Letter to the editors

Reply to comment by Jackson, Ringwood and McCammon with further observations on wüstite and magnetite

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Received 1983 August 30

We would like to thank Jackson, Ringwood & McCammon (1984) for their comments on our paper on wüstite. They have prompted us to re-examine our data and the data of others. As a result, we would like not only to respond to their comments on our paper but also to discuss some additional observations that bear on the subject.

In Fig. 1 we give the curves that are pertinent to this discussion: (1) the shock Hugoniot of magnetite, (2) the shock Hugoniot of Fe$_{0.94}$O, and (3) the 25°C isotherm of Fe$_{0.75}$O calculated by us in our original paper (Liu, Shen & Bassett 1982, fig. 4). We calculated the value of $x$ from a series of isotherms of Fe$_x$O and the shock Hugoniot of Fe$_{0.94}$O by correcting for the differences in temperature and iron content. We carefully stated the sources of temperature (7000 K) and expansivity ($3.3 \times 10^{-5}$ deg$^{-1}$) used for Fe$_{0.75}$O 'wüstite'.

Jackson et al. have calculated a hypothetical family of 'Hugoniot' curves from our Fe$_{0.75}$O isotherm for comparison with the shock Hugoniot curve of magnetite. They concluded that the discrepancy between their calculated hypothetical Fe$_{0.75}$O curve and the magnetite Hugoniot provides 'compelling evidence that Liu et al. have overestimated the high-pressure densities of the proposed very non-stoichiometric wüstites...'. However, to calculate their hypothetical curve from our isotherm, they introduce the Mie–Grüneisen relation and four new parameters, the mean initial density, $\rho'_0$; the Grüneisen parameter, $\gamma_0$; the exponent, $n$; and the transition energy $E_{TR}$ without giving any information about the source of the values they used for these parameters (except $\rho'_0$, which may not be appropriate for the non-stoichiometric Fe$_{0.75}$O 'wüstite'). As a result, we are unaware of any errors or incorrect assumptions that we might have made in our original calculations.

Jackson et al. comment that the bulk modulus we give for Fe$_{0.75}$O ($K_0 = 515$ kbar) is only 32 per cent of the bulk modulus of magnetite itself and is 'implausibly low' relative to materials such as MgO, Al$_2$O$_3$, SiO$_2$ and MgSiO$_3$ (perovskite). We have never considered the very non-stoichiometric wüstite to be like magnetite or any other oxides. In fact, its very difference is what makes it an unusual and interesting material to study.

Even if our calculations may have caused us to overestimate the density of the very non-stoichiometric wüstites at high pressures, we do not agree with Jackson et al. that this invalidates our main point that the so-called phase transition observed in the shock Hugoniot
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Figure 1. Comparison of shock Hugoniot of wüstite (Fe$_{0.94}$O) with that of magnetite (Fe$_{0.75}$O). Also shown is the 25°C isotherm of Fe$_{0.75}$O 'wüstite' proposed by Liu et al. (1982). Point A is based on the density calculated by subtracting off the density of iron from that of Fe$_{0.94}$O to give the density of Fe$_{0.75}$O.

can be interpreted as a change in stoichiometry, as we suggested in our original paper. As a matter of fact, recent static experiments of Shen, Bassett & Liu (1983) at 560 kbar and 275°C for 72 hr and 300°C for 67 hr have yielded a non-stoichiometric wüstite with $a_0 = 4.299$ Å (approximately Fe$_{0.93}$O). The effect of a pressure of 560 kbar in a static experiment may be comparable to or even greater than that of 700–800 kbar in a shock experiment on oxides or silicates.

We propose to present a new interpretation of the Hugoniot data of magnetite and wüstite as follows. Fig. 1 shows all the available shock data of magnetite and wüstite (see references in Jackson et al.). The wüstite Hugoniot has a higher density than the magnetite curve as one would expect. The two curves, however, converge at 2.4 Mbar as originally pointed out by Liu (1982). This is a peculiar trend, and two possible explanations may be proposed. First, the Hugoniot data of Fe$_{0.94}$O in the vicinity of 2 Mbar may be in error, especially if one compares it with all other Hugoniots of the relevant materials of the Earth's core as shown in fig. 4 of Liu (1982). Secondly, there may be yet another phase transition in magnetite between 1.4 and 3.0 Mbar (dashed line in Fig. 1). In this interpretation the Hugoniot point near 3 Mbar would lie beyond that phase transition and belong to the high-
pressure phase. If the wüstite point at 2.3 Mbar represents a mixture of magnetite and metallic iron, then the magnetite curve should pass through A in Fig. 1. Point A is based on the density calculated by subtracting off the density of iron (Al’tshuler, Bakanova & Trunin 1962; McQueen et al. 1970) from the density of wüstite (Jeanloz & Ahrens 1980) to give the density of magnetite. Additional measurements by the shock method need to be made before these questions can be resolved.

In conclusion, we wish to emphasize that in making our argument on change in stoichiometry as an explanation for the ‘phase transition’ in the Hugoniot of Jeanloz & Ahrens, we wanted only to suggest an alternative explanation. We undertook the research in part because we found the B1—B8 transition proposed by Jackson & Ringwood (1981) inadequate. It is well known that the structural relationship between B1 (rocksalt) and B8 (niccolite) parallels that between B3 (sphalerite) and B4 (wurtzite) and that between A1 (fcc) and A3 (hcp). If ideal values for the \( c/a \) ratio and \( u \) parameter for B8, B4 and A3 are assumed, these structures have the same packing index as B1, B3 and A1 respectively (e.g. Liu 1981). It is the departure from ideal values of the \( c/a \) ratio and \( u \) parameter in these structures that makes them slightly more close-packed than B1, B3 and A1. The largest volume change associated with the B1—B8 transition known is only 2–3 per cent. Yet, the volume (or density) change in the Hugoniot of FeO,\( _9\)O claimed by Jackson & Ringwood (1981) is on the order of 10–25 per cent. Clearly more careful work on this important material is needed in order to clarify some of the inconsistencies mentioned above.

References


