

[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.