Effect of Light Elements on the Sound Velocities in Solid Iron: Implications for the Composition of Earth's Core

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Abstract

We measured compressional sound velocities in light-element alloys of iron (FeO, FeSi, FeS, and FeS$_2$) at high pressure by inelastic x-ray scattering. This data set provides a mineralogical constraint on the composition of Earth's core, and completes the previous set formed by the pressure–density systematics for these compounds. Based on the combination of these data sets and their comparison with radial seismic models, we propose an average composition model of Earth's core. We show that sulphur is not a good candidate for the light alloying element in the core. On the other hand, the incorporation of small amounts of silicon or oxygen is compatible with geophysical observations and geochemical abundances. In our model, the inner core contains 2.7 wt% silicon and 0.2 wt% oxygen, and the outer core contains 8 wt% oxygen and 3.2 wt% silicon.

The composition of the Earth's core is a standing problem in the field of Earth sciences (*1-4*). Seismic wave propagation and normal mode oscillation are available probes to study the core, and their inversion yields a distribution of sound velocity, density, and compressibility profiles (*5, 6*). However, these models cannot directly constrain the chemical and structural properties of Earth materials. In order to understand and investigate the composition of the Earth, one has to use mineralogical and geochemical models that in turn have to be in accord with these seismological models. Using shockwave measurements on iron, Birch (*7*) proposed that Earth's core was too light to be made of pure iron. Since then, multiple studies (*8-10*) have revealed that indeed iron is too dense to be the only constituent not only of Earth's core as a whole, but also more specifically of the solid inner core.

From a methodological viewpoint, high-pressure mineralogy provides sets of data that can be combined with seismic data in order to check the self-consistency of the models. In this sense, the study of Earth materials under extreme conditions (high pressure and high temperature) in recent years unveiled information on the density and compressibility of minerals (*11*) in the conditions of the deep Earth from the *in situ* study of their crystal structure by x-ray diffraction. It was only very recently that probing static sound velocities in extreme conditions (*9, 12*) became available, making it important to measure sound velocities of iron alloyed with lighter elements, among which sulphur, oxygen and silicon are the

geochemical choice candidates. The question now is how to constrain the relative abundances of these light elements, and eventually rule out some of them based on a cross-correlation of seismic observations, geochemical considerations, and mineralogical data.

Here, we report direct high-pressure measurements of sound velocities in iron compounds with elements supposedly entering in the composition of the Earth's core, *i.e.* iron oxide (FeO–wüstite), iron sulphide (FeS–troilite and FeS_2–pyrite) and iron silicide (FeSi), and address the question of the composition of the core. For modelling sound velocities in the combined composite mineral model within a first-order approximation, the composite compressional sound velocity in the $(1-\varepsilon_1-\varepsilon_2-\varepsilon_3)Fe + \varepsilon_1O + \varepsilon_2Si + \varepsilon_3S$ system is considered equal to that in the $(1-2.\varepsilon_1-2.\varepsilon_2-2.\varepsilon_3)Fe + \varepsilon_1FeO + \varepsilon_2FeSi + \varepsilon_3FeS$ system where ε_1, ε_2, ε_3 stand for the molar fraction of O, Si, and S in the inner core, respectively.

Sound velocities were measured at high pressure by very-high resolution inelastic x-ray scattering at the European Synchrotron Radiation Facility (ESRF) on beamline ID28, using the (8,8,8) reflection of a backscattering silicon monochromator at an energy of 15.618 keV (3.9 meV resolution). The details of the experimental setup have been reported elsewhere (*13*). The samples were loaded in Mao-Bell type diamond anvil cells, except for the FeS experiment where the sample was loaded in a high-temperature resistant membrane-driven cell. The dispersion of longitudinal acoustic (LA) phonons was measured for 5 values of the momentum transfers between 4 and 12 nm^{-1}. The sound velocity, which is equal to the slope of the dispersion curve at zone center, can thus be directly obtained. At each pressure, an x-ray diffraction pattern was collected in order to obtain directly the molar volume and hence, the density (without using otherwise unreliable if not unavailable equations of state). The measurements were performed to pressures of 90 GPa at room temperature for FeO, FeS_2 and FeSi. In the case of FeS, the measurements were performed at high pressure and high temperature in the stability field of phase IV (*14*) which is the non-quenchable phase relevant to sulphur-rich planetary cores, between 4 GPa at 375 K and 13.5 GPa at 610 K.

In the case of iron, we used a compilation of previously published experimental results, combining shockwave data (*15*) with static work (*9, 16*), and limiting ourselves to pressures below 78 GPa for the static dataset (figure 1). This limitation is due to the fact that the measurements above that pressure need to be corrected for elastic anisotropy. Indeed, it was shown (*16*) that the angular dependence of the P-wave velocity (elastic anisotropy) could be measured with that technique. The elastic anisotropy could be extracted from differences in velocities measured in various geometries, thanks to the preferential alignment of grains of iron uniaxially compressed in a diamond anvil cell. This is shown in figure 2, where the P-wave velocity is plotted as a function of pressure for various values of the angle between the compression axis and the incident and scattered photons. It is clear that there is no measurable anisotropy up to 78 GPa, because the P-wave velocities are independent of orientation. At 112 GPa, differences in velocities can be measured, and the elastic anisotropy of iron can be inferred. This information, although very useful for the comprehension of the anisotropic properties of Earth's inner core, impedes all use of such data for comparison with averaged radial models, as is the case here. The surprising correlation with the shockwave data (taken at high temperature) suggests that the compressional-wave velocity has no intrinsic dependence on temperature (Birch's law), but scales rather linearly with density. This is at odds with a recent measurement of composite sound velocities at high pressure and high temperature (*17*), based on NRIXS; with this technique however, one has to note that the compressional and shear velocities cannot be obtained directly, since a precise knowledge of the equation of state is required at high temperature, which is not available yet.

The sound velocities measured as a function of density are reported in figure 3, along with the linear regressions and their parameters. For the reasons pointed out above, the linear regression for iron was calculated only taking into account the IXS datasets up to 78 GPa grouped with the shockwave data. It is worthy to note that the densities were not obtained using previously published equations of state, but rather by direct measurement of the molar volumes by x-ray diffraction at each pressure point and for each compound, hence reducing all systematic errors transferred from the equations of state. It can be seen from figure 3 that all compounds follow the empirical "Birch law" in the investigated pressure and temperature range, which states that the compressional sound velocity of a material is proportional to its density. This behaviour is essential, because it means that sound velocities do not depend on a particular set of P and T, but rather on the combination of both as reflected by density. This allows the interpolation of the value of sound velocity of any such material to any given pressure or temperature inside the Earth, as long as we know its equation of state in order to calculate density.

Unfortunately, P-V-T equations of state of iron alloys are not readily available, and very little data are present in order to calculate their densities at the P–T conditions of Earth's core. Nevertheless, knowing the P–V–T equation of state of the major compound, namely ε-iron in the present case (*18*), it is possible based on our measurements, to reconstruct the composition–velocity–density profiles of terrestrial solid core models constituted of iron and one light element. Indeed, the average density ρ and compressional sound velocity V of a two-component ideal solid is given in first approximation by $\rho = \dfrac{\rho_1 \cdot \rho_2}{(1-x)\rho_1 + x\rho_2}$ and $V = \dfrac{V_1 \cdot V_2}{(1-x)V_1 + xV_2}$, respectively, where $1-x$ is the molar fraction of component 1. Forcing $\rho = \rho_{PREM}$ and $V = V_{PREM}$, and knowing ρ_1 (density of iron), V_1 and V_2 (Birch relations for iron and the light element), we are left with two equations that can be solved to give unique solutions to the two variables that are x (the molar fraction of the alloying compound) and ρ_2 (density of the light element). Unlike most previous studies, we did not attempt to extrapolate measurements made on solid state phases to the liquid outer core, but used partitioning data in the literature to estimate the composition of the outer core from that constrained for the inner core with the method described above. The results are summarised in table 1.

The most striking observation is that a very high concentration of sulphur (in the FeS form) would be needed to account for the density and velocity profile of Earth's inner core, significantly above typical values inferred from geochemistry (*1-3, 19, 20*). If sulphur were to be the only light element entering in the composition of the inner core, the latter would have to contain around 10 wt% (all percentages hereafter are in weight) sulphur in order to exhibit the density and compressional sound velocity profiles obtained by PREM, and would also require a very low bulk modulus for FeS, since the compression (V_0/V) needs to be 2.49, which is unrealistic for any core-forming material under such pressures. Since geochemical models tend to exclude such large amounts of sulphur in the core, a value of more than 5% of S in the core is unlikely (*1-3*). Moreover, the very low bulk modulus would dramatically soften the inner core, similarly to what was already shown for the outer core in a structural study of the Fe-S liquid system (*21*). The case of FeS_2 was also considered, mainly because of the different bonding properties of sulphur in this compound (different oxidation state, low-spin compound). Although the abundances may sound reasonable (table 1), the elasticity is unacceptable, because it requires FeS_2 to have the same density at core pressures and temperatures than at normal room conditions. On these bases, sulphur whether in the S^{2-} or S^- form, cannot be considered as a good candidate for the light element in the inner core.

The abundances obtained for silicon and oxygen in binary assemblages, namely 2.7% and 1.7% respectively (see table 1), are in the range given by various geochemical models. Moreover, the compression ratios given by our model are in reasonable accord with existing equations of state. In order to discriminate between these two components, a closer look at inner-core–outer-core interactions is necessary. This can also help constrain the composition of the outer core. Theoretical calculations show that the partition coefficient for silicon and oxygen between the liquid and solid phases of iron is $D^{Liq/Sol}(Si)=1.2$ and $D^{Liq/Sol}(O)=40$ (*22*). Thus, one has to rule out the possibility that oxygen be a major light element component of the inner core, because putting 1.7% oxygen in the inner core as a light element in order to satisfy PREM requires an outer core having unrealistic large oxygen contents of 12%. It was pointed out by a theoretical study (*22*) that about 8 mol% oxygen (2.1 wt%) is required in the outer core in order to obtain the density contrast at the ICB, since this density jump cannot be obtained with Si or S. With the partition coefficient given above, this results in traces (0.2%) of oxygen in the inner core. Therefore, the light element in the inner core is mainly silicon, amounting to 2.7%, with traces (0.2%) of oxygen. Using the liquid-solid partition coefficients, we find 8% oxygen and 3.2% Si in the outer core.

Our final model is synthesised in table 1. Based on these considerations from experimental and theoretical mineral physics and seismology, and by ruling out certain possibilities on the basis of cosmochemical abundances, we propose that the light alloying element in Earth's inner core is silicon, constituting 2.7% of its weight, along with traces of (0.2%) oxygen. The outer core would then bear 3.2% silicon along with 8% oxygen. Sulphur would be ruled out as a light element on the basis of our study; this is in agreement with recent theoretical (*23*) studies and experimental work on the Fe-S liquid (*21*). We note that the most recent geochemical studies (*24*) do not favour large amounts of sulphur in the core, in accord with cosmochemical models of the core. The total light element content of the inner core is 3 wt%, and that of the outer core is around 11 wt%.

This study reveals the need for further experimental (whether in the static or dynamic domain) and theoretical data, in order to constrain such composite models; most importantly, P-V-T equations of state (*18*) and compressional sound velocities (*9*) in iron need to be measured with increased accuracy to very high pressures and temperatures, since this is the dataset that plays the most significant role in the inversion of the sound velocity and density data, iron being the major element in the core. Secondly, similar measurements need to be performed on light-element alloys. Last, state-of-the-art solid-liquid elemental partitioning data in iron (*25*) is required to infer the composition of the outer core, on the basis of an inverted composition model of the inner core. Such measurements can be combined with structural (density) and dynamic (sound velocities) information on liquid iron. Obtaining such a model for the composition of the core would help address many standing issues in Earth sciences, ranging for the conditions of core formation (*26*), to the nature of the material that formed the Earth during the phase of planetary accretion (*1, 2*).

TABLES AND FIGURES

Element / Mineral		Fraction for one element (wt%)	Compression (V_0/V)	Model fraction inner core (wt%)	Model fraction outer core (wt%)
Si	FeSi	2.7	1.28	2.7	3.2
O	FeO	1.7	1.33	0.2	8.0
S	FeS	9.8	2.51	0	0
S	FeS$_2$	3.2	1.0	0	0

Table 1: Results from our model for the major-element composition of the core. The first two columns give the weight fraction and compressions obtained by resolving our doubly-constrained sound velocity and density model for the inner core according to PREM. It shows that both forms of sulphur cannot reasonably fit the model, either because of extreme values of the compression ratios (huge compression for FeS, no compression for FeS$_2$), or because of the unrealistic content (12 wt% sulphur). Silicon and oxygen on the other hand can both satisfy the double-constraints for the inner core. Our final preferred model is given in the last two columns, and is based on theoretically predicted solid-liquid partition coefficients.
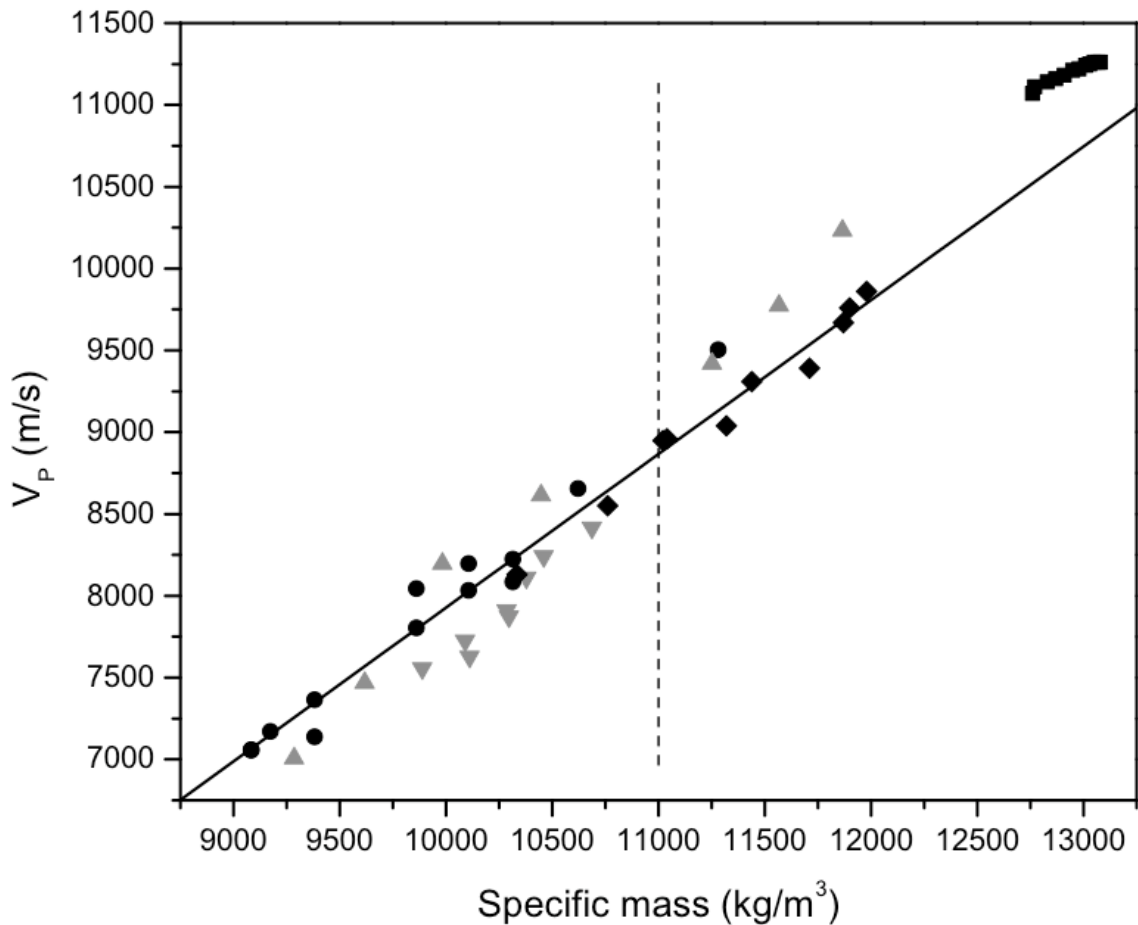
Figure 1: Compressional (P-wave) sound velocities for ε-iron form static IXS work (black circles), static NRIXS work (gray up- and down- triangles), and shockwave measurements (black diamonds). The scatter in the NRIXS data is too large and can therefore not be used to obtain reliable velocity-density relationships. The IXS data was combined with the shockwave data, and the linear fit obtained is $V_P = 0.94\rho - 1466$. The dashed line shows the cut-off density above which the static data was not used, due to contributions of anisotropy to the measured sound velocity (see Fig. 2). The black squares represent the inner-core's velocity-density profile as obtained from PREM.
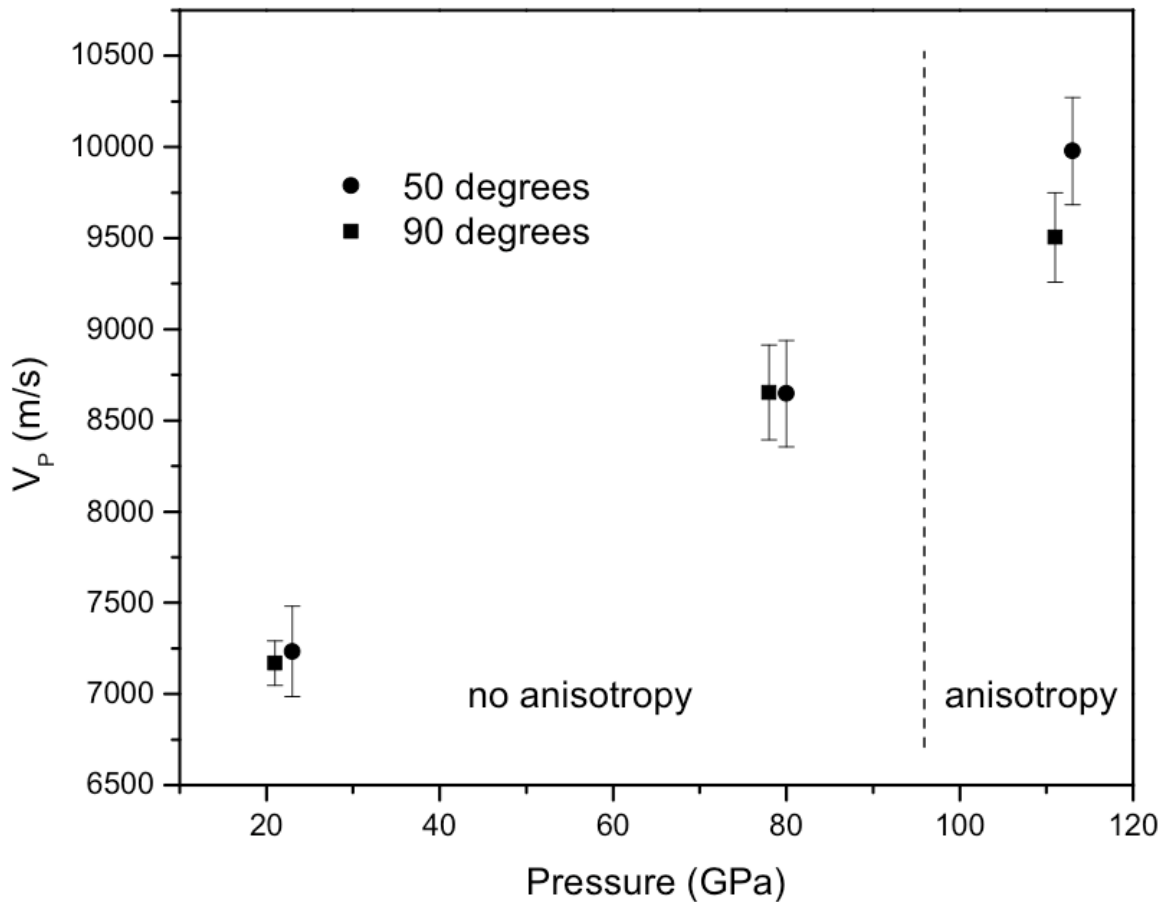

Figure 2: Compressional (*P*-wave) wave velocities in iron for various angles with respect to the compression axis; the data at 22 GPa and 116 GPa is from Antonangeli *et al.* (*16*). This clearly shows that there is no measurable anisotropy up to at least 78 GPa. The measurement of an anisotropy at higher pressures allows determining its elastic anisotropy, but at the same time impedes using the datasets to model radial seismic profiles. Hence, all static data used in this work to derive a velocity-density relationship was limited to pressures of 78 GPa.
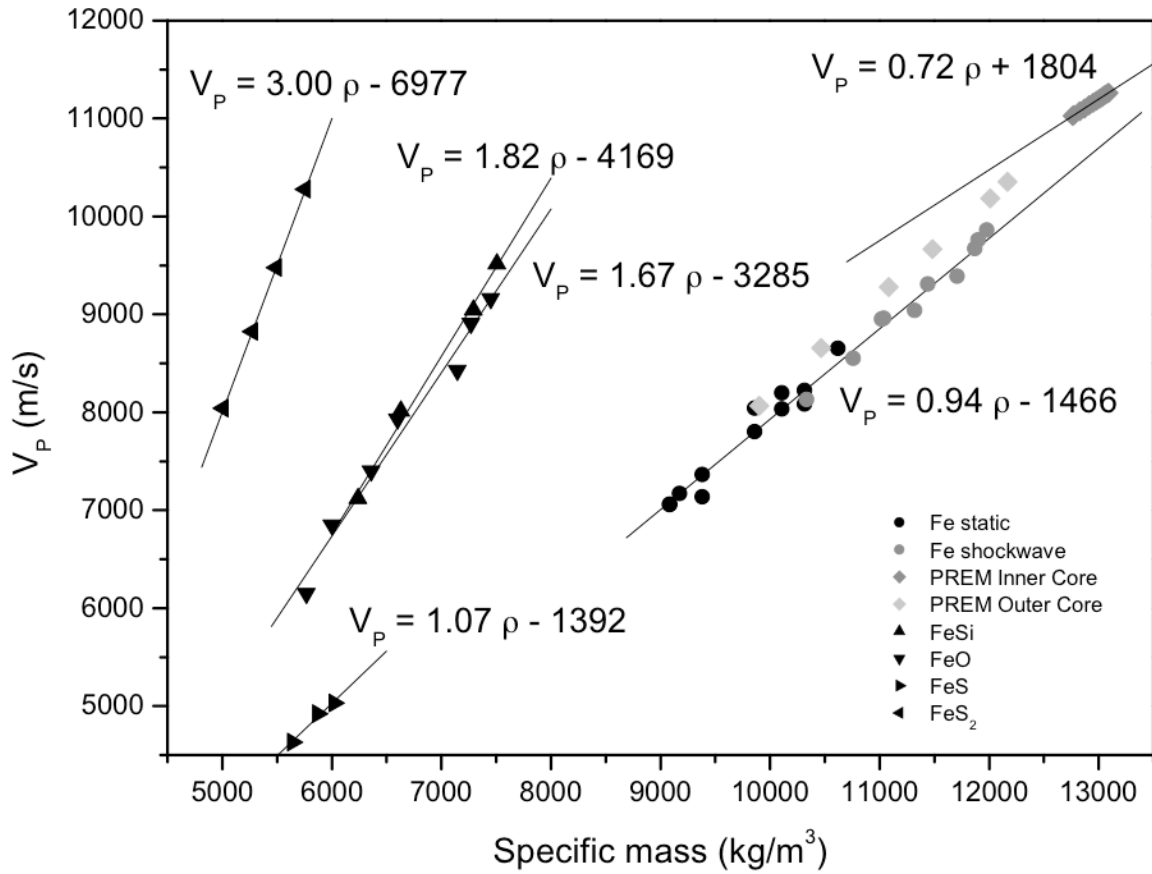
Figure 3: Compressional (*P*-wave) wave velocities in Fe, FeS, FeO, FeS$_2$ and FeSi as a function of density. Seismic velocity profiles from the radial PREM model for the inner and outer core are also reported, along with the parameters of the linear regressions used for each compound.

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