

greater than the 'mixed oxide' densities, as has been predicted on the basis of high-pressure static experiments on related compounds [e.g., Ringwood, 1969] (see also later discussion). In addition, the new Φ 's are close to the mixed-oxide Φ 's, which is in accord with the suggestion made by D. L. Anderson [1969] that Φ could be estimated from that of the component oxides. This result is a consequence of constraining Φ and ρ to lie on a line passing through the MgO, Al₂O₃, and SiO₂ points (Figure 2). Since these are the main components of most of the compounds considered, and since the densities are close to the mixed-oxide densities, Φ is constrained to be close to the mixed-oxide Φ . Thus the use of the revised seismic equation of state is approximately equivalent to the hypothesis of the molar additivity of Φ [D. L. Anderson, 1969].

The iron-rich compounds show systematically different behavior—in Figure 2 we see that K' is systematically lower for Fe₂O₃, Fe₃O₄, and fayalite. Exceptional behavior might be expected, since the $\Phi - \rho$ point for FeO (Table 1) apparently does not line up with the other oxides in Figure 2, and since it has been noted [D. L. Anderson, 1969] that the parameter $\Psi_0 = \rho_0 \Phi_0^{-1/2} / (M)$ (cf. equation 6) increases with iron content. To allow for this, the iron-rich compounds were re-analyzed using $\Phi_0 = 0.0510$ (corresponding to roughly 70 wt % FeO), and the results are given in Table 1. K'_0 is greater, and ρ_0 and Φ_0 are less than previously. For fayalite, ρ_0 and Φ_0 now seem to be anomalously low compared to the mixed-oxide values. The same may be true of Fe₂O₃, but Fe₃O₄ seems not unreasonable. Since decisive tests are difficult, considerable uncertainty must still attach to the iron-rich compounds.

EFFECT OF THE BIRCH-MURNAGHAN EQUATION

Consider the functional form of dK/dP yielded by the Birch-Murnaghan equation. Differentiating (1), we get

$$\frac{dK}{dP} = \frac{1}{3} \left[\frac{(49x^2 - 25) - \xi(81x^4 - 98x^2 + 25)}{(7x^2 - 5) - \xi(x^2 - 1)(9x^2 - 5)} \right] \quad (8)$$

The zero-pressure ($x = 1$) value is $K'_0 = 4 - 4/3 \xi$. Note that if $\xi = 0$, (8) gives a high-pressure ($x = \infty$) limit of $7/3$, whereas if

$\xi \neq 0$, the high-pressure limit is 3. Figure 3 shows dK/dP plotted against x for several values of ξ . For $\xi = 0$ ($K'_0 = 4$), dK/dP decreases monotonically toward the high-pressure limit. For $\xi < 0$ ($K'_0 > 4$), dK/dP again decreases monotonically toward the high-pressure limit of 3, but for $\xi > 0$ ($K'_0 < 4$) a singularity occurs for some value of $x > 1$. In the latter case dK/dP first decreases to minus infinity before changing sign and approaching the high-pressure limit. For $K'_0 = 2$, for instance, dK/dP becomes zero at about $x = 1.08$, i.e., about 15% compression. Since it is found that $K'_0 < 4$ for many of the materials analyzed here, it is evident that the Birch-Murnaghan equation must be used with caution. If K'_0 is found to be less than 4, then the Birch-Murnaghan equation will be physically reasonable only within a restricted pressure range.

This singular behavior of the Birch-Murnaghan equation is not usually a problem. It arises

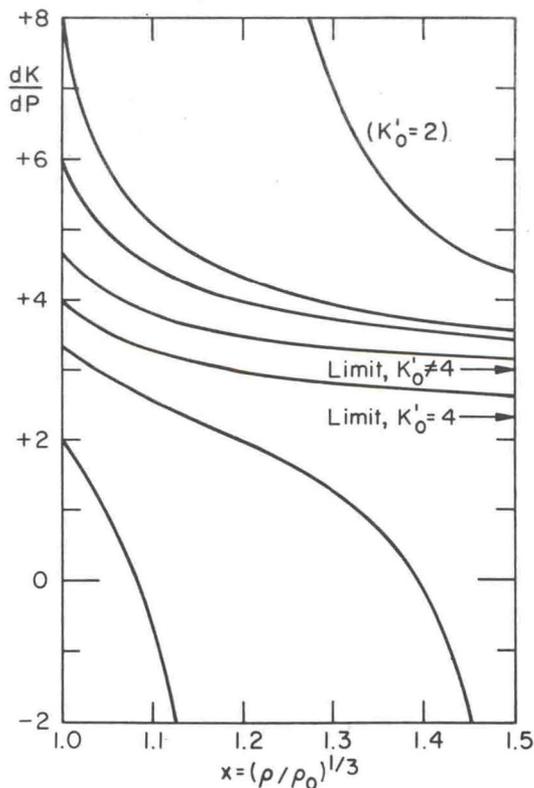


Fig. 3. dK/dP derived from Birch-Murnaghan curve, equation 8, versus compression, for various starting values $K'_0 = (dK/dP)_{x=1}$.

here because the uncertainty of the zero-pressure density is reflected in large uncertainties in the other equation-of-state parameters. Alternative equations have recently been proposed that specifically have the property that dK/dP approaches the high-pressure limit smoothly [Keane, 1954; O. L. Anderson, 1968; Fritz and Thurston, 1970].

For some of the substances with the lowest K_0' in Figure 1, the anomalous results have apparently been exaggerated by an additional effect. Ahrens *et al.* [1969] calculated the Grüneisen ratio from the formula

$$\gamma = \gamma_0 \rho_0 / \rho \quad (9)$$

where γ_0 was taken as the zero-pressure Dugdale-Macdonald value, which, from (4), is

$$\gamma_0 = \frac{2}{3} - \frac{2}{3}\xi \quad (10a)$$

$$= \frac{1}{2}(K_0' - 1) \quad (10b)$$

When K_0' is small, γ can be unreasonably small, and in some such cases γ was arbitrarily set equal to 1. This has the effect of further decreasing the adiabatic value of K_0' . The affected substances are forsterite, fayalite, oligoclase, albitite, and microcline. It is clear that K_0' must have been low in spite of this effect, and that many of the other substances still had very low values of K_0' .

INFERRED CRYSTAL STRUCTURES OF HIGH-PRESSURE PHASES

Because of the slightly lower ρ_0 obtained with the use of the revised seismic equation of state, the possible crystal structures of the high-pressure phases must be reconsidered. Table 2 compares the old and new ρ_0 and Φ_0 to the mixed-oxide densities and Φ 's, and lists the suggested structures, together with their densities. As noted earlier, the densities are close to, or slightly greater than, the mixed-oxide densities. Because of the use of the revised seismic equation of state, the same systematic behavior can now be seen in Φ_0 (see earlier discussion). Since the possible structures were discussed in detail by Ahrens *et al.* [1969], they will be discussed here only as the interpretation differs from theirs. The variety of arguments that may be used to determine likely crystal structures, in particular the estimation of the density of the structure (Table 2) from

the systematics of isostructural compounds discussed more fully by Ahrens *et al.* [1969] and, for example, by Reid and Ringwood [1969].

Olivine group. Although the inferred densities of Twin Sisters dunite, Hortonolite dunite, and fayalite are slightly below the strontium plumbate structure densities, especially for fayalite, they are still comparable, and the fact that density, Φ_0 , and K_0' all change systematically with iron content suggests that these three substances are in the same structure. In contrast, for forsterite and olivinite I, ρ_0 and Φ_0 are higher and K_0' is lower than would be expected from the above trends, so that the closer packed $K_2\text{NiF}_4$ structure is favored for both of these. The concordance obtained between the forsterite and olivinite I (Table 2 and Figure 2) is in striking contrast to the earlier results (Figure 1), and encourages both the above interpretation and the use of the revised seismic equation of state. A further consideration is that the low iron-content olivines do not transform from the olivine to the spinel phase, but transform into a distortion of this phase, the $\beta\text{-Mg}_2\text{SiO}_4$ structure [Ringwood, 1969]. Possibly, anomalous behavior could be expected at the higher pressure transformation from spinel (or $\beta\text{-Mg}_2\text{SiO}_4$) to the 'post-spinel' phases being considered here. It is not clear why the olivinite and Twin Sisters dunite should behave differently since they have similar iron contents, but the reaction kinetics may be sensitive to small differences in the sample porosities [Ahrens *et al.*, 1969].

The 'low-spin' (LS) state structures in Table 2 will be discussed below in conjunction with the other high-iron content compounds.

Hematite, magnetite, spinel. The perovskite structure density for Fe_2O_3 of 5.8 g/cm³ is somewhat higher than the revised density of 5.7 g/cm³, but may still be considered compatible. If allowance is made in the shock analysis for the higher iron content, however (see earlier discussion), the shock density of 5.44 g/cm³ is considerably lower than the perovskite structure density. An alternative is the β -rare earth structure, which would give a density of about 5.56 g/cm³ [Reid and Ringwood, 1969] which is quite compatible with the shock-wave results. By calculating the heat of formation, Gaffney and Ahrens [1970] showed that Fe_2O_3 would only be stable in the perovskite structure if the