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## INNER CORE COMPOSITION

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### Why is the inner core important?

The solid inner core is complex and not yet fully understood. This is hardly surprising given that the temperature of the Earth's core (*q.v.*) is in the range 5000–6000 K and inner core pressures are ~330–360 GPa. Knowledge of the exact composition and structure of the Earth's inner core would enable a better understanding of the internal structure and dynamics of the Earth as a whole; in particular, better constraints on *core composition (q.v.)* would not only have fundamental implications for models of the formation, differentiation, and evolution of the Earth, but would also enable successful interpretation of seismic observations which have revealed *inner core anisotropy (q.v.)*, layering and heterogeneity (e.g., Creager, 1992; Song 1997; Beghein and Trampert, 2003; Cao and Romanowicz, 2004; Koper *et al.*, 2004). The elastic anisotropy of the inner core is well established: *seismic velocities of the inner core (q.v.)* show P-wave velocities ~3% faster along the polar axis than in the equatorial plane (e.g., Creager, 1992). However, more recent seismic observations suggest further complexity. The evidence is for a seismically isotropic upper layer, with lateral variations in thickness of ~100–400 km, overlaying an irregular, nonspherical transition region to an anisotropic lower layer (Song and Helmberger, 1998; Ouzounis and Creager, 2001; Song and Xu, 2002). The existence of an isotropic upper layer implies that the magnitude of the seismic anisotropy in the lower inner core must be significantly greater than previously thought, possibly as much as 5%–10%. The observed layering also implies that the upper and lower inner core are compositionally or structurally different. Small-scale heterogeneities in the Earth's inner core have also been observed, possibly associated with phase changes, a “mushy layer,” melt inclusions and/or compositional differences (Cao and Romanowicz, 2004; Koper *et al.*, 2004). The question now arises as to the mechanisms by which such complexity can occur, all of which could be highly compositionally dependent. Therefore, we cannot test any hypotheses for the observed features without knowing the inner core composition.

### The inner core is not just made of iron

The exact composition of the Earth's inner core is not very well known. On the basis of cosmochemical and geochemical arguments, it has been suggested that the core is an iron alloy with possibly as much as ~5 wt% Ni and very small amounts (only fractions of a wt % to trace) of other siderophile elements such as Cr, Mn, P, and Co (McDonough and Sun, 1995). On the basis of materials-density/sound-wave velocity systematics, Birch (1964) further concluded that the core is composed of iron that is alloyed with a small fraction of lighter elements. The light alloying elements most commonly suggested include S, O, Si, H, and C, although minor amounts of other

elements, such as K, could also be present (e.g., Poirier, 1994; Gessmann and Wood, 2002). From seismology it is known that the density jump across the inner core boundary is between ~4.5% and 6.7% (Shearer and Masters, 1990; Masters and Gubbins, 2003) indicating that there is more lighter element alloying in the outer core. The evidence thus suggests that the outer core contains ~5%–10% light elements, while the inner core has ~2%–3% light elements. Our present understanding is that the Earth's solid inner core is crystallizing from the outer core as the Earth slowly cools and the partitioning of the light elements between the solid and liquid is therefore crucial to understanding the evolution and dynamics of the core.

### Which phase of iron exists in the inner core?

Before tackling the more detailed problem of *inner core composition (q.v.)* in terms of alloying elements, it is essential to know what crystalline structure(s) are present and also their seismic properties, as these will greatly affect both interpretations made from seismic data and also the possible alloying mechanism. Many experimentalists have put an enormous effort over the last 10–15 years into obtaining a phase diagram of pure iron under core conditions, but above relatively modest pressures and temperatures there is still much uncertainty. Experimental techniques have evolved rapidly in recent years, and today, using diamond anvil cells or *shock wave experiments (q.v.)*, the study of minerals at pressures up to ~200 GPa and temperatures of a few thousand kelvin are possible. These studies, however, are still far from routine and results from different groups are often in conflict. At low pressures and temperatures the phase diagram of iron is well understood: the body-centered-cubic (bcc) phase is stable at ambient conditions, transforming to the hexagonal close-packed phase (hcp) at high pressure (>10–15 GPa) and to the face-centered-cubic phase at high temperature (>1200 K). Both experiments and also theoretical calculations of the static, zero-Kelvin solid (Stixrude *et al.*, 1997; Vočadlo *et al.*, 2000), have suggested that the hcp phase has a wide stability field at high pressures *and* temperatures right to the conditions of the Earth's inner core. However, this assumption that iron must have the hcp structure at core conditions has recently been challenged (Brown 2001; Beghein and Trampert, 2003), especially if the presence of lighter elements is included (Lin *et al.*, 2003). It now seems very possible that a bcc phase might be formed (Vočadlo *et al.*, 2003). Previously, the bcc phase of iron was considered an unlikely candidate for an inner core-forming phase because athermal calculations show it to be elastically unstable at high pressures, with an enthalpy considerably higher than that of hcp iron (Stixrude and Cohen, 1995; Söderlind *et al.*, 1996; Vočadlo *et al.*, 2000). However, more recent *ab initio* molecular dynamics calculations at core pressures and temperatures have suggested that the bcc phase of iron becomes entropically stabilized at core temperatures. Although for pure iron the thermodynamically most stable phase is still the hcp phase, the free energy difference is so very slight that a small amount of light element impurity could stabilize the bcc phase at the expense of the hcp phase (Vočadlo *et al.*, 2003).

## Alloying elements

It is generally assumed that the small amount of nickel alloyed to iron in the inner core is unlikely to have any significant affect on *core properties* (*q.v.*) as nickel and iron have sufficiently similar densities to be seismically indistinguishable, and addition of small amounts of nickel are unlikely to appreciably change the physical properties of iron. However, the presence of light elements in the core does have an affect on core properties. The light element impurities most often suggested are sulfur, oxygen, and silicon. Although these alloying systems have been experimentally studied up to pressures of around 100 GPa (e.g., Li and Agee, 2001; Lin *et al.*, 2003; Rubie *et al.*, 2004) there seems little prospect of obtaining experimental data for iron alloys at the highly elevated pressures and temperatures of the Earth's inner core.

An alternative approach to understanding inner core composition (*q.v.*) is to simulate the behavior of these iron alloys with *ab initio* calculations which are readily able to access the pressures and temperatures of the inner core. Alfè *et al.* (2000, 2002) calculated the chemical potentials of iron alloyed with sulfur, oxygen, and silicon. They developed a strategy for constraining both the impurity fractions and the temperature at the inner core boundary (ICB) based on the supposition that the solid inner core and liquid outer core are in thermodynamic equilibrium at the ICB. For thermodynamic equilibrium the chemical potentials of each species must be equal both sides of the ICB, which fixes the ratio of the concentrations of the elements in the liquid and in the solid, which in turn fixes the densities. If the core consisted of pure iron, equality of the chemical potential (the Gibbs free energy in this case) would tell us only that the temperature at the ICB is equal to the *melting temperature of iron* (*q.v.*) at the ICB pressure of 330 GPa. With impurities present, the *ab initio* results reveal a major qualitative difference between oxygen and the other two impurities: oxygen partitions strongly into the liquid, but sulfur and silicon, both partition equally in the solid and liquid. Having established the partitioning coefficients, Alfè *et al.* (2002) then investigated whether the known densities of the outer and inner core, estimated from seismology, could be matched by one of their calculated binary systems. For sulfur and silicon, their ICB density discontinuities were considerably smaller than the known seismological value at that time of 4.5%/0.5% (Shearer and Masters, 1990); for oxygen, the discontinuity was markedly greater than that from seismology. Therefore none of these binary systems were plausible, i.e., the core *cannot* be made solely of Fe/S, Fe/Si, or Fe/O. However, the seismic data can clearly be matched by a ternary/quaternary system of iron and oxygen together with sulfur and/or silicon. A system consistent with seismic data could contain 8 mol% oxygen and 10 mol% sulfur and/or silicon in the outer core, and 0.2 mol% oxygen and 8.5 mol% sulfur and/or silicon in the inner core (Alfè *et al.*, 2002). However, it should be remembered that it is likely that several other light elements could exist in the inner core and would therefore have to be considered before a true description of inner core composition could be claimed.

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## Cross-references

- Core Composition
- Core Properties, Physical
- Core Properties, Theoretical Determination
- Core Temperature
- Inner Core Anisotropy
- Inner Core Seismic Velocities
- Melting Temperature of Iron in the Core, Experimental
- Melting Temperature of Iron in the Core, Theory
- Shock Wave Experiments