

$\text{Fe}^{3+}\text{-O}_6 \approx -80$ kcal/mole (see further discussion below for Fe_2O_3).

$\text{Fe}^{2+}\text{-O}_4 = -88 \pm 5$ kcal/mole

$\text{Fe}^{3+}\text{-O}_6 \approx -110$ kcal/mole

(The quoted uncertainties represent the total spread between values calculated for different compounds.)

The relative covalent energy of stishovite and the silicate spinels is as one would expect. In stishovite each Si^{4+} is bonded to six O^{2-} ions at a distance of ≈ 1.77 Å, whereas in the spinels each Si is bonded to only four O^{2-} at ≈ 1.62 Å. The lower coordination will favor covalent bonding more than the higher. Similarly shorter bonds may also favor covalency. This relation between covalency and coordination also holds for the two iron ions, Fe^{2+} and Fe^{3+} .

The energies for hematite indicate a rather large covalent contribution of about 150 kcal/mole. However, a closer examination of the isostructural Al_2O_3 indicates that such an estimate is much too high. The multipole term in general is due primarily to dipole effects with a smaller effect due to quadrupoles. However, in Al_2O_3 the dipole terms are negligible and the quadrupole terms dominate (HAFNER and RAYMOND (1968)). This is not required by the general corundum lattice but only by the specific one for Al_2O_3 . We should expect therefore that for Fe_2O_3 as for most oxides the dipole terms would be larger than the 25 kcal/mole in Al_2O_3 . This will decrease the covalent contribution (probably to less than 100 kcal/mole).

For the compounds whose heat of formation and structure is unknown we can use the arguments given at the beginning of this section to evaluate the correctness of the proposed structure. If our calculated heat of formation is much less than that of a stable phase we conclude that the structure is not correct in some respect.

AHRENS *et al.* (1969) have proposed several possible shock-induced high-pressure structures for MgSiO_3 and Fe_2O_3 . The high-pressure equation of state as well as zero-pressure pressure-density of MgSiO_3 (≈ 4.25 g/cm³) is poorly known. This severely limits the accuracy of our calculation.

For MgSiO_3 the high-pressure phase proposed for the shocked state was either a perovskite structure or an ilmenite structure. The latter was favored because it gives a density which is closer to that inferred from the shock data. Our calculation for MgSiO_3 (perov-

skite) for a density of 4.25 g/cm³ gives a heat of formation about 100 kcal/mole less than that of the natural phase, enstatite. In addition, Si^{4+} in six-fold coordination with oxygen should contribute about -150 kcal/mole to heat of formation (cf. stishovite) making MgSiO_3 (perovskite) much more stable than MgSiO_3 (enstatite). We know that this can not be true, so we conclude that either this proposed structure or the density is incorrect. A density of 4.07 g/cm³ gives a heat of formation about 20 kcal/mole less than that of enstatite even after including the covalent effects (see fig. 2). A density of ≈ 3.95 g/cm³ gives an enthalpy of formation which would be consistent with the perovskite structure. The reported shock data for enstatite (MCQUEEN and MARSH (1966)) are not sufficiently definitive to exclude this value. Unfortunately no Madelung constant is available for ilmenite so we can not check that structure.

AHRENS *et al.* (1969) also proposed that Fe_2O_3 , which has the corundum structure at low pressure, goes into a perovskite structure at high pressures. We have investigated two cases: the first in which the iron remains trivalent (forming a 3-3 perovskite) and the second in which an electron is transferred from one iron ion to the other yielding one divalent and one tetravalent ion for each pair of Fe^{3+} (forming a 2-4 perovskite (REID and RINGWOOD, 1969)). The latter case leads to some major difficulties which will be discussed after considering the first, simpler, case.

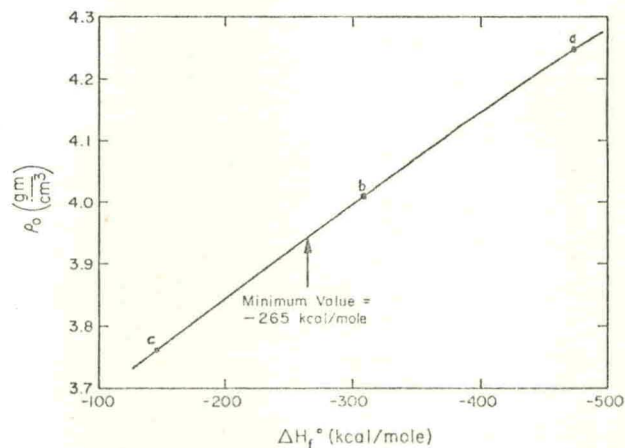


Fig. 2. Relation between calculated ionic enthalpy of formation and density for MgSiO_3 (perovskite). Arrow indicates minimum permissible value for this high pressure phase. Perovskites (a) and (b) are not stable.