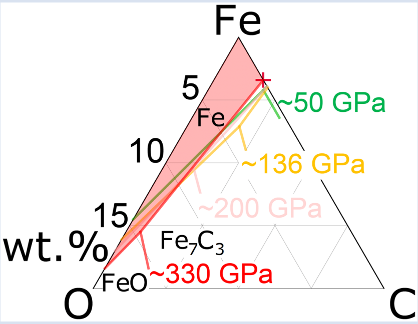
Geochemical Perspectives Letters

Melting experiments on Fe-C-O to 200 GPa; liquidus phase constraints on core composition

F. Sakai[1*], K. Hirose[1,2], K. Umemoto[2]

https://doi.org/10.7185/geochemlet.2218

Abstract



Recent theoretical calculations suggested that carbon and oxygen are important light elements in the Earth's inner and outer core, respectively. We performed melting experiments on the Fe-C-O system and obtained ternary liquidus phase relations at ~50, ~136, and ~200 GPa based on textural and compositional characterisations of recovered samples. Considering the previously reported Fe-C binary eutectic liquid composition, these results are extrapolated to 330 GPa, which constrains C and O concentrations in the liquid outer core that crystallises Fe at the inner core. Theory has predicted a possible range of the solid inner core composition in Fe-C-S-Si that explains seismological observations. The compositions of liquids Fe-C-O-S-Si in equilibrium with such solid Fe-C-S-Si alloys are calculated with the solid-liquid partition coefficient of C obtained in this study along with those of S and Si in the literature. These liquid compositions, however, do not satisfy constraints from both outer core observations and the liquidus phase relations examined in this study, suggesting that the inner core is not Fe-C-S-Si alloy but may include H as an important impurity element.

Received 14 December 2021 | Accepted 21 April 2022 | Published 17 May 2022

Introduction

The ~8 % density deficit and ~4 % velocity excess of the Earth's outer core with respect to pure Fe (Kuwayama *et al.*, 2020) are attributed to the presence of light elements such as C, O, S, Si, and H (*e.g.*, Hirose *et al.*, 2021). The recent *ab initio* simulations by Li *et al.* (2018) showed a possible range of the solid inner composition in the Fe-C-S-Si system and argued that C is essential to explain the density, and compressional and shear velocities, observed in the inner core. It suggests that the outer core is also rich in C when considering its low solid metal/liquid metal partition coefficients obtained in the Fe-C system (Mashino *et al.*, 2019). Contrarily, O is known to be almost insoluble in solid Fe (Alfè *et al.*, 2002) and should thus be nearly absent in the inner core. Instead, O can account for the density difference observed across the inner core boundary (ICB) (Alfè *et al.*, 2002; Kuwayama *et al.*, 2020) and is likely to be a major light element in the outer core (Badro *et al.*, 2014; Umemoto and Hirose, 2020). Both C and O could thus be important light elements in the core. Morard *et al.* (2017) argued that both C and O largely diminish the liquidus temperatures of Fe alloys, which is important for the core-mantle boundary (CMB) temperature to be lower than the melting temperature of the lowermost mantle.

Melting phase relations and eutectic liquid compositions have been examined in Fe-rich portions of both the Fe-C (Mashino *et al.*, 2019) and Fe-O binary systems (Oka *et al.*, 2019), but those in the Fe-C-O ternary systems are not known yet. When two or more light elements are present, interactions between them affect phase relations and element partitioning in ternary systems. The composition of the outer core liquid should be within the liquidus field of Fe such that it crystallises the dense inner core.

Here we performed melting experiments on the Fe-C-O system at high pressure and temperature (*P-T*) in a laser heated diamond-anvil cell (DAC) (see Supplementary Information S-1 for Methods) and determined the ternary liquidus phase relations and solid-liquid partitioning based on the textural and chemical analyses of recovered samples at ~50 (39–49) GPa, ~136 (128–138) GPa, and ~200 (190–211) GPa. These results are then extrapolated to the ICB pressure of 330 GPa by employing earlier data on the Fe-C system (Mashino *et al.*, 2019). The range of the possible inner core composition in the Fe-C-S-Si system has been recently proposed by Li *et al.* (2018). We examine the validity of such Fe-C-S-Si inner core and suggest that H may be an additional important light element not only in the outer core (Umemoto and Hirose, 2020) but also in the inner core (Wang *et al.*, 2021).

Results

We performed five separate melting experiments on three samples with different C/O ratios at pressures around 50 GPa, 136 GPa, and 200 GPa (Table S-1). From the textural and compositional characterisations of sample cross sections, we determined liquid compositions and their liquidus phases (Figs. 1,

1. Department of Earth and Planetary Science, The University of Tokyo, Tokyo 113-0033, Japan
2. Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo 150-8550, Japan
* Corresponding author (email: f.sakai@eps.s.u-tokyo.ac.jp)

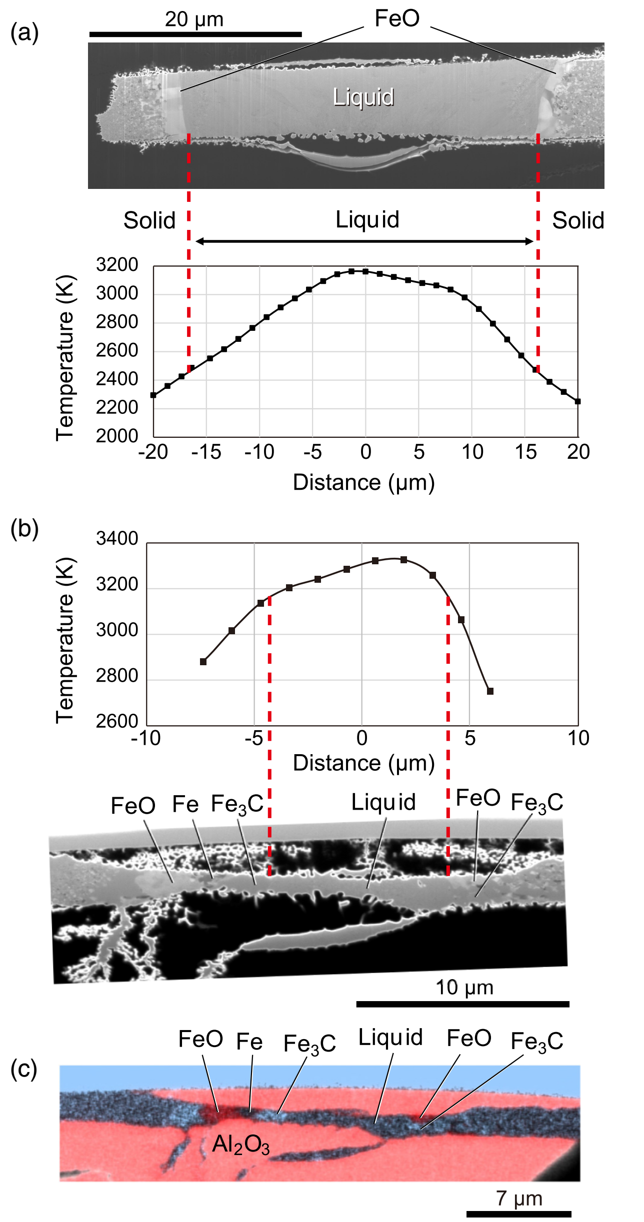


Figure 1 Scanning ion microscope (SIM) images and the X-ray elemental map of sample cross sections and corresponding temperature profiles obtained in **(a)** run #1 at 46 GPa and **(b, c)** run #3 at 128 GPa. The X-ray map **(c)** is combined for C (light blue), O (red), and Al (white). In run #3, we found Fe_3C and FeO in direct contact with liquid at 3170 K and Fe at a slightly lower temperature portion (3040 K), suggesting that the liquid obtained closely represents the ternary eutectic liquid at ~3110 K.

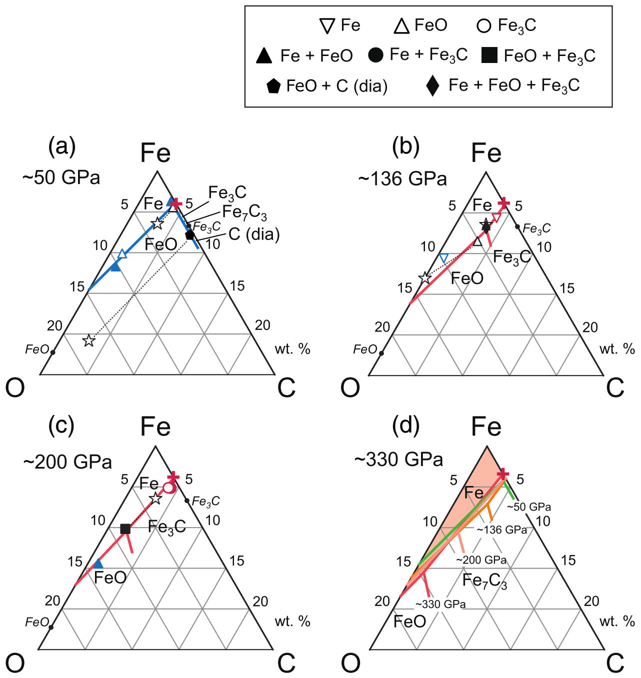


Figure 2 Liquidus phase relations of the Fe-C-O ternary system in weight percent at **(a)** ~50 GPa, **(b)** ~136 GPa, **(c)** ~200 GPa, and **(d)** ~330 GPa. Liquids obtained in the present experiments (black) are plotted along with those from Oka *et al.* (2019) (blue) and Mashino *et al.* (2019) (red). Pluses indicate the Fe-C binary eutectic composition at each pressure. Stars show the compositions of starting materials and are connected by dotted lines to those of liquids formed. Contamination by carbon explains the mass balance in each run. The present results indicate higher O concentration in the Fe-FeO eutectic liquid than earlier studies in which the presence of C in liquid was not quantitatively taken into account (Morard *et al.*, 2017; Oka *et al.*, 2019). Since the inner core consists of light element depleted solid Fe, the outer core composition should be in the liquidus field of Fe at inner core pressures as shown by the red area in **(d)** for 330 GPa.

S-1; Supplementary Information S-2). The Fe-C-O ternary diagrams were obtained at each pressure based on these present data along with those reported in Mashino *et al.* (2019) and Oka *et al.* (2019), both of which reported the EPMA analyses of C and O concentrations in liquids along with their liquidus phases. We employ the Fe-C binary eutectic composition at each pressure from Mashino *et al.* (2019) considering uncertainty in their determinations (see red pluses in Fig. 2).

At ~50 GPa, the Fe-C-O liquids containing only 0.4–0.6 wt. % O coexisted with FeO, indicating that the liquidus field of FeO extends to a low O portion (Fig. 2a). Moreover, the compositions of liquids coexisting with FeO ± Fe (runs #1 and #O7) are close to that of the Fe-C binary eutectic liquid that coexists with Fe + Fe_3C (Mashino *et al.*, 2019), suggesting that they approximate the ternary eutectic composition at this pressure. The Fe + FeO cotectic line and the C-free, Fe-FeO binary eutectic composition are obtained by combining such ternary eutectic composition with those of O-rich (8.8–10.3 wt. %) liquids coexisting with FeO ± Fe (runs #O3 and #O4).

At ~136 GPa (Fig. 2b), we obtained the ternary eutectic liquid which coexisted with Fe + FeO + Fe_3C (run #3; Fig. 1b,c). The Fe + Fe_3C cotectic line is drawn between the ternary eutectic and the Fe-C binary eutectic compositions (Mashino *et al.*, 2019) and is consistent with the liquid composition obtained in run #M3 coexisting with Fe. The Fe-FeO binary eutectic composition was found at ~50 GPa and ~200 GPa from the positions of the Fe + FeO cotectic line in the Fe-C-O ternary diagrams and is estimated for ~136 GPa by interpolation considering the pressure effect works linearly, based on the previous observations that the Fe-FeO eutectic composition increases approximately in proportion to pressure above 50 GPa (Oka *et al.*, 2019). The Fe + FeO cotectic line obtained at this pressure is compatible with the results of runs #4 and #O5. Also at ~200 GPa (Fig. 2c), we obtained an Fe-C-O liquid coexisting with FeO + Fe_3C in run #5 in addition to those from runs #M4, #M7, and #O6. This liquid should almost represent the ternary eutectic liquid since its composition is plotted near the tie line between those of the Fe-C eutectic liquid and the liquid coexisting with Fe + FeO (run #O6).

These results well constrain the Fe-C-O ternary liquidus phase diagram at ~50 GPa, ~136 GPa, and ~200 GPa (Fig. 2a–c). The ternary eutectic temperature is found to be about 2460 ± 110 K at ~50 GPa (run #1), 3110 ± 150 K at ~136 GPa (run #3), and 3660 ±240 K at ~200 GPa (run #5), and they are extrapolated to ~4100 K at the ICB pressure (Fig. S-2). Figure 2d shows the liquidus phase relations at 330 GPa, in which we employed the C concentration in the Fe-C binary eutectic liquid (Mashino *et al.*, 2019) and extrapolated the ternary eutectic liquid composition and the O content (~18 wt. %) in the Fe-O eutectic liquid by considering the linear pressure effect above 50 GPa where mixing between the Fe-rich metallic liquid and FeO-rich ionic liquid becomes ideal (Oka *et al.*, 2019). It is noted that the ternary eutectic composition is located close to the tie line connecting the Fe-Fe_3C and Fe-FeO binary eutectic compositions at each pressure. In other words, the liquidus field of Fe, a compositional range of liquids that first crystallise Fe rather than light element-rich phases of Fe_3C (or Fe_7C_3 above 203–255 GPa according to Mashino *et al.*, 2019) and FeO, can be estimated by interpolation between the Fe-C and Fe-O eutectic liquid compositions.

Discussion

Fe-C-O or Fe-C-O-S-Si outer core? If the outer core is an Fe-C-O liquid, it crystallises the Fe-C inner core because a negligible amount of O can be included in solid Fe (Alfè *et al.*, 2002; Yokoo *et al.*, 2019). C alone cannot account for the observed density and velocities (Li *et al.*, 2018). It is likely that 1.7 wt. % S is present in the outer core according to cosmochemical and geochemical studies (Dreibus and Palme, 1996). When we apply the solid Fe/liquid partition coefficient of sulfur, $D_S = 0.8$ (by weight) at 330 GPa determined by both theory (Alfè *et al.*, 2002) and experiment (Yokoo *et al.*, 2019), the inner core may include 1.4 wt. % S in addition to C. The recent *ab initio* calculations gave possible C concentrations in solid Fe-C-1.4 wt. % S alloys that explain the inner core density, compressional and shear velocities (the Fortran code provided in Li *et al.*, 2018); 1.5–2.3, 1.0–1.6, and 0.7–1.1 wt. % C for $T_{360GPa} = 5500$, 6000, and 6500 K, respectively. We can calculate the C contents in Fe-C-O-1.7 wt. % S liquids that are in equilibrium with such Fe-C-1.4 wt. % S solids at the ICB with D_C that depends on the amount of O (Fig. 3; Supplementary Information S-3). Regardless of the O content, such liquid compositions are, however, far outside the liquidus field of Fe in the Fe-C-O-1.7 wt. % S system at inner core conditions (Fig. S-3), which is estimated considering 5 wt. % S in the Fe-S binary eutectic liquid at 330 GPa (Mori *et al.*, 2017) (see Supplementary Information S-4). The Fe-C-1.4 wt. % S inner core (and Fe-C-O-1.7 wt. % S outer core) is therefore not feasible.

Next we additionally consider the presence of Si. The range of solid Fe-C-Si-1.4 wt. % S compositions that satisfy the observed inner core density and velocities has been also calculated by Li *et al.* (2018) at $T_{360GPa} = 5500$, 6000, and 6500 K. The C and Si abundances in Fe-C-O-Si-1.7 wt. % S liquids which coexist with such Fe-C-Si-1.4 wt. % S solids at the ICB are calculated by employing D_C and D_{Si} (= 1.0) (Alfè *et al.*, 2002). In addition, the remaining O content is obtained for the liquids Fe-C-O-Si-1.7 wt. % S to account for the outer density and velocity (Umemoto and Hirose, 2020) when $T_{ICB} =$ 5320 K, 5800 K, and 6280 K that correspond respectively to 5500 K, 6000 K, and 6500 K at 360 GPa employed in Li *et al.* (2018) assuming adiabatic temperature profile and Grüneisen parameter $\gamma = 1.5$. On the other hand, we extend the estimate of the liquidus field of Fe to the Si-bearing system considering 8 wt. % Si in the Fe-Si binary eutectic liquid at 330 GPa (Hasegawa *et al.*, 2021) (see Supplementary Information S-4). Nevertheless, the range of liquid compositions based on constraints from seismological observations of both the inner and outer core again do not overlap with the liquidus field of Fe in the Fe-C-O-Si-1.7 wt. % S system (Fig. 4).

Hydrogen in the core? None of the alloys in the Fe-C-O-S-Si system satisfy the liquidus phase constraint on core composition examined in this study in addition to the seismological constraints. This is primarily because high concentrations of C are required in the inner core when H is not considered (Li *et al.*,

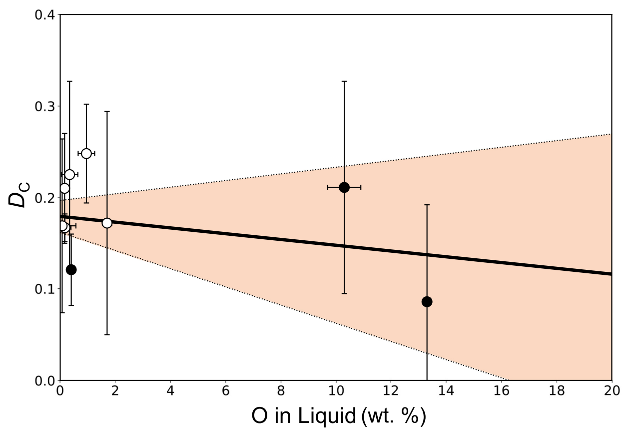


Figure 3 The solid Fe/liquid partition coefficient of C, D_C plotted as a function of O concentration in liquid, calculated by weight percent. Solid and open circles indicate data obtained in this study and Mashino *et al.* (2019), respectively. The regression line is based on maximum likelihood estimation with weighting based on the inverse of uncertainty in each data; $D_C = -0.003(7) \times [O]_{liq} + 0.18(2)$. The shaded band indicates ±1σ uncertainty.

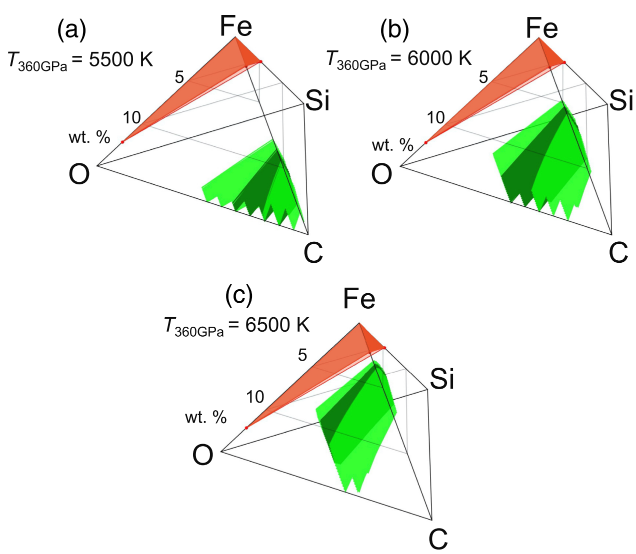


Figure 4 Compositional range of liquids (green) that are in equilibrium with the Fe-C-Si-1.4 wt. % S solids for the inner core proposed by Li *et al.* (2018). Green and dark green areas indicate compositions estimated using D_C with and without ±1σ uncertainty, respectively. $T_{360\ GPa} = 5500$ K **(a)**, 6000 K **(b)**, and 6500 K **(c)**. The O contents are calculated to account for the outer density and velocity at corresponding $T_{ICB} = 5320$ K, 5800 K, and 6280 K (Umemoto and Hirose, 2020). The red area shows the liquidus field of Fe in the Fe-C-O-Si-1.7 wt. % S system. There are no Fe-C-O-Si-1.7 wt. % S liquids that satisfy both the seismological (green) and liquidus phase (red) constraints.

2018), which leads to too much C in the outer core due to the low D_C (= 0.1 to 0.2) (Fig. 3). It is likely that the inner core solid contains only a minor amount of C and may instead include a substantial amount of H. Indeed, the more recent *ab initio* simulations by Wang *et al.* (2021) demonstrated that solid Fe-Si-H alloys can explain the seismological observations of the inner core. The inclusion of H in the inner core requires its presence in the outer core as well. Indeed, it has been already supported by *ab initio* calculations of the density and compressional velocity of H-bearing liquid Fe alloys (Umemoto and Hirose, 2020) and by the high metal/silicate partition coefficient of H under high *P-T* conditions of core segregation (Li *et al.*, 2020; Tagawa *et al.*, 2021).

In future studies, it is important to elucidate liquidus temperatures of Fe alloys not only at the eutectic point but also for the entire liquidus field of Fe. With a narrow range of possible T_{ICB}, we will then be able to tightly constrain the compositions of liquids that crystallise Fe at the inner core. Conversely, the liquidus temperatures of a possible range of the outer core composition can constrain T_{ICB}, which remains highly controversial (Hirose *et al.*, 2021).

Acknowledgements

We thank Y. Kuwayama, S. Yokoo, and K. Yonemitsu for their help in experiments. Comments from Y. Fei and two anonymous reviewers were valuable to improve the manuscript. This work was supported by the JSPS grant 21H04968.

Editor: Francis McCubbin

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2218.

Cite this letter as: Sakai, F., Hirose, K., Umemoto, K. (2022) Melting experiments on Fe-C-O to 200 GPa; liquidus phase constraints on core composition. *Geochem. Persp. Let.* 22, 1–4. https://doi.org/10.7185/geochemlet.2218

References

Alfè, D., Gillan, M.J., Price, G.D. (2002) Composition and temperature of the Earth's core constrained by combining ab initio calculations and seismic data. *Earth and Planetary Science Letters* 195, 91–98. https://doi.org/10.1016/S0012-821X(01)00568-4

Badro, J., Cote, A.S., Brodholt, J.P. (2014) A seismologically consistent compositional model of Earth's core. *Proceedings of the National Academy of Sciences* 111, 7542–7545. https://doi.org/10.1073/pnas.1316708111

Dreibus, G., Palme, H. (1996) Cosmochemical constraints on the sulfur content in the Earth's core. *Geochimica et Cosmochimica Acta* 60, 1125–1130. https://doi.org/10.1016/0016-7037(96)00028-2

Hasegawa, M., Hirose, K., Oka, K., Ohishi, Y. (2021) Liquidus Phase Relations and Solid-Liquid Partitioning in the Fe-Si-C System Under Core Pressures. *Geophysical Research Letters* 48, e2021GL092681. https://doi.org/10.1029/2021GL092681

Hirose, K., Wood, B., Vočadlo, L. (2021) Light elements in the Earth's core. *Nature Reviews Earth & Environment* 2, 645–658. https://doi.org/10.1038/s43017-021-00203-6

Kuwayama, Y., Morard, G., Nakajima, Y., Hirose, K., Baron, A.Q.R., Kawaguchi, S.I., Tsuchiya, T., Ishikawa, D., Hirao, N., Ohishi, Y. (2020) Equation of state of liquid iron under extreme conditions. *Physical Review Letters* 124, 165701. https://doi.org/10.1103/PhysRevLett.124.165701

Li, Y., Vočadlo, L., Brodholt, J.P. (2018) The elastic properties of *hcp*-Fe alloys under the conditions of the Earth's inner core. *Earth and Planetary Science Letters* 493, 118–127. https://doi.org/10.1016/j.epsl.2018.04.013

Li, Y., Vočadlo, L., Sun, T., Brodholt, J.P. (2020) The Earth's core as a reservoir of water. *Nature Geoscience* 13, 453–458. https://doi.org/10.1038/s41561-020-0578-1

Mashino, I., Miozzi, F., Hirose, K., Morard, G., Sinmyo, R. (2019) Melting experiments on the Fe–C binary system up to 255 GPa: Constraints on the carbon content in the Earth's core. *Earth and Planetary Science Letters* 515, 135–144. https://doi.org/10.1016/j.epsl.2019.03.020

Morard, G., Andrault, D., Antonangeli, D., Nakajima, Y., Auzende, A.L., Boulard, E., Cervera, S., Clark, A., Lord, O.T., Siebert, J., Svitlyk, V., Garbarino, G., Mezouar, M. (2017) Fe–FeO and Fe–Fe_3C melting relations at Earth's core–mantle boundary conditions: Implications for a volatile-rich or oxygen-rich core. *Earth and Planetary Science Letters* 473, 94–103. https://doi.org/10.1016/j.epsl.2017.05.024

Mori, Y., Ozawa, H., Hirose, K., Sinmyo, R., Tateno, S., Morard, G., Ohishi, Y. (2017) Melting experiments on Fe–Fe_3S system to 254 GPa. *Earth and Planetary Science Letters* 464, 135–141. https://doi.org/10.1016/j.epsl.2017.02.021

Oka, K., Hirose, K., Tagawa, S., Kidokoro, Y., Nakajima, Y., Kuwayama, Y., Morard, G., Coudurier, N., Fiquet, G. (2019) Melting in the Fe-FeO system to 204 GPa: Implications for oxygen in Earth's core. *American Mineralogist* 104, 1603–1607. https://doi.org/10.2138/am-2019-7081

Tagawa, S., Sakamoto, N., Hirose, K., Yokoo, S., Hernlund, J., Ohishi, Y., Yurimoto, H. (2021) Experimental evidence for hydrogen incorporation into Earth's core. *Nature Communications* 12, 2588. https://doi.org/10.1038/s41467-021-22035-0

Umemoto, K., Hirose, K. (2020) Chemical compositions of the outer core examined by the first principles calculations. *Earth and Planetary Science Letters* 531, 116009. https://doi.org/10.1016/j.epsl.2019.116009

Wang, W., Li, Y., Brodholt, J.P., Vočadlo, L., Walter, M.J., Wu, Z. (2021) Strong shear softening induced by superionic hydrogen in Earth's inner core. *Earth and Planetary Science Letters* 568, 117014. https://doi.org/10.1016/j.epsl.2021.117014

Yokoo, S., Hirose, K., Sinmyo, R., Tagawa, S. (2019) Melting Experiments on Liquidus Phase Relations in the Fe-S-O Ternary System Under Core Pressures. *Geophysical Research Letters* 46, 5137–5145. https://doi.org/10.1029/2019GL082277