



ELSEVIER

Earth and Planetary Science Letters 195 (2002) 91–98

EPSL

www.elsevier.com/locate/epsl

# Composition and temperature of the Earth's core constrained by combining ab initio calculations and seismic data

D. Alfè<sup>a,b</sup>, M.J. Gillan<sup>b,\*</sup>, G.D. Price<sup>a</sup>

<sup>a</sup> *Research School of Geological and Geophysical Sciences, Birkbeck College and University College London, Gower Street, London WC1E 6BT, UK*

<sup>b</sup> *Physics and Astronomy Department, University College London, Gower Street, London WC1E 6BT, UK*

Received 11 May 2001; received in revised form 21 September 2001; accepted 26 October 2001

## Abstract

It is shown how ab initio techniques based on density functional theory can be used to calculate the chemical potentials of the leading candidate impurity elements (S, O and Si) in the Earth's solid inner core and liquid outer core. The condition that these chemical potentials be equal in the solid and liquid phases provides values for the ratios of the impurity mol fractions in the inner and outer core. By combining the estimated ratios with ab initio values for the impurity molar volumes in the two phases, and demanding that the resulting density discontinuity across the inner-core boundary agree with free-oscillation data, we obtain estimates for the concentrations of S, O and Si in the core. The results show that O partitions much more strongly than S and Si from solid to liquid, and indicate that the presence of O in the core is essential to account for seismic measurements. We suggest that if compositional convection drives the Earth's magnetic field, then the presence of O may be essential for this compositional convection. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* chemical composition; core; seismology; simulation

Ever since the discovery of the Earth's core 90 years ago, its composition and temperature have been controversial. The work of Birch [1] and others in the 1950s made it clear that the core consists mainly of iron with a minor fraction of nickel, but that unidentified light impurities must also be present, since the density of the core is significantly lower than that of iron: modern estimates [2–5] indicate that the outer core is lower

in density by 5–10%, and the inner core by 2–3%. The main obstacle to further progress has been the lack of reliable thermodynamic data for the relevant iron alloys under core conditions, and it has been stressed recently [6] that ab initio calculations of thermodynamic functions can make an important contribution. We show here how ab initio calculations of the chemical potentials of the main impurity candidates can provide strong new constraints on both the composition and the temperature of the core, and we present numerical values both for the impurity mol fractions in the inner and outer core and for the temperature at the inner-core/outer-core boundary (ICB).

\* Corresponding author. Fax: +44-20-7679-1360.  
E-mail address: m.gillan@ucl.ac.uk (M.J. Gillan).

Cosmochemical abundances of the elements, combined with models of the Earth's history, limit the possible impurities to a few candidates [2]. The most often discussed are S, O and Si, and we shall confine ourselves to these three here, though C and H have sometimes been proposed [2]. Our strategy for constraining the impurity fractions and the temperature is based on the fact that the solid inner core has grown from the liquid outer core over many hundreds of millions of years, so that the solid and liquid should be in thermodynamic equilibrium at the ICB. This implies that the chemical potentials of Fe and of each impurity must be equal on the two sides of the ICB.

If the core consisted of pure Fe, equality of the chemical potential (Gibbs free energy in this case) would tell us only that the temperature at the ICB is equal to the melting temperature  $T_m$  of Fe at the ICB pressure of 330 GPa. With impurities present, equality of the chemical potentials for each impurity element imposes a relation between the mol fractions in the liquid and the solid, so that with S, O and Si we have three such relations. But these three relations must be consistent with the accurate values of the mass densities in the inner and outer core deduced from seismic and free-oscillation data [7–9]. We shall show that ab initio results for the densities and chemical potentials in the liquid and solid Fe/S, Fe/O and Fe/Si alloys determine with useful accuracy the mol fraction of O and the sum of the S and Si mol fractions in the outer and inner core, as well as giving the temperature at the ICB.

The chemical potential  $\mu_X$  of a solute X in a solid or liquid solution is conventionally expressed as  $\mu_X = \mu_X^\dagger + k_B T \ln a_X$ , where  $\mu_X^\dagger$  is a constant and  $a_X$  is the activity [10]. To reflect the fact that  $a_X$  becomes equal to the mol fraction  $c_X$  in the dilute limit  $c_X \rightarrow 0$ , it is common practice to write  $a_X = \gamma_X c_X$ , where the activity coefficient  $\gamma_X$  has the property  $\gamma_X \rightarrow 1$  as  $c_X \rightarrow 0$ . The chemical potential can therefore be expressed as:

$$\mu_X = \mu_X^\dagger + k_B T \ln(\gamma_X c_X) = \mu_X^\dagger + k_B T \ln \gamma_X + k_B T \ln c_X \quad (1)$$

which we rewrite as:

$$\mu_X = \tilde{\mu}_X + k_B T \ln c_X \quad (2)$$

where  $\tilde{\mu}_X = \mu_X^\dagger + k_B T \ln \gamma_X$ . It is helpful to focus on the quantity  $\tilde{\mu}_X$  for two reasons: first, because it is a convenient quantity to obtain by ab initio calculations [6]; second, because at low concentrations the activity coefficient  $\gamma_X$  will deviate only weakly from unity by an amount proportional to  $c_X$ , and by the properties of the logarithm the same will be true of  $\tilde{\mu}_X$ .

By Eq. 2, equality of the chemical potentials  $\mu_X^l$  and  $\mu_X^s$  in coexisting liquid and solid (superscripts l and s, respectively) then requires that:

$$\tilde{\mu}_X^l + k_B T \ln c_X^l = \tilde{\mu}_X^s + k_B T \ln c_X^s \quad (3)$$

or equivalently:

$$c_X^s / c_X^l = \exp [(\tilde{\mu}_X^l - \tilde{\mu}_X^s) / k_B T] \quad (4)$$

This means that the ratio of the mol fractions  $c_X^s$  and  $c_X^l$  of X in the solid and liquid solution is determined by the liquid and solid thermodynamic quantities  $\tilde{\mu}_X^l$  and  $\tilde{\mu}_X^s$ . Although liquid–solid equilibrium in the Fe/S and Fe/O systems has been experimentally studied up to pressures of around 60 GPa [11,12], there seems little prospect of obtaining experimental data for  $\tilde{\mu}_X^l - \tilde{\mu}_X^s$  for Fe alloys at the much higher ICB pressure. However, we have shown recently that the fully ab initio calculation of  $\tilde{\mu}_X^l$  and  $\tilde{\mu}_X^s$  is technically feasible [6].

Our ab initio methods employ density functional theory (DFT) implemented using pseudopotentials and plane-wave basis sets (for a non-technical review, see e.g. [13]). Virtually all ab initio work on Earth's core materials has been based on DFT, and recent work indicates that with the ultra-soft type of pseudopotential employed here the pseudopotential/plane-wave technique has essentially the same accuracy as all-electron methods such as FLAPW (full-potential linearised augmented plane-wave) or PAW (projector augmented wave) when applied to iron [14,15]. DFT calculations using the generalised-gradient approximation (GGA) for exchange-correlation energy [16] have been shown to give very accurate

results for the low-pressure elastic, vibrational and magnetic properties of body-centred cubic (b.c.c.) Fe, the b.c.c.  $\rightarrow$  h.c.p. (hexagonal close packed) transition pressure, and the pressure–volume relation for h.c.p. Fe up to over 300 GPa [15,17,18]; they also appear to give good predictions of the phonon density of states of h.c.p. Fe up to Earth’s core pressures [19]. The present calculations were performed with the VASP code [20], which is exceptionally stable and efficient for metals. Technical details of the pseudopotentials, plane-wave cut-offs etc. for Fe and the Fe/S and Fe/O alloys are the same as in our previous work [21,22]; the pseudopotentials and cut-off for the Fe/Si system are based on the same principles. The GGA of Perdew et al. [16] is used throughout.

Our techniques for making ab initio calculations of chemical potentials and densities in liquid and solid alloys have been reported earlier [6], and we summarise them only briefly here. The chemical potential  $\mu_X$  of chemical component X can be defined as the change of Helmholtz free energy when one atom of X is introduced into the system at constant temperature  $T$  and volume  $V$ . In ab initio simulation, it is awkward to introduce a new atom, but the awkwardness can be avoided by calculating  $\tilde{\mu}_X - \tilde{\mu}_{\text{Fe}}$ , which is the free energy change  $\Delta F$  when an Fe atom is replaced by an X atom. For the liquid, this  $\Delta F$  is computed by applying the technique of ‘thermodynamic integration’ [23] to the (hypothetical) process in which an Fe atom is continuously transmuted into an X atom, as described in [6]. Results for  $\mu_S$  for liquid Fe/S at  $T=7000$  K and  $P=370$  GPa were reported earlier [6]. We have now performed calculations for O and Si at the same thermodynamic condition, and our  $\mu_X$  results for all three impurities in liquid Fe/X are summarised in Table 1. Technical details of our ab initio molecular dynamics simulations on liquid Fe/O and Fe/Si were similar to those of [6]: simulations were performed at constant volume and temperature on systems of 64 atoms; the duration of the simulations after equilibration was typically 6 ps in order to reduce statistical errors to an acceptable level; the number of thermodynamic integration points used in transmuting Fe into X was 3, and

Table 1

Calculated chemical potentials (eV units) of impurities in the Earth’s liquid outer core and solid inner core

Impurity	$\mu_X^s - \mu_X^l$	$\lambda_X^l$	$\lambda_X^s$
Sulphur	$0.25 \pm 0.04$	$6.15 \pm 0.2$	$5.9 \pm 0.2$
Silicon	$0.05 \pm 0.02$	$3.6 \pm 0.1$	$2.7 \pm 0.1$
Oxygen	$2.6 \pm 0.2$	$3.25 \pm 1.3$	

Chemical potential  $\mu_X = \tilde{\mu}_X + k_B T \ln c_X$  of impurity X is represented at low mol fraction  $c_X$  by the linearised form  $\tilde{\mu}_X = \mu_X^\dagger + \lambda_X c_X$ , with superscripts l and s indicating liquid and solid.

we carefully checked the adequacy of these numbers of points. To account for the dependence of  $\tilde{\mu}_X$  on mol fraction  $c_X$ , we report it in the low-concentration regime as  $\tilde{\mu}_X = \mu_X^\dagger + \lambda_X c_X$ . As mentioned after Eq. 2, this representation of  $\tilde{\mu}_X$  reflects the weak deviation of the activity coefficient  $\gamma_X$  from unity at low  $c_X$ . Table 1 reports values of  $\mu_X^\dagger$  and  $\lambda_X$ , with superscripts l and s indicating liquid and solid.

The chemical potential difference  $\tilde{\mu}_X - \tilde{\mu}_{\text{Fe}}$  of X dissolved substitutionally in h.c.p. Fe is readily computed in the low-concentration limit, assuming the harmonic approximation for lattice vibrations. The Helmholtz free energy difference  $\Delta F \equiv \Delta U - T\Delta S$  when an Fe atom is replaced by an X atom is  $\Delta U$ , the difference of total energies of the non-vibrating equilibrium systems, minus  $T\Delta S$ , where  $\Delta S$  is the difference of vibrational entropies, which is readily obtained from the ab initio vibrational frequencies of the Fe/X and Fe systems. We shall see that the low-concentration limit suffices for the O impurity, but not for S and Si. To obtain the term in  $\tilde{\mu}_X - \tilde{\mu}_{\text{Fe}}$  that is linear in  $c_X$ , we employ calculations on the Fe system containing nearest-neighbour pairs of X atoms, as described earlier [6]. All the indications are that the harmonic approximation is good for S and Si. However, it is very poor for substitutional O, because the small size of the O atom gives it a large vibrational freedom [24]. The use of thermodynamic integration to account for the large anharmonicity of O in calculating  $\tilde{\mu}_O - \tilde{\mu}_{\text{Fe}}$  was reported recently [24]. Our ab initio results for  $\mu_X$  for the Fe/X solid solutions, again for 7000 K and 370 GPa, are also shown in Table 1, where we report values of  $\mu_X^\dagger$  and  $\lambda_X$  in the linearised ex-

pansion  $\tilde{\mu}_X = \mu_X^\dagger + \lambda_X c_X$ . (Technical details of the calculations on the solid Fe/Si alloy were the same as those of [6] on Fe/S; specifically, calculations were performed on systems of 64 atoms and the phonons were calculated using our implementation of the small displacement method [25].)

These results reveal a major qualitative difference between O and the other two impurities: For S and Si,  $\tilde{\mu}_X$  is almost the same in the solid and the liquid, the differences being at most 0.3 eV, i.e. markedly smaller than  $k_B T \approx 0.5$  eV; but for O the difference of  $\tilde{\mu}_X$  between solid and liquid is  $\sim 2.6$  eV, which is much bigger than  $k_B T$ . This means that added O will partition strongly into the liquid, but added S or Si will have similar concentrations in the two phases.

We now consider the density changes caused by alloying. In general, the density of the binary solid or liquid system is  $\rho = [(1-c_X) m_{\text{Fe}} + c_X m_X]/v$ , where the mean volume per atom  $v$  is given by  $v = [(1-c_X) v_{\text{Fe}} + c_X v_X]$ , with  $m_{\text{Fe}}$ ,  $m_X$  the atomic masses of Fe and X and  $v_{\text{Fe}}$ ,  $v_X$  the partial atomic volumes, given by  $v_{\text{Fe}} \equiv (\partial \mu_{\text{Fe}} / \partial P)_{T, c_X}$  and  $v_X \equiv (\partial \mu_X / \partial P)_{T, c_X}$ . The partial atomic volumes can be thought of as the change of volume of the whole system when one atom of Fe or X is added at constant  $P$  and  $T$ , so that  $v_X - v_{\text{Fe}}$  is the volume change when one Fe atom is replaced by an X atom. Equivalently, the pressure change when one atom of Fe is replaced by X at constant volume is given by  $(v_X - v_{\text{Fe}}) B_T / V$ , where  $B_T$  is the isothermal bulk modulus and  $V$  is the total volume. For the liquid, we obtain  $v_X - v_{\text{Fe}}$  from the pressure change  $\delta P$  in a constant- $(V, T)$  simulation when  $N_X$  of the Fe atoms are replaced by X atoms, which is given by  $\delta P \approx (v_X - v_{\text{Fe}}) B_T N_X / V$ . Estimates were reported earlier [21,22] for the S and O mol fractions required to give the observed density reduction relative to pure liquid Fe. We summarise these estimates and our new results for liquid Fe/Si by stating that  $v_X$  for S, Si and O has the values 6.65, 6.65 and 4.25 Å<sup>3</sup>, compared with the volume per atom in pure liquid Fe of 6.97 Å<sup>3</sup>. Once again, O differs markedly from S and Si, since  $v_O$  is considerably less than  $v_{\text{Fe}}$ , whereas  $v_S$  and  $v_{\text{Si}}$  are almost the same as  $v_{\text{Fe}}$ . Our calculations show that S and Si create little strain in the h.c.p. lattice, and the volume per atom is essen-

tially the same as that of Fe. This is not true for O, where we find  $v_O = 4.65$  Å<sup>3</sup>. (This volume is obtained by calculating  $\mu_O$  at two nearby pressures and estimating  $v_O \equiv (\partial \mu_O / \partial P)_{T, c_O}$  by finite difference.) Interestingly, O has a larger volume in the solid than in the liquid. This is expected, because the Fe neighbours in the liquid can accommodate themselves to the smaller size of the O atom, but the rigidity of the lattice hinders this accommodation in the solid.

We now use our numerical results for chemical potentials and densities to determine whether the known densities in the liquid and solid core can be accounted for by any binary Fe/X model with  $X = \text{S, O or Si}$ . (Since the core contains Ni, we should strictly consider (Fe,Ni)/X models. However, the mol fraction of Ni is believed to be only  $\sim 10$ – $12\%$  [26], and the Fe and Ni atoms have almost the same masses and electronic properties, so for present purposes we commit only small errors by ignoring the presence of Ni. In particular, the replacement of 10% of Fe atoms by Ni will change the density of both solid and liquid by only  $\sim 0.5\%$ , and the Fe/Ni ratio should be almost identical in the two phases, so the presence of Ni should not affect our arguments about partitioning of light impurities between inner and outer core.) In studying the densities, we must pay careful attention to possible errors both in the measured densities and in our ab initio results. The densities of the liquid and solid core are  $\rho^l = 12166$  and  $\rho^s = 12764$  kg m<sup>-3</sup>, with a probable error of  $\pm 1\%$  [7–9]. The relative density discontinuity  $(\rho^s - \rho^l) / \rho^s$  across the ICB is quite tightly constrained by free-oscillation data, which give  $(\rho^s - \rho^l) / \rho^s = 0.045 \pm 0.005$  [8,9]. Recent ab initio calculations of the melting properties of pure Fe at ICB pressures [27,28] agree in giving a density change on melting of only ca. 1.7%, which suggests the need for a strong partitioning of impurities from solid to liquid to explain the value of  $(\rho^s - \rho^l) / \rho^s$  in the real core. The density of pure liquid Fe at  $P = 330$  GPa and the corresponding  $T_m$  of 6700 K given by our original ab initio melting curve [27] is 12908 kg m<sup>-3</sup>, i.e. 6.1% higher than the known liquid core density. However, in the 2 years since [27] was published we have improved our ab initio calculations of the free en-

ergy of solid Fe, and we have obtained independent ab initio results for  $T_m$  using the coexistence approach of [28]. The revised  $T_m$  value at  $P=330$  GPa that emerges from this more recent work is 6350 K (or 6200 K after a correction due to our estimate of likely DFT errors), as will be reported elsewhere [29]. There will be a depression of melting point due to the impurities, which we estimate below to be 600–700 K. We therefore provisionally take the temperature at the ICB to be 5600 K. Since the expansion coefficient of the liquid is  $1.05 \times 10^{-5} \text{ K}^{-1}$  (this value is the result of our calculations, in agreement with the estimates of [3]), we estimate the density of pure liquid Fe at ICB ( $P, T$ ) to be  $13059 \text{ kg m}^{-3}$ . As a final correction, we note that our DFT calculations overestimate the density of low- $T$ /high- $P$  h.c.p. Fe by  $\sim 0.7\%$ , and we assume that this error will carry over to the liquid, so that our best estimate of  $\rho^l$  for pure Fe at ICB ( $P, T$ ) is  $12968 \text{ kg m}^{-3}$ , i.e. 6.6% higher than the liquid core density.

Using our calculated partial volumes of S, Si and O in the binary liquid alloys, we find that the required mol fractions required to reproduce the liquid core density are 16, 14 and 18% respectively (Fig. 1, panel (a) displays our predicted liquid density  $\rho^l$  as a function of  $c_X^l$  compared with the seismic density). Our calculated chemical potentials in the binary liquid and solid alloys then give mol fractions in the solid of 14, 14 and 0.2% respectively (see Fig. 1, panel (b)). Finally, our partial volumes in the binary solids give density discontinuities of  $2.7 \pm 0.5$ ,  $1.8 \pm 0.5$  and  $7.8 \pm 0.2\%$  respectively (Fig. 1, panel (c)). As expected, for S and Si, the discontinuities are considerably smaller than the known value of  $4.5 \pm 0.5\%$ ; for O, the discontinuity is markedly greater than the known value. We conclude that none of the binary systems can account for the discontinuity quantitatively. However, it clearly can be accounted for by O together with either or both of S and Si. Ab initio calculations on general quaternary alloys containing Fe, S, O and Si will clearly be feasible in the future, but currently they are too demanding, so for the moment we assume that the chemical potential of each impurity species is unaffected by the presence of the others. Our estimated mol fractions needed to account

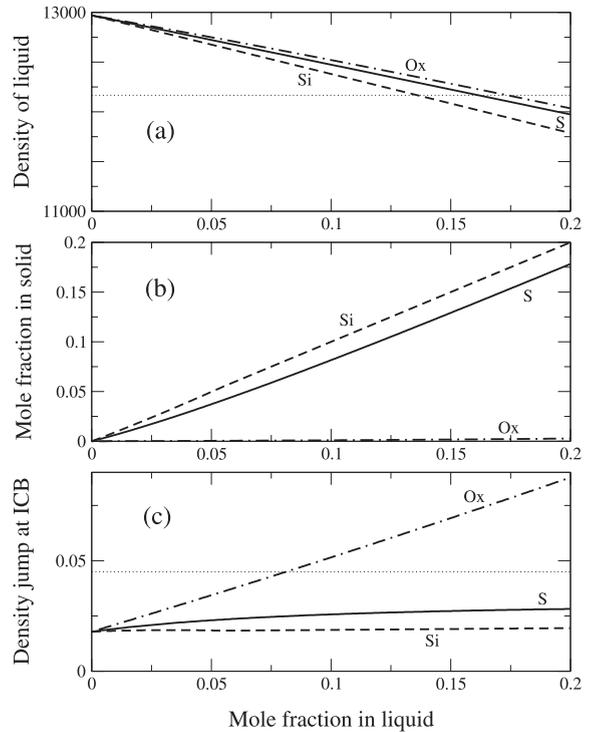


Fig. 1. Liquid and solid impurity mol fractions  $c_X^l$  and  $c_X^s$  of impurities X=S, Si and O, and resulting densities of the inner and outer core predicted by ab initio simulations. Solid, dashed and chain curves represent S, Si and O respectively. (a) Liquid density  $\rho^l$  ( $\text{kg m}^{-3}$  units); horizontal dotted line shows density from seismic data [7–9]. (b) Mol fractions in solid resulting from equality of chemical potentials in solid and liquid (Eq. 4). (c) Relative density discontinuity  $\delta\rho/\rho^l$  at the ICB; the horizontal dotted line represents free-oscillation data [8,9].

for the ICB density discontinuity, reported in Table 2, show that we must have  $\sim 8\%$  of O in the outer core and a slightly larger amount of S and/or Si.

With our calculated impurity chemical potentials, we can now use the Gibbs–Duhem relation [10] to compute the change of Fe chemical potential caused by the impurities in the solid and liquid. By requiring the chemical potential of Fe in the two phases to be equal, we obtain the change  $\Delta T$  of  $T_m$  relative to that of pure Fe. Our estimate is  $\Delta T = -700 \pm 100 \text{ K}$ .  $T_m$  of pure Fe at ICB pressure has long been controversial, but almost all modern estimates, including recent ab initio calculations, cluster in the range 5300–6700 K (for a

review of experimental work, see [30]; ab initio values are reported in [27–29]). Our own ab initio value of the ICB  $T_m$  of 6200–6350 K [29], is in good agreement with that inferred from shock data (for a discussion, see [29] and references therein), which are, however, still at variance with the DAC data of Boehler [31]. Our  $\Delta T$  value therefore implies an ICB temperature of ca. 5600 K, interestingly in close agreement with the value of 5700 K inferred from very recent ab initio calculations on the elasticity properties of the inner core [32].

The heart of our results is the weak partitioning of S and Si and the strong partitioning of O from solid into liquid. The mechanism of this effect is rather simple. The atoms S and Si have about the same size as Fe, and substitute for Fe in the crystal lattice without appreciable strain; their coordination numbers in the Fe/S and Fe/Si liquid alloys [21] are about the same ( $\sim 13$ ) as the coordination number of Fe. By contrast, the small O atom replaces Fe in the lattice rather uneasily [24], and is unable to bond effectively with its neighbours, but yet is too large to be accommodated interstitially. In the Fe/O liquid [22], O has a considerably smaller coordination number of  $\sim 9$ , and this makes the bonding with its neighbours more effective in the liquid. The consequence is that O is thermodynamically much more stable in the liquid than in the solid. The strong partitioning of O may be important for another reason. It is widely believed that the Earth's magnetic field is powered by compositional convection [33,34], i.e. convection driven by the release of light elements into the liquid as the inner core grows by freezing of the outer core. If O is, indeed, the only credible impurity that partitions strongly, then the presence of O may be indispen-

sable for the generation of the magnetic field. A quantitative analysis of compositional convection and its influence on the geodynamo requires a detailed consideration of the entropic and enthalpic effects of the crystallisation of the inner core, and we shall report separately on this [35].

In spite of the strong partitioning of O, our calculations require an O mol fraction of  $\sim 0.3\%$  in the inner core. At first sight, this appears to conflict with the earlier finding [36] that substitutional O dissolved in close-packed Fe at core pressures is thermodynamically unstable with respect to decomposition into Fe and FeO. This finding was based on ab initio calculation of the enthalpy of formation  $\Delta H$  of the  $\text{Fe}_{1-x}\text{O}_x$  solid solution from Fe and FeO perfect crystals, and our own recent ab initio work [22,24] found that  $\Delta H$  has a large positive value of  $\sim 4$  eV, which is similar to that found in [36]. This large value arises from the small size of the O atom and its ineffective bonding to its neighbours in the solid solution. However, it has also become clear recently that the loose fit of substitutional O in the Fe lattice leads to extremely large entropic effects at core temperatures [24], which are probably sufficient to stabilise the solid solution at concentrations of up to  $\sim 3\%$ . In view of this, we do not believe that there is any objection to our proposed inner-core O concentration.

We have deliberately avoided geochemical arguments, since we regard them as less certain than the physical data of seismology. However, geochemistry may ultimately be able to give guidance about the ratio of S and Si, which our methods cannot determine. Because of the high volatility of S, a high S content in the core is difficult to reconcile with the observed depletion in the Earth of less volatile elements like K and Zn. From the mantle abundance of Zn, it was argued by Dreibus and Palme [37] that the core cannot contain more than  $\sim 3$  mol% of S. If this were correct, then our results (Table 2) would require the presence of  $\sim 7$  mol% of Si together with  $\sim 8$  mol% of O. It is not entirely clear whether Si and O can coexist in the core without precipitating to form  $\text{SiO}_2$ , but future ab initio calculations should be able to help with this question. We note that the model of Allègre et al. [38], based on the as-

Table 2

Estimated molar percentages of sulphur, silicon and oxygen in the solid inner core and liquid outer core obtained by combining ab initio calculations and seismic data

	Solid	Liquid
Sulphur/silicon	$8.5 \pm 2.5$	$10 \pm 2.5$
Oxygen	$0.2 \pm 0.1$	$8.0 \pm 2.5$

Sulphur/silicon entries refer to total percentages of sulphur and/or silicon.

sumption of a chondritic Earth composition, also calls for the simultaneous presence of substantial amounts of Si and O. At present, we do not believe there is a firm basis for making definitive statements about the S/Si ratio.

In summary, the requirement that the densities of the inner and outer cores be reproduced provides two constraints on the mol fractions of impurities, and we have shown how *ab initio* calculation of densities and chemical potentials allows these constraints to be exploited; restricting the impurity candidates to S, Si and O, we find that the outer core must contain  $\sim 8$  mol% of O and a similar amount of S and/or Si; the need for the presence of O stems from the similarity of sizes of the S, Si and Fe atoms, and the markedly smaller size of O; we estimate the temperature at the inner-core/outer-core boundary to be ca. 5600 K.

### Acknowledgements

The work of D.A. was supported by NERC Grant GR3/12083 and by a Royal Society University Research Fellowship, and that of M.J.G. by GEC and Daresbury Laboratory. D.A. also acknowledges support from CNR. The calculations were run on the Cray T3E machine at Manchester CSAR Centre and on the Origin 2000 machine at the UCL HiPerSPACE Centre. **[BW]**

### References

- [1] F. Birch, Density and composition of mantle and core, *J. Geophys. Res.* 69 (1964) 4377–4388.
- [2] J.P. Poirier, Light elements in the Earth's outer core: A critical review, *Phys. Earth Planet. Inter.* 85 (1994) 319–337.
- [3] W.W. Anderson, A.T.J. Ahrens, An equation of state for liquid iron and implications for the Earth's core, *J. Geophys. Res.* 99 (1994) 4273–4284.
- [4] A. Jephcoat, P. Olson, Is the inner core of the Earth pure iron?, *Nature* 325 (1987) 332–335.
- [5] L. Stixrude, E. Wasserman, R.E. Cohen, Composition and temperature of the Earth's inner core, *J. Geophys. Res.* 102 (1997) 24729–24739.
- [6] D. Alfè, M.J. Gillan, G.D. Price, Constraints on the composition of the Earth's core from *ab-initio* calculations, *Nature* 405 (2000) 172–175.
- [7] A.M. Dziewonski, D.L. Anderson, Preliminary reference Earth model, *Phys. Earth Planet. Inter.* 25 (1981) 297–356.
- [8] T.G. Masters, P.M. Shearer, Summary of seismological constraints on the structure of the Earth's core, *J. Geophys. Res.* 95 (1990) 21691–21695.
- [9] P.M. Shearer, T.G. Masters, The density and shear velocity contrast at the inner core boundary, *Geophys. J. Int.* 102 (1990) 491–498.
- [10] P.W. Atkins, *Physical Chemistry*, Ch. 7, Oxford University Press, Oxford, 1994.
- [11] R. Boehler, Fe–FeS eutectic temperatures to 620 kbar, *Phys. Earth Planet. Inter.* 96 (1996) 181–186.
- [12] E. Ohtani, A.E. Ringwood, W. Hibberson, Composition of the core: I. Solubility of oxygen in molten iron at high temperatures, *Earth Planet. Sci. Lett.* 71 (1984) 85–93.
- [13] M.J. Gillan, The virtual matter laboratory, *Contemp. Phys.* 38 (1997) 115–130.
- [14] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* 59 (1999) 1758–1775.
- [15] D. Alfè, G. Kresse, M.J. Gillan, Structure and dynamics of liquid iron under Earth's core conditions, *Phys. Rev. B* 61 (2000) 132–142.
- [16] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids and surfaces: Applications of the generalized gradient approximation for exchange and correlation, *Phys. Rev. B* 46 (1992) 6671–6687.
- [17] L. Stixrude, R.E. Cohen, D.J. Singh, Iron at high pressure: Linearized-augmented-plane-wave computations in the generalized-gradient approximation, *Phys. Rev. B* 50 (1994) 6442–6445.
- [18] P. Söderlind, J.A. Moriarty, J.M. Wills, First-principles theory of iron up to earth-core pressures: Structural, vibrational and elastic properties, *Phys. Rev. B* 53 (1996) 14063–14072.
- [19] H.K. Mao, J. Xu, V.V. Struzhkin, J. Shu, R.J. Hemley, L. Vočadlo, D. Alfè, G.D. Price, M.J. Gillan, W. Sturhahn, M.Y. Hu, E.E. Alp, M. Schwoerer-Böhning, D. Häusermann, P. Eng, G. Shen, H. Giefers, R. Lübbers, G. Wörtemann, Phonon density of states of iron up to 153 GPa, *Science* 292 (2001) 914.
- [20] G. Kresse, J. Furthmüller, Efficient iterative schemes for *ab-initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 54 (1996) 11169–11186.
- [21] D. Alfè, M.J. Gillan, First-principles simulations of liquid Fe–S under Earth's core conditions, *Phys. Rev. B* 58 (1998) 8248–8256.
- [22] D. Alfè, G.D. Price, M.J. Gillan, Oxygen in the Earth's core: A first-principles study, *Phys. Earth Planet. Inter.* 110 (1999) 191–210.
- [23] D. Frenkel, B. Smit, *Understanding Molecular Simulation*, Ch. 4, Academic Press, New York, 1987.
- [24] D. Alfè, G.D. Price, M.J. Gillan, Thermodynamic stability of Fe/O solid solution at inner-core conditions, *Geophys. Res. Lett.* 27 (2000) 2417–2420.

- [25] G. Kresse, J. Furthmüller, J. Hafner, Ab-initio force-constant approach to phonon dispersion relations of diamond and graphite, *Europhys. Lett.* 32 (1995) 729–734.
- [26] F.D. Stacey, *Physics of the Earth*, Ch. 1, J. Wiley and Sons, New York, 1977.
- [27] D. Alfè, M.J. Gillan, G.D. Price, The melting curve of iron at the pressures of the Earth's core from ab initio calculations, *Nature* 401 (1999) 462–464.
- [28] A. Laio, S. Bernard, G.L. Chiarotti, S. Scandolo, E. Tosatti, Physics of iron at Earth's core conditions, *Science* 287 (2000) 1027–1030.
- [29] D. Alfè, G.D. Price, M.J. Gillan, Iron under Earth's core conditions: Liquid-state thermodynamics and high-pressure melting curve from ab initio calculations, *Phys. Rev. B*, submitted. Preprint available in electronic form at <http://arXiv.org/ps/cond-mat/0107307>.
- [30] O.L. Anderson, A. Duba, Experimental melting curve of iron revisited, *J. Geophys. Res.* 102 (1997) 22659.
- [31] R. Boehler, Temperatures in the Earth's core from melting point measurements of iron at high static pressures, *Nature* 363 (1993) 534.
- [32] G. Steinle-Neumann, L. Stixrude, R.E. Cohen, O. Gülseren, Elasticity of iron at the temperature of the Earth's inner core, *Nature* 413 (2001) 57.
- [33] S.I. Braginsky, *Dokl. Akad. Nauk SSSR Engl. Transl.* 149 (1963) 1311.
- [34] P.H. Roberts, D. Gubbins, in: J.A. Jacobs (Ed.), *Geomagnetism*, Vol. 2, Academic Press, London, 1987, pp. 185–249.
- [35] D. Gubbins, D. Alfè, G. Masters, G.D. Price, M.J. Gillan, Gross thermodynamics of 2-component core convection, *Geophys. J. Int.*, submitted.
- [36] D. Sherman, Stability of possible Fe–FeS and Fe–FeO alloy phases at high pressure and the composition of the Earth's core, *Earth Planet. Sci. Lett.* 132 (1995) 87–98.
- [37] G. Dreibus, H. Palme, Cosmochemical constraints on the sulphur content of the Earth's core, *Geochim. Cosmochim. Acta* 60 (1996) 1125–1130.
- [38] C.A. Allègre, J.-P. Poirier, E. Humler, A.W. Hofmann, The composition of the Earth, *Earth Planet. Sci. Lett.* 134 (1995) 515–526.