ESRF	**Experiment title:** Spin state of Earth materials: clinopyroxene $CaFeSi_2O_6$	**Experiment number:** He95
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Names and affiliations of applicants (* indicates experimentalists):

Prof. S.S. Hafner, Institute of Mineralogy, University of Marburg, Lahnberge, 35032 Marburg, Germany
* Dr. Li Zhang, Institute of Mineralogy, University of Marburg, Lahnberge, 35032 Marburg, Germany
* Dr. J. Stanek, Department of Physics, Jagiellonian University, Cracow, Poland
*D. Sontowski, Institute of Mineralogy, University of Marburg, Lahnberge, 35032 Marburg, Germany

Introduction Studying the role of iron in the physics and chemistry of Earth's deep interior is of great significance to the structure and dynamics of the Earth. This report concerns high-pressure properties of ferrous iron in major mineral compounds of the Earth's mantle such as wuestite FeO,

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clinopyroxene $CaFeSi_2O_6$, olivine Fe_2SiO_4, etc. We have started with measurements on $CaFeSi_2O_6$ because it has been extensively studied in our group at high pressures: its electronic structure has been studied using Mössbauer spectroscopy up to 10 GPa. Its crystal structure has been studied using single crystal diffraction up to 20 GPa. With these experimental data as constraints, *ab initio* calculation has been performed to clarify the pressure induced changes in hyperfine parameters. Furthermore, theoretical calculation has been made, predicting a high - low spin transition of Fe^{2+} in $CaFeSi_2O_6$ in the pressure range of 30 to 50 GPa.

Experimental The proposed experiment was carried out in the forward scattering set-up at Nuclear Scattering Beamline ID18 in the ESRF. The 93.5% ^{57}Fe enriched polycrystalline sample was pressed in discs. Diamond anvils with culets from 300 to 600 µm in the pressure cells were used. Rhenium plates preindented to about 40 - 90 µm with holes of 300 - 400 µm served as gaskets. The sample discs with diameters of 110 - 300 pm, thickness of 20 - 50 µm were loaded together with pressure calibrant rubys in presssure cells. Helium gas was confined in pressure cell and used as hydrostatic pressure transmitting medium. This loading technique guaranteed the highest degree of hydrostaticity possible at very high pressures and effectively reduced the pressure gradient aross the sample area (see insert in (d) of Fig. 1). The pressure gradient at 68 GPa, the highest pressure of this experiment, accounted to about 3% across the sample hole. It was crucial to keep this gradient small in our experiment since a distribution of pressure would result in a distribution of hyperfine parameters, severely complicating a more accurate evaluation of the time spectra

Results The time spectra of $CaFeSi_2O_6$ were measured up to 68 GPa, partly with stainless steel (natural and enriched in ^{57}Fe) outside of the pressure cell as reference for determination of isomer shift. The typical count rates were between 1 and 4 Hz due to small samples in the pressure cell. For collecting a high pressure time spectrum of reasonable statistics, 2 - 4 hours were needed. The time spectra were fitted by use of the programs of CONUSS and MOTIF. The fits of selected standards yielded hyperfine parameters identical to those known from conventional Mössbauer spectra. From the evaluation of thick samples highly enriched in ^{57}Fe, it was concluded that taking inhomogeneity of sample thickness into account was essential for our evaluation.

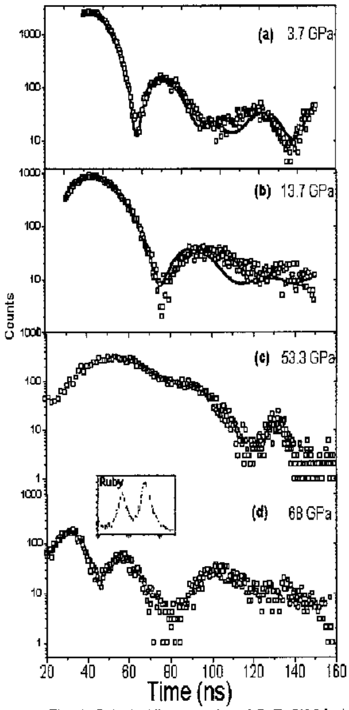

Fig. 1. Selected time spectra of CaFeSi2O6 at different pressures. The insert in (d) shows hydrostatic pressure in He pressure medium.

The evaluated results of $CaFeSi_2O_6$ up to 10 GPa agree with our previous Mössbauer data. The spectra above 50 GPa showed clear evidence of a phase transformation, corresponding to the pressure range predicted for a spin transition of Fe^{2+} (Fig.1). Since there are various possibilities to evaluate these spectra, reasonable interpretation of the spectra is only possible with an unambiguous in situ phase identification of the high pressure induced new phases by x-ray diffraction in the same pressure range. The nature of the phase transformation is still open, for example, if a spin transition of Fe^{2+} is indeed involved as predicted. Further clarification of this question is of crucial implication to the geophysics of the Earth's deep interior and experiment of x-ray diffraction is now proposed

Reference Li Zhang, S.S. Hafner, J. Stanek, M. Stanek, J. Metge, H. Grüensteudel High pressure studies of Earth's upper mantle minerals using nuclear forward scattering of synchrotron radiation. XXX11 International School of Physics, Zakopane, Poland, May 12.17,1997.

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