ESRF	**Experiment title:** XANES study of Fe alloys end-members under high pressure	**Experiment number**: ES-1043
Beamline: BM23	**Date of experiment**: from: 08/09/2021 to: 14/09/2021	**Date of report**: 05/10/2021
Shifts: 18	**Local contact(s)**: Angelika Rosa	*Received at ESRF:*

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Report:

The aim of this beamtime was to record accurate XANES and EXAFS signal for different Fe end-members as a function of pressure at room temperature.

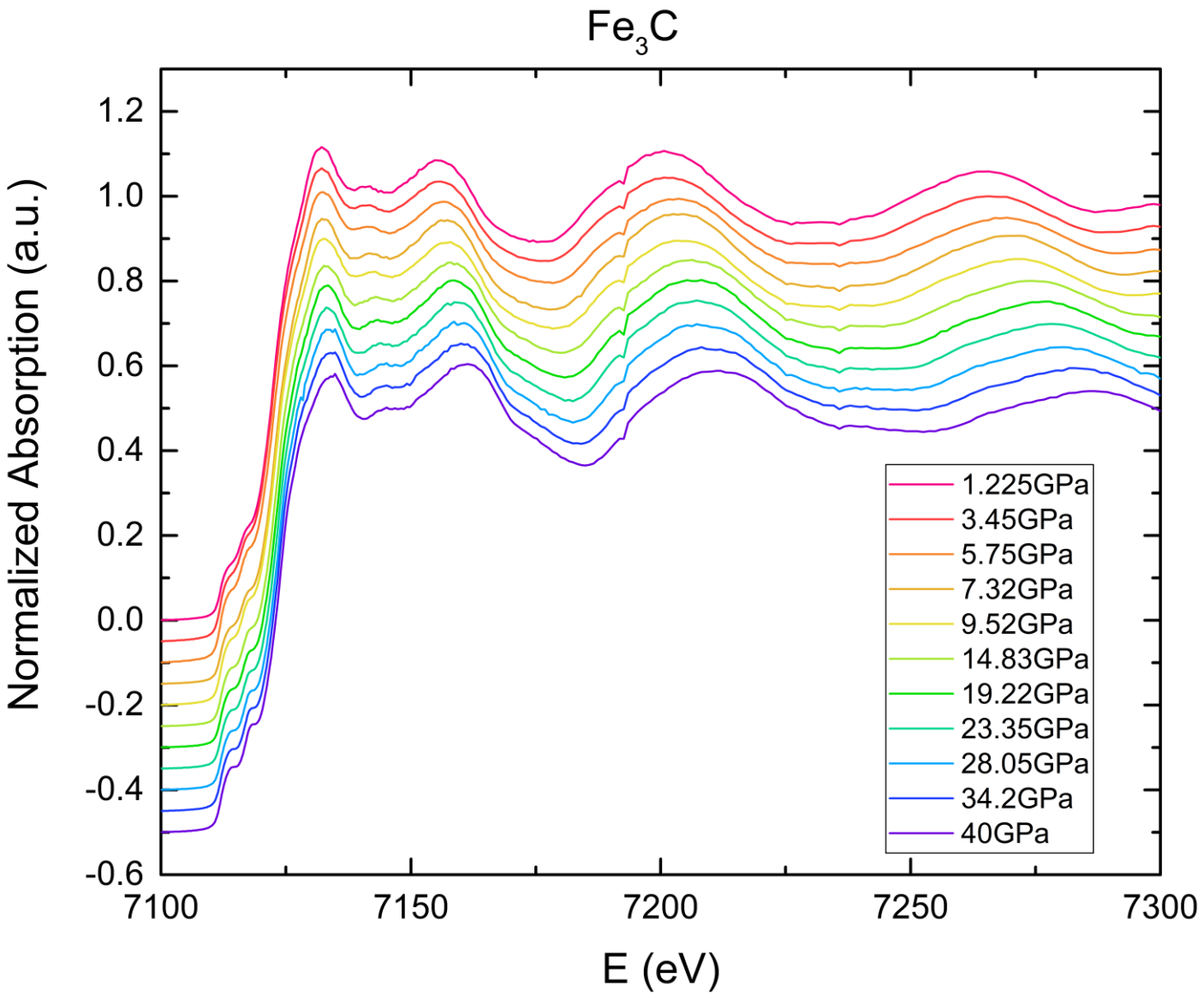
We used the experimental setup now available on BM23, allowing us to simultaneously record XRD patterns, ruby fluorescence to measure pressure and high-quality EXAFS signal at the Fe-k-edge in a Diamond Anvil Cell.

Unfortunately, we were not able to analyse the XANES region of the spectra with a 0.2 eV energy resolution using the Si (311) crystal, as previously mentioned in our proposal, as the absorption of the diamond was too high, even using drilled Nano Polycrystalline Diamonds (NPD).

The experiment has been mainly carried out using a solid pressure medium, KCl. This pressure medium could also be used as pressure calibrant above 40 GPa, when due to non-hydrostaticity the ruby fluorescence signal becomes too weak. Our first trials using Ne as pressure medium were not successful, potentially related to small cracks in the fragile drilled nanopolycrystalline diamonds.

We carried out cold compressions on four different samples in different pressure ranges: carbides (Fe-15wt%C, Fe_3C and Fe_7C_3) between 1bar and 50 GPa, as well as oxides (FeO) up to ~150 GPa.

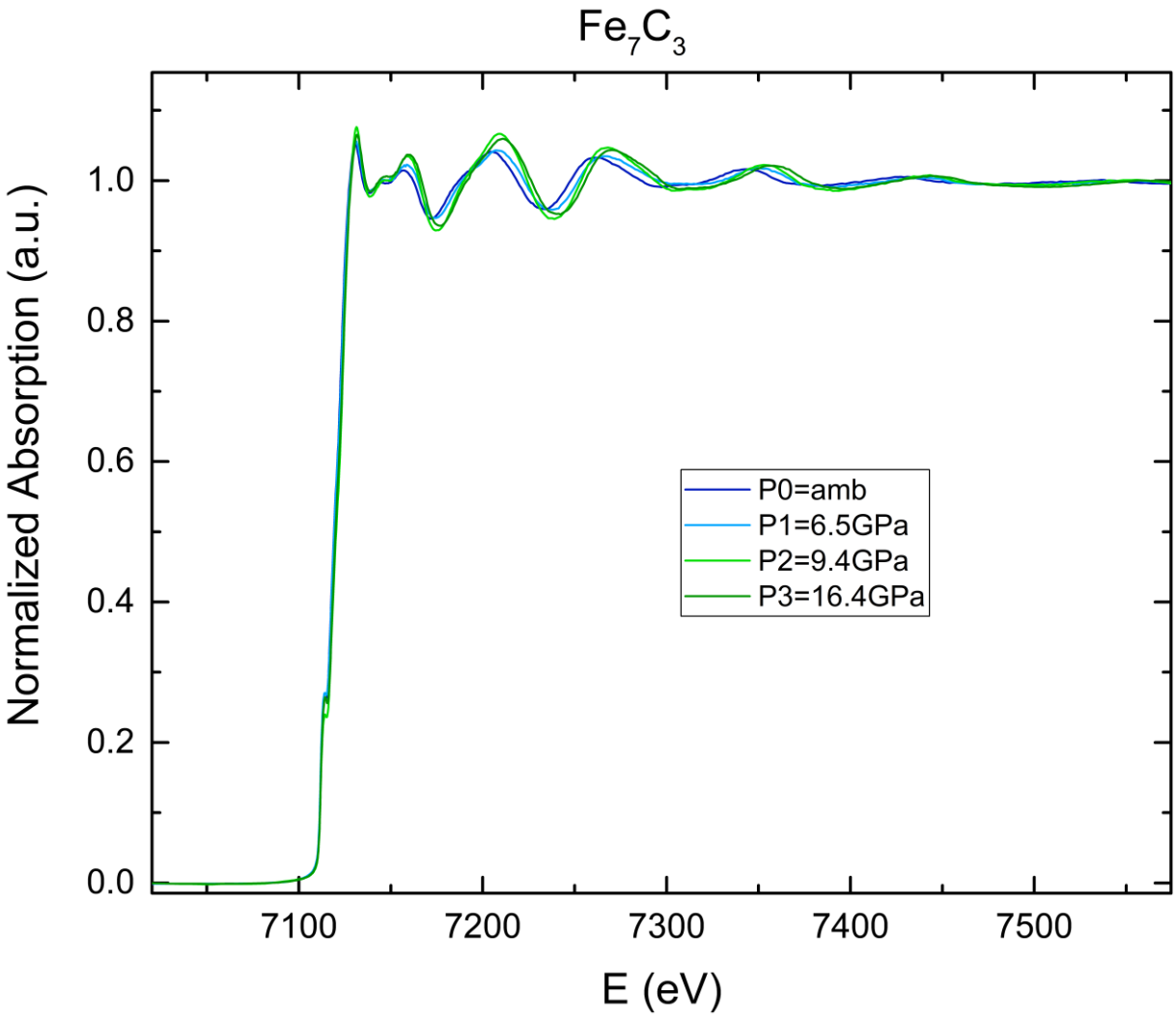
Here are shown the different experimental results we obtained. These raw data will be carefully analysed and compared with ab initio calculations performed by the group of Prof. Kim of the University of Toronto (i.e. Blair Lebert and PhD student Christopher Heath).



Fe_3C purity was carefully analysed prior to experiment by Y. Nakajima from Kumamoto University. This sample was synthetized under high pressure using a multi-anvil platform available at the Institute for Planetary Materials, Misasa, Japan.

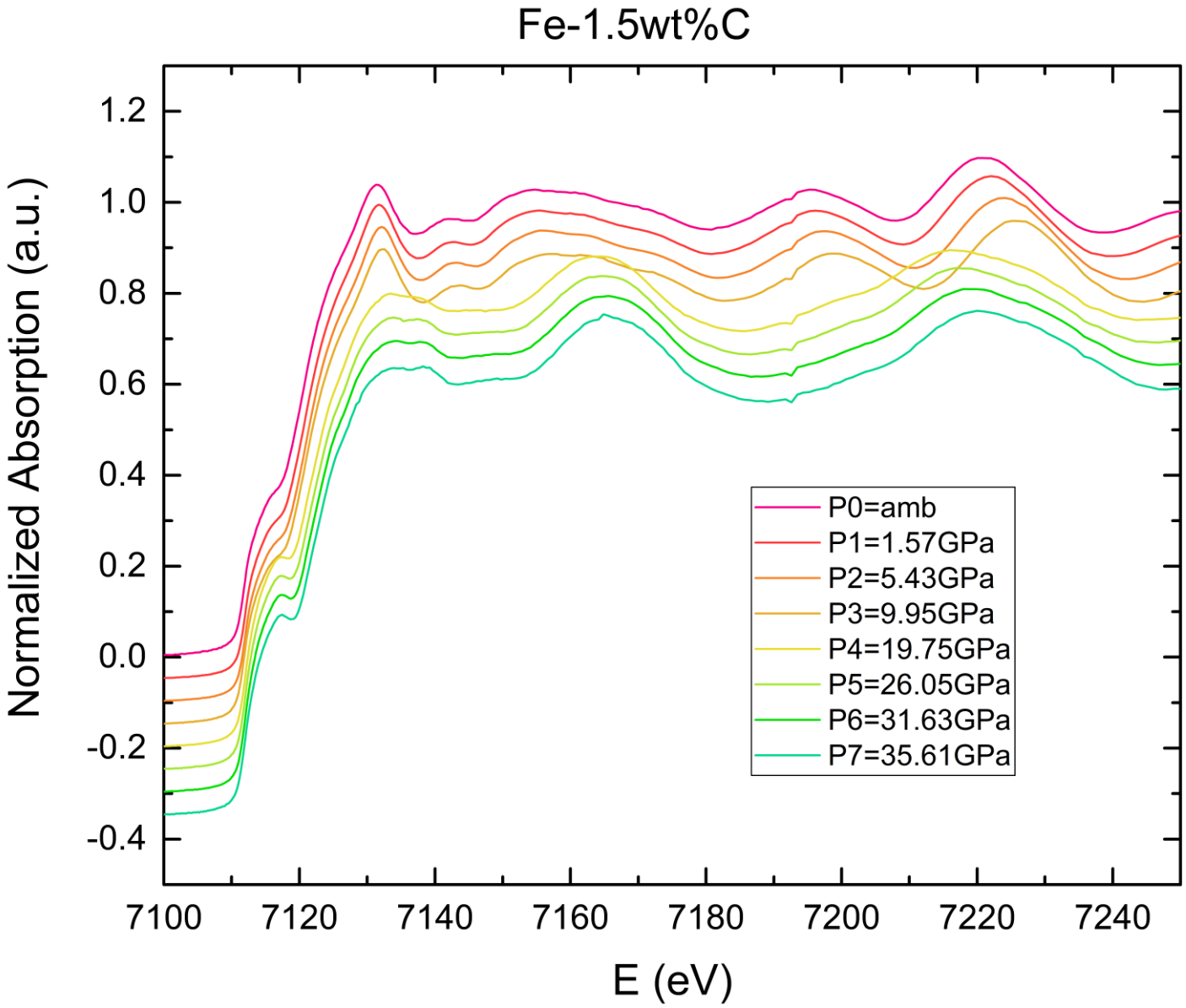
For this sample, we were able obtain a signal up to 14 $Å^{-1}$.

Careful analysis of the XANES spectra will be carried out, as well as the EXAFS signal, in order to decipher if the ferromagnetic to paramagnetic transition previously observed around 5-10 GPa (Gao et al., 2008; Litasov et al., 2013) could be identified here.



This carbide with a stoichiometry Fe_7C_3 was also synthetized and characterized by Yoichi Nakajima.

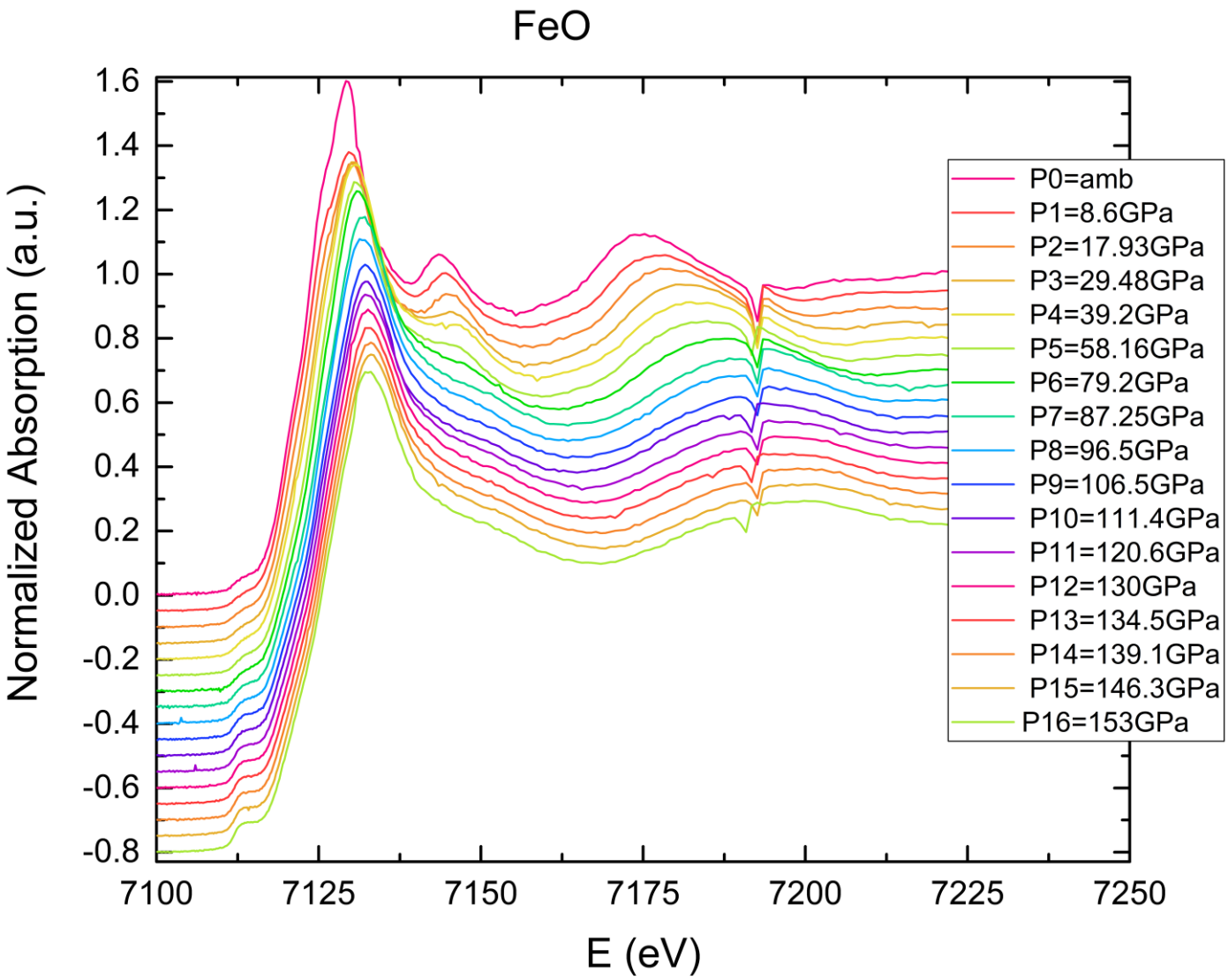
The XANES signal seems to highlight a structural change between 6.5 GPa and 9.4 GPa, in correlation with a previously observed ferromagnetic to paramagnetic transition in this compound at **7** GPa (Chen et al., 2012). This transition seems to have a more obvious signature in Fe_7C_3 rather than in Fe_3C compound.



This sample is a Fe alloy containing 1.5wt%C. It has been synthesized by an ultrarapid quench method at the Institut de Chimie et des Matériaux de Paris-Est (ICMPE), Paris, France (Morard et al., 2017). Previous cold compression dataset of such sample has shown that it stays into a unique phase and do not decompose into Fe + Fe_3C.

For this sample, valid signal from the sample was measured up to 18 $Å^{-1}$. This is important in order to finely compare this structure with pure Fe recorded in a previous inhouse test run. This will allow to deduce the effect of C incorporation on the structure of pure bcc/hcp Fe under high pressure.

A bcc to hcp structural transition between 10 and 20 GPa can be easily noticed both in the XANES and the EXAFS.



Starting material for this run was Fe_xO (x=0.92 following (McCammon and Liu, 1984)) synthesized under reducing conditions from hematite at 1200°C for 24 hours (courtesy of Prof S. Jacobsen from Northwestern University).

The first gradual change observed here between 30 and 60 GPa is correlated with the structural transition between B1 and B8 structure.

For higher pressure, we successfully covered the intended pressure range for which a spin transition is expected in solid FeO, around 120 GPa (Ozawa et al., 2011). However, no obvious change in the spectra could be noticed in this pressure range. In addition, the XRD spectra of the sample is not clearly showing a volume change, expected to be of 2.5% at 120 GPa, in the present study. Our results are therefore in strong disagreement with the previous study.

In conclusion, these different runs will be used as reference for analysis of quenched samples in future Laser Heated DAC studies, to determine melting relations of iron alloys in the Fe-C-O ternary system under high pressure, as well as determine potential C contamination in different Fe melting experiments.

References :

Chen, B., Gao, L., Lavina, B., Dera, P., Alp, E.E., Zhao, J., Li, J., 2012. Magneto-elastic coupling in compressed Fe7C3 supports carbon in Earth's inner core. Geophys. Res. Lett. 39, 2–5. https://doi.org/10.1029/2012GL052875

Gao, L., Chen, B., Wang, J., Alp, E.E., Zhao, J., Lerche, M., Sturhahn, W., Scott, H.P., Huang, F., Ding, Y., Sinogeikin, S. V., Lundstrom, C.C., Bass, J.D., Li, J., 2008. Pressure-induced magnetic transition and sound velocities of Fe3C: Implications for carbon in the Earth's inner core. Geophys. Res. Lett. 35, 1–5. https://doi.org/10.1029/2008GL034817

Litasov, K.D., Sharygin, I.S., Dorogokupets, P.I., Shatskiy, A., Gavryushkin, P.N., Sokolova, T.S., Ohtani, E., Li, J., Funakoshi, K., 2013. Thermal equation of state and thermodynamic properties of iron carbide Fe3C to 31 GPa and 1473 K. J. Geophys. Res. Solid Earth 118, 5274–5284. https://doi.org/10.1002/2013JB010270

McCammon, C.A., Liu, L., 1984. The Effects of Pressure and Temperature on Nonstoichiometric Wustite , FexO : The Iron-rich Phase Boundary. Phys. Chem. Miner. 10, 106–113.

Morard, G., Andrault, D., Antonangeli, D., Nakajima, Y., Auzende, A.L., Boulard, E., Cervera, S., Clark, A.N., Lord, O.T., Siebert, J., Svitlyk, V., Garbarino, G., Mezouar, M., 2017. Fe – FeO and Fe – Fe 3 C melting relations at Earth ' s core – mantle boundary conditions : Implications for a volatile-rich or oxygen-rich core. Earth Planet. Sci. Lett. 473, 94–103. https://doi.org/10.1016/j.epsl.2017.05.024

Ozawa, H., Hirose, K., Ohta, K., Ishii, H., Hiraoka, N., Ohishi, Y., Seto, Y., 2011. Spin crossover, structural change, and metallization in NiAs-type FeO at high pressure. Phys. Rev. B - Condens. Matter Mater. Phys. 84, 1–6. https://doi.org/10.1103/PhysRevB.84.134417