



## In-situ extreme condition x-ray study of calcite, aragonite, platinum and rhenium

Vivien Mohrholz, Friedrich Schiller University of Jena, Germany  
September 8, 2015

### **Abstract**

This report is about high pressure and high temperature x-ray diffraction experiments on Rhenium, Platinum, Calcite and Aragonite at the extreme condition beamline (ECB) P02.2 of PETRA III. It will focus on the steps of the experiment and then the results of the rhenium experiment will be presented and evaluate. The main question was if there is any differences in the behavior of rhenium during fast (40 bar/min) and slow compression (1 bar/min). Also it was an interest if the different gaskets influence the experiment.

## Content

1. Introduction.....	3
2. Experiment.....	4
2.1 Diamond Anvil Cell.....	4
2.2 Extreme Condition Beamline P02.2.....	5
3. Measurement.....	6
4. Results.....	8
5. Literature.....	13

## 1. Introduction

In the geoscience it is important to understand the processes in the Earth's crust, mantle and also in the core, like subduction zones and volcanos. Because, it is impossible to watch these processes in nature, they have to be rebuild at experiments in laboratories. The pressure and the temperature are the main parameters in the kinetic of rocks and minerals. Next to them, also the content of liquids influence the processes. In the last decades of years there were many researches at extreme condition that found several new phases of minerals that are formed at high pressure and or temperature. Some of them are only stable at these extreme conditions, like the most phases of ice [1]. Also shock compressed rocks at impact craters shows such high pressure and high temperature phase transitions.

These phase transitions can be determined with x-ray powder and single crystal diffraction. The position of the Bragg peaks in the diffraction pattern allows to determining the symmetry and cell volume. The intensity of the peaks leads to the atomic arrangement. With the equation of state (EOS) and the change of the cell volume it is possible to calculate the pressure by Birch–Murnaghan:

$$P(V) = \frac{K_0}{K'_0} \left[ \left( \frac{V}{V_0} \right)^{-K'_0} - 1 \right]$$

Carbonates are one of the common minerals in the mantle of the earth, especially Magnesite ( $\text{MgCO}_3$ ), Dolomite ( $(\text{Ca,Mg})(\text{CO}_3)_2$ ) and Calcite ( $\text{Ca}(\text{CO}_3)$ ) [2]. They are important for the C cycle between the mantle and the surface through subduction zones and volcanism. Next to the decarbonation it was found out, that at really high pressure, also dissolution of carbonates by fluids, brought from the earth's surface, produce C in the lower mantle. [3]. But the high pressure forms of the carbonates are not that well known. Calcite has at high pressure two different forms  $\text{Ca}(\text{CO})_2\text{-III}$  and  $\text{Ca}(\text{CO})_2\text{-IV}$  both were found by Frezotti, 2011[4]. We had searched for any different metastable phase between these structures.

Rhenium is a rare earth element and is only found bound in molybdenum. Pure rhenium has one of the highest melting points what makes it also useful in heated Diamond Anvil Cells during high pressure and high temperature experiments. Rhenium has a hexagonal closed package.

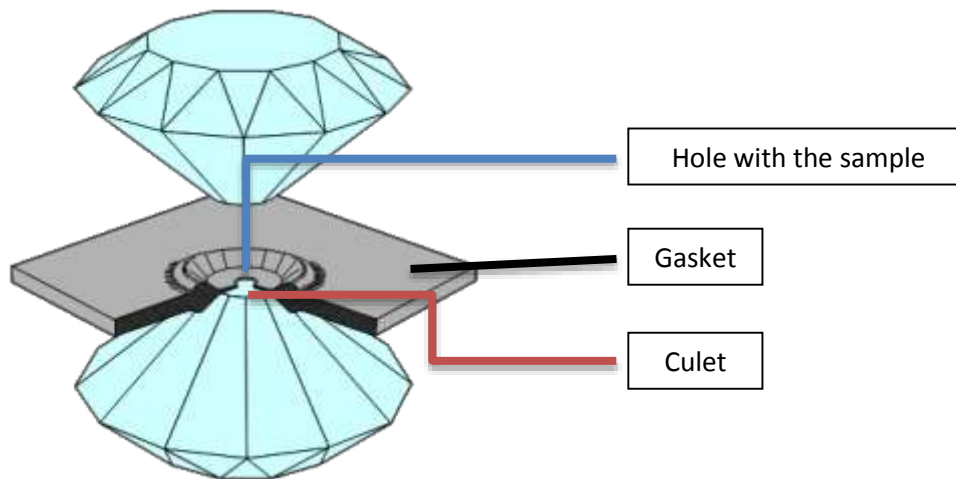
Platinum is also a rare element in the earth crust and has also one of the highest melting points, even higher then rhenium. It has a face centered cubic crystal structure. Platinum can be found bound in copper and nickel in the nature.

Such extreme condition experiments can be made with different Anvils, like the multi anvil cell or the diamond anvil cell. In the experiment we used the Diamond Anvil Cell.

## 2. Experiment

### 2.1 Diamond Anvil Cell (DAC)

For the high-pressure experiments diamond anvil cells (DAC) were used. They getting load with rhenium, platinum, calcite ( $\text{CaCO}_3$ ) and aragonite ( $\text{Mg}_3(\text{CO}_3)_2$ ). To expect the pressure in the DAC calcite and aragonite had also platinum in the cell.



Picture 1 Diamond Anvil Cell

The picture 1 shows the construction of a DAC. At first the diamonds have to be clued and align them. If they are not perfectly aligned, they will break at high pressure. After this the gasket between the diamonds would be the next step. It can be formed out of different materials, e.g. rhenium or steel. In the experiment a rhenium and two times a steel gasket was used. To thin down the gasket, the two diamonds were used and pushed slowly together. The gaskets of the experiment were around  $30\text{ }\mu\text{m}$  thin. Furthermore, in the center of the gasket there has to be a hole, where the sample will get filled in. The hole was at the experiment  $100\text{ }\mu\text{m}$  thick and was done with a mechanical driller. The diamonds and the gasket have to be cleaned. After that the gasket is put back on the culet of the diamond. The culets of the diamonds were  $200$  and  $300\text{ }\mu\text{m}$ . After that the sample can be filled in under a microscope with a needle, till the whole space in the hole is filled. Only a bit of platinum (depending on the experiment) is also filled in the hole, to know the pressure during the experiment. Then the DAC can be lightly closed. During the whole loading process the diamonds has to be cleaned after every step.

### 2.2 Extreme Condition Beamline (ECB) P02.2

The experiment was done at the extreme condition beamline P02.2 at PETRA III during July 31, 2015 to August 2, 2015. We have done several runs on calcite, aragonite, platinum and

rhenum. The pressure, loading, compression rate and further information can be seen on the table 2 in the chapter 'Measurements' of this report.

a) Experimental Settings

Energy	25,6 keV
Wavelength	0,4847 Å
Detector	Perkin Elmer (XRD1621)
Sample to detector distance	351,8468 mm
Used compression rates	1; 2; 10; 20; 40 bar/min
Pressure control	Membrane-driven DAC

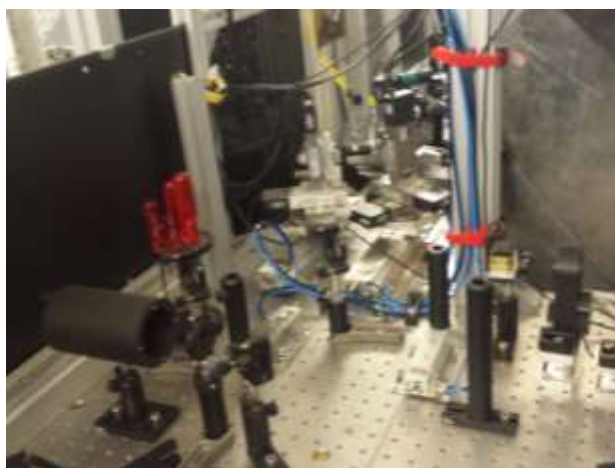
Table 1) Experimental Settings

For the experiment we used an energy of the beam of 25,6 keV and got a wavelength of 0,4847 Å. The wavelength gives a nice distance of peaks in the diffraction pattern and also a good intensity, which was good for the evaluation of them.

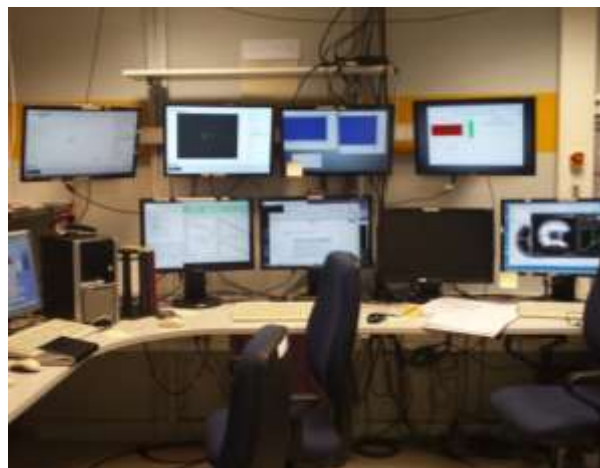
We used different compression rates during the experiment that are also shown in the table 1 above. On rhenum only 1 and 40 bar/min were used.

A membrane was used to control the pressure. The highest possible compression rate was 40 bar/min. The membrane is put into the cell and produces the pressure with a gas, like at P02.2 with Argon.

After placing the sample on the table of the experiment (picture 3) and connecting the membrane cell with the pipeline of the gas, the alignment of the beam need to be done, by a laser. This is made at the control station (picture 2) of the beamline. The room with the experiment is already closed.



Picture 3 Table on which the sample is put on



Picture 2 Control station of P02.2

After checking the alignment and taking a dark shot the expose time (how often a pattern will be made, often 0,2 – 5 s) and the pressure can be scheduled. During the experiment the diffraction pattern shows up on the right screen in the picture 2. After going to the set pressure, the rate of the decompression can be set.

### 3. Measurement

The table shows the samples that we used during the experiments.

DAC	runs	Load	Pressure medium	Gasket	Compression rate	Pressure	Information
SYN9		Calcite	Platinum	Re	1 bar/min	50 bar	Expose time 5s – 50 bar (47 GPa), short break at #610, decom: #1011, min 16 GPa
SYN9		Calcite	Platinum	Re	20 bar/min	30 bar	Expose time 1s, #183 decom, P=13 GPa
Vas6a		Calcite	Platinum	Re	1 bar/min	40 bar + heating	<b>Run 1:</b> T=1689+3 K, decom: #92, P=53 GPa, sample moved #174, #187 decom complete, #200 laser off
Vas6a		Calcite	Platinum	Re	2 bar/min		<b>Run 2:</b> 1 GPa -> Calcite II, 4GPa start heating
Vas6a		Calcite	Platinum	Re	10 bar/min		P=60,5 GPa
SYN9		Aragonit	Platinum	Re	20 bar/min		3s expose time, up to 50 GPa, after decom 10 GPa
#4	3x	Rhenium	-	Re	40 bar/min		<b>Run 1:</b> 68 GPa, #1012 down to 40 GPa, opened <b>Run 2:</b> 30 – 40 – 50 bar, #3000 decom, keep closed <b>Run 3:</b> from 13 GPa to 48 GPa to 14 GPa
#4	3x	Rhenium	-	Re	1 bar/min		1s expose time <b>Run1:</b> 49 GPa, decom: #_d to 15 GPa <b>Run2:</b> 15 GPa, 4219 to 50 bar, max at 40 bar -> 37 GPa
#4	5x	Rhenium	-	Steel	40 bar/min		<b>Run1:</b> 4 bar – 40 bar – 4 bar – 30 bar <b>Run 2 (continue):</b> Down #476, up #860 Down #1460, up #1950, Down #2550, end #3281
SYN9	5x	Rhenium	-	Steel	1 bar/min		<b>Run1:</b> #1032 4 GPa, #2346 62 GPa, #2390

							decom, end #3000 <b>Run2:</b> not completed, shutter closed <b>Run3:</b> #2490 43,5 GPa, #5280 2,5 GPa <b>Run4:</b> #2830 44 GPa, #4877-4906 shutter closed <b>Run5:</b> #1552-1757 shutter closed Diamond broke #1699
SYN7		Rhenium	-	Re	49bar/min		Diamond broke
#17		Platinum	Neon	Re	40 bar/min	40 bar	From 20 GPa to 75 GPa, decom: #572
#17		Platinum	-	Re	1 bar/min	38 bar	1 s expose, 60 GPa #1693, stabilize around 65 GPa #1799-1916 #1919 decompr, shutter closed, 25 GPa
#4	3x	Platinum	-	Re	40 bar/min		Wrong name

Table 2) Experiments

## 4. Results

In this chapter I will only show the results on rhenium as an example how to evaluate the data.

The picture 1 shows the last spectrum of the rhenium run in the DAC SYN7 with the identified hkl.

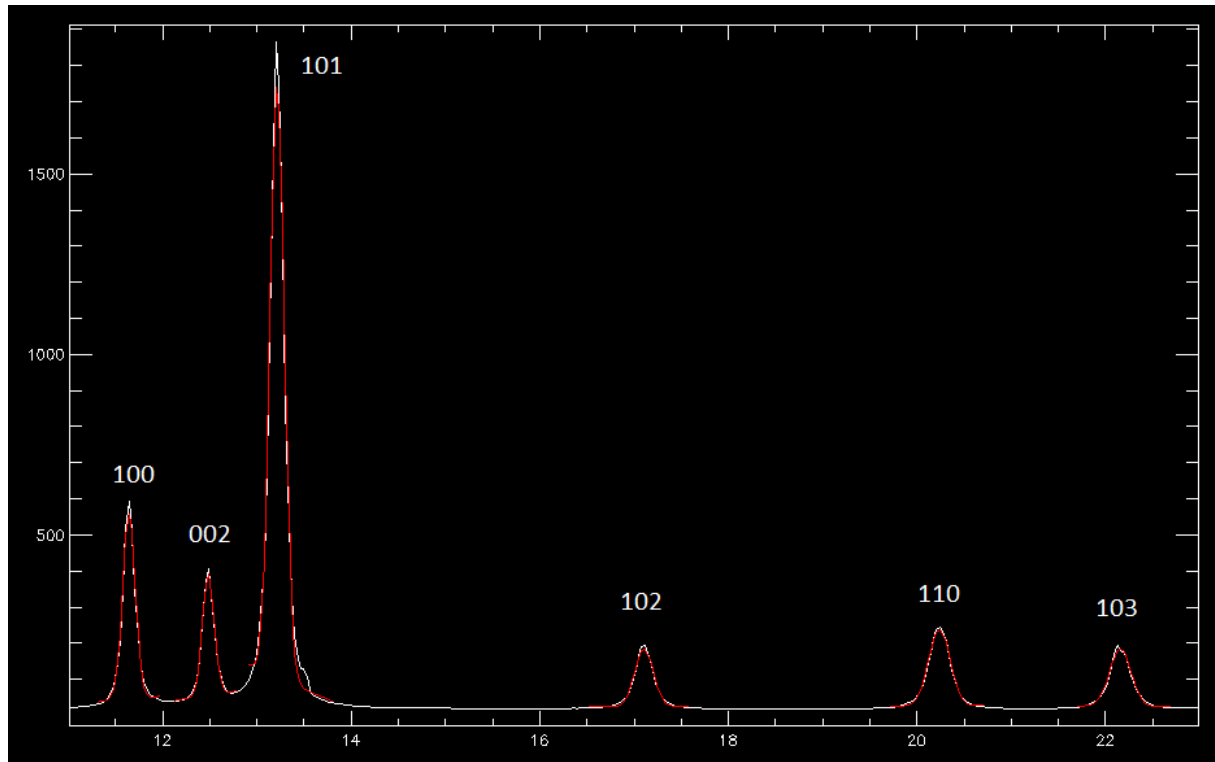


Figure 1) Spectrum of Rhenium without pressure

The main program that was used is the P02 Processing Tool, which is written by André Rothkirch.

hkl	2θ
100	11.644029
002	12.185244
101	13.214941
102	17.106707
110	20.238823
103	22.155115

Table 3) hkl of the peaks and 2theta angle



The following Figures 2 till 5 shows the change in volume and pressure during the experiment of rhenium with 1 bar/min as compression rate.

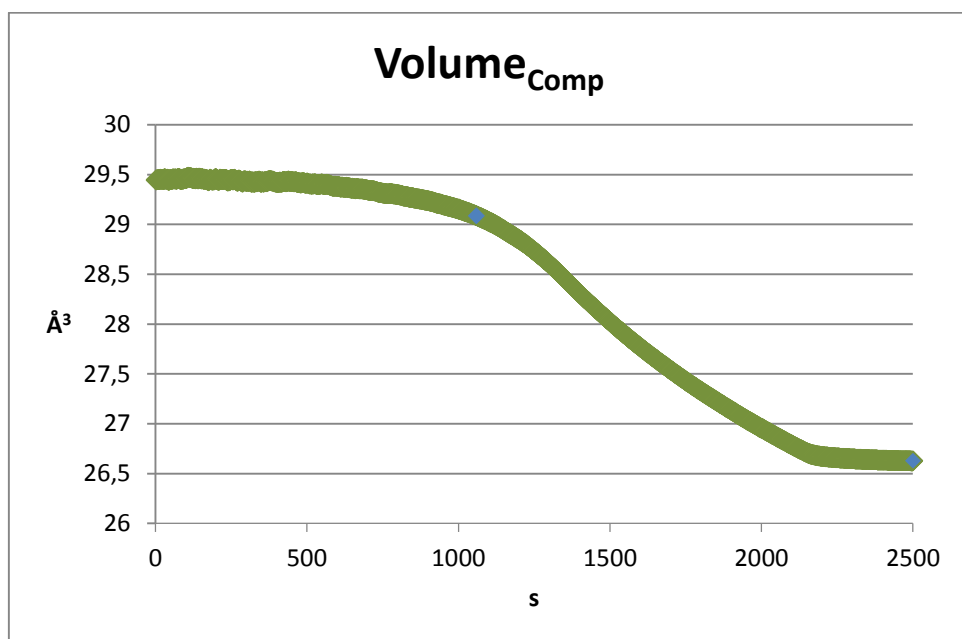


Figure 2) Volume change of Rhenium during compression.

With increasing pressure the volume of the cell decreases. This relationship can be seen in the figure 2 and 3 and also in the following figures 4 and 5. When the pressure decreases the cell volume increases.

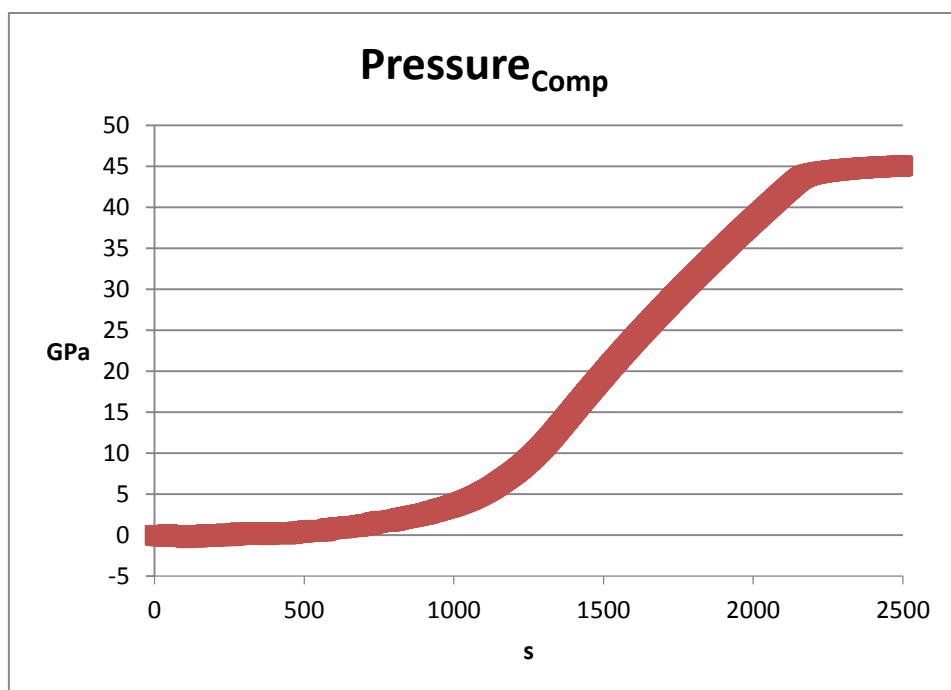


Figure 3) Pressure change of Rhenium during compression.

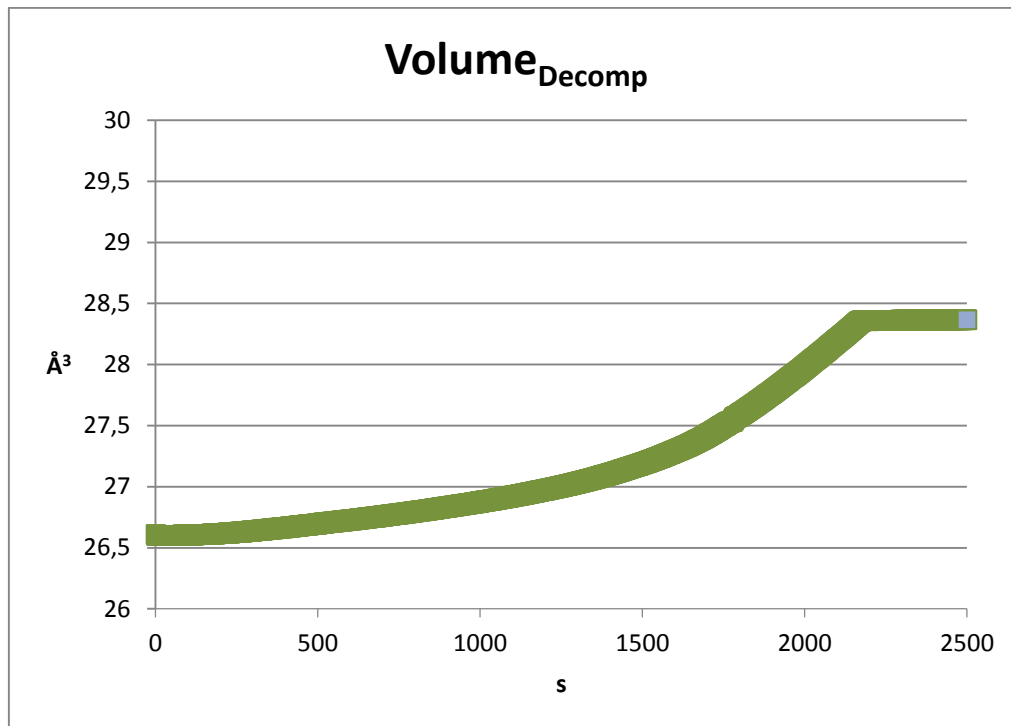


Figure 4) Volume change of Rhenium during decompression.

At these figures 4 and 5 it can be seen, that the pressure (during the decompression) in the cell did not going back to zero. Also the cell volume does not going fully back to its basic value. This could caused by the membrane that there is after full decompression some gas inside that produce the rest of the pressure.

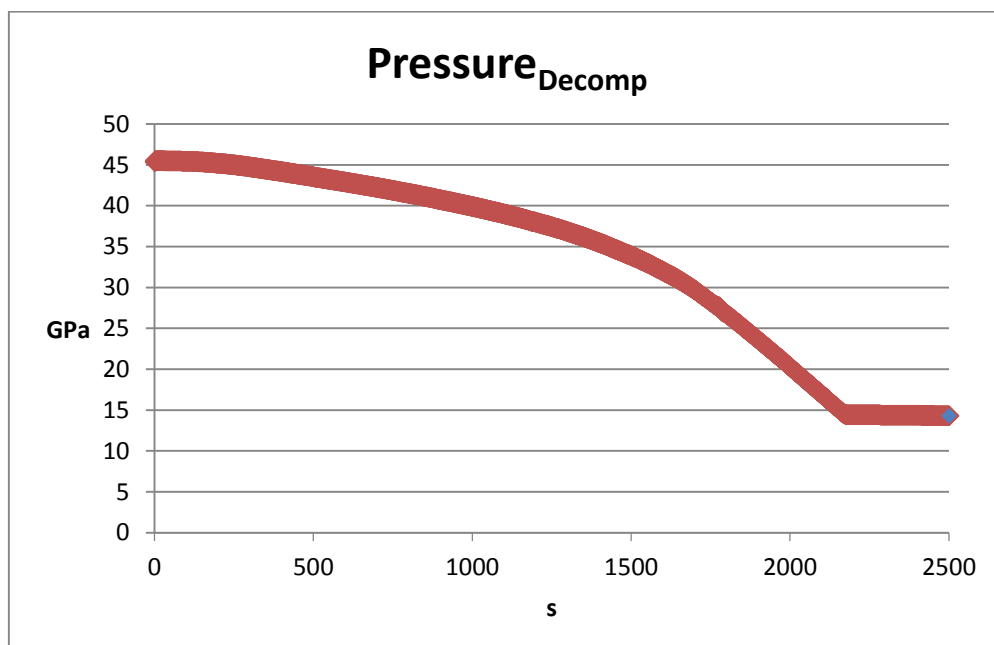


Figure 5) Pressure change of Rhenium during decompression.

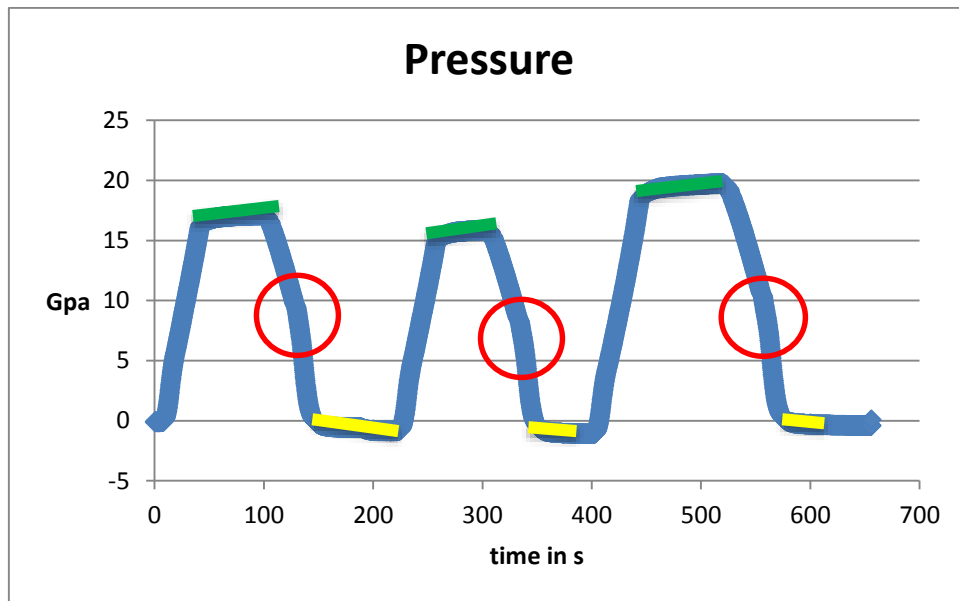


Figure 6 Pressure change of rhenium

In the figure 6 there can be seen also an effect that is caused by the membrane. The compression rate is changing during the process of compression and decompression (red marked). Furthermore after stopping the compression and decompression the pressure in the cell is also increasing (after compression – green marked) and decreasing (after decompression – yellow marked).

In the next Figure 7 and 8 it can be seen what happened when the diamonds broke during compression. The experiment was done with the DAC SYN7 with a compression rate of 40 bar/min. The volume and the pressure went instant back to the basic value at the beginning of the experiment.

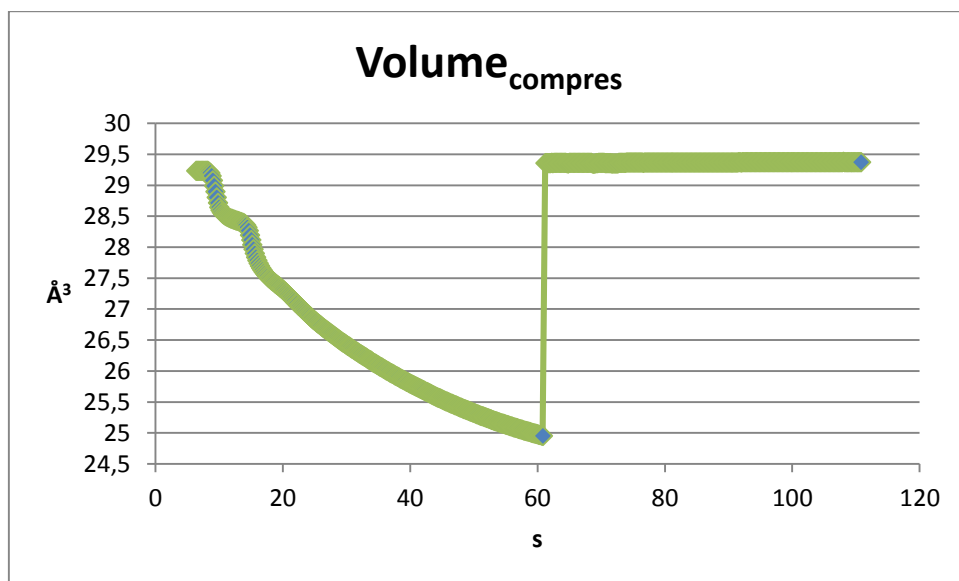


Figure 7) Volume change of Rhenium during compression.

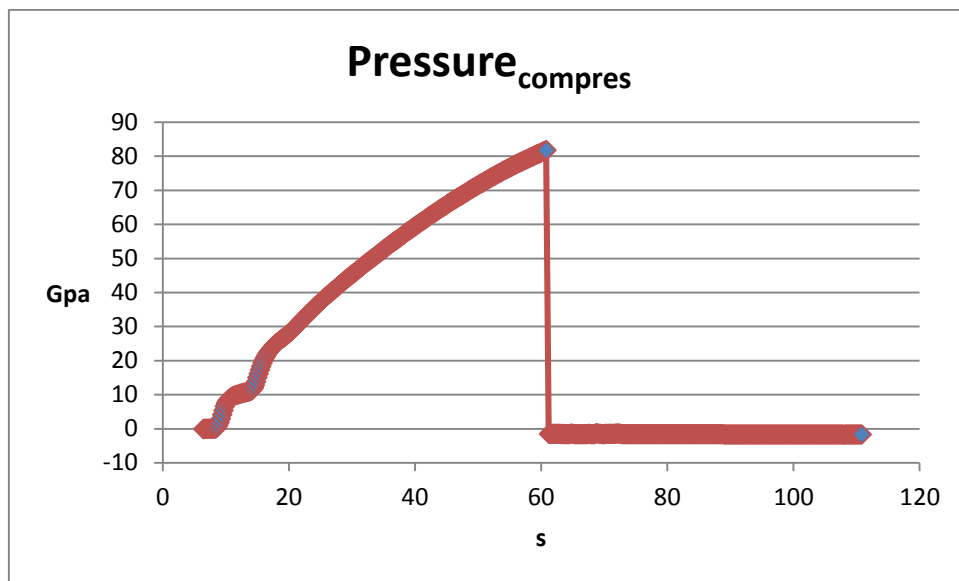


Figure 8) Pressure change of Rhenium during compression.

## 5. Literature

### *a) Book:*

Oliver H. Seeck, Bridget M. Murphy; X-Ray Diffraction – Modern Experimental Techniques; Chapter X-ray Diffraction at Extreme Conditions: Today and Tomorrow (H.-P. Liermann); Pan Stanford Publishing; 2015

### *b) Paper:*

[1] R. Ramírez, N. Neuerburg, and C. P. Herrero; The phase diagram of ice: A quasi-harmonic study based on a flexible water model; The Journal of Chemical Physics 139, 084503; 2013

[2] Marco Merlini, Wilson A. Crichton, Michael Hanfland, Mauro Gemmi, Harald Müller, Ilya Kuzenko, and Leonid Dubrovinsky; Structures of dolomite at ultrahigh pressure and their influence on the deep carbon cycle; PNAS, Vol. 109, No. 34, Page. 13509 - 13514; 2012.

[3] M. Merlin, M. Hanfland, W.A. Crichton; CaCO<sub>3</sub>-III and CaCO<sub>3</sub>-VI, high-pressure polymorphs of calcite: Possible host structures for carbon in the Earth's mantle; Elsevier; 2012.

[4] M. L. Frezzotti, J. Selverstone, Z. D. Sharp and R. Compagnoni; Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps; nature geoscience letters; 2011.

### *c) Picture*

(1) [http://www.mawi.tu-darmstadt.de/df/dispersefeststoffe/forschung\\_3/hochdruckverfahren/hochdruckverfahren.en.jsp](http://www.mawi.tu-darmstadt.de/df/dispersefeststoffe/forschung_3/hochdruckverfahren/hochdruckverfahren.en.jsp)