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Density measurements of liquid Fe-S alloys at high-pressure

C. Sanloup,¹ F. Guyot,² P. Gillet,¹ G. Fiquet,¹ M. Mezouar,³ I. Martinez,⁴

Abstract. We present the first static measurements of the density of metallic liquids in the Fe-S system in the pressure and temperature range 1.5 GPa–6.2 GPa and 1500 K–1780 K. Density is inferred from X-ray absorption experiments carried out with a large volume press at the European Synchrotron Radiation Facility. It is shown that increasing the amount of sulfur in liquid iron decreases the bulk incompressibility by -2.5 GPa per 1 weight% of S. These data are important for constraining the presence and amount of sulfur in the cores of small planetary bodies.

1. Introduction

The density of the Earth's core is less than that of a pure Fe-Ni liquid alloy. This statement relies on the comparison between density of the core extracted from seismic and gravimetric data, and laboratory measurements of the equation of state of liquid iron extrapolated to core pressures (P) and temperatures (T) [Birch, 1952]. The core is thus expected to contain up to 10–15 weight % of light elements (H, C, O, N, Si and S) [Poirier, 1994], but there is no consensus on which of these elements (or which mixture of them) are actually present in the core of the Earth and other planets (Mars, galilean satellites). Deciding which element may be alloyed with Fe in the core cannot be simply derived from geochemical mass-balance calculations because the candidate elements are more or less volatile [O'Neill and Palme, 1997]. One alternative is to come back to the seminal work of Birch [Birch, 1952] and to compare the observed core density with that of candidate liquid alloys measured under the relevant P-T conditions. However, the experimental data are very scarce and getting them is still an experimental challenge. The development of large volume presses and high-brilliance synchrotron sources has permitted significant improvements in such density measurements.

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Existing density data on Fe and Fe-alloys liquids were collected either at ambient pressure by ultrasonic [Nasch *et al.*, 1997; Hixson *et al.*, 1990] or pycnometric/Archimedean methods [Lucas, 1964; Kaiura *et al.*, 1979] or in the 100 GPa range by shock wave techniques [Anderson *et al.*, 1994]. The results we present are the first obtained under moderate static pressure conditions, following the recent X-ray absorption method developed in the 0–5 GPa and 300–900 K ranges [Katayama, 1996; Katayama *et al.*, 1998]. They encompass the pressure and temperature conditions of small planetary bodies and those of planetary differentiation. They also provide a basis for extrapolation to pressures relevant to the martian and Earth cores.

2. Experimental Techniques

We used a large volume apparatus [Besson *et al.*, 1992; Mezouar, 1997] installed on the ESRF beamline ID 30. The cell-assembly (Fig.1) is designed to minimize the absorption of X-rays by the furnace (graphite), the pressure transmitting medium (boron epoxy + hBN) and the sample container (sapphire cylinder). The samples consist of pure fine powders of Fe and FeS mixed in different proportions : Fe-10wt%S, Fe-20wt%S, Fe-27wt%S. The non-contamination of the samples by impurities and the accuracy of the Fe/S ratios were also a posteriori checked by SEM analysis on recovered cell-assemblies (Fig. 2-A). A monochromatic X-Ray beam goes through the whole cell assembly (Fig.1 and 3); for density measurements, it is crucial to reduce the absorption by the cell-assembly relative to the sample itself.

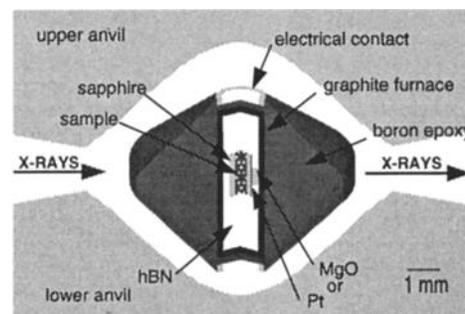


Figure 1. The cell-assembly consists of a boron epoxy medium, a graphite furnace, a hBN cylinder acting both as a pressure transmitter and P-T calibrant and a sample filling a sapphire cylinder. For P-T calibration, a Platinum microfoil (4 μm thick) is used or MgO powder is packed in a 200 μm lateral hole drilled in hBN.

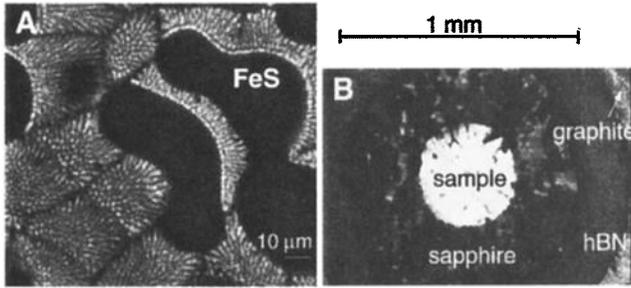


Figure 2. A– SEM photograph of an experimental run (Fe-27wt%S) after quenching, two generation of dendrites are observed, attesting a fully liquid state prior to quenching: 50 μm -size FeS dendrites and then the eutectic Fe-FeS intergrowth; B– cross section of a typical recovered cell-assembly.

As the absorption coefficient of X-rays, μ , for a given element increases both with its atomic mass and with the wavelength, a good compromise was found for $E=46.7$ keV in the Fe-S chemical system. The crystalline *vs* molten state of the sample is checked by recording diffraction patterns on imaging plates. P-T conditions (Table 1) are inferred from the diffraction patterns of hBN and Pt (polycrystalline microfoil) or MgO powder located near the sapphire cylinder (Fig.1) and isochoric calculations on their molar volumes [Touloukian *et al.*, 1977; Jamieson *et al.*, 1982; Isaak *et al.*, 1989; Zhao *et al.*, 1997; LeGodec, *personal communication*]. The absorption method consists of measuring the intensity of the X-ray beam with two photodiodes before (I_0) and after (I) the crossing of the whole cell assembly (Fig.3). The absorption profile is recorded during the movement of the whole press perpendicular to the X-ray beam axis.

3. Results

The intensity ratio obeys the Beer-Lambert law

$$\frac{I}{I_0} = \iint_{x,y} \exp(-(\mu\rho d)_{liq} - (\mu\rho d)_{env} - (\mu\rho d)_{sa}) dx dy \quad (1)$$

where μ is the mass absorption coefficient, ρ the density, d the X-ray path length and y the vertical size of the X-ray beam (50 μm width \times 100 μm height). The subscripts *liq*, *env* and *sa* stand for liquid, sample environment and sapphire respectively. The exact shape of the absorption scans departs somehow from what it should be for a perfect cylindrical sapphire container. Its actual geometry is inferred from an as close as possible match of the scan shape, leading to the correct d values for each P-T conditions, in relation (1) within 0.5%. Deviations of sapphire shapes from perfect cylindricity are below 1% and are accounted for in the calculations. It should be mentioned that to the maximum pressures reached in the experiments, the total variation of the radius of sapphire is below 3%. It follows that the relative error on the X-ray path length

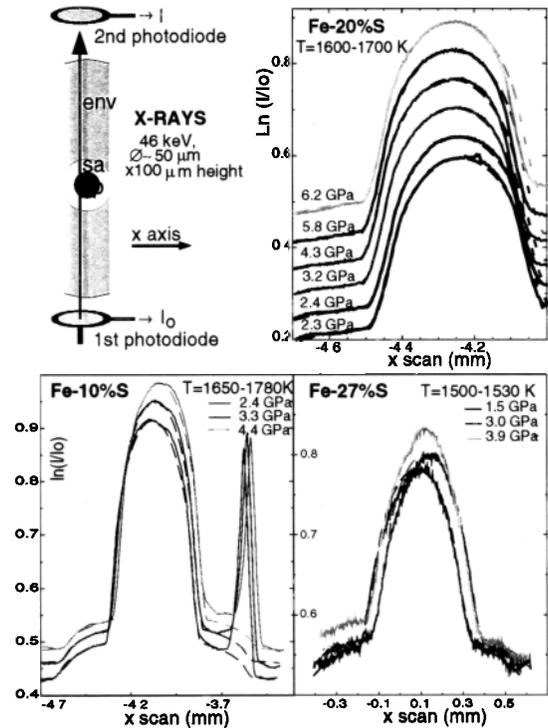


Figure 3. Absorption scans for liquid Fe- $x\%$ S (for the Fe-27%S experiment, the energy was fixed to 58 keV) and sketch of the scan geometry through the cell-assembly (upper left). Dashed lines are fits of the data; subscripts *liq*, *env* and *sa* stand for liquid, sample environment and sapphire; the peak at $x \sim -3.55$ mm (lower left) corresponds to the Pt microfoil used for internal P-T calibration.

between different points used for an equation of state determination is below 1%. For each experiment, the cell-assembly was recovered and cross-sections showed very small deformations of the sapphire (Fig. 2-B). The density of the liquids as a function of P and T is obtained in the following way. Each absorption scan is simulated with relation (1) leading to values of $(\mu\rho)_{liq}$. Density is obtained if μ_{liq} is known. It is assumed that μ is the same for solids and liquids of the same composition and is independent of pressure and temperature. We estimate μ of the samples just before melting from the density measured by the X-ray diffraction patterns and the $\mu\rho$ product inferred from the absorption scans. For one given chemical composition, the total range of relative variations of measured μ is contained within 2.5%. Densities of the solid S-bearing samples are calculated from the geometric mean value of ρ_{Fe} and ρ_{FeS} as determined by a fit of their respective volumes inferred

Table 1. Experimental P-T conditions.

composition (wt% S) :	P range	T range
10%	2.1–6.0 GPa	1650–1780 K
20%	2.3–6.2 GPa	1600–1700 K
27%	1.5–4.0 GPa	1500–1530 K

from the diffraction spectra. The estimated values of μ are : $\mu_{10\%S} = 0.186 \text{ m}^2 \cdot \text{kg}^{-1}$, $\mu_{20\%S} = 0.170 \text{ m}^2 \cdot \text{kg}^{-1}$ and $\mu_{27\%S} = 0.115 \text{ m}^2 \cdot \text{kg}^{-1}$ (this last composition was studied at 58 keV, this is the reason why μ is lower). We also carefully checked that μ is not affected by solid state phase transitions neither in Fe nor in FeS. ρ_{liq} is then calculated with a precision of about 2.5%. Errors on pressure and temperature determinations are due to uncertainties on unit-cell parameters, temperature gradients and equations of state of calibrants. These errors result in uncertainties on pressure and temperature of 50 K and 0.3 GPa respectively. Examples of these relative errors on density-pressure relations are given in figure 4-A and their effects on the imprecision in the determination of K_T in figure 4-B.

Experiments were performed under quasi-isothermal conditions ($\pm 50 \text{ K}$), resulting in density variations less than the error bar. For a given composition, ρ_{liq} values at different pressures are fitted to a third order isothermal Birch-Murnaghan equation of state in which $\rho_{liq}(P_o, T, x_S)$, considered as regular data points and not as input parameters, are provided by picnometric and Archimedeian data [Lucas, 1964; Kaiura et al., 1979].

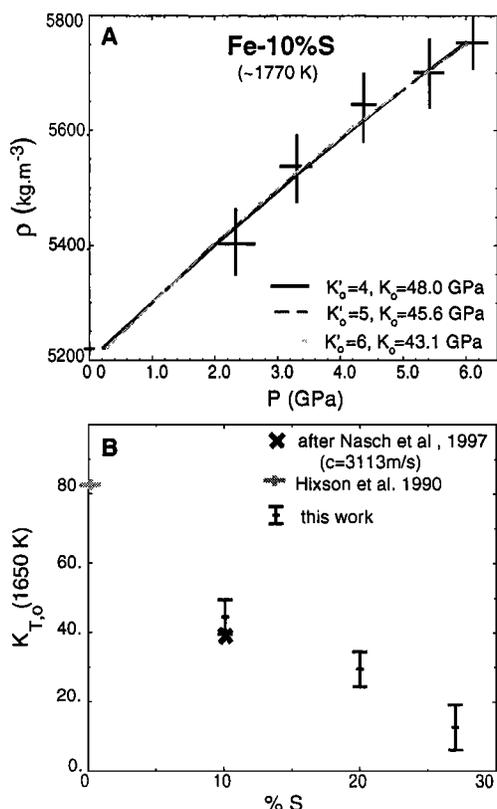


Figure 4. A- Density as a function of pressure for the Fe-10wt%S experiment; B- bulk incompressibility, K_T , as a function of the wt% S content. For convenient comparison, the plotted K_T values all correspond to the same 1650 K isotherm; error bars on K_T include tests for a 4-7 K'_o range as well as uncertainties on density measurements.

The results for Fe-10wt%S composition along a 1770 K isotherm are presented in Figure 3. The derived values of K_T along this isotherm range between 48 and 42 GPa, corresponding to K'_o values of 4 and 7 respectively.

4. Discussion and Geophysical Implications

To quantify the effect of sulfur on K_T and to minimize temperature corrections, all the data have been reduced to a common isotherm (1650 K) for which the adiabatic bulk incompressibility, K_S , of molten Fe-5wt%Ni-10wt%S has been measured [Nasch et al., 1997]. We have assumed that $(\partial K/\partial T)_P$ of the Fe-S liquids is similar to that of liquid iron (-0.0104 GPa/K) [Hixson et al., 1990]. It should be noticed that such temperature corrections concern relatively small temperature differences (less than 200 K) and that varying dK/dT by 100% will result in errors on K of less than 4 GPa.

The K_T values are shown in Figure 4-B. The K_T value for pure iron is inferred from previous work. K_T decreases from 80 GPa for pure iron [Hixson et al., 1990; Anderson et al., 1994] down to around 20 GPa for 27 wt% S. These results can be compared to ultrasonic velocities measurements [Nasch et al., 1997]. For Fe-5wt%Ni-10wt% S liquids, these authors have derived $K_S(1650 \text{ K}, P_o)=63 \text{ GPa}$ leading to $K_T=45 \text{ GPa}$ using the relation : $K_S=K_T \times (1 + \alpha\gamma T)$ with $\gamma=1.9$ and $\alpha=1.10 \cdot 10^{-4} \text{ K}^{-1}$ [Hixson et al., 1990]. To obtain this K_S from ultrasonic velocities, they used a value for the density at 1650 K of $6500 \pm 500 \text{ kg} \cdot \text{m}^{-3}$ which has been derived from data on solid pyrrhotite [Brown et al., 1984] and not real zero pressure density of liquid FeS. A different value for the density of their liquid ($5333 \text{ kg} \cdot \text{m}^{-3}$) is obtained if pycnometric data for FeS liquids are used [Kaiura et al., 1979]. Using this more realistic density value, we infer $K_T=40 \text{ GPa}$ for their liquid composition which is in agreement with the present data for a similar sulfur content (Fig.4-B). Combining ultrasonic data and the present results emphasizes the strong effect of S on the liquid iron compressibility. Moreover, it implies that the K'_o values of such liquids are higher than 4 and probably close to 7, and also that there is little frequency dependence of K_T .

Some geophysical perspectives can now be outlined. For a "planetary" plausible S content, e.g. 0-20wt%, 1%S implies a decrease in K_T of 2.5 GPa (first order approximation). As our experimental P-T conditions are directly relevant to galilean satellites such as Ganymede, this result can be applied to dynamic and structural studies of these small planetary bodies. Unless an electrolyte-rich deep ocean exists on Ganymede, the discovery of an intrinsic magnetic field by the Galileo probe [Kivelson et al., 1996] implies the presence of a liquid metallic core. Given the small size of the planet, that is its most probably low accretion heat, this requires in turn a low melting point for the core metallic component. The presence of sulfur is therefore

strongly expected both as an antifreeze element and as a cosmologically favoured candidate. Our data show that neglecting the effect of S on K_T could lead to errors in relating core density and composition. For example, in an hypothetical galilean-like small planetary body (2000 km in radius, with a Fe-15wt%S liquid core and an adiabatic temperature core profile anchored at 1350 K at the upper core boundary, 1000 km in depth), the mean core density would be calculated 4.5% too low if K_T were assumed equal to that of pure liquid Fe. Concerning the formation of the Earth and martian cores, at least part of the formation process happened in the 0–10 GPa pressure range, either in the first hundreds kilometers of the planet or in small pre-planetary differentiated bodies [Stevenson, 1990; Karato et al., 1997]. The measured densities of Fe-S melts we present should therefore be taken into account in early history models of the Earth and Mars. Considering present day state of Mars, if its core is indeed liquid and its sulfur content is as high as predicted by cosmochemical models [Dreibus and Wanke, 1985; Sanloup et al., 1999] i.e. around 15 wt%, then the effect of sulfur on the physical properties of the core has to be taken into account, especially for moment of inertia calculations.

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