65	37.4	5.8	14.3	7.0	5.2	19.0	29.6	73	0.73
9	Monteponite CdO	8.24	128.41	15.6	64.2	7.8	19.2	5.2	3.8	10.8	13.1	40	0.54
10	Rutile TiO ₂	4.26	79.9	18.8	26.6	6.25	11.5	8.7	3.2	21.5	50.5	111	0.59
11	Cassiterite SnO ₂	7.0	150.70	21.55	50.3	7.17	13.2	7.6	2.8	19	27	85	0.79
12	Stishovite SiO ₂	4.35	60.09	13.8	20.0	4.6	8.6	11.6	4.3	44	100	200	1.21
13	Pyrolusite MnO ₂	5.21	86.93	16.61	29	5.5	10.2	9.8	3.6	31*	59*	141	1.01
14	Baddeley. ZrO ₂	5.82	123.22	21.15	41.2	7.0	13.0	7.7	2.8	—	—	86	0.81
15	Quartz SiO ₂	2.65	60.09	22.70	20.0	7.55	13.9	7.2	2.65	3.7	14	76	0.75
16	Coesite SiO ₂	3.0	60.09	20.0	20.0	6.67	12.7	7.9	2.9	8.0*	26.7	91	0.82
17	Corundum Al ₂ O ₃	3.98	101.96	25.6	20.4	5.1	10.4	9.6	4.7	25	63	135	1.00
18	Hematite Fe ₂ O ₃	5.27	159.7	30.2	31.9	6.0	12.3	8.1	4.0	20.6	39	97	0.84
19	Ilmenite FeTiO ₃	4.78	151.75	31.71	30.4	6.35	13.0	7.7	3.8	18.5	39	88	0.80
20	Spinel MgAl ₂ O ₄	3.64	141	38.8	20.2	5.55	12.2	8.2	4.6	20	55	100	0.85
21	Gahnit. ZnAl ₂ O ₄	4.59	183.3	40.0	26.2	5.7	12.0	8.3	4.5	20*	43*	100	0.85
22	Hercynite FeAl ₂ O ₄	4.4	173.8	39.4	24.8	5.6	12.5	8.0	4.4	21*	48*	94	0.83
23	Magnetite Fe ₃ O ₄	5.24	231.55	44.3	33	6.4	13.7	7.3	4.0	18	37	78	0.76
24	Chrom. FeCr ₂ O ₄	5.07	223.87	44.0	31.9	6.3	13.6	7.3	4.1	~20	~40	80	0.77
25	Chrysoberyl BeAl ₂ O ₄	3.69	126.97	34.2	18.1	4.9	10.6	9.4	5.3	27*	73*	133	0.99
26	Spinel-I Mg ₂ SiO ₄	3.53	140.73	40.0	20.1	5.7	12.3	8.1	4.5	15*	41*	97	0.85
27	Spinel-II Mg ₂ SiO ₄	3.87	140.73	36.3	20.1	5.2	11.2*	8.9*	4.94*	27.5*	~71*	118	0.94
28	Spinel-I Fe ₂ SiO ₄	4.85	203.78	42	29.1	6.0	12.9	7.8	4.3	13.5*	28*	90	0.81
29	Spinel-II Fe ₂ SiO ₄	5.37	203.78	37.9	29.1	5.4	11.6*	8.6*	4.7*	25.8*	48*	108	0.90
30	Forsterite Mg ₂ SiO ₄	3.22	140.73	43.67	20.1	6.24	13.4	7.5	4.1	13	40	79	0.78
31	Fayal. Fe ₂ SiO ₄	4.39	203.78	46.4	29.4	6.57	14.2	7.0	3.9	11	25	72	0.73
32	Monticellite CaMgSiO ₄	3.05	156.49	51.37	22.3	7.32	15.8	6.3	3.5	—	—	59	0.66
33	Phenak. Be ₂ SiO ₄	2.96	110.16	37.2	15.8	5.32	11.5	8.7	4.9	21*	71*	114	0.91
34	Zircon ZrSiO ₄	4.68	183.31	39.27	30.6	6.54	12.0	8.3	3.1	20	43	103	0.87
35	Sphene CaSiTiO ₅	3.52	196.07	55.70	24.5	6.95	13.6	7.3	3.2	—	—	77	0.76

Table 1 (Continued)

No.	Mineral and formula	ρ , g/cm ³	M, g/mole	$\nu = \frac{M}{\rho}$, cm ³ /mole	$\bar{M} = \frac{M}{n}$, g	$\bar{\nu} = \frac{M}{\rho n}$, cm ³	v_0 , (Å) ³	$l = \frac{1}{v_0}$	b	$K \cdot 10^{-10}$, kg/cm ³	$\Phi = \frac{K}{\rho}$, (km/sec) ²	$d_1 = 0.1 \frac{b}{\omega l}$, (Å) ⁻³	χ
36	Pyrope Mg ₃ Al ₂ Si ₃ O ₁₂	3.58	403.19	112.5	20.1	5.62	11.5	8.7	4.2	~1	46	111	0.91
37	Almandine Fe ₃ Al ₂ Si ₃ O ₁₂	4.32	497.78	115.2	24.88	5.76	11.80	8.5	4.2	~16	37	107	0.88
38	Spessartine Mn ₃ Al ₂ Si ₃ O ₁₂	4.19	495.02	118.0	24.75	5.9	12.1	8.2	4.1	~15.5	37	102	0.86
39	Grossularite Ca ₃ Al ₂ Si ₃ O ₁₂	3.59	450.47	126.3	22.70	6.3	12.8	7.8	3.8	~15	42	90	0.81
40	Andradite Ca ₃ Fe ₂ Si ₃ O ₁₂	3.86	508.21	131.67	25.4	6.6	13.5	7.4	3.6	~15	39	81	0.77
41	Kyanite Al ₂ SiO ₅	3.66	162.05	44.1	20.2	5.52	10.8	9.3	4.1	19*	52*	125	0.97
42	Sillimanite Al ₂ SiO ₅	3.24	162.05	49.91	20.2	6.23	12.2	8.2	3.6	13*	40*	97	0.85
43	Andalusite Al ₂ SiO ₅	3.14	162.05	51.54	20.2	6.43	12.6	7.9	3.5	11*	35*	91	0.82
44	Staurolite Fe(OH) ₂ ·Al ₂ SiO ₅	3.65	413.8	114	21.8	6.0	—	—	—	12.8	34	—	0.52
45	Cordierite Mg ₂ Al ₃ [AlSi ₅ O ₁₈]	2.51	585	232.8	20.17	8.0	15.9	6.3	2.8	—	—	—	0.65
46	Enstatite MgSiO ₃	3.20	100.41	32.50	20.0	6.5	12.9	7.8	3.8	11	34	89	0.79
47	Enstatite-II MgSiO ₃	4.0*	100.41	25.0	20.0	5.0	10.0*	10	4.9*	32*	80*	147	1.02
48	Ferrosillite FeSiO ₃	3.99	131.94	33.07	26.4	6.6	13.5	7.4	3.7	10*	25*	82	0.77
49	Ferrosillite-II FeSiO ₃	5.10*	131.94	25.85	26.4	5.3	10.8*	9.3	4.6*	29.7*	58*	128	0.99
50	Hypersthene Mg, Fe)SiO ₃	3.5	116.0	33.0	34	6.8	13.2	7.6	3.7	9.6	28	84	0.77
51	Diopside CaMgSi ₂ O ₆	3.26	216.58	66.4	21.66	6.64	13.5	7.4	3.6	12	37	80	0.77
52	Jadeite NaAlSi ₂ O ₆	3.33	202.15	60.98	20.2	6.1	12.5	8.0	4.0	13.5	41	96	0.83
53	Hornblende Ca ₂ (Mg, Fe) ₅ × [Si ₄ O ₁₁] ₂ (OH) ₂	3.15	820	260	20.3	6.8	—	—	—	9.5	30	—	0.78
54	Orthoclase KAlSi ₃ O ₈	2.56	278.35	109	21.40	8.4	16.7	6.0	2.7	5.2	21.8	53	0.63
55	Albite NaAlSi ₃ O ₈	2.61	262.2	100.2	20.2	7.72	15.5	6.4	3.0	5.7	21.8	62	0.68
56	Anorthite CaAl ₂ Si ₂ O ₈	2.76	278.2	100.7	21.4	7.72	15.5	6.4	3.0	8.7	31.5	62	0.68

**n was deduced by an additivity calculation.

EFFECTS OF OXYGEN PACKING DENSITY ON PHYSICAL AND THERMODYNAMIC PARAMETERS

Figure 1 shows the bulk modulus K as a function of v_0 . The oxides and silicates form

two independent groups as parallel lines; the oxides having the higher K for a given v_0 . Quartz has a somewhat special position, since its K is too low for an oxide which is related to the lower K for silicates. There is no exact relation of K to ρ for oxides. For

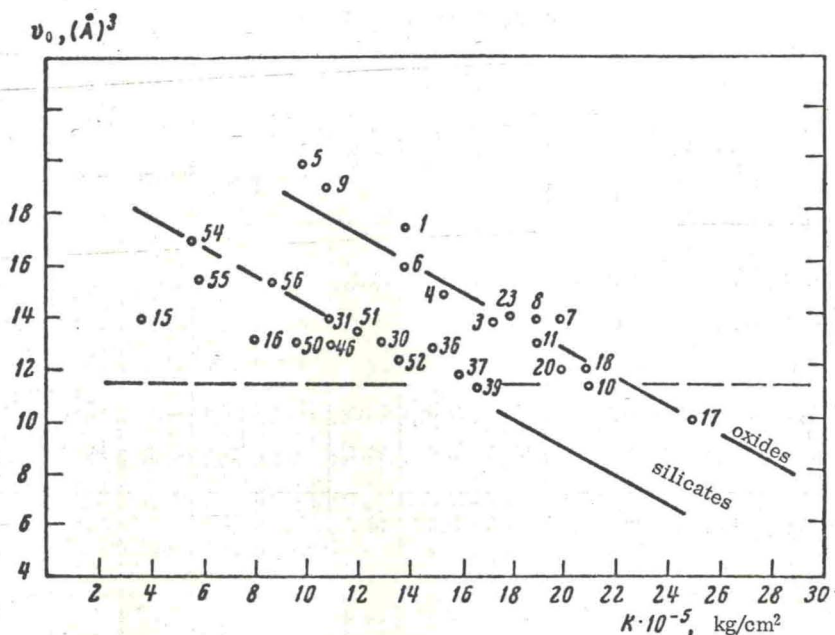


Fig. 1. K in relation to v_0 . The numbers are those of the minerals in Table 1.

instance, monteponite (CdO) has $\rho = 8.24$ g/cm^3 , which is largely due to the high atomic weight of Cd (112.41), where its K is close to that for CaO ($\rho = 3.35$ g/cm^3). Also, bromellite ($\rho = 3.0$ g/cm^3) has a very high K , as have stishovite (4.35 g/cm^3) and corundum (3.98 g/cm^3). The density involves two components [3, 23]: 1) the weight, 2) the packing density d , so there can be low-density substances with close packing and high K (BeO) and high-density ones with more open packing (CdO , ZnO , MnO , FeO).

The silicates (Fig. 1) also show no direct relation of K to ρ , but the groups feldspars, quartz, pyroxenes, olivines, and garnets in general lie on a line $K = f(v_0)$ in order of increasing density, and so igneous rocks often show a correlation between ρ and K (and also the wave speed) [23]. There is an indirect relation between ρ and K for silicates because these usually consist of elements similar in weight, and increase in ρ corresponds to an increase in d .

Analogy with other ionic crystals indicates that K for these compounds is dependent not only on d but also on factors such as the cation radius and valency, and also the number of bonds per unit volume [25]. These effects are reflected in the additional parameters b and d_1 (Table 1), in which b

(dimensionless) is the number of cations per 100 \AA^3 and is

$$b = \frac{n_c \cdot z}{v_c} \cdot 100, \quad (3)$$

in which n_c is the number of cations in the chemical formula. Also, d_1 is

$$d_1 = b \cdot \omega \cdot l(\text{\AA})^{-3}, \quad (4)$$

in which ω is the mean cation valency and $l = 1/v_0$ is the oxygen packing density. Then ω equals the cation valency for a simple oxide; for complex oxides, it is calculated as the ratio of the cation charges to the number of cations. For instance, $\omega = 8/3$ for spinel, and forsterite, or $\omega = 24/8$ for garnets.

Figure 2 shows $K = f(d_1)$. The oxides and silicates form two fairly narrow bands having the same slope, with the silicates above the oxides. Quartz in the silicates deviates from the general scheme, as does bromellite in the oxides. In general, $K = f(d_1)$ resembles $K = f(v_0)$, but the correlation is closer. Figure 2 can be used with known d_1 to determine K approximately.

A full elucidation of the relation of K to structure would involve other parameters

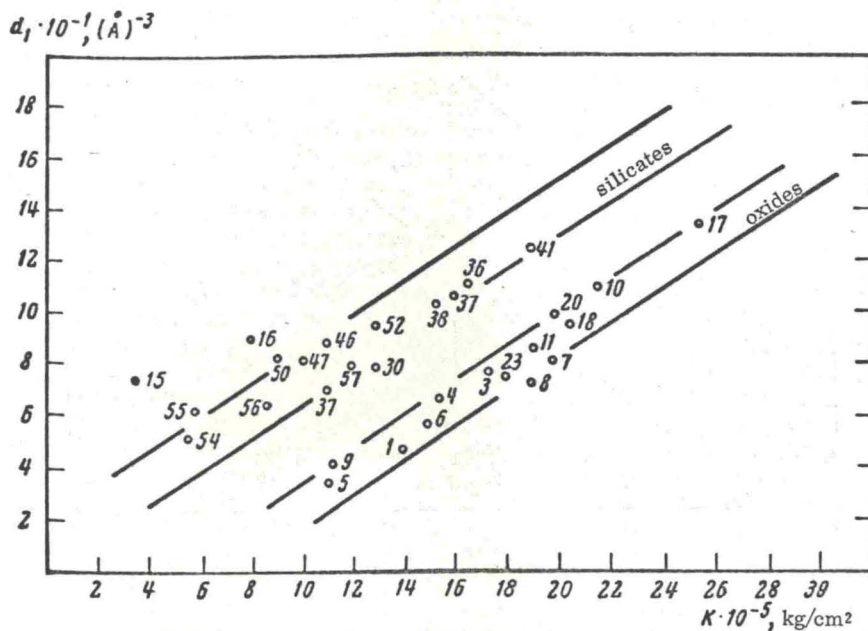


Fig. 2. K in relation to d_1 . The numbers are those of the minerals in Table 1.

such as the degree of filling of holes of a given sort (tetrahedral, octahedral, etc.). The energy of a cation is [2] dependent on whether it is in a tetrahedral hole or an octahedral one, because of the effects of the surrounding electric field on the electron distribution in the ion.

Figures 3 and 4 show the entropy S and Gibbs free energy Z as functions of v_0 , the abscissa in Fig. 3 being the entropy per g-atom. There is some dependence of S on volume, as minerals with low volumes (bromellite, stishovite, corundum, kyanite) tend to have low S . There is a clearer relation of S to the properties of the cations; Fig. 3 shows the cation series in order of increasing S , which is also the order of increasing atomic weight.

Figure 4 shows that the mean Gibbs free energy $\Delta Z/n$ has no clear relation to v_0 but is related to the properties of the cations, being anomalously low for compounds of Fe, Mn, Zn, and Sn but high for Ti, Al, and Zr. The corresponding cation series is shown. The mean enthalpy has a similar relation to v_0 (graph not shown).

Recently, \bar{v} and ΔZ have been used to elucidate the depth distribution of paragenetic mineral associations [8, 24, 26]. If the mean mineral composition of a metamorphic facies is considered from the viewpoint of the mean atomic volume [24], there is no clear division of minerals into groups, but \bar{v} tends to fall as the depth increases (some uncertainty is introduced by the wide stability ranges of quartz and the plagioclases). The significance of \bar{v} for the depth distribution of minerals should be considered over a wider range with due allowance for the effects of T , which makes fairly clear the crystallochemical nature of the Mohorovičić discontinuity, M , which coincides approximately with $\bar{v} = 7$ and separates two regions of occurrence of oxides and silicates. Above M we find typical crustal minerals with a fairly open structure, which contain large cations such as Na, K, and Ca; below M we find minerals with close packing of the oxygen ions (olivine, spinel, garnets, etc.). This shows that below M , in the upper and lower parts of the mantle, we should find geospheres differing primarily in oxygen packing density. We may say roughly that differences in v_0 characterize major geospheres, while differences in ΔZ make themselves felt within each such sphere.

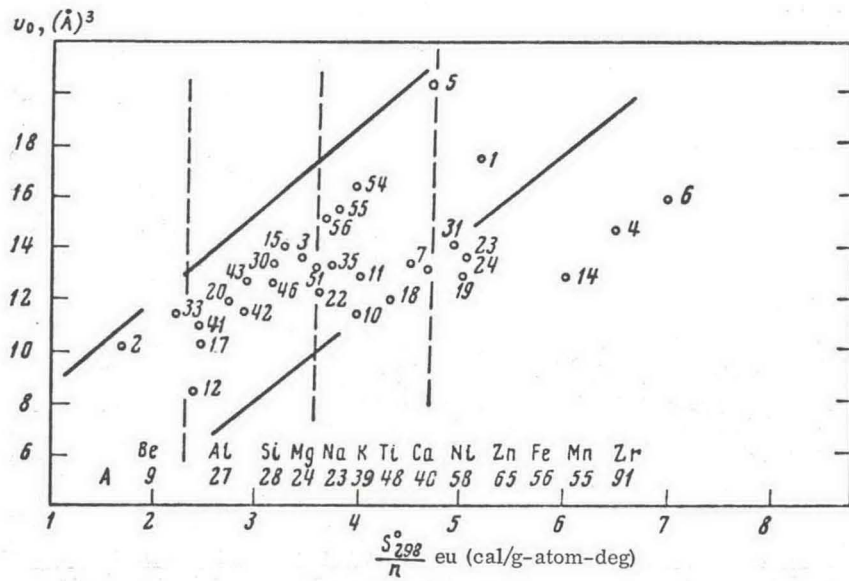


Fig. 3. \bar{S}_{298}^0 (mean standard entropy) in relation to v_0 . The numbers are those of the minerals in Table 1.

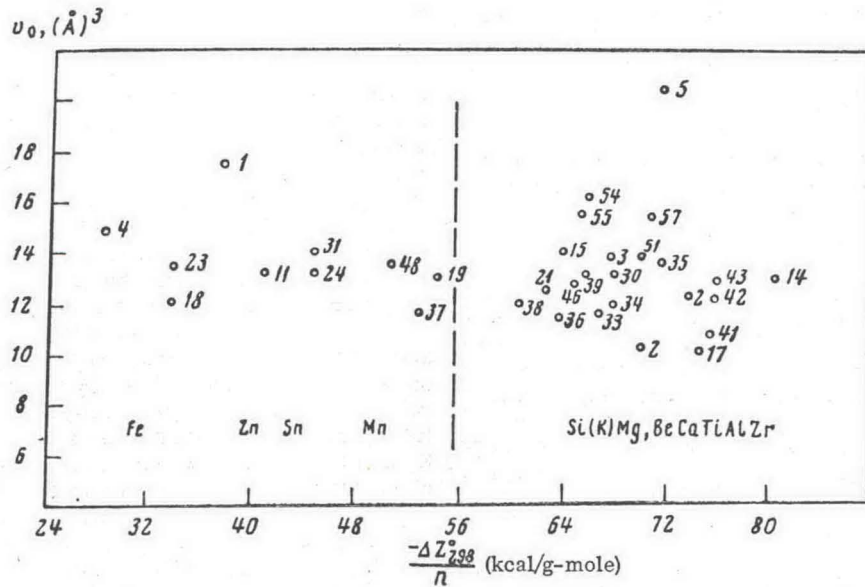


Fig. 4. Mean Gibbs free energy $-\Delta Z_{298}^0/n$ in relation to v_0 . The numbers are those of the minerals in Table 1.

ADDITIVITY IN THE PHYSICAL AND THERMODYNAMIC PARAMETERS OF OXIDES AND SILICATES

The molecular volume or density of a compound oxide may be determined approximately by summing the volumes of the corresponding simple oxides. This applies also to K , l , b , d_1 , and the thermodynamic parameters. The summation is by volume and in proportion to the volume, not by the number of simple oxides in the formula or by the molecular weights of these.

Table 2 gives the actual values (experimental or calculated, bottom line) as well as those found by additivity (top line). Not all parameters have been determined for certain substances (dash in the bottom line). The oxides give good agreement between the two figures when the cation in the simple oxide has the same coordination as in the compound. For instance, Mg^{2+} in periclase has $k = 6$, whereas in spinel it has $k = 4$, so we do not obtain very good agreement for spinel on summing over the volumes of periclase and corundum, but the ratio of the corresponding quantities usually corresponds to the MgO/Al_2O_3 volume ratio. Another case occurs in zinc spinel and chrysoberyl, where the coordination is retained and the agreement is better.

The silicates give a more complicated picture. Low values for the densities are obtained on summing the volumes of the corresponding metal oxides and quartz: this suggests that the silicon-oxygen tetrahedra in silicates (which involve oxygen close packing) are packed more closely than in quartz. This agrees well with the known structure of quartz, which in Belov's representation [1] is derived from a cell with an A_3X_2 pattern of eight cube-octahedra by filling two tetrahedra in each cube-octahedron along a three-fold axis. The energy relationships of the cations and anions cause the silicon-oxygen tetrahedra to rotate somewhat into a more stable position; the diad axes of those tetrahedra in quartz are parallel to the triad axis in the structure. The result is fairly open framework of tetrahedra that does not correspond to closest packing of the oxygen ions (about 1/3 of the close-packed positions are empty). Coesite has a denser structure, in which those diad axes are turned somewhat one with respect to another [2]. Belov's scheme [1] allows one to imagine also a closer packing of the tetrahedra.

The additivity method can give the parameters of forsterite, fayalite, enstatite, ferrosilite, phenakite, etc. with fair accuracy if we use SiO_2 in the form of coesite (molecular volume $20 \text{ cm}^3/\text{mole}$, density 3.0 g/cm^3) as the basis. K has not yet been determined for coesite, which causes difficulty in calculating K for silicates. The dependence of K on the mean atomic volume [23] and a reverse calculation by additivity give $K = 8 \times 10^5 \text{ kg/cm}^2$ as an approximate result, which was used in calculating the other K .

However, certain minerals (e.g., kyanite and garnet) have the tetrahedra more closely packed than in coesite; they correspond to a modification of SiO_2 having the parameters $M/\rho = 18.5 \text{ cm}^3/\text{mole}$, $\rho = 3.25 \text{ g/cm}^3$, and $K = 11 \times 10^5 \text{ kg/cm}^2$. Such a modification is not known, but the features of quartz and coesite enable us to assume that it could occur, at least in the metastable state. This allows us to calculate the properties of kyanite, garnets, and the spinel modifications of forsterite and fayalite having densities of 3.53 and 4.85 g/cm^3 respectively (spinel I in Table 1).

K has not been determined for kyanite; the calculation gives about $19 \times 10^5 \text{ kg/cm}^2$. To test this I derived approximately the longitudinal wave speeds V_p along the [001], [010], and [100] directions in a kyanite crystal as 10.8 , 10.2 , and 8.0 km/sec respectively. For transverse waves, V_s was 6.3 , 5.3 , and 4.5 km/sec for different directions of displacement. K was calculated via the mean values $V_p = 9.70 \text{ km/sec}$ and $V_s = 5.70 \text{ km/sec}$ ($V_p/V_s = 1.73$, as for corundum), which gave K as $18.7 \times 10^5 \text{ kg/cm}^2$. Higher K are implied by $K = f(\bar{v})$ [23].

It is difficult to calculate the parameters of sillimanite and andalusite in this way because some of the Al^{3+} ions have $k = 4$, and the physical properties of these tetrahedra are unknown. The situation is similar for the feldspars. The divalent cations in garnets have $k = 8$ (at centers of Thomson cubes) [1] and their properties are unknown. Somewhat high values for the volumes are obtained if we use as a basis the properties in 6:6 coordination in conjunction with $18.5 \text{ cm}^3/\text{mole}$ for silica.

The additivity principle may be used to find approximate densities, volumes, etc. for high-pressure phases, e.g., the spinel II modification of forsterite or enstatite (Table 1),

Table 2

Additivity Calculation of Physical and Thermodynamic Parameters

Parameter	Spinel MgO·Al ₂ O ₃	Garnet ZnO·Al ₂ O ₃	Hercynite FeO·Al ₂ O ₃	Chrysoberyl BeO·Al ₂ O ₃	Magnetite FeO·Fe ₂ O ₃	Ilmenite FeO·TiO ₂
	Oxides					
M/ρ, cm ³ /mole	36.85/ 38.8	39.94/ 40.0	37.65/ 39.4	33.92/ 34.22	42.25/ 44.3	31.3/ 31.71
ρ, g/cm ³	3.86/ 3.64	4.59/ 4.59	4.54/ 4.4	3.73/ 3.70	5.42/ 5.24	4.83/ 4.78
K·10 ⁵ , kg/cm ²	22.6/ 6.20	21/ —	22/ —	28/ 27	19.1/ 18	19.1/ 18.5
l, (Å) ⁻³	8.4/ 8.2	8.2/ 8.3	6.72/ 6.2	9.6/ 9.4	6.07/ 5.7	7.9/ 7.7
b	4.9/ 4.6	4.52/ 4.50	4.8/ 4.4	5.3/ 5.3	4.92/ 4.06	4.74/ 3.8
S ₂₉₈ ^o , cal/mole-deg	19.2/ 19.3	23.2/ —	25.0/ 25.4	15.55/ —	34.4/ 35	24.9/ 25.3
ΔZ ₂₉₈ ^o , kcal/mole	512.8/ 517.5	452.7/ —	435.1/ 441.9	515.7/ 515.5	235.5/ 242	269.4/ 277.5
C _{p,298} ^o , cal/mole-deg	27.82/ —	28.50/ —	31.08/ —	24.9/ —	37.2/ 34.2	25.8/ 23.78

Silicates

Parameter	Forsterite 2MgO·SiO ₂	Fayalite 2FeO·SiO ₂	Enstatite MgO·SiO ₂	Ferrosilite FeO·SiO ₂	Phenakite 2BeO·SiO ₂	Kyanite Al ₂ O ₃ ·SiO ₂
M/ρ, cm ³ /mole	42.50/ 43.67	44.1/ 46.4	31.95/ 32.5	32.0/ 33	36.6/ 37.2	44.1/ 44.1
ρ, g/cm ³	3.32/ 3.22	4.62/ 4.39	3.27/ 3.20	4.1/ 3.99	3.0/ 2.97	3.66/ 3.66
K·10 ⁵ , kg/cm ²	12.5/ 13	11.5/ 11	11/ 11.0	10.7/ —	21/ —	19/ —
l, (Å) ⁻³	7.5/ 7.5	7.2/ 7.0	7.7/ 7.8	7.5/ 7.4	8.5/ 8.7	—
b	4.1/ 4.1	3.9/ 3.9	3.7/ 3.8	3.7/ 3.7	4.87/ 4.9	—
S ₂₉₈ ^o , cal/mole-deg	22.8/ 22.7	35/ 34.7	15.4/ 16.2	21.9/ 23	15.7/ 15.4	—
ΔZ ₂₉₈ ^o , kcal/mole	472/ 480	317/ 316	336/ 337	258/ 257.7	478/ 470	—
C _{p,298} ^o , cal/mole-deg	28.4/ 28.2	35/ 31.7	19/ 19.6	21.2/ —	22.7/ 22.8	—

or enstatite and ferrosilite with the ilmenite structure. In that case we should use stishovite (6:3 coordination) as the basis. Table 1 gives the results.

It is not important as regards the additivity principle whether a substance occurs in the depths of the Earth as simple oxides or

as a compound of spinel, garnet, etc. type; but the chemical composition and the cation coordination (in an oxygen environment) are important. The principle can give reasonably reliable results for the properties of a substance of known composition, provided that we have a clear conception of the stability ranges of oxides and silicates at the P and T prevailing within the Earth.

EFFECTS OF P AND T ON PHYSICAL PARAMETERS

The effects of P are fairly well known from two somewhat interconnected sources: 1) experiments on pure substances (crystals and pure monomineralic aggregates) by isothermal compression, dynamic compression, ultrasonics, and X-rays, 2) experiments on rocks and natural monomineralic aggregates. Theoretical studies could also be important, but so far they have been concerned with extrapolation of the experimental results rather than to fundamental research.

Figure 5 summarizes results on $\Delta V/V_0$ for some oxides and silicates up to 10 or 20 - 25 kbar [5, 12 - 14]. The results for certain substances (diopside, garnets, etc.) are somewhat conflicting, but the order of decreasing compressibility is generally as

follows: quartz, (micas), feldspars (from orthoclase to anorthite), (amphiboles), pyroxenes (from augite to jadeite and spodumene), olivine, zircon, garnets (from andradite to pyrope), periclase, hematite, magnetite, ilmenite, chromite, cassiterite, spinel, rutile, corundum, bromellite, (stishovite). This series in general reflects the decrease in molecular volume and only indirectly (for silicates) is related to the density. The $\Delta V/V_0 = f(P)$ curves differ in slope. The compressibility β is deduced from the linear parts as

$$\beta p = \frac{\Delta v}{v_0}, \quad (5)$$

which gives $K = 1/\beta$ as linearly varying with P; $K' = dK/dP$ varies with the mineral, being largest for quartz (about 6.0) and least for bromellite or stishovite. Exact values for K'

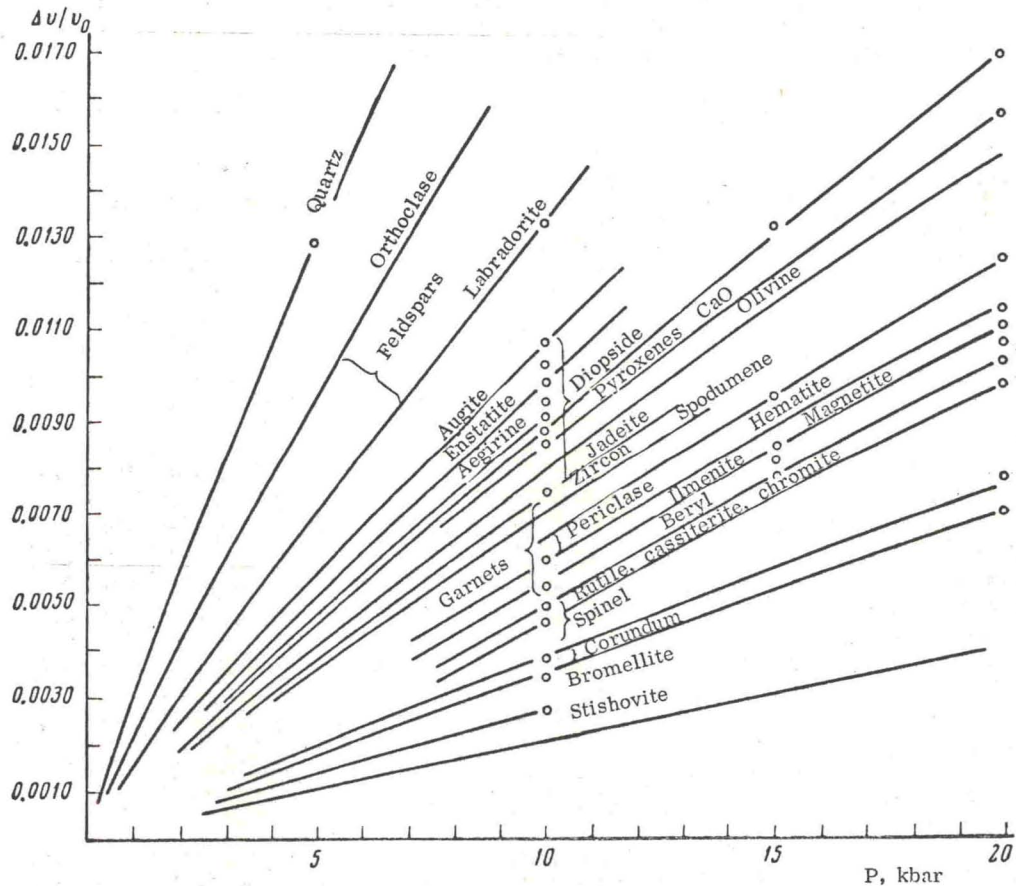


Fig. 5. $\Delta V/V_0$ as a function of P for oxides and silicates.

enite
TiO₂
31.71
/ 4.78
18.5
/ 7.7
/ 3.8
25.3
277.5
23.78

enite
SiO₂
44.1
/ 3.66

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are hard to derive at present, as the experiments are only of limited accuracy, the range in K' being usually 3.5 - 4.5 (mean 4.0). Here we must note that the K from static methods differ from those obtained by dynamic methods, but the poor accuracy does not allow us to distinguish the adiabatic compressibility β_S from the isothermal value β_T .

This trend in K persists to higher P (up to a polymorphic transition to a denser modification, if there is one) [5, 9 - 14], though there is a tendency for K' to decrease as P increases. Shock-compression data [10 - 13] indicate that K' decreases discontinuously at the above transition point; for instance, the high P phases corresponding to quartz, spinel, magnetite, hematite, forsterite, fayalite, dunite, diabase, bronzitite, and plagioclase have [13] K' of 1 - 3.5 and average K' of 2.5 - 3.0, instead of the average 4.0 for low P . These are only preliminary values, since extrapolation via the Birch-Murnahan equation of state was used [12, 13] in calculating the zero parameters for the high-pressure phases. All the above minerals and rocks showed polymorphic transitions,

but none were detected for MgO , Al_2O_3 , and MnO_2 .

In spite of some spread in the values, pure substances give a fairly clear picture of the change in K with P . The picture is more complex for rocks and natural minerals, which may have grossly defective structures: K' is generally larger and varies nonlinearly with pressure, especially up to 2 - 5 kbar. The topic may be examined via the published data for wave speeds up to 10 kbar [5] and my own results up to 20 kbar [14, 27]. Table 3 summarizes the results for certain rock types, this being based on my recent results for wave speeds in igneous rocks from the Kola peninsula and for basalts of various types. Only for granites and dense fine-grained basalts does K' approach the theoretical value deduced from the corresponding minerals.

Little is known about $K(T)$ for oxides and silicates. The results are most complete for $\alpha - Al_2O_3$ from 4.2 to 1300°C at atmospheric pressure [15]: $\partial K_S / \partial T$ is -0.08 to -0.09 kbar/deg below 300°C K , as against

Table 3
Changes in Bulk Modulus K , Young's Modulus E , and the Shear Modulus μ at High Pressures in Igneous Rocks

Rock	P range, kbar	Values at initial and final points				$\frac{\partial K_S}{\partial P}$	$\frac{\partial E}{\partial P}$	$\frac{\partial \mu}{\partial P}$
		ρ , g/cm ³	$K_S \cdot 10^{-5}$, kg/cm ²	$E \cdot 10^{-5}$, kg/cm ²	$\mu \cdot 10^{-5}$, kg/cm ²			
Olivinites	2-20	3.29-3.33	12.8-13.8	17.4-19.1	6.8-7.5	5.5	9.5	3.9
Bronzites	2-20	3.25-3.30	10.7-11.9	16.0-17.8	6.4-7.1	6.6	10.0	3.8
Harzburgites	2-20	3.30-3.34	11.9-13.3	17.0-18.7	6.8-7.4	7.7	9.4	3.3
Gabbro-norites	2-20	2.98-3.03	8.40-9.35	12.0-13.2	4.7-5.2	5.3	6.6	2.3
Pechenga diabase	2-20	3.05-3.12	8.0-8.95	11.0-12.1	4.3-4.7	5.0	6.1	2.2
Frederik diabase	2-10	3.03-3.05	8.3-9.0	11.1-11.6	4.3-4.6	9.1	6.8	2.5
Saint Reville diab.	2-10	2.98-3.01	8.12-8.66	10.5-11.1	4.1-4.4	6.7	7.5	3.4
Medium-grained dolerite	2-10	2.83-2.86	7.2-7.60	9.0-9.6	3.5-3.7	5.0	7.5	3.7
Fine-grained dolerite	2-20	2.96-3.03	7.60-8.35	10.2-11.0	3.9-4.34	4.2	4.5	2.8
Porous basalt	2-20	2.89-2.97	6.30-7.82	8.5-9.8	3.34-3.8	8.4	7.2	2.9
Fine-grained oceanic basalt	2-20	2.96-3.03	7.05-7.62	9.0-10.2	3.5-3.98	3.5	6.7	2.7
Granites	2-20	2.64-2.72	5.33-6.43	8.5-9.75	3.3-3.9	6.1	6.9	3.3

-0.22 to -0.25 from 300 to 1300°K. Anderson et al. [16] have collected results for corundum, periclase, spinel, forsterite, garnet, hematite, quartz, CaO, zincite, and bromellite, for which the values are -0.14, -0.12 and -0.16 (MgO as polycrystal and single crystal -0.13, -0.11, -0.20, -0.17, -0.10, -0.14, -0.13, and -0.12. The $(\partial K_S/\partial T)_P$ may be compared with $(\partial K_S/\partial P)_T$, which are given [16] for the above minerals as 3.98, 4.58, 4.18, 4.78, 5.43, 4.53, 6.4, 5.23, 4.78, and 5.52.

An open structure should produce a low K , a high K' , and a low $\partial K/\partial T$. Such a substance should also have considerable thermal expansion and a high specific heat. Quartz meets this condition (apart from the thermophysical parameters), as do CaO and zincite to a certain extent. A future paper will examine the relation between these parameters on more extensive evidence.

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	$\frac{\partial E}{\partial p}$	$\frac{\partial \mu}{\partial p}$
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3	10.0	3.8
7	9.4	3.3
3	6.6	2.3
0	6.1	2.2
1	6.8	2.5
7	7.5	3.4
0	7.5	3.7
2	4.5	2.8
4	7.2	2.9
5	6.7	2.7
1	6.9	3.3

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Received for publication
February 3, 1969

UDC 550.890