

On the (γ , ϵ , l) Triple Point of Iron and the Earth's Core

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Summary

The triple point (γ , ϵ , l) of iron has been located at 0.94 ± 0.20 Mbar and $2970 \pm 200^\circ\text{C}$ by means of extrapolations of recent data on the melting temperature of the γ phase of iron to 200 kbar and of the revised γ – ϵ phase boundary. The slope for the ϵ – l boundary is calculated to be 1.4 ± 0.3 deg/kbar at the triple point. For a core composition dominated by iron and for all realistic estimates of the slope of the γ – ϵ phase boundary, the ϵ phase appears to be the appropriate iron phase for the inner core. Using the linear relationship between melting temperature and volume compression of the solid phase proposed by Kraut and Kennedy, the melting temperature of the ϵ iron at a pressure corresponding to the mantle–core boundary is calculated to be $3500 \pm 200^\circ\text{C}$ and that at a pressure corresponding to the inner–outer core boundary to be $4650 \pm 500^\circ\text{C}$. The present calculated melting temperature difference throughout the outer core is more than twice as great as that estimated by Higgins and Kennedy who have not considered the effect of the γ – ϵ transformation on the melting curve. Hence, the obstacle preventing adiabatic convection in the liquid outer core has been removed without resort to the suggestions of other investigators.

Introduction

Geophysicists are interested in the phase diagram of iron because the inner core is believed to be primarily composed of solid iron in equilibrium with the adjacent liquid outer core (see, e.g. Birch 1972). Knowledge of the composition and temperature of the core governs the hypotheses of the origin, formation, and evolution of the Earth and other planets as well.

Iron displays two known triple points, (α , γ , ϵ) and (δ , γ , l), with a third hypothetical triple point of (γ , ϵ , l) in the temperature–pressure plane; α is the standard bcc phase of iron, γ the fcc phase, ϵ the hcp phase, δ the high temperature bcc phase, and l the liquid phase (see Fig. 1 for a general review). Of these three triple points, only the hypothetical one, (γ , ϵ , l), has direct relevance to the core. Our lack of knowledge of this triple point has led many previous investigators to ignore the complications of Fig. 1 in extrapolating the fusion of iron to pressures corresponding to core conditions (e.g. Simmons 1953; Strong 1959; Knopoff & MacDonald 1960; Boyd & England 1963; Sterrett, Klement & Kennedy 1965; Higgins & Kennedy 1971; Leppaluoto 1972; Boschi 1974).

Birch (1972) first considered the effect of the γ – ϵ transformation in detail. He

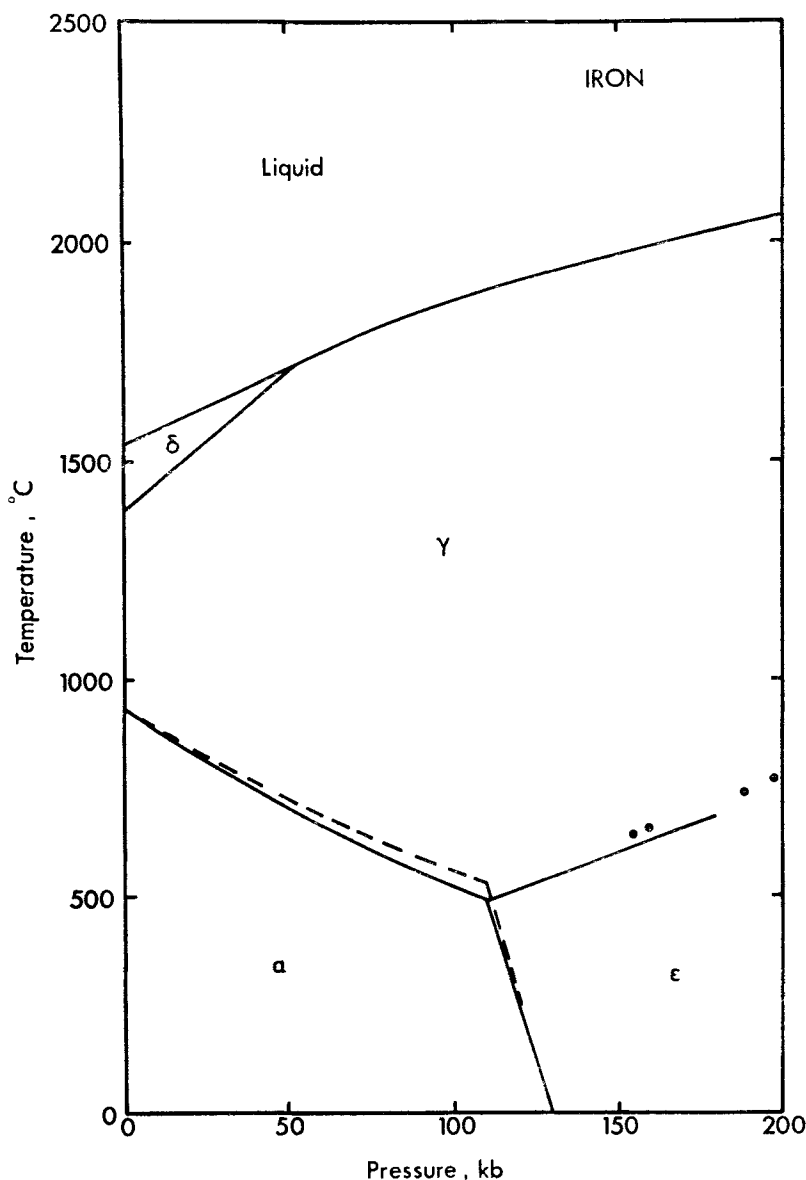


FIG. 1. Phase diagram of iron to 200 kilobars. After Liu & Bassett (1975).

discussed two rather arbitrary locations of the (γ , ϵ , I) triple point of iron: (1) at about 5100°K and 4 Mbar and (2) at about 3800°K and 1 Mbar. The former implies that the inner core consists of γ iron and the latter that the inner core consists of ϵ iron. Without new evidence, Birch (1972) concluded that neither of these two alternatives (nor the third that the triple point lies somewhere within the pressure range of the outer core) can be dismissed.

Utilizing new data for the γ - ϵ phase boundary, for the (δ , γ , I) triple point (Strong *et al.* 1973) and for the fusion curve of iron up to 200 kbar (Liu & Bassett 1975), we wish in this paper to estimate the co-ordinates (P , T) of the (γ , ϵ , I) triple point and the fusion curve of the ϵ iron at core conditions.

The γ - ε phase boundary

The absence of direct observation of the (γ , ε , l) triple point restricts discussion to indirect estimates based on the intersection of the γ - ε and γ - l phase boundaries (see Fig. 1). One would generally expect the calculation of a solid-solid phase boundary (e.g. γ - ε) to be more straightforward than calculation of a fusion curve (e.g. γ - l), but this is not the case for iron.

The initial slope of the γ - ε boundary at the (α , γ , ε) triple point was first estimated by Takahashi & Bassett (1964) to be 2 ± 1 deg/kbar in agreement with Bundy's (1965) measured value of 2.8 deg/kbar. Birch (1972) adopted the 'smaller' value (see Table 1 of his paper). This preference has prevented Birch from choosing among the alternatives mentioned in the previous section (see also comments of Strong *et al.* 1973). It should be pointed out here, however, that the small value estimated by Takahashi & Bassett (1964) is apparently due to an error in their calculation. Using their estimated values of slope for the α - γ (-2.6 deg/kbar) and α - ε (-93.5 deg/kbar) phase boundaries and those of volume changes for α - γ (-0.16 cm³/mole) and α - ε (-0.20 cm³/mole), the calculated value for the slope of the γ - ε phase boundary should be 0.7 ± 0.4 deg/kbar instead of 2 ± 1 deg/kbar.

More elaborate measurements on the volume change associated with the α - ε phase transition was reported by Mao, Bassett & Takahashi (1967). They gave a value of -0.34 ± 0.01 cm³/mole. When this value is used in conjunction with the estimates made by Takahashi & Bassett (1964) for the other parameters, the slope for the γ - ε phase boundary is calculated to be 3.1 ± 0.5 deg/kbar. This revised value is in good agreement with the measured value reported by Bundy (1965) and is almost identical to the high value reported by Liu & Bassett (1975). The present calculated slope, 3.1 ± 0.5 deg/kbar, is not sensitive to the estimated values of the slopes for the α - γ and α - ε boundaries. For instance, slopes of -2.3 deg/kbar for the α - γ boundary and -35 ± 15 deg/kbar for the α - ε boundary (Bundy 1965) yield a calculated slope of the ε - γ boundary of 3.0 ± 0.5 deg/kbar. Thus, a value of 3.0 ± 0.5 deg/kbar is the best estimate we can make for the slope of the γ - ε phase boundary.

The γ - ε phase boundary was found to be linear up to 200 kbar (Bundy 1965; Liu & Bassett 1975). Since the slope of the γ - ε boundary is governed by the Clapeyron equation, deviations from linearity arise from the temperature and pressure dependence of the volume (ΔV) and entropy (ΔS) differences. Only in the rare cases where marked curvature exhibits, solid-solid phase boundaries are generally linear as functions of pressure and temperature. We are making the assumption that the linearity of the γ - ε phase boundary is valid in the present study.

The volume difference (ΔV) between the metastable α iron and the ε iron is nearly a constant in the pressure range between 130 and 300 kbar and room temperature according to the semi-empirical equations of state of Andrews (1973). Since γ iron is less compressible than α iron, we expect that ΔV between the γ and ε phases is likely to be also independent of pressure in the range between 130 and 1000 kbar. Thus, the entropy difference (ΔS) between the γ and ε phases is not sensitive to the changes of pressure and temperature either.

The (γ , ε , l) triple point

Having estimated the slope of the γ - ε boundary at the triple point (α , γ , ε) and justified its linear extrapolation to pressures of ca 1000 kbar, we turn to the extrapolation of the γ - l boundary determined up to 200 kbar by Liu & Bassett (1975). Following Birch's (1972) suggestion that the linear law between the melting temperature and volume proposed by Kraut & Kennedy (1966) is probably a good approxi-

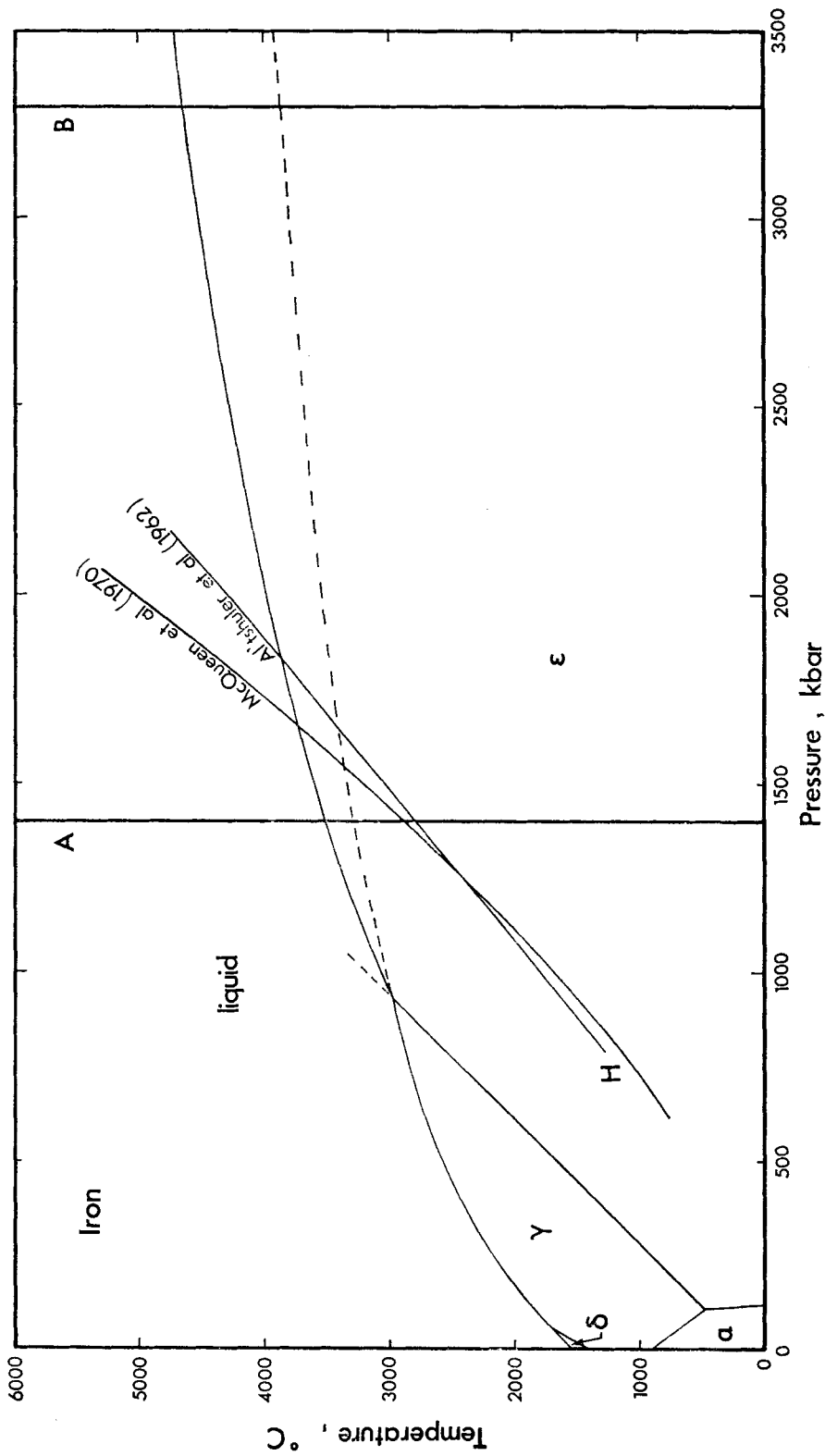


FIG. 2. Estimated phase diagram of iron to core conditions. The (γ , ϵ , δ) triple point is estimated to be 940 ± 200 kbar and 3000 ± 200 °C; A indicating the pressure corresponding to the mantle-core boundary, B to the inner-outer core boundary, and H the Hugoniot temperature-pressure curve of Al'tshuler *et al.* (1962) and of McQueen *et al.* (1970).

mation for extrapolating the melting temperatures to high pressure, Liu & Bassett (1975) have fitted their experimental data to the linear law. Among the four equations reported by Liu & Bassett (1975) in their Fig. 6, the author prefers the following one,

$$T_m = 1506(1 + 4.16 |\Delta V/V_{\epsilon, 0}|) \quad (1)$$

for the purpose of extrapolating the melting temperature of γ iron. The reasons are: (1) the remaining three are based on or influenced by data of the α iron; (2) even though the compression data for the γ iron are not available, one would expect that the γ and ϵ phases might behave similarly under compression since each iron atom is surrounded by 12 nearest-neighbours in both phases; (3) the isothermal compression of the ϵ phase has been measured to pressures in excess of 300 kbar (Mao *et al.* 1967) and its merits have been reviewed recently by Andrews (1973). The compression curve for the ϵ iron in the form of the Murnaghan equation reported by Mao *et al.* (1967) can be rewritten as

$$|\Delta V/V_{\epsilon, 0}| = 1 - \left(1 + \frac{P}{325}\right)^{-0.196} \quad (2)$$

where P is the pressure in kilobars. Combining equations (1) and (2), one can readily plot the γ - l boundary in a P - T diagram (see Fig. 2). This melting curve intersects the linear γ - ϵ boundary at 935 kbar and 2966 °C, which almost coincides with one of Birch's (1972) estimates. In considering various uncertainties, the triple point of (γ , ϵ , l) can be best estimated to be at 0.94 ± 0.20 Mbar and 2970 ± 200 °C.

Since the estimated triple point of (γ , ϵ , l) is far below the pressure corresponding to the mantle-core boundary (1.4 Mbar), any attempt to locate this triple point in the inner core requires an unrealistic change in the slope of the γ - ϵ phase boundary. If the core is mainly composed of iron, we conclude that the solid inner core is in the ϵ phase.

The ϵ - l boundary

Estimation of the initial slope dT/dP of the ϵ - l boundary requires knowledge of the slopes of the γ - l and γ - ϵ phase boundaries at the (γ , ϵ , l) triple point. We have assumed

Table 1

Calculated thermodynamic constants at the triple point of (γ , ϵ , l), $P = 935$ kbar, $T = 2966$ °C.

Transition	ΔV (cm ³ /mole)	ΔS (cal/deg. mole)	dT/dP (deg/kbar)
$\gamma \rightarrow \epsilon$	-0.18 ^a	-1.43 ^b	3.0 ^c
$\epsilon \rightarrow l$	0.25	3.61	1.7 ^b
$l \rightarrow \gamma$	-0.07 ^b	-2.18 ^d	0.8 ^e
	$\Sigma = 0$	$\Sigma = 0$	

(a) Calculated from the data of volume differences at the triple point of (α , ϵ , γ) in the present work and assumed to be independent of pressure and temperature within the interested region.

(b) From other data in the table using the Clapeyron equation.

(c) This work.

(d) From Strong *et al.* (1973) assuming independent of P and T .

(e) From equation (3) of this work.

that the γ - ϵ boundary has a constant slope of 3.0 deg/kbar and the slope of the γ - l boundary can be evaluated from equations (1) and (2) as

$$\frac{dT_m}{dP_{\gamma-l}} = \frac{[6265] \times 0.196}{325} \left(1 + \frac{P}{325}\right)^{-1.196} \quad (3)$$

Equation (3) yields a slope of 0.8 deg/kbar for the γ - l boundary at the triple point. Other data required to compute the ϵ - l boundary are listed in Table 1, which gives the initial slope for the ϵ - l boundary to be 1.7 deg/kbar. This value should probably be regarded as the upper limit since, in Table 1, one of the assumptions that ΔS is constant used to evaluate the volume difference (ΔV) between the γ and liquid phases at the (γ , ϵ , l) triple point would lead to an overestimate of the value of ΔV (see e.g. Slater 1939; & Clark 1963). Various considerations suggest that the initial slope of the γ - l boundary can be best estimated to be 1.4 ± 0.3 deg/kbar. Using this slope, the constant in brackets in the right-hand side of equation (3) can be evaluated for the ϵ - l boundary, and a form of the Kraut-Kennedy law can be constructed for the fusion curve of the ϵ iron as

$$T_m = 228(1 + 51.4 |\Delta V/V_{\epsilon, ol}|) \quad (4)$$

Equation (4) has also been plotted in Fig. 2 and it intersects the mantle-core boundary at c. 3500 °C with a slope of 1.0 deg/kbar and the inner-outer core boundary at c. 4650 °C with a slope of 0.4 deg/kbar.

Shock-wave Hugoniot of iron

Early shock-wave studies (Bancroft, Peterson & Minshall 1956) on iron revealed a single kink in the Hugoniot curve at ca 130 kbar which was associated with the α - ϵ phase boundary. Subsequent work by Al'tshuler *et al.* (1958) and McQueen & Marsh (1960) to pressures of 4.9 and 1.7 Mbar, respectively failed to reveal any further changes in slope of the particle *vs* shock velocity trajectory. More recent investigation by Al'tshuler, Bakanova & Trunin (1962) and McQueen *et al.* (1970), however, showed that the slope of the Hugoniot varies slightly in the vicinity of 1.9 and 1.6 Mbar respectively. This has been attributed to phase changes in iron from ϵ to γ , from solid to liquid, or both by McQueen *et al.* (1970).

Using the Hugoniot pressure-temperature data tabulated by Birch (1972), we also plot the Hugoniot data of Al'tshuler *et al.* (1962) and McQueen *et al.* (1970) in Fig. 2. Their data intersect the fusion curve of the ϵ iron computed from equation (4) at c. 1.85 and 1.65 Mbar, respectively. Although this might be quite fortuitous, especially when the experimental scatter of the Hugoniot data and uncertainties of the extrapolation of the fusion curve are taken into consideration, it does appear to strengthen the possibility that melting is responsible for the curvature in the Hugoniot in the pressure range 1.5-2.0 Mbar.

Temperature of the core

The motivation of the present work is neither to the precise location of the (γ , ϵ , l) triple point, nor the determination of precise melting temperatures of iron at pressures corresponding to the mantle-core and the inner-outer core boundaries. We are interested instead in what the most likely phase of iron is at the P-T conditions of the solid inner core and in suggesting more appropriate methods for estimating the melting temperature of iron at core conditions. Strictly speaking, the inner-outer core boundary may well represent the solid-liquid phase boundary in a multi-com-

ponent system dominated by iron. Nevertheless the study of the phase diagram of pure iron, at present, provides the basic framework for an understanding of the thermal regime of the core.

The recent work concerning this subject by Higgins & Kennedy (1971) and Kennedy & Higgins (1973a, b) has been criticized by several authors on various grounds. Birch (1972) accepts their use of the melting law but stresses that the implications of the complicated phase diagram of iron have been overlooked. Birch's effort in clarifying the phase diagram of iron was hindered by his difficulty in choosing among the various alternatives for the location of the (γ , ϵ , I) triple point. However, his estimates for the melting temperature of iron at the mantle-core boundary and at the inner-outer core boundary are within 200° of those arising from the present study. In view of the uncertainties the estimates of the present work are in excellent agreement with Birch's.

Verhoogen (1973) has discussed the inadequacy of the melting data (Sterrett *et al.* 1965) upon which the Higgins & Kennedy extrapolation is based. He also doubts the validity of the linear dependence of melting temperature on compression and points out that Leppaluoto's (1972) significant structure theory calculations yield quite different results. Frazer (1973) pointed out that the relevant thermal properties of the core (coefficient of thermal expansion and specific heat at constant pressure) are not sufficiently well known for reliable estimation of the adiabatic temperatures of the core. Further, he claims that the methods used by Higgins & Kennedy to estimate the adiabatic temperature gradient are inappropriate (see also Jacobs 1973). Boschi (1974) obtained quite different results from those of Higgins & Kennedy on the basis of a generalized Lindermann melting law, which carries a quadratic term in the melting temperature and volume relationship. In conclusion, all of these authors have raised objections to Higgins & Kennedy's work and produced solutions which circumvent the difficulties for convection in the liquid outer core raised by Higgins and Kennedy, but they have all based their arguments on the low-pressure α phase of iron (with the exception of Frazer).

We could adopt the generalized Lindemann law for computing the melting temperature of the ϵ iron in core conditions. It is expected that the melting temperatures thus obtained would be a few thousand degrees higher than the present estimates; but this does not necessarily mean that the estimates from the generalized law are close to the reality.

In conclusion, we emphasize that any attempts to estimate the melting temperature of iron at core conditions must take the (γ , ϵ , I) triple point into account. The consequence of considering this triple point is that the melting temperatures of iron at core conditions thus estimated would be a few hundred degrees greater than those estimated from the low pressure α iron, and what is more, the melting temperature gradient throughout the outer core is greater than those obtained without consideration of the triple point. For instance, the melting temperature difference throughout the outer core calculated in the present study is *c.* 1150° with an average gradient of *ca.* $0.6^\circ/\text{kbar}$. The former figure is more than twice as that estimated by Higgins & Kennedy (1971) and is equivalent to the temperature difference of 1250° required for the outer core to convect adiabatically (Kennedy & Higgins 1973b). The average temperature gradient is $3/4$ of that obtained by Boschi (1974) based on the generalized Lindermann law. Hence, the suggestions by various authors for overcoming the difficulties for convection in the outer core appear unnecessary.

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