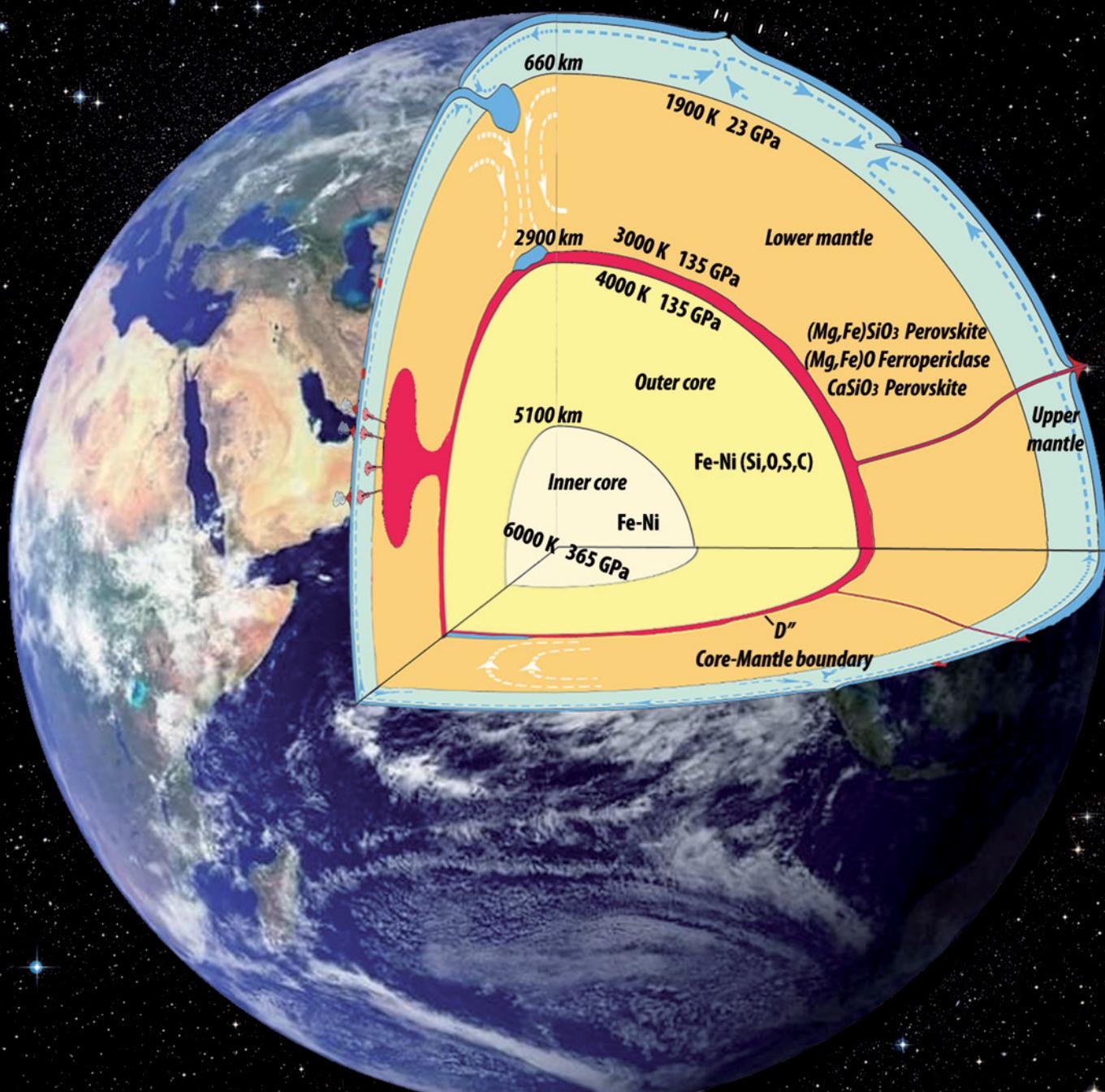


# A new spin on Earth's deep mantle

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Earth's mantle is the largest distinct layer within the Earth, between the crust and the core. It accounts for roughly 2/3 of Earth's mass and is composed mainly of dense iron-bearing silicates. Laboratory experiments have recently shown that iron in mantle minerals undergoes a high-spin to low-spin transition driven by pressure, occurring at mid to lowermost mantle depths. This introduces a paradigm shift in our understanding of the physics and chemistry of the deep Earth.



**S**eismic wave analysis is the main tool for studying Earth's deep structure (figure 1). Radial seismological (1D) models, obtained from inversion of seismic travel times and normal mode spectra, give the compressional and shear wave velocities, as well as density, in the Earth as a function of depth. These profiles are characterised by smooth variations punctuated by sharp discontinuities. They reflect either chemical boundaries such as the core-mantle boundary at 2900 km depth, or physical boundaries such as the inner-core boundary at 5100 km.

Earth's mantle is composed mainly of silicates, and starts at 10 km below the oceanic crust and up to 70 km below the continental crust. It ends at the core-mantle boundary, at 2900 km depth. It is subdivided in Upper Mantle (shallower than 410 km), Transition Zone (410–660 km) and Lower Mantle (660–2900 km); the subdivision is derived from clear seismic discontinuities at the corresponding depths.

In one of their major achievements, high-pressure experiments have shown that the seismic discontinuities in the mantle are a direct consequence of phase transformations in mantle minerals and rocks. The behaviour and properties of terrestrial rocks and minerals can be studied at high pressure and high temperature, using presses such as the piston-cylinder press, the belt and toroidal presses, the multi-anvil press, or the laser-heated diamond anvil cell (LH-DAC) depicted in figure 2. The LH-DAC allows covering the entire pressure and temperature range in Earth's mantle, and a significant portion of that in the core. LH-DAC labs around the world can nowadays routinely achieve pressures in excess of 135 GPa (pressure at Earth's core-mantle boundary), while simultaneously heating the samples above 3000 °C using infrared lasers.

## Composition

Although the question of a difference in bulk chemical composition between the upper and lower mantle is still a matter of debate, the mineralogy of these two reservoirs is, at any rate, fundamentally different. The upper mantle (and transition zone) is mainly composed of four-fold-coordinated silicate framework minerals (olivine, pyroxenes, garnets, and their high-pressure structural modifications), whereas the bulk of the lower mantle consists mainly of six-fold coordinated silicates – magnesium silicate perovskite (*pv*),  $(\text{Mg}, \text{Fe})\text{SiO}_3$  and calcium silicate perovskite (*Ca-pv*),  $\text{CaSiO}_3$  – and a dense oxide ferropericlase (*fp*),  $(\text{Mg}, \text{Fe})\text{O}$ .

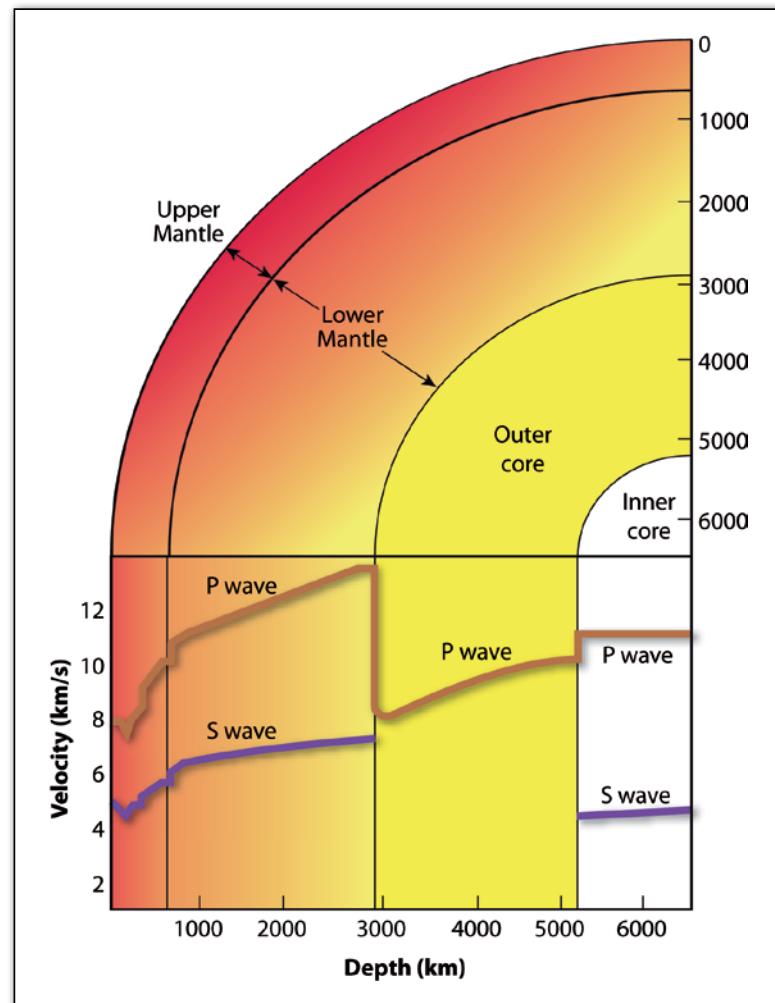
Iron-bearing minerals have complex physical and chemical properties, in contrast to the iron-free end-members. This is due to the electronic complexity of iron. The specificity of iron derives from the fact that it is a transition metal. Unlike the other major elements (Mg, Ca, Si, Al) of the bulk Earth, it has partially filled  $3d$  orbitals that give rise to a series of possible electronic configurations

that depend on its atomic environment [1]. As a consequence, iron in mantle minerals adopts different valences such as ferrous ( $\text{Fe}^{2+}$ ) and ferric ( $\text{Fe}^{3+}$ ) iron, and different electronic configurations such as high-spin (HS) and low-spin (LS) iron.

## Spin pairing

Half a century ago, William Fyfe [2] argued that elevated pressure could induce spin pairing in nominally HS minerals, and there was a possibility that this could occur in the pressure range of Earth's mantle, although the exact structure of the phases was still unknown. This is due to the fact that the spin state is determined by the balance between two energies: the crystal field stabilisation energy (favours the LS state) that increases with pressure, and the pairing energy (favours the HS state) that is essentially unaffected by pressure [3]. Thus, an iron-bearing mineral consisting of HS iron in the shallow mantle can undergo a pressure-driven transition to an LS state in the deeper mantle.

▼ FIG 1: (a) Schematic representation of the layers inside Earth: the names of the layers, their pressure, temperature, depth, and their composition. (b) The seismic wave velocity profiles (compressional and shear waves) as a function of depth. Except for the 2900-km boundary (the core-mantle boundary) which is compositional, the discontinuities have all been linked to phase transitions in the mantle or the core.



The fundamental differences in the physical and chemical properties of HS and LS iron can then play a crucial role inside the Earth, and affect the thermochemistry, elasticity, and dynamics of the entire planet; the hunting season for spin transitions in mantle minerals was open! It wasn't until recently that the breakthroughs in x-ray spectroscopy instruments on 3<sup>rd</sup> generation synchrotron sources combined with the enhanced LH-DAC technology allowed the direct probing of the spin state of geophysically relevant minerals at high pressure.

Using high-resolution x-ray emission spectroscopy, one

## This introduces a paradigm shift in our understanding of the physics and chemistry of the deep Earth

spin magnetic moment of the Fe atom. In order to investigate the possibility of spin pairing at depth in the mantle, lower-mantle minerals ( $Mg_{0.83}Fe_{0.17}$ )O *fp* and ( $Mg_{0.9}Fe_{0.1}$ )SiO<sub>3</sub> *pv* were pressurised in a LH-DAC [4,5], to pressures of 145 GPa (above mantle's maximum pressure of 135 GPa). A series of experiments were conducted in 2003 and 2004 at the ID16 inelastic scattering beamline of the European Synchrotron Radiation Facility, where a high-brightness 10 keV synchrotron x-ray beam was focussed onto the sample through the diamond anvils. The spin magnetic moment of iron in both minerals was measured as a function of pressure by monitoring the intensity of the K $\beta'$  line (figure 3). For the first time since Fyfe's

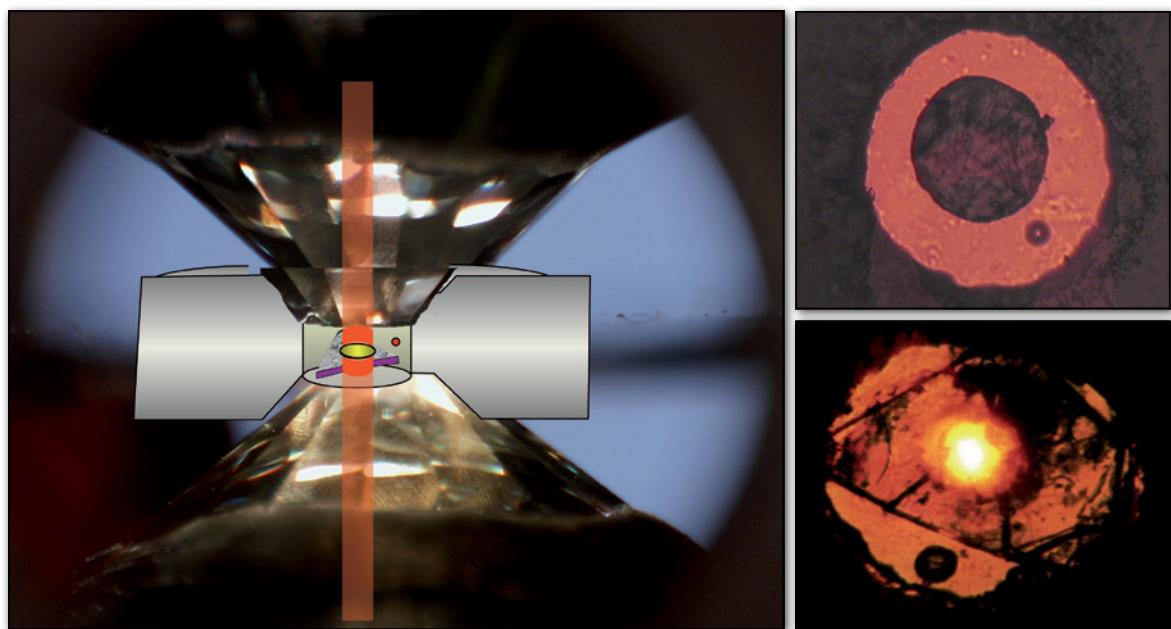
can measure iron K $\beta$  emission and resolve the K $\beta'$  line from the main K $\beta_{1,3}$  emission line. The intensity of the K $\beta'$  line is linked to the

conjecture, spin pairing was observed in lower-mantle minerals at high pressure. The measurements show that iron in *fp* undergoes a change from HS to LS between 50 and 70 GPa at room pressure. It was later shown that increasing temperature increases the transition pressure (90 GPa at mantle temperatures) and broadens the HS-LS coexistence domain. In *pv*, a sharp transition to a full LS state is observed at 120 GPa (figure 3). Mantle minerals in the bottom 300 km (120 GPa) are entirely low-spin.

### Geophysical differences

Geophysical interest in these transitions could seem odd, but is highly justified: spin pairing has a radical effect on important physical parameters, and on the lower mantle as a whole. LS minerals have a smaller molar volume (because LS Fe is smaller than HS Fe) and therefore a higher density than their HS counterpart, as well as a higher bulk modulus. Very accurate [6] x-ray diffraction experiments on *fp* around the spin transition pressure have confirmed the density effect: a subtle yet distinguishable kink in the equation of state V(P,T) of *fp* is observed, as one crosses the spin transition, and the LS *fp* lies on a denser isotherm than the HS phase. The adiabatic bulk modulus also changes and increases, but in such a way that the seismic parameter  $K_s/\rho$  (where  $K_s$  is the adiabatic bulk modulus and  $\rho$  is the density) is unchanged. This has been proven recently [7] by inelastic x-ray scattering experiments, where density variations are observed, but wave speeds are not affected. Wave speeds are one of the seismological observables in the Earth, and it is remarkable that no change in the radially averaged 1D seismic parameter is observed. From

**▼ FIG 2:** Schematic representation of the laser-heated diamond anvil cell. The sample is compressed in a small metallic chamber in between two opposed diamond anvils. Pressures well above a megabar (100 GPa) can be routinely reached. By focusing infrared lasers on the sample through the anvils, we can simultaneous heat under pressure, to temperatures above 3000 K. Upper right: a sample (disk) seen through the diamond anvils, along the compression axis. The small ball is made of ruby and is used as a pressure gauge. The transparent medium surrounding the sample is usually a noble gas or an alkali halide. Lower right: a quartz sample heated by an infrared laser. The temperature at the center of the spot can routinely reach 3000 °C.



an observational point of view, and as opposed to the crystallographic transitions in the mantle that have their associated seismic discontinuities, these (spin-pairing) transitions are seismically transparent.

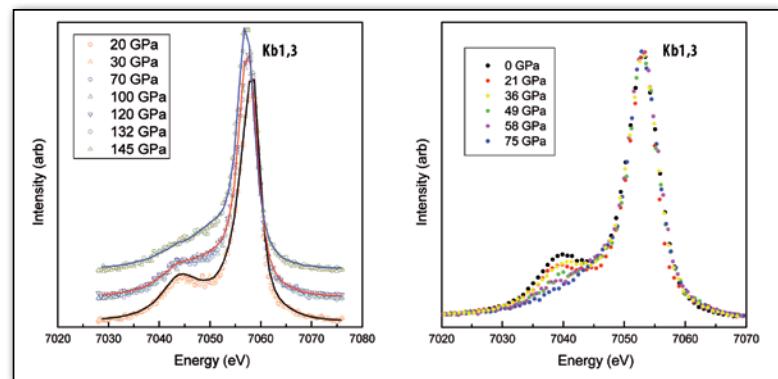
The thermodynamics and phase equilibrium between minerals can be affected by spin transitions (bear in mind that the  $P\Delta V$  term in Gibbs free energy is order of magnitudes larger at mantle pressures than at ambient). Iron in the mantle is distributed in a solid solution by substitution with magnesium, in *fp* ( $\text{Mg},\text{Fe}\text{O}$ ) and *pv* ( $\text{Mg},\text{Fe}\text{SiO}_3$ ). The relative concentration of iron in the two phases, or partition coefficient, is constrained by the minimisation of the Gibbs free energy for the substitution (or exchange) reaction:  $\text{Mg}^{fp} + \text{Fe}^{pv} \rightleftharpoons \text{Mg}^{pv} + \text{Fe}^{fp}$ . The fact that the LS iron atom has a smaller volume than its HS counterpart will favour the enrichment of Fe in the LS phase over to the HS phase. Although the rocks' bulk chemistry is constant, the distribution of elements in the minerals that make up the rock is changing. The rheological and physical properties of the rocks become very different. Since *pv* is likely the interconnected phase, its depletion in iron should increase its viscosity and stiffen the mantle at large depth. An important effect on the dynamics in the mid-mantle (1800 km) has been suggested, where the transition has been proposed to enhance plume (hot rising material) upwelling [8], by adding a spin-related buoyancy to hot upwelling material in the mid-mantle.

## Heat transport

Dynamical simulations have suggested that a fully LS lowermost (2600–2900 km) mantle would stabilise large thermal structures (super-plumes) while trimming small-scale structures [9]. Indeed, heat can be transported in the mantle by conduction, radiation, or convection. Convection in the lower mantle is only initiated if the other two processes fail to transfer heat, *e.g.*, if the ratio between heat transport through convection and heat transport through conduction and radiation is high enough. Changes in the conduction or radiation properties of lower-mantle mineral assemblages will therefore strongly affect lower-mantle dynamics. One of the main and intrinsic characteristics of LS iron-bearing minerals resides in the blue-shift of iron absorption bands (the absorption bands initially in the infrared shift to the visible). This would increase the radiative thermal conductivity of the minerals [10,11]. A mantle with a thermal conductivity jump (due to spin pairing) can stabilise a thermal boundary layer atop the core–mantle boundary [12], in which large upwellings are favoured, and could be the birthplace of super-plumes.

## Important consequences

As we see, a small unexpected effect (spin pairing in mantle minerals) can have important consequences on the dynamics of the Earth as a whole, and as was mentioned by Fyfe [2] in 1960, and subsequently relayed by Burns and Sherman [1,3]:



**▲ FIG 3:** X-ray K $\beta$  emission spectra of iron in the lower mantle's principal minerals: Mg-perovskite (*pv*, left) and ferropericlase (*fp*, right), at various pressures. The intensity of the K $\beta^1$  peak, characteristic of the spin quantum state, vanishes at high pressure, indicative of a pressure-driven spin-pairing transition (the spectra have been shifted vertically for *pv* for clarity). The high-spin (HS) and low-spin (LS) states coexist over a rather large pressure interval (tens of GPa), and the conversion to the LS state is complete at 60–70 GPa for *fp* and 120 GPa for *pv*. In the latter case, this corresponds to 300 km above the core–mantle boundary. According to those findings, the base of the mantle should be entirely made of LS iron.

*The effect of pressure deep inside Earth's mantle may be to collapse the atomic orbitals of iron from the high-spin to the low-spin state. The transition represents a major change in the chemical bonding character of one of Earth's most important elements. Density, elastic moduli, thermal conductivity, electrical transport, and other physical and chemical properties of Fe-bearing minerals could thus be dramatically altered at depth.*

## About the Author

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