

In situ ^{57}Fe Mössbauer spectroscopy of iron and olivine at high pressure and temperature

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Abstract—*In situ* Mössbauer measurements have been performed at high pressure and temperature by use of a diamond anvil cell equipped with a resistivity furnace. Iron-57 enriched iron metal and olivine are investigated in this study to set up the routine conditions for this type of Mössbauer spectroscopy. Sample temperatures in the DAC are calibrated using the second order Doppler shift of α -iron and pressures are determined from the shift of the fluorescence line from Sm:YAG. Methods are developed to prevent the point source from being heated during the experiment. The pressure dependent centre shift of α -iron is observed to be $-4.0 \cdot 10^{-3} \text{ mms}^{-1} \text{ GPa}^{-1}$ at temperatures up to 600 K.

INTRODUCTION

THERE IS a growing need for *in situ* measurements of minerals and rocks at elevated temperatures and pressures to simulate conditions during rock formation. The kinetics of transformation reactions at the high temperatures prevailing in the Earth's mantle and core, are so rapid that physical-chemical properties of solids at high temperatures usually cannot be preserved by quenching. The application of different spectroscopic methods *e.g.* such as Raman spectroscopy, optical spectroscopy, X-ray diffraction, neutron diffraction and Mössbauer spectroscopy (HAWTHORNE, 1988), all in combination with the diamond anvil cell allow for determining properties of earth materials under conditions resembling their natural origin. Because of the simple alignment of a Mössbauer spectrometer with a diamond anvil cell device, this method has the potential to become an important method for such types of measurements.

Early use of a high-pressure device for obtaining high pressure Mössbauer spectra was developed by DEBRUNNER *et al.* (1966) to study the valence electron behaviour in metal organic complexes. Later several groups have developed diamond anvil cells for ultrahigh pressure Mössbauer spectroscopy (see STERER and PASTERNAK, 1990). The advantage of using diamond as anvils in high pressure Mössbauer spectroscopy is the low absorption of gamma rays by the diamonds. AMTHAUER *et al.* (1979) used B_4C as anvils, in conjunction with a hydraulic system, to apply pressure on their investigated samples. The use of B_4C was favoured because it allows large area samples to be examined, but limits the pressure to moderate values compared to conditions in the Earth's interior. In the present paper we have performed high pressure Mössbauer spectroscopy using the diamond anvil

cell fitted with an external Pt-wired furnace to obtain high temperatures in the sample simultaneously. We discuss the difficulties in using this technique before it can be applied as a routine method for measuring minerals under these conditions.

EXPERIMENTAL SET UP

We have used a modified type of diamond anvil cell (DAC) described by MING *et al.* (1987) for performing X-ray diffraction at high pressure and temperature. The main parts of the DAC are depicted in Fig 1. There are several precautions one has to take before Mössbauer measurements can be performed using the DAC.

- (1) the small sample size necessitates the use of ^{57}Fe in the sample which results in thickness effects of the absorption lines.
- (2) reasonable counting rates need the source close to the sample and a strong point source, in our case 50 mCi. At the same time heating of the source has to be avoided.
- (3) the pressure and temperature calibration is very sensitive to the mounting of the sample in the DAC.
- (4) the measurements must be performed in an inert or reduced atmosphere to avoid oxidation of diamonds, gasket, rockers and sample which may limit the maximum temperature used in the experiment.

Our exploratory experiments have resulted in a new Mössbauer technique. We have investigated powdered samples of metallic iron produced by reducing Fe_2O_3 in hydrogen, and a medium iron-rich olivine $\text{Fa}_{41}\text{Fo}_{59}$ obtained from hydrothermal experiments (see below). All synthetic samples contained ^{57}Fe enriched to 95%. Samples, approximately 0.1–0.2 mg, and chips of Sm:YAG crystals were placed together with a 1:4 mixture of ethanol/methanol in a 350 μm diameter hole of a Ta-gasket on the diamond anvil face. The closed cell was then wrapped tightly with tape and the inner part of the pressure cell was slowly flushed with argon gas. The upper and lower part of the cell was connected to a water cooling system. Note the copper shield (Fig. 1), in contact with the cooled pressure cell, preventing the radioactive point source, ^{57}Co in Rh, from becoming heated during the experiments.

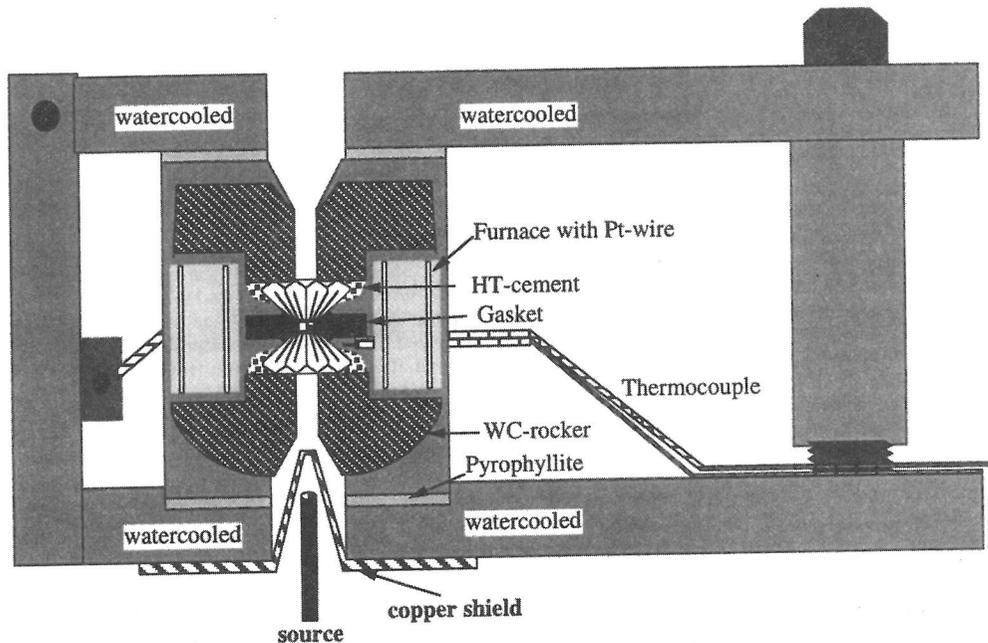


FIG. 1. Schematic cross section of the diamond anvil cell (not in scale).

Temperature calibration

A circular Pt wired furnace around the diamonds was temperature regulated using a thermocouple Pt₁₀₀/Pt₉₀Rh₁₀ attached close to the gasket (see Fig. 1). We believe that there is no larger temperature gradient in the sample due to the shape of the furnace and the good thermal conductivity of diamonds. However there are several positions in the DAC where the temperature of the system is of vital concern.

The temperature of the sample between the diamonds was calibrated using two different procedures:

- (1) comparing melting temperatures observed under the microscope of congruently melting oxides placed in the sample chamber with well known melting points;
- (2) measuring the temperature dependent centre shift of metallic iron in the sample chamber under ambient pressure due to the second order Doppler shift (SOD).

The result of the temperature calibration is shown in Fig. 2. Similar to MING *et al.* (1987) we observed a somewhat lower temperature of the sample (real temperature) compared to the set value of the regulator using calibration method 1. At a set value of 473 K a real temperature of 448 K was recorded, and at a set value of 823 K the real temperature in the sample chamber was observed to be 723 K; a similar difference was observed by MING *et al.* (1987) in their melting calibration. However when using the well known SOD ($-7.3 \times 10^{-4} \text{ mms}^{-1} \text{ deg}^{-1}$) INGALLS (1967), much larger deviations are observed from the set value (see Fig. 2). At 873 K a sample temperature of only 613 K is estimated from the SOD value. The SOD measurements were most similar to the actual Mössbauer spectroscopy set up with the DAC in a horizontal position, the source cooling shield in place and a

steady flow of argon gas. A plausible explanation for the observed large temperature difference in the diamond anvil cell could be the high thermal conductivity of diamonds, in combination with the cooling media brought close to the lower rocker and the diamond anvils (see Fig. 1). It is possible that the horizontally situated diamond anvil cell will enhance thermal convection in the system. The obtained temperature calculated from the SOD values are further supported by the observed changes in the hyperfine fields of α -iron with temperature (PRESTON *et al.*, 1962).

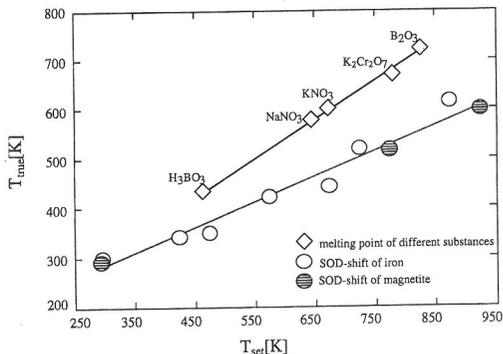


FIG. 2. Results of calibration of the sample chamber temperature. Diamonds: from salt oxides, Circles: from ⁵⁷Fe second order Doppler shifts. The size of the symbols indicates the estimated errors.

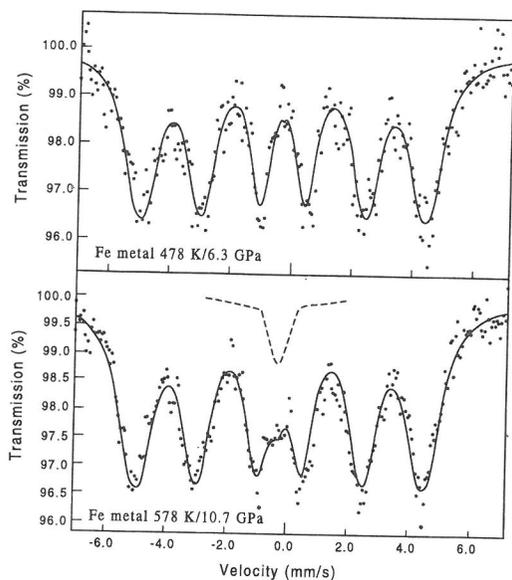


FIG. 3. Mössbauer spectra of ^{57}Fe at a) 478 K/6.3 GPa, b) 578 K/10.7 GPa. The dashed line represents the fitted single absorption line due to the ϵ -phase. Note the intensity ratio of individual lines indicating substantial thickness effect of the resonance.

The use of the SOD as a temperature calibration would be incorrect if the source were heated, which would result in too high centre shift values. In order to establish the temperature of the source during heating experiments,

centre shifts of a thin iron foil above the cell, ventilated at room temperature, were measured while operating the empty pressure cell over a range of temperatures with the source cooled in the usual manner. At a DAC temperature of 873 K the first signs of an elevated temperature of the source was noticed. The SOD indicated that the source was approximately 10 K above room temperature. It is therefore justified to assume that heating of the source is negligible when performing experiments below 873 K.

Pressure calibration

The pressure calibration of the sample chamber was carried out at each set temperature *in situ* before and after each Mössbauer measurement. A laser optical system, situated close to the Mössbauer source, was used to determine the pressure dependent shift of the fluorescence line at 617.7 nm (ambient pressure) of a Sm doped YAG, excited by a 20 mW Ar-laser operating at 488 nm (Bi *et al.*, 1990). Pressure calibration measurements were performed with the DAC in a vertical position after which it was put back over the Mössbauer source for Mössbauer spectra collection in a horizontal position without disconnecting the power and cooling lines. Use of ruby was avoided since the shift of the fluorescence lines depends on both pressure and temperature. In the laser optical system an Oriel Multispec spectrograph was used to measure the shift of the fluorescence line. Precision of pressure measurements are estimated to be within ± 0.02 GPa. The pressure dependence of the centre shift is too small ($\approx -8.0 \times 10^{-3} \text{ mms}^{-1} \text{ GPa}^{-1}$) to allow for a practical calibration of the pressure.

RESULTS

In our aim to explore the routine performance of *in situ* high P and T Mössbauer spectroscopy we

Table 1. Hyperfine parameters of iron at different temperatures and pressures

Pressure [GPa]	Temperature [K]	CS [mm/s]	B [Tesla]	FWHM [mm/s]	
6.3	478	-0.15	31.0	0.39	
	555	-0.21	29.8	0.38	
	573	-0.24	29.5	0.39	
	590	-0.24	29.5	0.39	
	605	-0.26	29.13	0.30	
10.7	471	-0.17	30.7	0.39	
	522	-0.21	30.1	0.39	
	522	-0.39		0.77	ϵ -phase
	522	-0.22	30.1	0.33	
	522	-0.35		0.83	ϵ -phase
	574	-0.26	29.3	0.32	
	574	-0.35		0.53	ϵ -phase

The uncertainty in pressure is ± 0.2 GPa, and in temperature ± 20 K. The uncertainty in the centre shift (CS) and the full width at half maximum (FWHM) are both ± 0.02 mm/s, and in the magnetic field (B) approximately ± 0.2 Tesla. The uncertainty in the parameters for ϵ -iron are larger because the singlet is mainly hidden under the sextet.

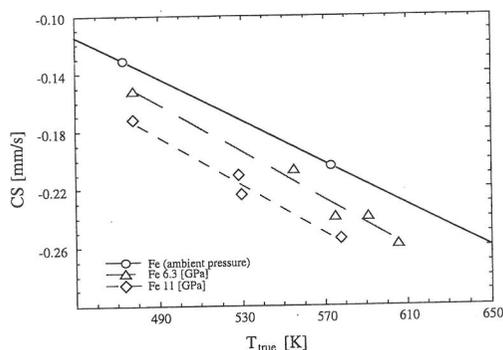


FIG. 4. Change in centre shift of ^{57}Fe with temperature and pressure.

have examined iron rich phases with well known properties. Metallic iron was chosen because it is the most iron rich phase, but with the present method it is also possible to investigate phases less rich in iron. For example, olivine with only 41% fayalite in solid solution can be measured within reasonable times, 20–24 hours.

Measurements on metallic iron

Our first spectra of metallic iron are shown in Fig 3. and the hyperfine parameters are given in Table 1. The spectra are broad and deviate considerably from the usual 3:2:1 peak intensity

ratio due to the strong thickness effects (effective thickness calculated to 150 compared to 2.0 for a thin absorber). At high temperatures, however, the broadening of the spectra decreases as a result of the decreasing recoil free fraction and accordingly give a more favourable situation for site population estimates, *e.g.* in Fe-Mg silicates.

The increase in pressure and temperature are clearly demonstrated in the decrease of the centre shift values, partly due to the SOD caused by temperature but also from the change in electron density around the nucleus, a pressure effect discussed by INGALLS (1967). This behaviour explains the parallel lines representing data at 6.3 and 10.7 GPa, respectively, below the SOD lines (see Fig. 4). The results indicate a pressure shift in α -iron in the order of $-4.0 \times 10^{-3} \text{ mms}^{-1} \text{ GPa}^{-1}$, somewhat less compared to the tabulated observations for α -iron, -7×10^{-3} to $-9 \times 10^{-3} \text{ mms}^{-1} \text{ GPa}^{-1}$, at room temperature in WILLIAMSON (1978).

Although we were not able to reach the α - γ transition, ϵ -iron appears in all spectra at 10.7 GPa in agreement with the phase diagram produced by AKIMOTO *et al.* (1987) for iron. The appearance of a single line demonstrates its paramagnetic state. The ϵ -phase seems always to occur simultaneously with the α -phase due to a sluggish phase transformation (MILLET and DECKER, 1969) and/or pressure gradients in the cell.

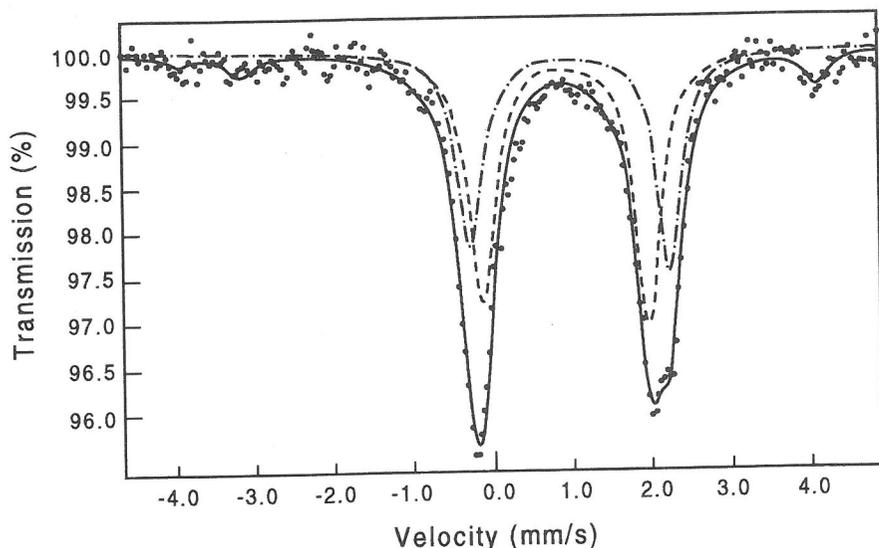


FIG. 5. Mössbauer spectrum of olivine $\text{Fa}_{41}\text{Fo}_{59}$ at 595 K/2.4 GPa. The weak magnetic pattern is due to trace amounts of magnetite.

Table 2. Mössbauer parameters of synthetic olivine $\text{Fa}_{41}\text{Fo}_{59}$ at 573 K

Pressure [GPa]	Intensity M1 [%]	Intensity M2 [%]	CS M1 [mm/s]	CS M2 [mm/s]	QS M1 [mm/s]	QS M2 [mm/s]	FWHM [mm/s]
0.4	55	45	0.90	0.97	2.08	2.43	0.35*
2.4	56	44	0.92	0.98	2.12	2.49	0.36*
3.0	59	41	0.95	0.96	1.97	2.41	0.40*

*Full width at half maximum (FWHM) for M1 and M2 doublets was constrained to be equal.

All velocities are given relative to α -iron at room temperature. The estimated error for CS, QS and FWHM is approximately ± 0.02 mm/s and for the intensity $\pm 3\%$. The uncertainty in pressure is approximately ± 0.2 GPa.

Measurements on olivine

The Mössbauer spectra of olivine have the advantage of showing an increased resolution when measured at elevated temperature reflecting the distribution of Fe among the available M1 and M2 sites in the olivine structure (ANNERSTEN *et al.*, 1982).

A synthetic olivine was produced from a reduced oxide mix (MgO , $^{57}\text{Fe}_2\text{O}_3$ and SiO_2) in cold sealed bombs at 0.2 GPa/975 K using graphite as an oxygen buffer. Small amounts of magnetite were present after the run and could clearly be seen in the Mössbauer spectra. From X-ray diffraction analysis of the run products the composition of the olivine was calculated according to the formula: $X_{\text{Fa}} = 7.522 - 14.9071(3.0199 - d_{130})^{1/2}$ (SCHWAB and KUSTNER, 1977) to be $\text{Fa}_{41}\text{Fo}_{59}$ instead of the original $\text{Fa}_{50}\text{Fo}_{50}$ oxide mixture and in agreement with the presence of small amounts of magnetite. Microprobe analysis could not be performed due to the small crystalline size of the olivine.

Figure 5 shows the spectra of olivine $\text{Fa}_{41}\text{Fo}_{59}$ at the temperature 575 K and the pressure 2.4 GPa. The resulting Mössbauer parameters obtained from the computer fit of the spectra are listed in Table 2. Over the small pressure range measured the centre shifts are constant within the error limit. The room temperature spectra are not resolved, as expected, that will allow a separation of the overlapping doublets.

It is interesting to observe that our data suggest a slight increase of iron preferring the M1 site with increasing pressure. Similar observations were made by AKAMATSU *et al.* (1993) on olivine samples quenched from high pressure. Our present data on iron site population in olivine are too sparse to confirm these data, but they are in qualitative agreement with the results of AKAMATSU *et al.* (1993).

CONCLUSIONS

Our work, so far, on high pressure-high temperature Mössbauer spectroscopy has shown the possibility of the DAC technique to study iron containing minerals in situ under those conditions under which rock forming processes prevail. Very high pressures can be reached with DAC but the temperature is limited to around 1200 K when the cell is put under vacuum. Studies at higher pressure and temperature are underway to further study the pressure influence on cation distribution in silicate minerals. Local heating, using laser radiation, may increase the temperature to higher values but will probably result in unpractically long measuring times due to the extreme low recoil free fractions of the absorber at such high temperatures.

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