

Fe^{3+} disproportionated into Fe^{2+} and Fe^{4+} , and even this possibility was open to doubt. The β -rare earth structure thus appears to be a reasonable candidate for this phase.

The revised densities of spinel (MgAl_2O_4) and magnetite (Fe_3O_4) are still significantly higher than the mixed-oxide densities. For MgAl_2O_4 the calcium ferrite structure density of 4.13 g/cm^3 is close enough to the derived density of 4.03 g/cm^3 to be acceptable. If the correction to the seismic equation of state allowing for the iron content of Fe_3O is made, the derived density of 6.0 g/cm^3 is much less than previously obtained (6.3 g/cm^3), and it does not seem necessary to invoke disproportionation to metallic iron via $3 \text{ Fe}_3\text{O}_4 = \text{Fe} + 4 \text{ Fe}_2\text{O}_3$. Either the calcium ferrite structure ($\approx 5.8 \text{ g/cm}^3$) or disproportionation into $\text{FeO} + \text{Fe}_2\text{O}_3$ (perovskite) ($\approx 5.9 \text{ g/cm}^3$) would not be unreasonable, the latter possibility depending on the interpretation of the high-pressure hematite phase as perovskite.

Electronic spin transitions. It has been suggested [e.g., *Strens*, 1969] that at high pressures and/or in certain coordinations the Fe^{2+} or Fe^{3+} ions (or both) would change their electronic configuration to a low-spin state in which one or more of the unpaired electrons in a higher energy level reverts to a lower energy level to form a 'spin-pair' in that level, with an accompanying decrease in ionic radius. In 6-coordination with O^{2-} , the Fe^{2+} ion has a 'high-spin' (HS) radius of 0.77 \AA and a low-spin (LS) radius of 0.61 \AA . For Fe^{3+} in 6-coordination these are 0.645 \AA (HS) and 0.55 \AA (LS) [*Shannon and Prewitt*, 1969]. The ionic volume changes are thus substantial. The transition to low spin is more favored in octahedral or square planar coordination, and less favored in tetrahedral or cubic eightfold coordination [*Strens*, 1969].

We have considered some possible phase changes of the iron-rich compounds that might involve spin transitions. The crystal structure may be unchanged during the transition, or the changed ratios of cation to anion radii may require an accompanying change in crystal structure.

The simplest structure to consider is hematite. The Fe^{3+} are in distorted octahedral coordination, so it is possible that the Fe^{3+} could undergo a spin transition (Gaffney, private com-

munication) while the corundum structure is retained. (Note that the Fe^{3+} LS ionic radius of 0.55 \AA is very close to the Al^{3+} radius of 0.53 \AA .) However, the density 6.05 g/cm^3 of this phase is considerably higher than that inferred from the shock data, and so it does not seem a very likely possibility.

There are several possibilities for Fe_3O_4 . At low pressure it has an inverse spinel structure, with the Fe^{2+} ions occupying one half of the octahedral sites and Fe^{3+} occupying the tetrahedral sites and the other one half of the octahedral sites. Thus either the Fe^{2+} or the Fe^{3+} occupying the octahedral sites, or both, could change to LS. Another possibility, much more likely, is to form a normal spinel with Fe^{3+} (LS) occupying all of the octahedral sites (the closely analogous FeAl_2O_4 is a normal spinel). The estimated densities of these structures are given in Table 2. Only the density 5.8 g/cm^3 of the inverse spinel with all octahedrally coordinated cations in the LS state approaches the shock density $6.0+ \text{ g/cm}^3$. Another possibility is a transition to the calcium ferrite structure coupled with a spin transition in the Fe^{3+} ions, which would occupy octahedral sites in this structure. The estimated density of this is 6.4 g/cm^3 , which is rather high. Then there are various possible dissociations with FeO (rocksalt, $\rho \approx 5.95$; rocksalt LS, $\rho \approx 7.8$) and Fe_2O_3 (corundum, $\rho = 5.27$; β -rare earth, $\rho = 5.56$; corundum LS, $\rho \approx 6.05$), of which the best possibilities seem to be FeO (LS) + Fe_2O_3 (β -rare earth; $\rho \approx 6.1 \text{ g/cm}^3$) and FeO (rocksalt) + Fe_2O_3 (corundum LS; $\rho \approx 6.0 \text{ g/cm}^3$). It is thus possible that spin transitions could be involved in the Fe_2O_3 and Fe_3O_4 phase changes, with the Fe^{2+} transition being a little more likely, but the evidence is not very strong.

If spin transitions are important in the earth, they are most likely to involve the Fe^{2+} ion in an olivine- or pyroxene-type solid solution. Although the Fe^{2+} sites in the olivine structure are octahedral, it can be seen from Table 2 that the shock-wave results for the dunites and fayalite cannot be explained by a spin transition in the olivine structure, since the density change would be too large for fayalite, but very small for the magnesium-rich olivines. In the strontium plumbate structure the Fe^{2+} is coordinated to 6 oxygen ions at the corners of a trigonal prism. In this coordination the spin pairing will

begin at a lower pressure and will be complete at a higher pressure than in octahedral coordination (Gaffney, private communication). For pyroxenes in the enstatite and ilmenite structures, but not perovskite, Fe^{2+} occupies octahedral sites. Thus olivines or pyroxenes containing some iron could have their densities increased by a few per cent through a spin transition, but the present shock-wave evidence is not sufficient to resolve this.

In summary, it is possible that spin transitions are involved in some of the shock-wave transformations, but there is little suggestion that they would occur in a mantle environment. If they did, the density changes would be a few per cent.

Enstatite, bronzitite. The density 3.93 g/cm^3 obtained here for enstatite is derived from the zero-pressure density of the hugoniot, since the data are so scattered that the iterative method used to calculate the adiabat would not converge. The density is comparable to that of the mixed oxides, and is intermediate between the ilmenite and perovskite structure densities. From the calculated heat of formation, Gaffney and Ahrens [1969] concluded that enstatite could only be stable in the perovskite structure if its density were less than about 3.9 g/cm^3 . While this is probably compatible with the shock data, it is considerably less than the inferred structure density. It is perhaps more reasonable that enstatite should be in the ilmenite structure.

The revised bronzitite density 3.33 g/cm^3 is dramatically less than the 3.74 g/cm^3 inferred by Ahrens *et al.* [1970], and is in fact close to the initial (untransformed) density of bronzitite (3.28 g/cm^3). The value 1.086 Mb of bulk modulus is close to the value 1.05 Mb found by Kumazawa [1969] on a single-crystal sample of a bronzite orthopyroxene of density 3.34 g/cm^3 . Thus, the bronzitite is probably only partially converted to a high-pressure phase. This conclusion is supported by the considerable scatter in the data.

Sillimanite, andalusite. The shock densities 3.94 and 3.84 g/cm^3 are intermediate between the estimated density 3.81 g/cm^3 of Al_2SiO_5 in the pseudobrookite structure and the mixed-oxide density 4.09 g/cm^3 . There is some doubt whether disproportionation into oxides is possible within the time of the shock pulse, and

the shock densities are closer to the pseudobrookite density, so this may be the favored structure. In this structure, both cations are octahedrally coordinated to oxygen.

Feldspars (microcline; albite, $\text{Ab}_{88}\text{An}_{12}$; oligoclase, $\text{Ab}_{81}\text{An}_{19}$; anorthosite, $\text{Ab}_{11}\text{An}_{89} + 10\%$ augite). Candidates for these high-pressure phases are the hollandite structure ($\sim 3.85 \text{ g/cm}^3$) or a disproportionation of the albite ($\text{NaAlSi}_3\text{O}_8$) into jadeite + stishovite and of the anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) into grossular + kyanite + stishovite. The disproportionation of microcline, KAlSi_3O_8 (Table 2), is speculative, since KAlSi_3O_8 is not known in the jadeite structure. The shock densities are intermediate, nearer the disproportionation densities than the hollandite densities. D. L. Anderson [1969] has suggested that the effect of calcium is to decrease the parameter Ψ_0 in the seismic equation of state. If sodium and potassium have the same effect, then the shock densities in Table 2 might be underestimates, but the anomalous results obtained from the original seismic equation of state [Ahrens *et al.*, 1969] (see Figure 1) suggest that this cannot be taken too far.

Westerly granite (quartz 27.5%, microcline 35.4%, oligoclase (An_{86}) 31.4%, mica 3.2%). The shock density 3.90 g/cm^3 is still in good agreement with the estimated density 3.94 g/cm^3 of a stishovite + hollandite mixture, and provides better evidence than the individual feldspar data that the feldspars have transformed to the hollandite structure.

Diabases (W1: augite 45%, labradorite 45%, microcline 3%; Frederick: augite 45%, olivine 1%, labradorite 48%, mica 1%). The shock densities given in Table 2 are extrapolated from those of Ahrens *et al.* [1970] and D. L. Anderson and Kanamori [1968], who used a seismic equation of state intermediate between the former and the present one. Since the presence of some aluminum in a pyroxene composition enhances the transformation to a garnet structure [Ringwood, 1969], we might expect that the augite has transformed to the garnet structure, with a density $\sim 3.65 \text{ g/cm}^3$. If the labradorite transformed to the hollandite structure, the resulting density would be $\sim 3.75 \text{ g/cm}^3$ which is in fairly good agreement with the shock densities. (The presence of calcium may again mean that the shock densities are underestimated.) The hypothesis that the pyrox-