ESRF	**Experiment title:** Kinetics of the high-pressure transformations in the binary Mg_2SiO_4 – Fe_2SiO_4 : toward a detailed understanding of the structure of the planets'interiors	**Experiment number**: HS3260
Beamline: ID27	**Date of experiment**: from: 25/04/07 to: 01/05/07	**Date of report**:
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Report:

Whithin the depth of the planets, values of the mantle thermodynamic properties are deduced through seismological and geodynamical probes. It has been shown recently that the incompressibilities calculated from these observations are very sensitive to the kinetics of phase transitions [1], and could bring tight constraints on mantle discontinuities, in particular in the transition zone (410-660 km in the Earth) where the $(Mg_{1-x},Fe_x)_2SiO_4$ α–β–γ transformations take place (Fig. 1). Moreover, when the characteristic times of a probe like seismic waves for instance and that of the kinetics of phase transition are nearly equal, the probe may causes chemical reactions, induced by the dissipation of the mechanical energy. The actual problem is that kinetics data of characteristic transitions of the planets' mantle at equilibrium are not yet available.

Therefore, we performed time-resolved X-ray diffraction experiments on two synthetic samples : $(Mg_{0.57},Fe_{0.43})_2SiO_4$ X_{Fe} = 0.43 and $(Mg_{0.42},Fe_{0.58})_2SiO_4$ X_{Fe} = 0.58, prepared at ambient pressure, high temperature, under controlled oxygen fugacity at the CRPG in Nancy (coll. G. Libourel). The starting materials are in the α form (space group Pbnm). At ESRF, they were pressurized in the Paris-Edinburgh press, and heated with $LaCrO_3$-Re furnace [2] to enter the α–γ transformation loop (Fig. 1).

5 loads could be performed, allowing the investigation of 10 (P,T) conditions. Sintered diamond anvils were used to reach 11 GPa, the maximum pressure in this experiment. The sample was hold in a MgO or h-BN capsule that serves as a pressure transmitting medium. Au and NaCl powders were added to the sample in order to calculate pressure and temperature using the cross-calibration method [3].

As the α–γ loop was scanned and the transformation proceeded, angle dispersive diffraction data were recorded at an incident wavelength of 0.6199 Å (Molybdenum K-edge). Patterns were acquired in 10s seconds every 45s within the standard configuration of the detector, the frequency limitation being the reading time of the MAR CCD. However, for the last run, we increased the binning of the MAR CCD detector, so that patterns could be acquired in 3s every 15 s, while keeping a very good signal/noise ratio. In that run, the frequency was limited by the motorization of the Soller slits.

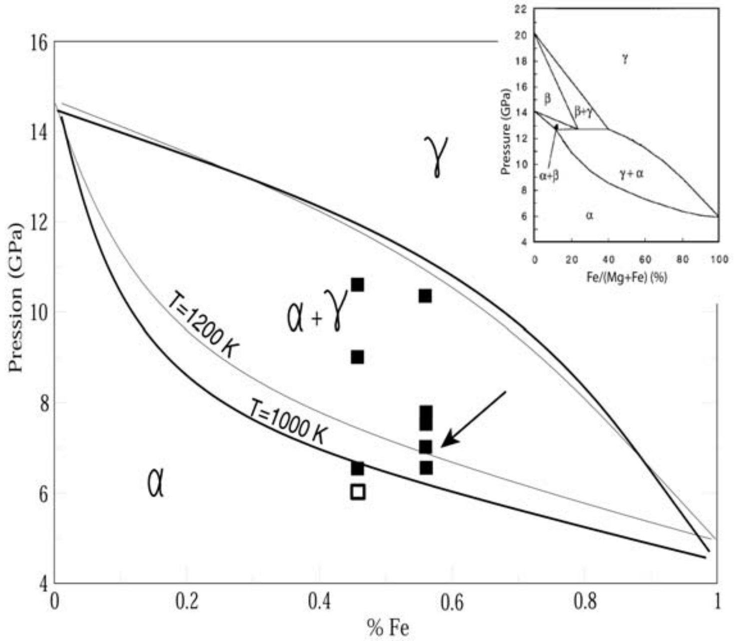

Fig. 1: Isothermal phase relations at 1000K and 1200K in the binary system Mg_2SiO_4-Fe_2SiO_4 between α and γ phases. In the upper right corner, the entire phase diagram including β phase is displayed at 1273 K.

As a pioneer time-resolved experiment, we concentrated on the α–γ transition, which occurs at pressures more affordable in the P.-E. press, i.e X_{Fe}=0.43 and 0.58. The 10 experimental P-T conditions are reported (filled squares 1000K, open squares 1200K,). Note that the transformation at 1200K was only of 4%. The right arrow points the data displayed in fig. 3.

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Preliminary Rietveld refinements of the integrated patterns using the GSAS package, show that equilibrium between the two phases could be reached within very contrasted timescale: 10 min to 5h (Fig. 2). Fe/Mg rearrangement could also be quantified during the transformation through the evolution of the unit cell parameters of α and γ. For instance, unit-the cell parameters of α decrease during the reaction, indicating a progressive depletion in iron, whereas the cell parameters increase of γ increase with its iron content.

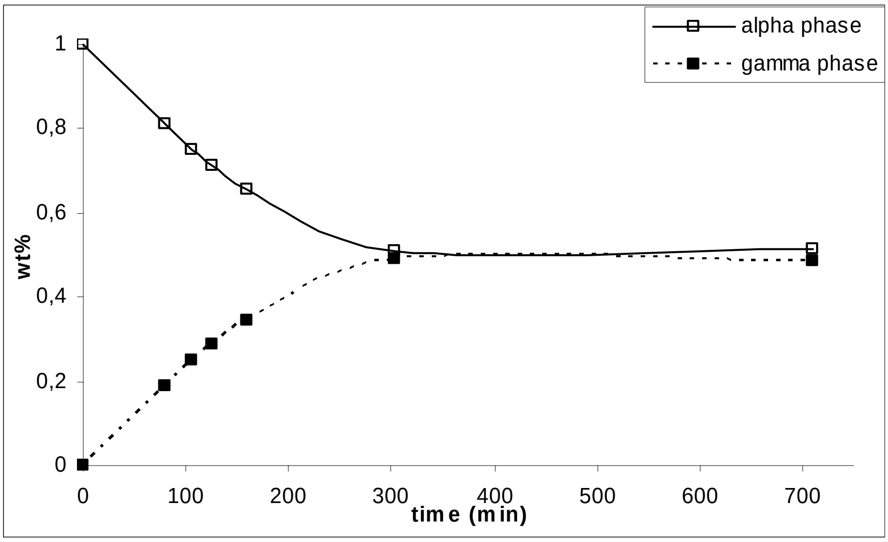

Fig. 2: Example of evolution with time of the relative amount of α and γ phases (in wt%) at 10.5 GPa, 950K, and for X_{Fe}=0.43.
This corresponds to a typical pattern of a 1st order transition kinetics.

Moreover, one series of measurements showed a very unexpected phenomenon: while transformation proceeds, the γ phase rapidly grows, whereas the α phase almost disappears in 3 min before growing again. This suggests that α phase might become highly disordered or amorphous.

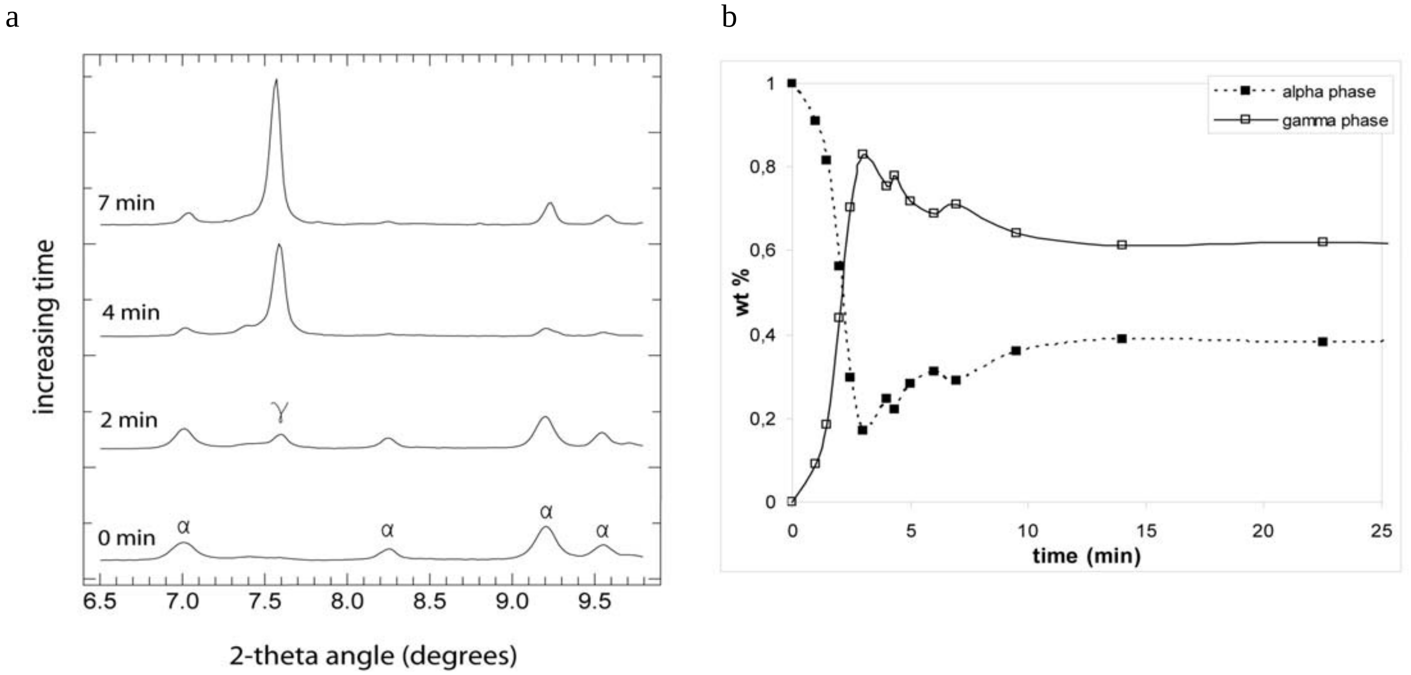

Fig. 3: (a) Short time series of selected XRD spectra acquired during α–γ transition at 1000 K, 7.5 GPa, X_{Fe}=0.58. (b) Evolution with time of the relative amount of α and γ (in wt%). Both diagrams emphasize the fast decrease of olivine (α) that almost disappears at t=4min. Later (t=7min), olivine increases again, with smaller unit cell parameters, indicating depletion in iron.

During this first set of experiments, we could only achieve half of our goals, approximately, due to the following technical problems:

- pressure was limited to 11 GPa, probably due to a ‘bad batch’ of B-epoxy gaskets that were too soft. The gap between the anvils closed at very low pressure. Temperature was limited to 1200 K, due to electrical arcs between the anvils. Consequently, the composition of major interest X_{Fe}=0.3 that corresponds to the mantle of Mars could not be investigated.
- Although, the measurements confirm that XRD patterns can be acquired with a very good signal/noise ratio in less than 1s, we could not reach such a high frequency, due essentially to the motorization of the Soller slits.

Given the interesting results already gathered during this first series of measurements, the identification of the current technical barriers, and the importance of investigating the composition of the martian mantle, we ask for a continuation of HS3260. Details, including the solutions to the previous problems are included in the proposal.

1. **Matas, J., F. Guyot, and Y. Ricard, *Chemical relaxation and seismic attenuation across phase transition.* in press.**
2. **Morard, G., et al., *Optimization of Paris-Edinburgh press cell assemblies for in situ monochromatic X-ray diffraction and X-ray absorption.* High Pressure Research, 2007. 27(2): p. 1-11.**
3. **Crichton, W. and M. Mezouar, *Noninvasive pressure and temperature estimation in large-volume apparatus by equation-of-state cross-calibration.* High Temperatures - High Pressures, 2002. 34: p. 235-242.**