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1 **Graphite Resistive heated Diamond Anvil Cell for**  
2 **simultaneous high-pressure and -temperature diffraction**  
3 **experiments**

4 Huijeong Hwang<sup>1,2,\*</sup>, Yoonah Bang<sup>3,#</sup>, Jinhyuk Choi<sup>3</sup>, Hyunchoe Cynn<sup>4</sup>, Zsolt Jenei<sup>4</sup>, William  
5 J. Evans<sup>4</sup>, Anita Ehnes<sup>1</sup>, Iris Schwark<sup>1</sup>, Konstantin Glazyrin<sup>1</sup>, G. Diego Gatta<sup>5</sup>, Paolo Lotti<sup>5</sup>,  
6 Chrystèle Sanloup<sup>6</sup>, Yongjae Lee<sup>3</sup>, Hanns-Peter Liermann<sup>1</sup>

7  
8  
9 <sup>1</sup>Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

10 <sup>2</sup> School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and  
11 Technology, 123 Cheomdan-Gwagiro, Gwangju 61005, Republic of Korea

12 <sup>3</sup>Earth System Sciences, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722,  
13 Republic of Korea

14 <sup>4</sup>Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA

15 <sup>5</sup>Dipartimento di Scienze della Terra ‘Ardito Desio’, Università degli Studi di Milano,  
16 Via Botticelli 23, Milan 20133, Italy

17 <sup>6</sup>Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Sorbonne  
18 Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD UR206, 75005  
19 Paris, France

20 <sup>#</sup>Present address: Korea Atomic Energy Research Institute (KAERI), Daedeok-daero 989 beon-  
21 gil, Daejeon 34057, Republic of Korea

22 <sup>\*</sup>Corresponding Author: Huijeong Hwang (huijeonghwang@gist.ac.kr)

24 **Abstract**

25 High pressure and temperature experiments using a resistively heated diamond anvil  
26 cell have the advantage of heating samples homogeneously with precise temperature control.  
27 Here, we present the design and performance of a graphite resistive heated diamond anvil cell  
28 (GRHDAC) setup for powder and single crystal X-ray diffraction experiments developed at  
29 the Extreme Conditions Beamline (P02.2) at PETRA III, Hamburg, Germany. In the GRHDAC,  
30 temperatures up to 2000 K can be generated at high-pressures by placing the GRHDAC in a  
31 water-cooled vacuum chamber. Temperature estimates from thermocouple measurements are  
32 within +/-35 K at the sample position up to 800 K and within +90 K between 800-1400 K when  
33 using a standard seat combination of cBN and WC. Isothermal compression at high-  
34 temperature can be achieved by employing a remote membrane control system. The advantage  
35 of the GRHDAC is demonstrated through the study of geophysical processes in the Earth's  
36 crust and upper mantle region.

37 **Introduction**

38 Exploring the physical properties of materials at high-pressure and simultaneous high-  
39 temperature, by X-ray diffraction at large scale synchrotron radiation facilities, is relevant to  
40 understanding the dynamics of the Earth interior<sup>1</sup> as well as in the characterization and  
41 synthesis of industrially relevant materials.<sup>2,3</sup> Heated diamond anvil cells (DAC) have been  
42 essential for these types of investigation, especially at pressures beyond the current capabilities  
43 of large volume press devices,<sup>4,5</sup> i.e. up to 150 GPa and at 2000-3000 K. Heating of the diamond  
44 anvil cell can be achieved by means of: a) external or internal electrical resistive heaters, which  
45 can reach temperatures up to 2000 K<sup>6</sup> and 3000 K<sup>7</sup>, respectively, and b) infrared laser heating  
46 through the transparent diamonds aiming at temperatures between 1200 to 6000 K.<sup>4</sup> Both DAC  
47 heating approaches have their advantages and disadvantages. While laser heated DACs can

48 reach high-pressures and -temperatures (up to 300 GPa and 6000 K), the temperature  
49 distribution in the sample is prone to steep temperature gradients. The uncertainty of  
50 temperature measurement to below 1200 K is also one of critical limitation of laser heated  
51 DACs. By inducing larger area laser heating and probing the sample with a smaller X-ray beam  
52 the issue of steep temperature gradient can be minimized but reduces the maximum temperature  
53 achievable. Furthermore, infrared laser heating of transparent samples can only be achieved  
54 when placing a dark coupler in the chamber adjacent to the sample. However, these metal  
55 couplers can induce contamination of and reaction with the sample as well as inhomogeneous  
56 heating. Far infrared lasers are slowly being implemented at different synchrotron radiation  
57 facilities. They do not require absorbers for transparent materials, have a larger heating spot,  
58 but temperature determination in the low temperature regime can still be very challenging. In  
59 addition, temporal fluctuations in the heating spot may contribute to the uncertainties in the  
60 temperature stability and consequently its estimation. Resistive heated DACs, on the other hand,  
61 are limited to lower pressure and temperature regimes, but offer excellent homogenous  
62 temperature distribution across the sample and can heat every material stably. There are two  
63 types of resistive heated DAC based on the location of the heater: internal and external. In the  
64 case of internal resistive heated DACs, the heater takes the form of a metal foil e.g.  $\text{Re}^7$  or fine  
65 wire and is placed in the sample chamber. As a result, heat is generated only within the sample  
66 chamber reaching temperatures up to 3000 K. However, the complexity of the gasket design  
67 required to install the insulator and heater in the small sample chamber can make handling of  
68 the setup difficult. External resistive heated DACs use heating wires that form a coil and are  
69 installed near the diamonds to heat either the entire DAC<sup>8</sup> or just the tip of the diamond anvil.<sup>9-</sup>  
70 <sup>11</sup> In comparison with internal resistive heated DACs, external resistive heated DACs are  
71 limited to temperatures of 2000 K and require auxiliary equipment such as water-cooled

72 vacuum chambers to prevent oxidation of the pressure cell and its components. Nevertheless,  
73 external resistive heated DAC is often preferred rather than internal resistive heated DACs due  
74 to their simpler preparation including that of the heater. Unfortunately, coil heaters installed  
75 around diamond tip either cannot reach high temperatures (above 1100 K) because the wire  
76 will eventually melt, or are extremely delicate, so that they easily shear off during heater  
77 preparation and pressurization. Thus, there has been a need for a robust externally resistive  
78 heated DAC that can reach high temperatures up to 2000 K and that can be employed at high-  
79 pressure beamlines for X-ray diffraction studies. Such external resistive heated DAC for  
80 powder X-ray diffraction has been developed over the last decade by using flexible<sup>12-15</sup> or rigid  
81 graphite sheets<sup>16-17</sup> which are very robust, can easily surround and heat the tip of the diamond  
82 anvils as well as the gasket and sample, thus reaching very high-temperatures without oxidation  
83 of the DAC components if used within a vacuum chamber. The flexible graphite resistive  
84 heated DAC (GRHDAC) has the advantage of directly touching the diamond and thus heating  
85 the tip of the diamond, as well as the gasket and the sample, by conductive heat transfer in  
86 contrast to the rigid graphite heater. Thus, the graphite heater in the GRHDAC ensures that  
87 temperature gradients that might arise from the high thermal conductivity of the diamonds, are  
88 minimized because the entire tip of the diamond is heated. The flexible graphite heater has also  
89 been used in single crystal X-ray diffraction studies by adapting the GRHDAC with large  
90 opening Bohler-Almax seats.<sup>18</sup> The flexible graphite heater has been tested extensively at the  
91 Extreme Conditions Beamline P02.2 at PETRA III by heating several internal standards in the  
92 GRHDAC to estimate temperature measurement uncertainties resulting from changing  
93 positions of the thermocouple junctions with respect to the sample positions. This work  
94 describes the GRHDAC setup in detail and its current ability to accurately estimate sample  
95 temperatures by comparing temperatures determined from thermocouple readings with those

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96 derived from unit cell volumes and equations of state (EoS) of known standards situated in the  
97 sample chamber. Finally, a brief overview of different applications of the GRHDAC is provided  
98 as well as an outlook on future developments necessary to further improve the performance of  
99 the internal GRHDAC.

## 00 **Experimental Method**

01 The GRHDAC consists of four main components: a diamond anvil cell, a direct current  
02 (DC) powered electrical heating circuit with thermocouple read out system, a vacuum vessel  
03 with water cooling, and a membrane drive system.

### 04 *Design of the GRHDAC*

05  
06 The GRHDAC is based on a modified 4-pin type DAC developed by the high-pressure  
07 group from Lawrence Livermore National Lab (LLNL) to accept flexible graphite sheet  
08 heaters.<sup>5</sup> The 4-pin DAC comprises two parts: a main body, and a cup that screws on to the  
09 main body from the downstream side securing the membrane between the main body and the  
10 cup. The cell is further equipped with a tungsten carbide (WC) seat, with a slit or cone shape  
11 opening on the upstream side, and a conical cubic boron nitride (cBN) or Böhler-Almax type  
12 seat on the downstream side to perform powder or single crystal X-ray diffraction  
13 measurements. A schematic diagram of the GRHDAC is shown in Fig. 1. In the GRHDAC,  
14 two pieces of flexible graphite sheets (Alfa Aesar, part 42953, graphite foil, 0.5 mm thick,  
15 99.8%) sandwich a Re gasket. Both the gasket and graphite sheets are indented to ensure tight  
16 contact of the graphite sheets with diamond and gasket. Each graphite sheet is pushed against  
17 L-shaped molybdenum electrodes that provide electricity from the outside through the DAC  
18 walls parallel to the compression axis from the upstream side to the graphite heaters. The Mo  
19 electrodes are insulated by alumina sleeves to isolate the electrical circuit from the DAC body.  
20 For the same reason, 0.5 mm thick alumina discs with central openings are glued to both seats,  
21 which also provide electrical insulation of the flexible graphite sheets (Fig. 1).

24 *Electrical Heating and Temperature Measurement System*

25 R-type thermocouples are employed to monitor the temperature up to 1723 K. They  
26 are located on the pavilion of each diamond anvil. The junctions of the thermocouples are fixed  
27 approximately 700  $\mu\text{m}$  below the culet edge of each diamond (Fig. 1). After fixing the position  
28 of thermocouple junctions on each diamond, the thermocouple junction is covered with cement  
29 (RESBOND 989 from Cotronics Corp.) to prevent contact to the graphite heater and gasket.  
30 This ensures accurate temperature measurements at the diamond tips to estimate the sample  
31 temperature in the gasket. The thermocouple electromotive force (EMF) is transferred to the  
32 outside of the vacuum vessel via a feedthrough (CF16-TCL2-CE-RS from VACOM) and read  
33 by a multimeter (Keithley 3706A) with a cold junction correction board. Mo rods of the  
34 GRHDAC are connected to the outside of the 4-pin DAC by means of copper rods that guide  
35 the electrical current to the outside of the vacuum chamber through a high-power electrical  
36 feedthrough and high-power welding cables connected to a DC power supply (Fig. 1(C),  
37 Agilent 6601, 220 A and 8V). The DC power supply and the thermocouple read out system  
38 have been incorporated into the control software of the P02.2 beamline.

39  
40 *Vacuum vessel, water cooling and membrane manifold*

41 In order to prevent heat loss and oxidation of the different components of the  
42 GRHDAC during heating, the entire setup is placed inside a customized vacuum-chamber. This  
43 chamber consists of a stainless-steel tube positioned in the vertical direction, which is welded  
44 shut with ConFlat (CF) vacuum flanges at the bottom and top. The tube has two cutouts at the  
45 height of the sample, one circular opening on the downstream side providing  $\pm 45^\circ$  access in  
46  $2\theta$  and a rectangular opening with  $\pm 60^\circ$  access on the upstream side. The openings are sealed  
47 with Kapton foil, permitting the X-rays to travel to and from the sample in the DAC without



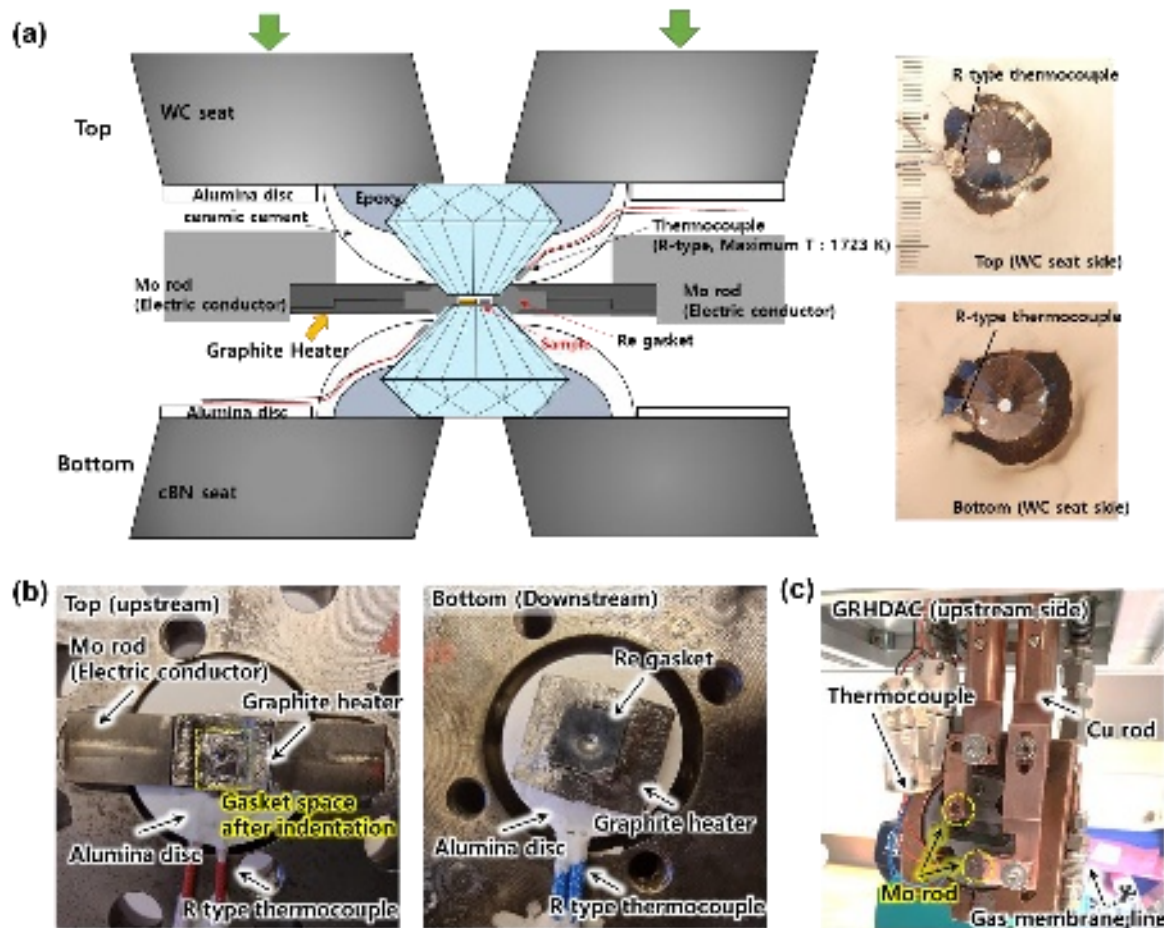
48 significant loss of X-ray intensity. The top CF flange has been modified to accept vacuum  
49 feedthroughs for the thermocouples (CF16-TCL2-CE-RS from VACOM), electrical power  
50 (CF40-HC8-2-CE-CU64 from VACOM), water cooling, and a membrane capillary, as well as  
51 a Quick Flange (QF)20 to connect a vacuum pump via a hose. The vacuum reached with a  
52 standard pump system from PETRA-III is better than  $1 \times 10^{-4}$  mbar, which is sufficient to  
53 prevent oxidation of the heated diamonds and metal components. To protect the sample  
54 positioning system underneath the vacuum chamber from heat transfer, the interface plate to  
55 the BKL-4 kinematic mount (Newport,) is water cooled, as is the outside of the main cell body  
56 of the 4-pin DAC. The pressure on the membrane that compresses sample is remotely  
57 controlled using either a pressure controller from Sanchez Technology (APD 200) or from  
58 General Electric (GE) (PACE 6000).

#### 60 *Temperature calibration using X-ray diffraction measurement in the GRHDAC*

61 Estimation of the sample temperature in the GRHDAC can be performed in different  
62 ways: a) using thermocouples placed close to the sample chambers or b) using internal X-ray  
63 diffraction standards. Because internal standards in the sample chamber may be subjected to  
64 reaction and pressure effects, temperature determination using thermocouples during  
65 simultaneous high-pressure and -temperature experiment is indispensable for estimating the  
66 accurate sample temperature. This approach, however, requires the placement of the  
67 thermocouples to be very reproducible, so that temperature gradients are minimal, and prior  
68 calibration of the temperature difference between the sample and thermocouple position can be  
69 applied to estimate an accurate sample temperature. In order to estimate the temperature  
70 difference between the sample and thermocouple position, X-ray diffraction standards (Al,  
71 NaCl, and Au) with a known high-temperature EoS were placed in the sample chamber and X-

72 ray diffraction patterns collected to measure the change of the unit-cell volume as a function  
73 of temperature at ambient pressure. Anhydrous NaCl powder with 99.999 % purity from Sigma  
74 Aldrich (Product no. 450006), Al and Au foils from Goodfellow were used as standards. The  
75 Al foil was separated from Au foil by NaCl powder to avoid the formation of alloys. Some of  
76 the X-ray diffraction patterns did not show any diffraction peaks from Al, and hence only  
77 diffraction data of NaCl and Au were used to determine the temperature in the sample chamber.

78 *In-situ* high-temperature and -pressure synchrotron X-ray diffraction measurements  
79 were conducted at beamline P02.2 at PETRA-III, Hamburg, Germany. Monochromatic  
80 synchrotron X-ray radiation was tuned to an energy of 25.6 keV ( $\lambda = 0.4828(1) \text{ \AA}$ ) with a beam  
81 size of 3 (h) x 8 (v)  $\mu\text{m}^2$  full width at half maximum (FWHM) focused by means of compound  
82 refractive lenses (CRLs). X-ray diffraction data were collected on a 2-dimensional Perkin  
83 Elmer XRD 1621 detector. Calibration of the sample-to-detector distance and detector tilt was  
84 performed using a CeO<sub>2</sub> standard from NIST (SRM 674b) with DIOPTAS,<sup>19</sup> which was also  
85 used to convert diffraction images to 1-dimensional  $2\theta$  values plots. All temperature and  
86 pressure calibration experiments were performed employing type-*Ia* standard-designed  
87 diamonds with 0.3 mm culet size and different seat configurations (see below). X-ray  
88 diffraction standards for the temperature calibration were loaded in a pre-indented rhenium  
89 gasket with an indentation thickness of 0.03 – 0.04 mm, and a hole of a 0.180 mm in diameter  
90 drilled by an electric discharge machine (EDM). X-ray diffraction data were collected after a  
91 stabilization period of approximately 10 minutes after reaching the desired temperatures in 50  
92 K intervals. In order to prevent the cell closure that would result in compression of the sample  
93 during heating, set screws were engaged.



**Fig. 1.** (a) Schematic image of GRHDAC setup (left) and photographs of the anvils (right) indicating the position of the R-type thermocouple on the pavilion of the diamond anvils. (b) Photographs of GRHDAC heater of the WC seat side (left) and cBN seat side (right). (c) Assembly of GRHDAC before placement into the vacuum chamber showing Mo electrodes, thermocouple wires and He gas membrane line.

06 **Results & Discussion**

07 **A. Thermal expansion of the temperature standards at ambient pressure**

08 Fig. 2 and 3 show the results of two calibration runs performed at ambient pressure. In  
 09 Fig. 2, we plot the results from the 1<sup>st</sup> calibration run with pure NaCl as an internal standard,  
 10 up to its melting temperature of 1074 K.<sup>20</sup> Results of the 2<sup>nd</sup> and 3<sup>rd</sup> run with mixed internal  
 11 standards (Al, NaCl, and Au) are presented in Fig. 3. In both experiments, the temperature of  
 12 the sample was estimated by determining the unit-cell volume from the diffraction pattern of  
 13 the standard in conjunction with the thermal EoS of NaCl,<sup>21</sup> and Au<sup>22</sup> at ambient pressure, until  
 14 the melting of the respective standards.<sup>23</sup> The melting temperatures of the standards were  
 15 determined by the disappearance of diffraction peaks and the appearance of diffuse scattering  
 16 signal. Fig. 2(B) and 2(C) indicate that, in 1<sup>st</sup> calibration run, the difference between the  
 17 temperature of the two thermocouple probes is relatively small (below 10 K) while the  
 18 difference to the actual sample temperature is below 30 K up to 800 K and below 90 K up to  
 19 the melting point of NaCl (1074 K). In the 2<sup>nd</sup> and 3<sup>rd</sup> runs, the difference in temperature  
 20 between the two thermocouples is much higher than in the 1<sup>st</sup> run, i.e., up to 800 K it is below  
 21 100 K, but at higher temperatures above 1100 K it can deviate by as much as 150 K. (Fig. 3(B)).  
 22 In the 3<sup>rd</sup> run, the gap between the temperature recorded by the thermocouple probes and  
 23 temperature estimated from known thermal EoS differs by as much 300 K, depending on the  
 24 standard used for the temperature estimate. However, the temperature difference of the  
 25 thermocouple located on the diamond of the cBN seat side is always no higher than +/-35 K  
 26 below 800 K and +75 above 800 K in comparison to the one mounted on the side with the WC  
 27 seat at the highest temperature. One can also observe that on the cBN side the temperature  
 28 difference increases significantly above 1000 K.

29 There is a slight difference between the temperature estimate using the EoS of NaCl

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30 and that of Au in the mixed phase experiments (Runs 2 and 3 displayed in Fig. 3), but the  
31 estimated temperature from the thermocouple on the cBN side is always lower than that on the  
32 WC side, as in run 1. In the case of NaCl, the temperature difference between the estimates in  
33 the sample chamber and the thermocouple fluctuate by +/- 35 K, while the difference between  
34 the sample chamber and the thermocouple on the WC side increase constantly until reaching a  
35 maximum of + 170 K at 1100 K. When using Au as a standard for estimating the temperature  
36 we find a similar behavior, except that the temperature differences are much larger, i.e. the  
37 temperature recorded by the thermocouple on the cBN side is lower than the temperature  
38 estimated from the Au EoS. At the same time the difference based on the temperature recorded  
39 on the WC side is much higher and reaches a value of as high as 300 K at 1300 K. We attribute  
40 the difference between the temperature estimates for NaCl and Au in the mixture to the fact  
41 that the Au foil was touching the diamond mounted on the WC side thus sensing the higher  
42 temperatures from this side.

43 The above observations indicate that in the original design, consisting of a small  
44 conical cBN seat and a large-slotted WC seat, the temperatures of the diamond on the cBN side  
45 is always lower than the temperature of the diamond on the WC seat, likely because of the  
46 higher thermal conductivity of the cBN seat that allows more heat to dissipate into the DAC  
47 body. Based on the calibration with an internal standard (NaCl or NaCl and Au mixture), the  
48 temperature of the sample is closest to that recorded on the cBN side. This means that there is  
49 a temperature gradient between the position of thermocouple on the diamond on the WC seat  
50 and the one on the cBN as described in Fig. 4. The distinct thermal conductivities of the seat  
51 materials resulted in a more efficient diversion of heat from the diamond tip on the cubic boron  
52 nitride (cBN) side compared to the tungsten carbide (WC) side. The gradient between the  
53 diamonds on the WC and the cBN seats becomes steeper at higher temperatures, when the heat

54 loss is more significant on the cBN seated side. This also explains the increased heating power  
55 consumption at higher temperatures. There may be a minimal temperature gradient within the  
56 sample itself, while the more significant gradient arises from the fact that the thermocouples  
57 are positioned on the diamonds located on different seats. Nevertheless, the difference to the  
58 temperature of the sample itself does not change significantly, so that one can always rely on  
59 the lowest recorded temperature (recorded with the thermocouple on the cBN side) being  
60 closest to the actual sample temperature. The temperature difference between the sample  
61 temperature and the recorded thermocouple temperature attached to the diamond of the cBN  
62 seated side in the three calibration runs of GRHDAC indicates that the maximum differences  
63 between the recorded temperature of the thermocouple attached to the cBN side and the sample  
64 is +/- 35 K until 800 K and above this + 90 K, +75 K, and +60 K, respectively (Fig. 2(d) and  
65 3(d)). Based on the maximum temperature differences, we conservatively estimated that the  
66 overall temperature uncertainty of the GRHDAC with the cBN and WC seats combination to  
67 be +/- 35 until 800 K and above + 90 K.

68 In order to reduce the temperature gradient across the diamonds and the sample area,  
69 tests were performed employing different seat materials and the combination thereof. Fig. 5(a)  
70 shows the results of the temperature calibration using seat combination of ZrO<sub>2</sub>(slit)-WC(BA)  
71 and of ZrO<sub>2</sub> (slit)-ZrO<sub>2</sub> (BA). The most homogenous temperature distribution was achieved  
72 when using both the slotted and the BA type seats consisting of ZrO<sub>2</sub> (which has a very low  
73 thermal conductivity) where the temperature difference between the thermocouple probes on  
74 the diamonds was less than 30 K at 1300 K and less than - 40 K to the sample up to 900 K (Fig.  
75 5(a) and 5(b)). Above 900 K, the diffraction peak of Au shifted to higher 2 $\theta$  values indicating  
76 pressurization of sample, so that it was not possible to estimate the real sample temperature  
77 from Au diffraction peaks alone. When combining a BA seat consisting of WC with a slotted

78 ZrO<sub>2</sub> seat, thermal gradient between the two thermocouples probing diamond temperature was  
79 much steeper in comparison to the combination of the slotted WC with the conical cBN seat.  
80 The thermal efficiency when using ZrO<sub>2</sub> seats on both sides was also significantly improved  
81 compared to when employing WC or cBN seat on either side. (Fig. 5(c)). At temperatures of  
82 about 1100 K, power consumption was cut by half when using ZrO<sub>2</sub> seat on both sides in  
83 comparison to other combination of seat materials. It has also become clear that the heating  
84 efficiency based on the electrical input power is relatively constant when the same combination  
85 of seat materials is used. Therefore, deployment of ZrO<sub>2</sub> seats on both sides is best for achieving  
86 precise sample temperature and pressure from the EoS of combined pressure and temperature  
87 standards during *in-situ* high pressure and temperature X-ray diffraction measurements using  
88 GRHDAC. Unfortunately, the BA type seats made of ZrO<sub>2</sub> are only stable up to 20 GPa. In  
89 summary, the overall temperature uncertainty when using the combination of a WC and cBN  
90 seat is  $\pm 35$  K until 800 K and above  $+ 90$  K while that for the ZrO<sub>2</sub> seats (regardless of the  
91 combination of seat shapes) is  $- 55$  K up to the highest temperatures of 900 K.

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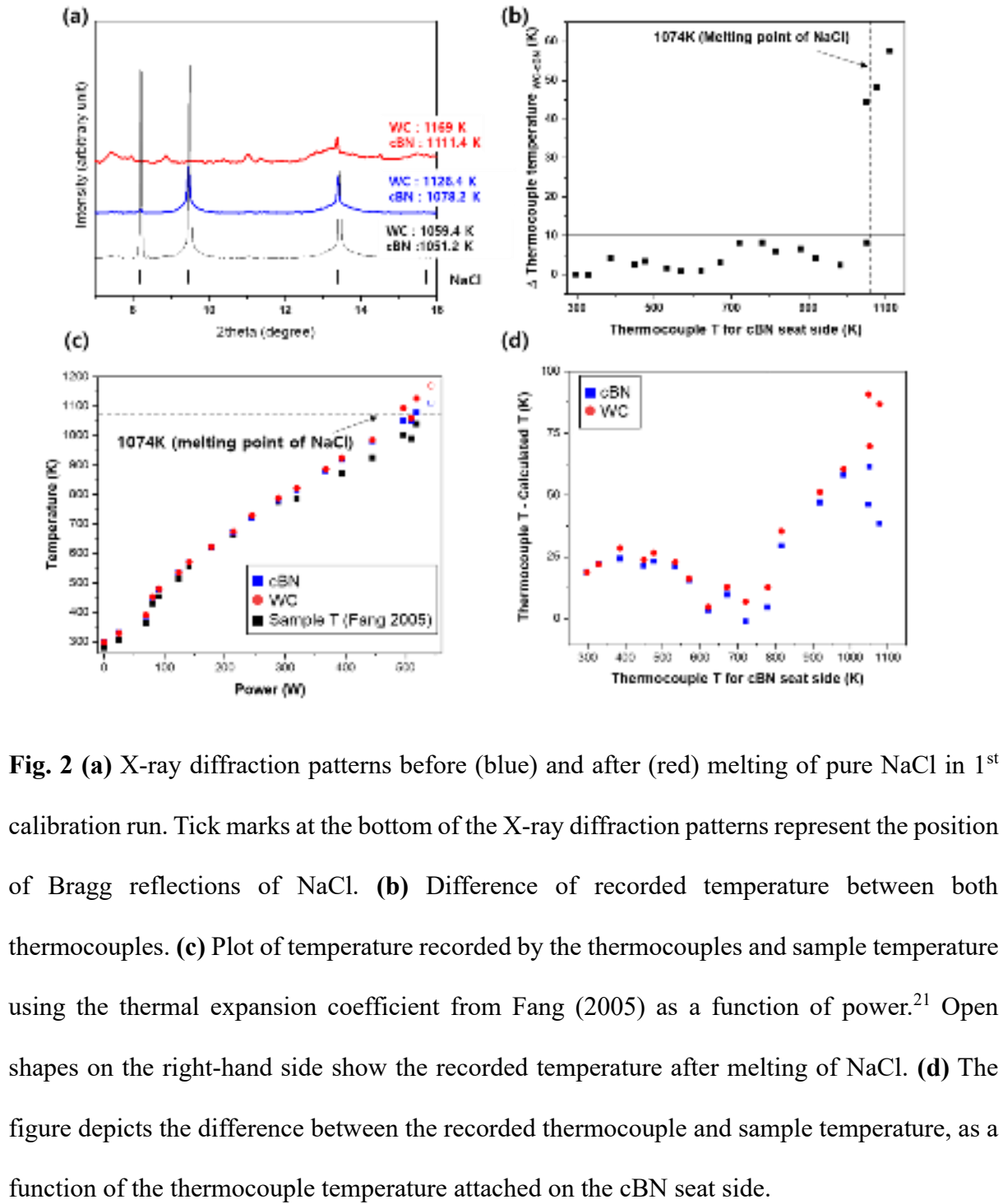
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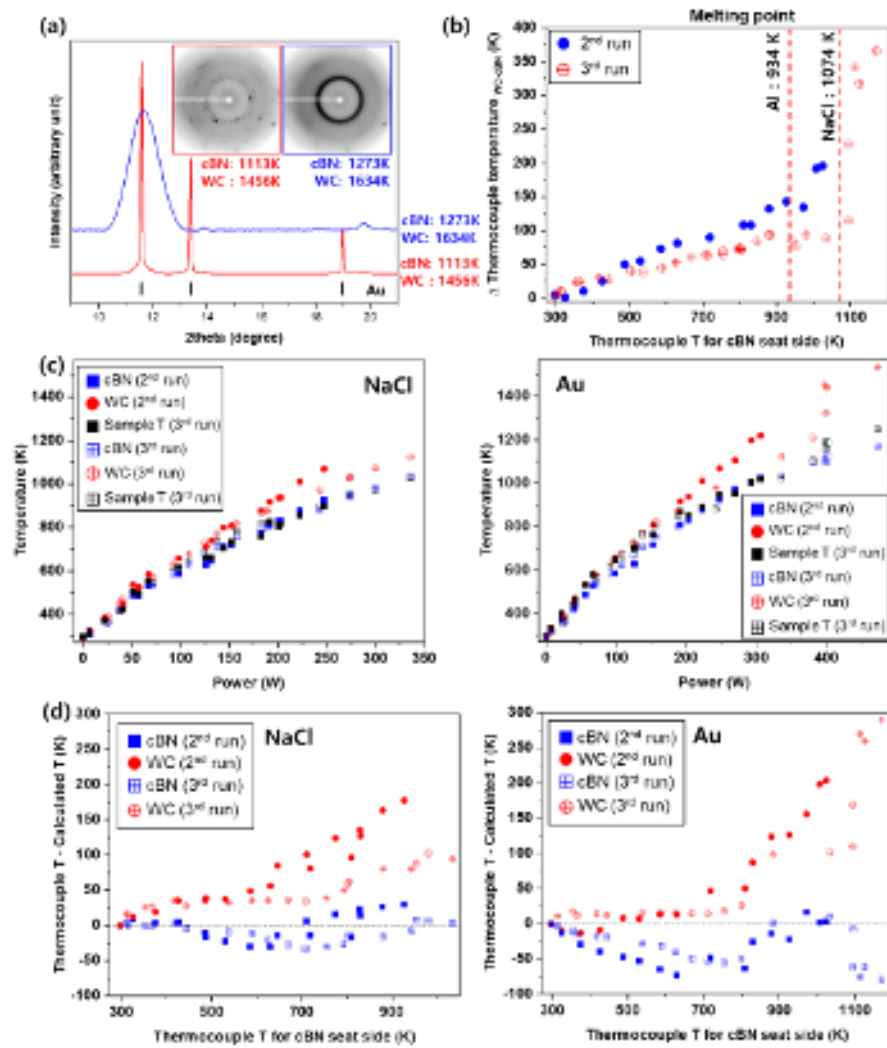
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**Fig. 2 (a)** X-ray diffraction patterns before (blue) and after (red) melting of pure NaCl in 1<sup>st</sup> calibration run. Tick marks at the bottom of the X-ray diffraction patterns represent the position of Bragg reflections of NaCl. **(b)** Difference of recorded temperature between both thermocouples. **(c)** Plot of temperature recorded by the thermocouples and sample temperature using the thermal expansion coefficient from Fang (2005) as a function of power.<sup>21</sup> Open shapes on the right-hand side show the recorded temperature after melting of NaCl. **(d)** The figure depicts the difference between the recorded thermocouple and sample temperature, as a function of the thermocouple temperature attached on the cBN seat side.

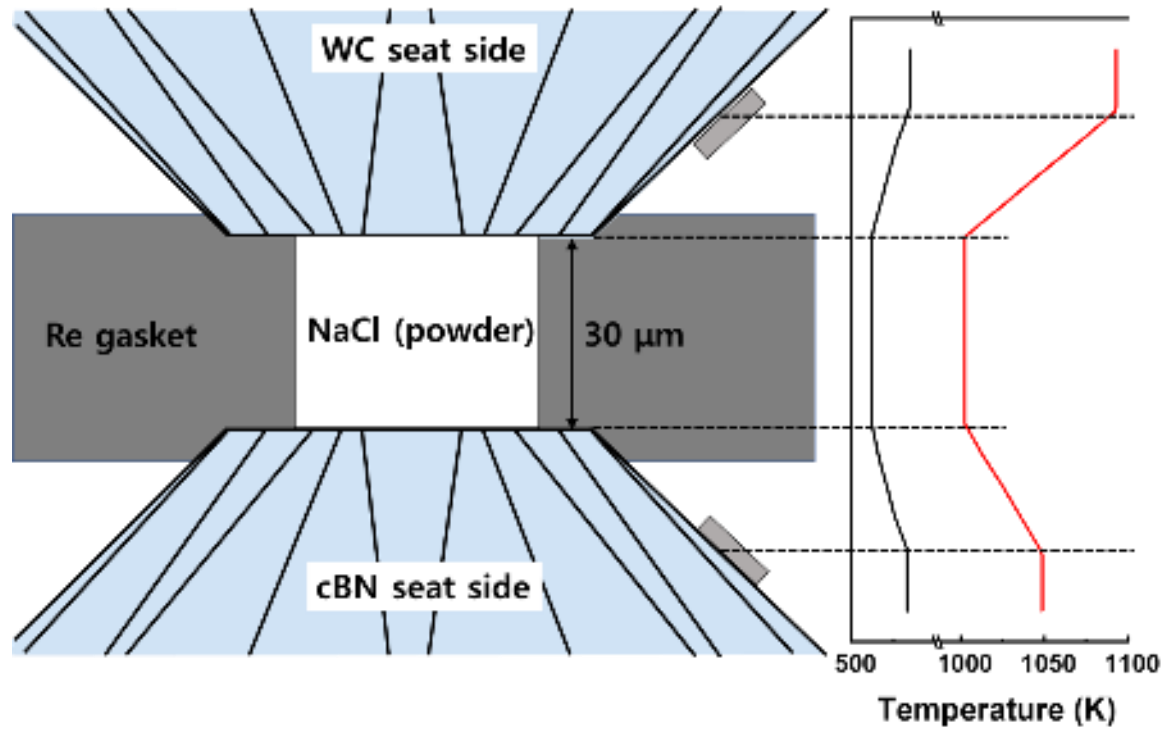


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**Fig. 3.** (a) Selected diffraction images and integrated diffraction patterns before and after melting of Au in the 2<sup>nd</sup> calibration run. (b) The temperature difference between the two thermocouples attached to the diamonds. (c) The correlation of power vs. temperature in the 2<sup>nd</sup> and 3<sup>rd</sup> calibration runs based on the temperatures measured by the thermocouples and the temperature calculated using the thermal expansion coefficient for NaCl from Fang (2005) and those for Au from Pamato et al. (2018).<sup>21-22</sup> (d) The differences between the recorded thermocouple temperature and the calculated temperature based on the thermal expansion coefficients of NaCl and Au, as a function of the measured thermocouple temperature for the cBN seat side.

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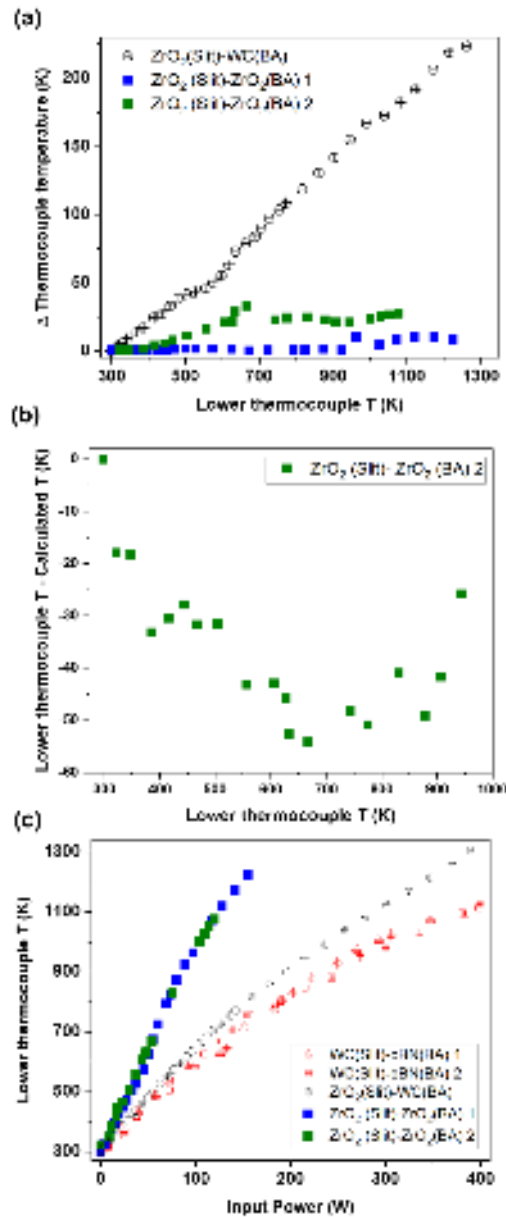
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**Fig. 4.** Schematic showing the temperature distribution between both diamonds during the 1<sup>st</sup> calibration run. The black and red lines denote the temperature distribution at the sample temperature of 512 and 1002 K, respectively.

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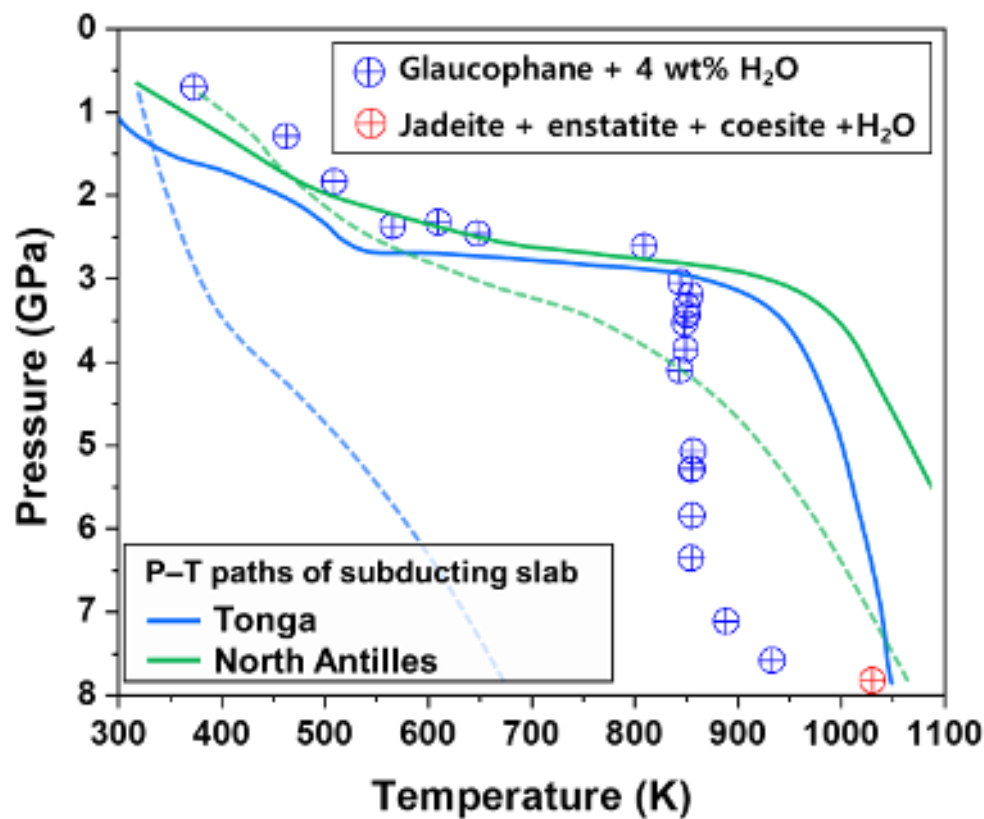


**Fig. 5. (a)** Probed temperature differences between two thermocouples attached to the pavilions of diamonds with different seat combinations. Open black circles with crosses represent the result from combining a BA seat comprised of WC with a slotted  $ZrO_2$  seat. The rest of the plots originate from experimental results using  $ZrO_2$  seats on both sides (Blue and Green squares). **(b)** Temperature differences between the temperature recorded by the thermocouples and the sample derived from the EoS of Au.<sup>22</sup> **(c)** Heating efficiency of different seat combinations as a function of power consumption.

29 **Applications of GRHDAC**30 **A. Stability of hydrous minerals under subduction zone conditions**

31 The stability of subducting hydrous minerals is critical for understanding the H<sub>2</sub>O  
32 transport process of the Earth's interior. The GRHDAC has been useful for generating  
33 simultaneous high-pressure and -temperature conditions encountered in the subduction zone.  
34 Through high-pressure and -temperature experiment using the GRHDAC combined with X-  
35 ray diffraction, the stability field and phase transition of hydrous minerals under subduction  
36 zone conditions can be studied. Fig. 6 shows the pressure and temperature path of the high-  
37 pressure and -temperature experiment for the hydrous mineral, glaucophane  
38 ( $\text{Na}_{2.09}(\text{Mg}_{2.7}\text{Fe}_{0.8}\text{Al}_{1.6})\text{Si}_{7.97}\text{O}_{22}(\text{OH})_2$ ), following a cold subduction geotherm using the  
39 GRHDAC. Au powder with a purity of 99.9 % (Sigma Aldrich, product no. 326585) was loaded  
40 as a pressure marker together with a powdered sample of glaucophane in the GRHDAC.  
41 Sample pressure was determined using the thermal equation of state of Au from Anderson  
42 (1989).<sup>24</sup> In order to realize a cold subduction environment, the sample was mixed with 4 wt.%  
43 of H<sub>2</sub>O<sup>25</sup> and loaded in the GRHDAC. In high-pressure and -temperature experiment of the  
44 glaucophane using GRHDAC, the pressure and temperature condition followed the geotherm  
45 models predicted for Tonga or North Antilles as described by Syracuse et al. (2010).<sup>26</sup> As the  
46 temperature increased to 850 K, a sample pressure increase was observed. Considering the  
47 reported thermo elasticity of glaucophane, the maximum thermal pressure that glaucophane  
48 can experience was estimated to be approximately 1 GPa.<sup>27,28</sup> Thus, the observed pressure  
49 increases to 3 GPa at 850 K cannot entirely be explained by thermal pressure. Additional  
50 pressurization during the heating is most probably due to the thermal expansion of components  
51 of the GRHDAC heated in the vicinity of the diamonds. To determine the high-temperature  
52 bulk modulus of glaucophane, isothermal X-ray diffraction data were collected at 850 K by

53 increasing the pressure through the gas membrane up to 6.3(3) GPa. At 7.8(3) GPa and 1030  
54 K, which is equivalent to ca. 250 km depth in the modeled geotherm, X-ray diffraction pattern  
55 confirmed the dehydration breakdown of glaucophane into jadeite ( $2\text{NaAlSi}_2\text{O}_6$ ), enstatite  
56 ( $1.5(\text{Mg}_{1-x}\text{Fe}_x)_2\text{Si}_2\text{O}_6$ ), coesite ( $\text{SiO}_2$ ), and  $\text{H}_2\text{O}$  fluid. When the compressibility of  
57 glaucophane at ambient temperatures is compared with that at high-temperature, we noted a  
58 suppression of the elastic anisotropy of glaucophane at high-temperature, which might  
59 contribute to the observed seismic anisotropy observed at the corresponding depth in the Tonga  
60 subduction zone. More details about this study may be found in Bang et al. (2021).<sup>15</sup>



161  
162 **Fig. 6.** Experimental pressure and temperature path explored in the study of glaucophane in the  
163 GRHDAC. Lines represent the pressure and temperature condition of the Tonga (Blue) and  
164 North Antilles (Green) subduction zone from Syracuse et al. (2010).<sup>26</sup> Dotted lines indicate the  
165 geotherms at Moho while continuous lines are representing the corresponding slab surface.

66 **B. Application of the GRHDAC in single crystal diffraction**

67 *In-situ* single-crystal X-ray diffraction experiments at combined high-temperature and  
68 high-pressure conditions (HPHT-SC-XRD) may provide data on the intrinsic structural  
69 stability of investigated samples, allowing not only the determination of  $P$ - $T$ - $V$  equations of  
70 state, but also the description of the structural mechanisms that govern, at the atomic scale, the  
71 bulk ( $P$ ,  $T$ )-behavior of the mineral (or synthetic compound) under investigation and its physical  
72 properties in general. These capabilities, made available by the use of the GRHDAC, are  
73 particularly relevant in tracking the occurrence and determining the critical  $T/P$  of phase  
74 transitions and corresponding structural evolutions.

75 Here we here report, as an example of *in-situ* HPHT-SC-XRD in the GRHDAC, the  
76 case study on scapolite. Scapolite is a group of open-framework aluminosilicates with general  
77 formula  $M_4T_{12}O_{24}A$ , where  $M$  are monovalent or divalent cations (usually Na, Ca and minor  
78 K),  $T$  are trivalent or tetravalent cations (mostly Al and Si) in tetrahedral coordination, and  $A$   
79 are anions such as Cl, CO<sub>3</sub> and SO<sub>4</sub>. Three mineral end members are recognized: marialite  
80 (Na<sub>4</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>Cl), meionite (Ca<sub>4</sub>A<sub>16</sub>Si<sub>6</sub>O<sub>24</sub>CO<sub>3</sub>), and silvialite (Ca<sub>4</sub>A<sub>16</sub>Si<sub>6</sub>O<sub>24</sub>SO<sub>4</sub>) even though  
81 most of the natural samples are of a given intermediate composition<sup>29</sup>. They are common rock-  
82 forming or accessory minerals, mainly encountered in metamorphic rocks of the amphibolite  
83 or granulite facies<sup>30-32</sup>. It is therefore of geological relevance to understand the behavior of  
84 scapolite-group members at non-ambient  $T$  and  $P$  conditions.

85 In a previous study on the compressional behavior at room temperature of an  
86 intermediate member of the scapolite solid solution,  
87 (Na<sub>1.86</sub>Ca<sub>1.86</sub>K<sub>0.23</sub>Fe<sub>0.01</sub>)(Al<sub>4.36</sub>Si<sub>7.64</sub>)O<sub>24</sub>[Cl<sub>0.48</sub>(CO<sub>3</sub>)<sub>0.48</sub>(SO<sub>4</sub>)<sub>0.01</sub>], Lotti et al. (2018)<sup>33</sup> reported  
88 the occurrence of a single-crystal to single-crystal phase transition from the tetragonal  $I4/m$  to  
89 the triclinic  $I\bar{1}$  space group, bracketed between 9.23 and 9.87 GPa. In order to investigate if the

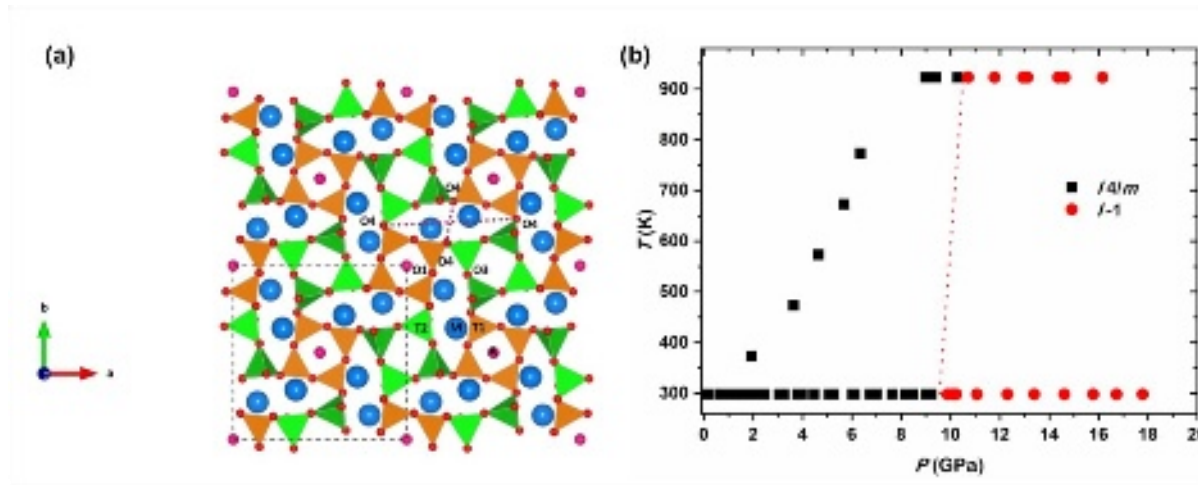
I-1

90 same phase transition would occur at higher temperature, an *in-situ* HPHT-SC-XRD  
91 experiment has been performed at beamline P02.2 at PETRA-III, DESY (Hamburg, Germany)  
92 using the GRHDAC. A single crystal fragment of the same sample studied by Lotti et al.  
93 (2018)<sup>33</sup> was loaded in the *P*-chamber (0.2 mm in diameter) obtained by spark-erosion of a  
94 rhenium gasket previously pre-indented to *ca.* 0.050 mm, along with ruby spheres and gold  
95 powder as pressure calibrants; silicone oil was used as the *P*-transmitting medium. Pressure  
96 was initially estimated using the ruby fluorescence shift<sup>34</sup> and at HPHT using the *P-T-V*  
97 equation of state of gold<sup>24</sup>, monitoring the shifts of the (111), (200) and (220) diffraction lines.  
98 A monochromatic X-ray beam (42.7 keV,  $\lambda = 0.2904 \text{ \AA}$ ) was used and the diffraction patterns  
99 were collected on a Perkin-Elmer XRD 1621 flat panel detector. For each dataset, the following  
00 data collection strategy was adopted: a step-wise  $\omega$ -scan from  $-25^\circ$  to  $+25^\circ$  (which allowed for  
01 a  $\sim 55\%$  completeness), with  $0.5^\circ$  step-scan and 1 second exposure time per frame. The  
02 instrumental model was calibrated using a crystal of ortho-enstatite [(Mg<sub>1.93</sub>,  
03 Fe<sub>0.06</sub>)(Si<sub>1.93</sub>,Al<sub>0.06</sub>)O<sub>6</sub>, (Space group, *Pbca*,  $a = 18.2391 (3)$ ,  $b = 8.8117 (2)$ ,  $c = 5.18320 (10)$   
04  $\text{\AA}$ ]. Data were collected using an in-house script and then converted to the “Esperanto” format  
05 in order to be processed in CrysAlisPro<sup>35-36</sup> for the indexing of the X-ray diffraction peaks,  
06 unit-cell refinements and intensity data reduction (corrected for Lorentz-polarization effects).  
07 The semi-empirical ABSPACK routine, implemented in CrysAlisPro, was applied to correct  
08 for absorption effects of the DAC components. Structure refinements were performed using  
09 JANA2006<sup>37</sup> starting from the model (and applying the same restrictions and assumptions)  
10 reported by Lotti et al. (2018)<sup>33</sup> for the refinements based on the high-pressure datasets. Three  
11 data collections at ambient-*T* were performed from 0.0001 up to 1.42 GPa and then the  
12 temperature was increased up to 923 K with data collections every 100 K. As described in  
13 section A, pressure also increased at this stage. At 923 K, an isothermal compressional ramp

14 from 8.98 up to 16.16 GPa was performed with ten dataset collections (Table 1). The tetragonal  
15  $I4/m$  structural model of scapolite has been successfully determined up to 10.30 GPa at 923 K,  
16 whereas, at 10.71 GPa, the triclinic  $I-1$  structure already described by Lotti et al. (2018)<sup>33</sup> was  
17 detected. The triclinic unit-cell parameters were indexed up to the highest pressure investigated  
18 of 16.16 GPa, even though observing a continuous and significant decrease in the intensity of  
19 the diffraction peaks with pressure. As shown in Fig. 7, based on the data reported here and  
20 those previously published<sup>33</sup>, it appears that the phase transition is significantly more controlled  
21 by pressure rather than by thermal excitation. Relevant structural parameters from the selected  
22 refinements are reported in Table 2. A comparison with the structural data reported from the  
23 isothermal compression at 298 K<sup>33</sup> shows that the same dominant structural mechanisms  
24 mainly controlled by pressure occur, with the anti-cooperative rotation of the 4-membered rings  
25 of tetrahedra **lying on the (001) plane**, which induces a compression of the channels along the shorter  
26 axis with related increase in ellipticity (Fig. 7 and Table 2). It is the dominant one. It is worth  
27 note that the structure refinements based on the HTHP data also suggest that the phase transition  
28 is likely induced by the saturation in the compressional trend of selected interatomic bonds  
29 involving the  $M$  cations (Table 3; see also Lotti et al. 2018)<sup>33</sup>, demonstrating the potential use  
30 of this experimental setup for thorough structural characterization and understanding of phase  
31 transitions at both high- $T$  and high- $P$  conditions.



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**Fig. 7. (a)** The crystal structure of scapolite viewed along the  $c$ -axis. Orange and green tetrahedra represent the independent  $T1$  and  $T2$  sites, respectively, whereas red, blue and purple spheres refer respectively to the oxygen, cations ( $M$ ) and anions ( $A$ ) positions. **(b)** Experimental phase diagram of tetragonal and triclinic scapolite at varying  $T$  and  $P$  conditions (based on data of Lotti et al., 2018<sup>33</sup>, and those reported in this manuscript).

**Table 1.** Unit-cell parameters of the tetragonal and triclinic polymorphs of scapolite at different temperature and pressure.

$T$ (K)	$P$ (GPa)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$V$ (Å <sup>3</sup> )
298*	0.0001*	12.1136(3)		7.5588(3)	90	90	90	1109.2(1)
298	1.27	12.0273(5)		7.5228(4)	90	90	90	1088.2(1)
298	1.42	12.0235(4)		7.514(2)	90	90	90	1086.3(2)
373	1.92	11.9869(8)		7.5117(7)	90	90	90	1079.3(1)
473	3.64	11.9497(13)		7.4733(14)	90	90	90	1067.1(3)
573	4.67	11.8578(5)		7.4491(4)	90	90	90	1047.4(1)
673	5.68	11.8541(5)		7.4422(4)	90	90	90	1045.8(1)
773	6.35	11.8371(4)		7.4273(4)	90	90	90	1040.7(1)
923	8.98	11.7378(5)		7.364(2)	90	90	90	1014.6(3)
923	9.41	11.7280(5)		7.311(2)	90	90	90	1005.6(3)
923	10.30	11.7206(11)		7.289(5)	90	90	90	1001.3(6)
923	10.71	11.714(4)	11.556(5)	7.319(3)	88.05(12)	89.88(6)	89.67(5)	990(2)
923	11.78	11.673(5)	11.573(11)	7.132(6)	86.86(7)	90.57(6)	89.72(6)	962(1)
923	12.93	11.684(5)	11.503(14)	7.164(7)	86.51(9)	90.26(6)	89.62(6)	961(1)
923	13.11	11.638(7)	11.507(11)	7.077(6)	86.19(7)	90.89(8)	89.51(7)	946(1)
923	14.36	11.619(9)	11.485(13)	7.103(8)	86.22(9)	90.94(10)	89.44(9)	946(2)
923	14.63	11.616(11)	11.40(2)	6.690(10)	85.05(12)	91.38(11)	88.97(10)	917(2)
923	16.16	11.59(2)	11.32(3)	6.83(2)	83.6(3)	91.7(2)	88.9(2)	889(4)

\* Crystal in the DAC without  $P$ -medium (prior to assembly in the GRHDAC)

48 **Table 2.** Angles ( $^{\circ}$ ), distances ( $\text{\AA}$ ) and volumes ( $\text{\AA}^3$ ) from selected refinements of tetragonal scapolite  
 49 at different temperatures and pressures. The O4-O4 distances refer to the diagonals of the  $8mR_{\text{short}}$  shown  
 50 in Figure 7a.

<i>T</i> (K)	<i>P</i> (GPa)	T1-O1- T1	T2-O2- T2	T2-O3- T2	T1-O4- T2	O1-O4- O3	$8mR_{\text{short}}$ O4-O4	$8mR_{\text{short}}$ O4-O4	$8mR_{\text{short}}$ $\epsilon^{**}$	<i>V</i> (M) $^{***}$
<b>298*</b>	0.0001*	157.8(3)	139.54(4)	146.3(2)	137.1(2)	93.34(9)	3.119(7)	9.335(8)	0.3341(10)	18.82(8)
<b>298</b>	1.27	157.7(3)	139.25(4)	146.0(2)	136.6(2)	92.43(9)	3.045(7)	9.323(8)	0.3266(10)	18.34(8)
<b>273</b>	1.92	157.5(4)	139.77(7)	146.5(3)	136.3(2)	92.06(10)	3.017(8)	9.313(8)	0.3240(11)	18.27(8)
<b>573</b>	4.67	157.6(5)	138.55(6)	145.4(4)	135.3(3)	90.90(13)	2.910(10)	9.290(10)	0.3132(14)	17.41(10)
<b>773</b>	6.35	157.6(5)	138.17(6)	144.5(4)	135.3(3)	90.6(2)	2.899(12)	9.275(12)	0.313(2)	17.37(12)
<b>923</b>	8.48	158.3(5)	137.8(2)	145.1(3)	135.8(5)	90.20(14)	2.846(12)	9.236(10)	0.308(2)	17.1(2)
<b>923</b>	9.41	158.0(5)	137.4(2)	144.6(3)	135.6(5)	90.1(2)	2.84(2)	9.230(12)	0.307(2)	17.0(2)
<b>923</b>	10.30	157.5(7)	136.7(3)	145.1(6)	134.1(7)	89.7(3)	2.78(3)	9.28(2)	0.300(3)	16.8(4)

\* Crystal in the DAC without *P*-medium; \*\* defined as ( $8mR_{\text{short}}$ -O4-O4 short)/( $8mR_{\text{short}}$ -O4-O4 long); \*\*\* volume of the *M* cation coordination polyhedron calculated using the tools implemented in VESTA3 (Momma and Izumi 2011)<sup>38</sup>

51  
 52 **Table 3.** Interatomic bonds ( $\text{\AA}$ ) of tetragonal scapolite involving the *M* cations coordination  
 53 environment from selected structure refinements at different T and P.

<i>T</i> (K)	<i>P</i> (GPa)	<i>M</i> -O2	<i>M</i> -O3 (x 2)	<i>M</i> -O4' (x 2)	<i>M</i> -O4'' (x 2)	<i>M</i> -A
<b>298*</b>	0.0001*	2.347(4)	2.516(3)	2.765(3)	2.888(3)	3.108(2)
<b>298</b>	1.27	2.347(5)	2.501(4)	2.746(4)	2.891(3)	3.116(2)
<b>373</b>	1.92	2.325(5)	2.481(4)	2.732(4)	2.845(4)	3.059(2)
<b>573</b>	4.67	2.296(7)	2.432(5)	2.693(5)	2.798(4)	3.021(2)
<b>773</b>	6.35	2.302(8)	2.418(6)	2.707(6)	2.788(5)	2.994(4)
<b>923</b>	8.48	2.297(9)	2.406(8)	2.689(7)	2.772(10)	2.943(3)
<b>923</b>	9.41	2.304(10)	2.394(9)	2.698(8)	2.751(11)	2.927(4)
<b>923</b>	10.30	2.287(14)	2.397(16)	2.683(13)	2.734(20)	2.920(4)

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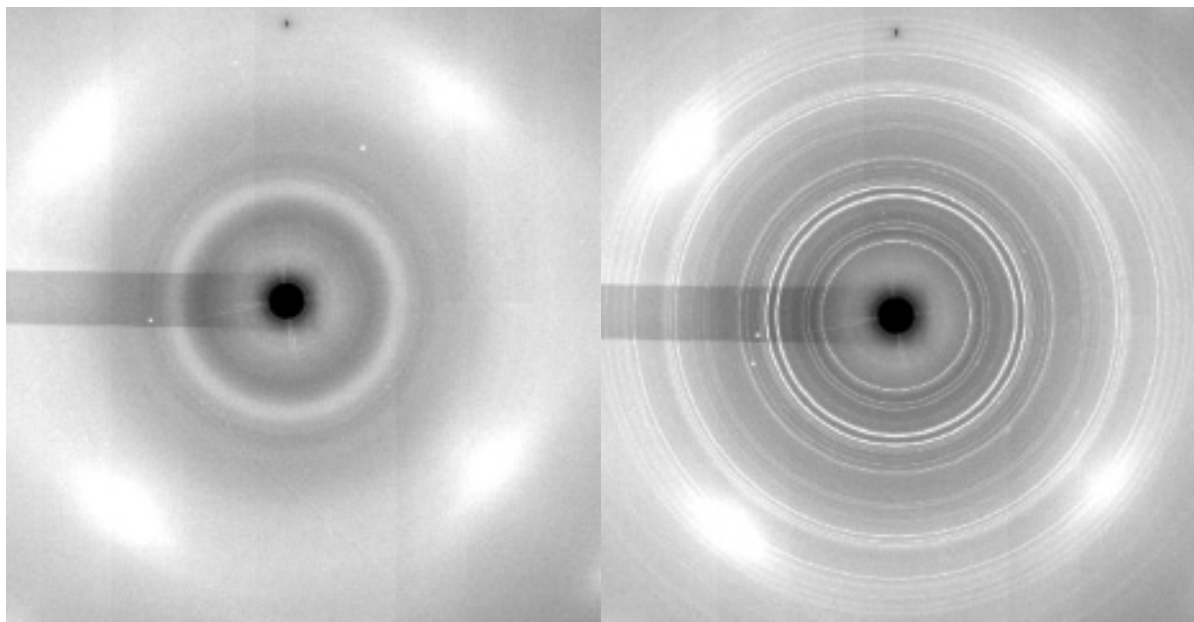
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### C. Xe retention in deep hydrous silicates

Atmospheric Xe is recycled at depth via subduction,<sup>39</sup> and potentially carried in cyclo-silicates due to their cage and channels like structures.<sup>40</sup> Xenon retention in compressed SiO<sub>2</sub> quartz and (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> olivine occurs through substitution of Xe with Si at high T, inducing the formation of Xe-O covalent bonds.<sup>41-44</sup> To investigate Xe retention in more complex naturally relevant systems, we have worked on the Xe-KNaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O system up to 9.7 GPa and 1473 K to target the P-T stability field of K-cymrite, the high P form of K-feldspar. Xenon is a very heavy element, hence strongly contributes to the X-ray diffracted signal. However, only 0.9 Xe wt% is retained in the crystalline structure, hence it is essential to optimize the quality of the X-ray diffraction patterns for accurate crystal structure refinement and proper identification of Xe crystal-chemistry. For that purpose, sample was loaded as a glass previously synthesised in a one atmosphere furnace, and further hydrated and doped with Xe using a piston-cylinder press.<sup>45</sup> Indeed, when the glass transition is crossed upon heating, it results in a powder pattern with very good ring statistics (see Fig.8).

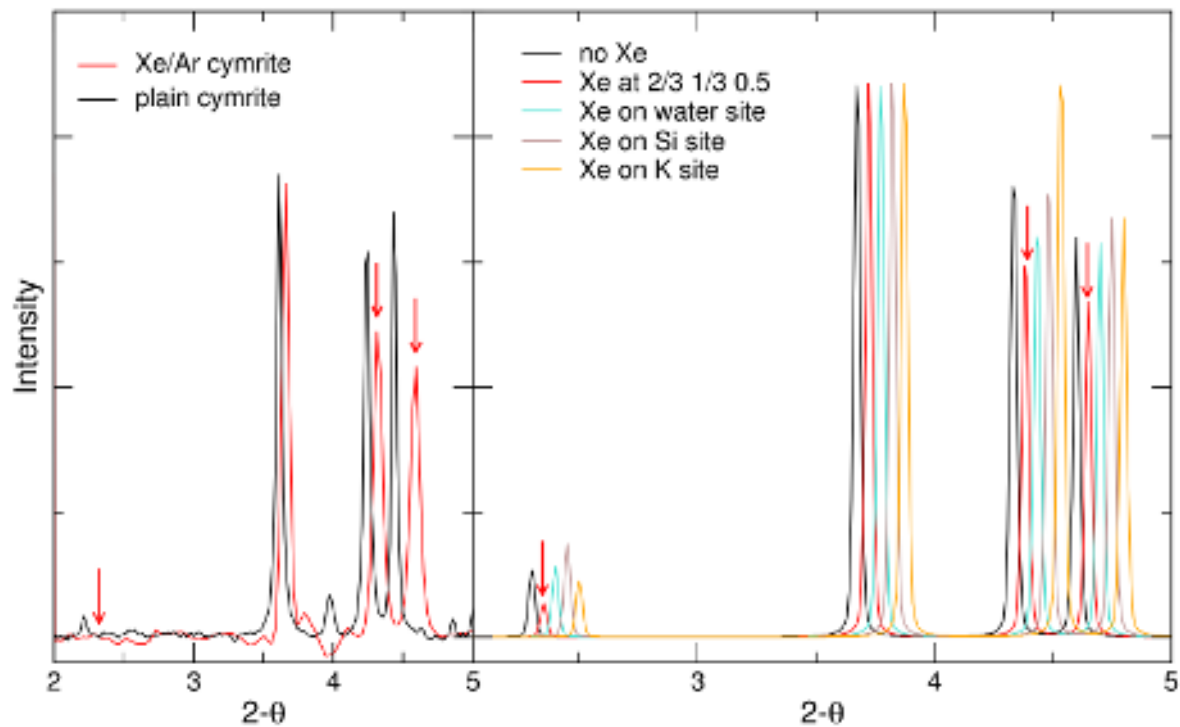
Such quality would not be obtained during laser heating in the DAC. Differences in intensity between plain and Xe-doped K-cymrite are small but still evident on the first four diffraction peaks (Fig.9), including disappearance of the lowest angle diffraction peak. Amongst the different crystallographic sites tested for Xe, only one matches the X-ray diffraction data. It does not correspond to rings site, as expected for other volatiles such as N<sub>2</sub>, Ar, or H<sub>2</sub>O,<sup>46</sup> but instead Xe sits in between sheets of [SiO<sub>4</sub>]<sup>4-</sup> tetrahedra, surrounded by six oxygen atoms in the same configuration as [XeO<sub>6</sub>]<sup>4-</sup> perxenate octahedra in K<sub>4</sub>Xe<sub>3</sub>O<sub>12</sub> perovskite.<sup>47</sup> However, a precise structure refinement will require collecting additional data with a higher Xe content. Indeed, the Xe content in recovered cymrite equals that in the starting glass, and no Xe bubbles were observed, attesting that 0.9wt% is below the Xe solubility for

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**Fig. 8.** 2-D X-ray diffraction signal of (left) glass sample (hydrous feldspar glass doped with 0.9 wt%Xe at 9.7 GPa and 880°C), and (right) re-crystallized pattern at 9.7 GPa and 1080°C. White shadows are diamond Bragg peaks from the anvils.

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90 **Fig. 9.** (Left) Integrated diffraction signal of Xe-doped and plain K-cymrite after re-  
91 crystallization from glass; the arrows point to the peaks which intensity decreases in the  
92 presence of Xe in the crystalline structure. (Right) Expected X-ray diffraction signal for K-  
93 cymrite without Xe and with Xe on different crystallographic sites. Note that coloured  
94 diffractograms are shifted horizontally to visualize intensity variations.

## 95 Outlook

97 Future work will focus on using a slotted and a conical  $\text{ZrO}_2$  seat for powder diffraction  
98 studies, in order to reach higher pressures at simultaneous high-temperatures and to overcome  
99 the 20 GPa pressure limit encountered when using the BA type  $\text{ZrO}_2$  seats. With this seat  
100 configuration, sample access to reciprocal space can only be reached when inverted the vacuum  
101 chamber so that slotted  $\text{ZrO}_2$  seat will be located on the downstream side. Furthermore,

02 fluorescence measurement of  $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$  will be implemented to estimate the pressure more  
03 precisely up to  $\sim 900$  K, since the  $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$  fluorescence lines are relatively insensitive to  
04 temperatures<sup>48-49</sup>. This will require reconfiguration of the online fluorescence microscope at  
05 P02.2 that is currently configured to monitor the sample chamber only from the downstream  
06 side.

## 08 **Conclusion**

09 We present the calibration of the 4-pin type GRHDAC based on X-ray diffraction  
10 measurements of materials with well-characterized melting points, such as NaCl, and Au, up  
11 to 1500 K at ambient pressure. Moreover, we demonstrated good heating capability and  
12 reproducibility of GRHDAC when comparing EoS temperature estimates based on synchrotron  
13 X-ray diffraction measurements of internal standards with thermocouple measurements. The  
14 differences between the temperature recorded by thermocouples placed on the diamond  
15 mounted on a cBN seat and the temperature derived from EoS of Au and NaCl standards were  
16 within 75 K below 1300 K. Significant improvement of the temperature stability can be  
17 achieved when employing  $\text{ZrO}_2$  type seat. As such, the GRHDAC presented in this paper  
18 enables access to simultaneous temperature and pressure regimes that is not possible to reach  
19 using the infrared laser heated DAC. Further development of the GRHDAC technique would  
20 help to establish high precision EoS and phase stability studies in a wide range of pressure and  
21 temperature conditions and in particular those where the laser heating experiment may fail.

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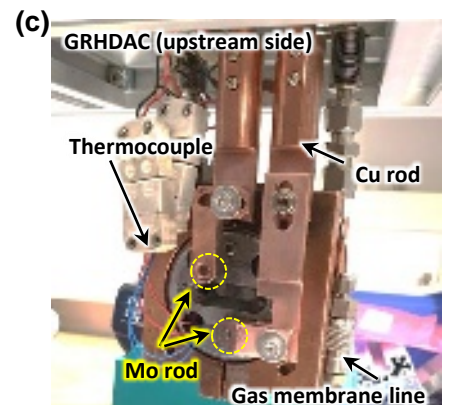
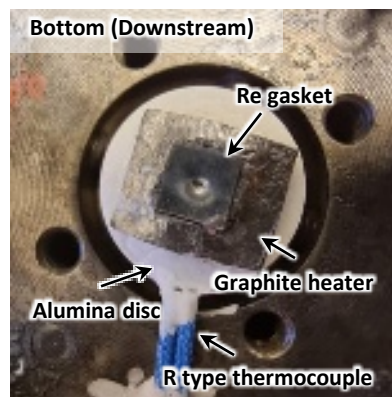
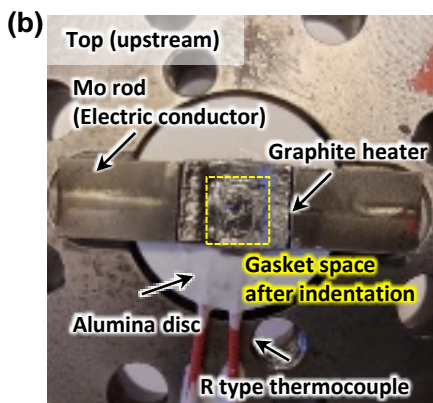
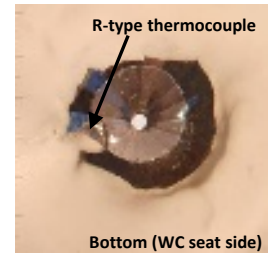
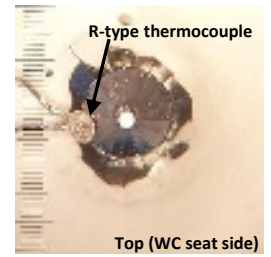
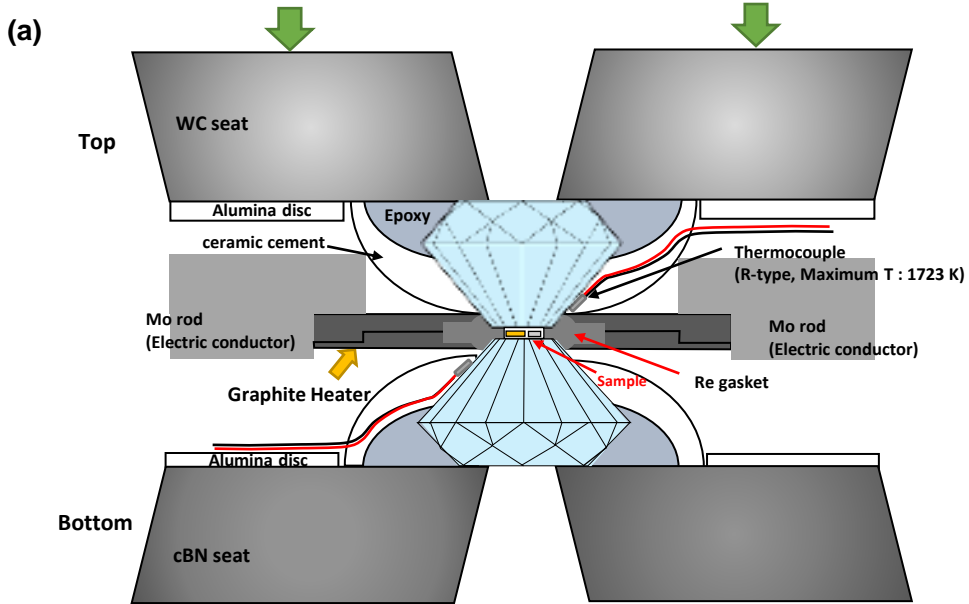
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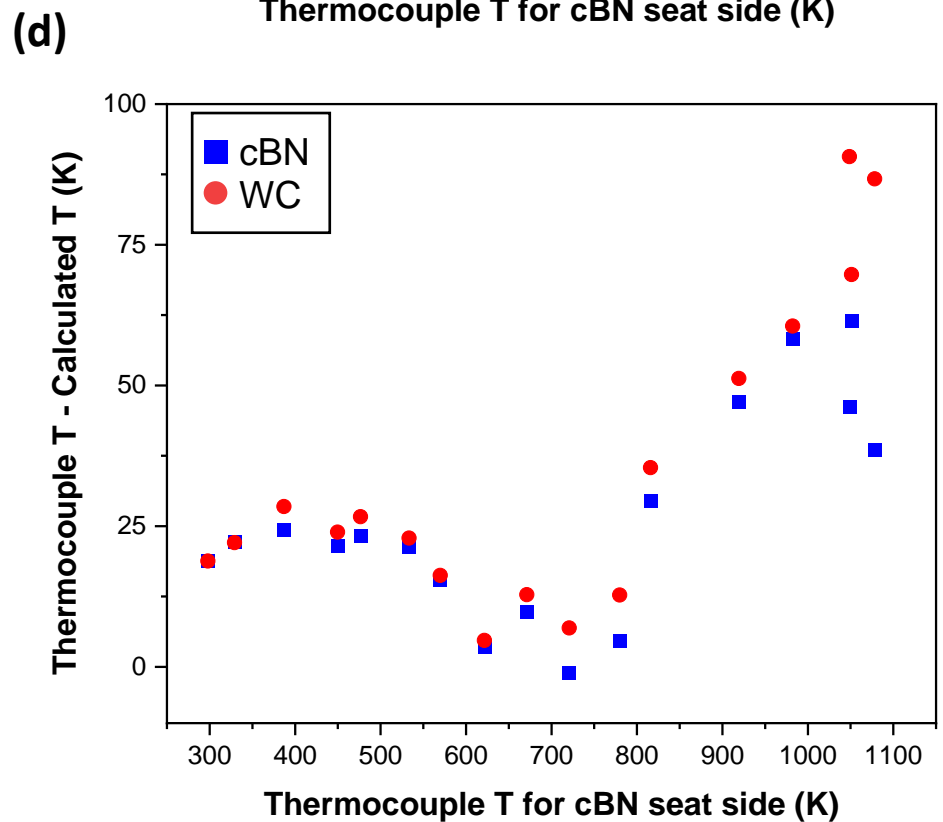
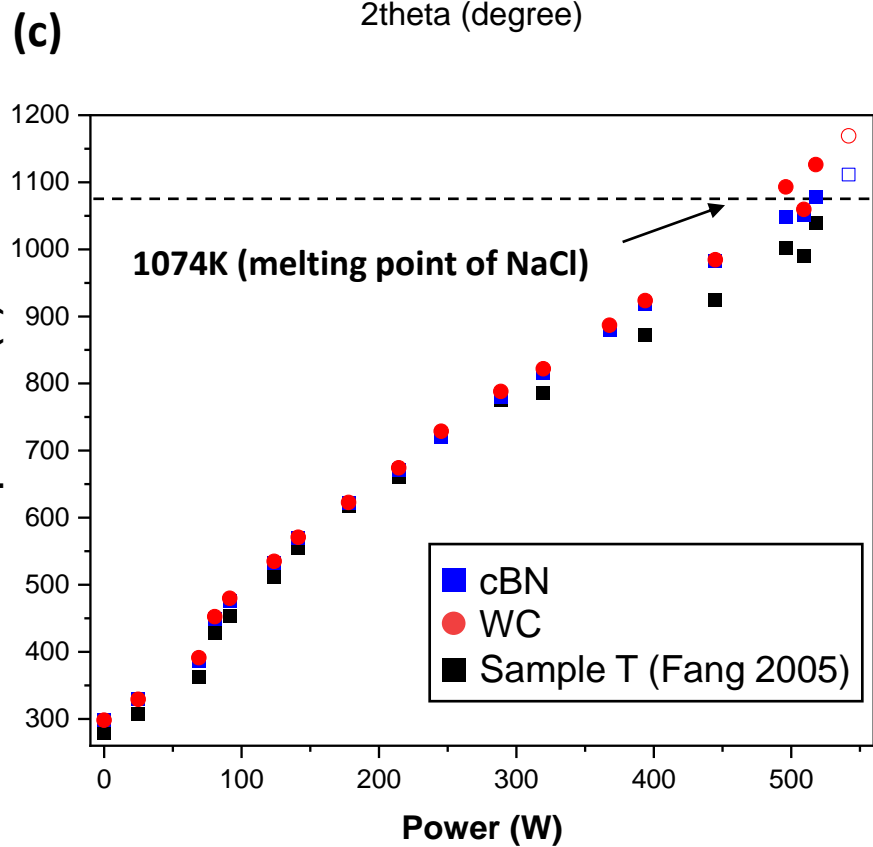
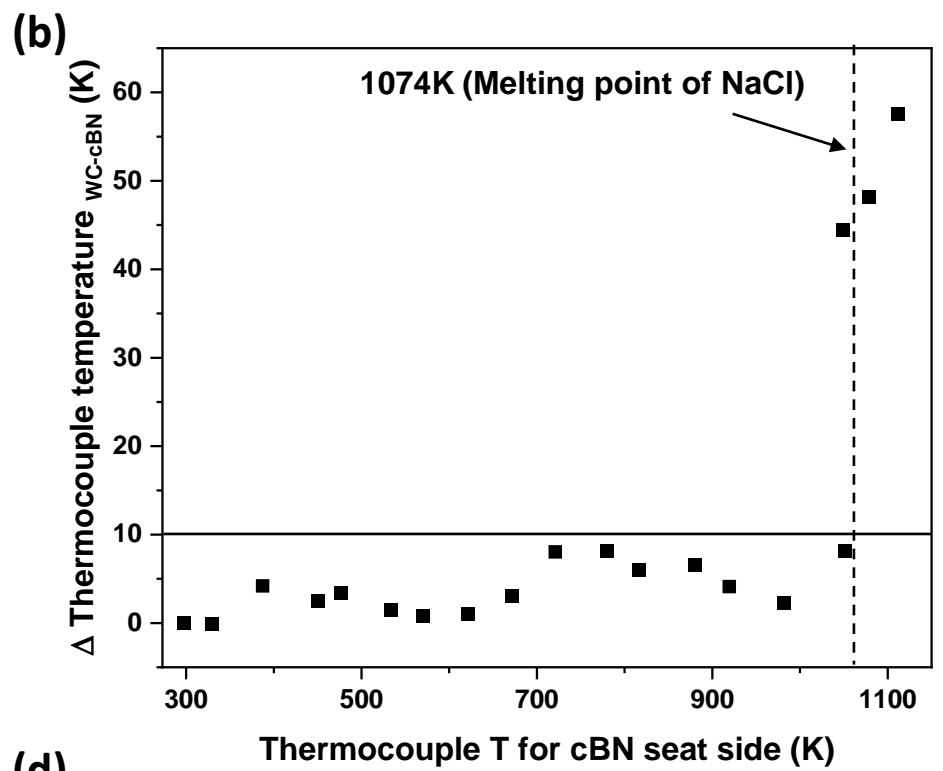
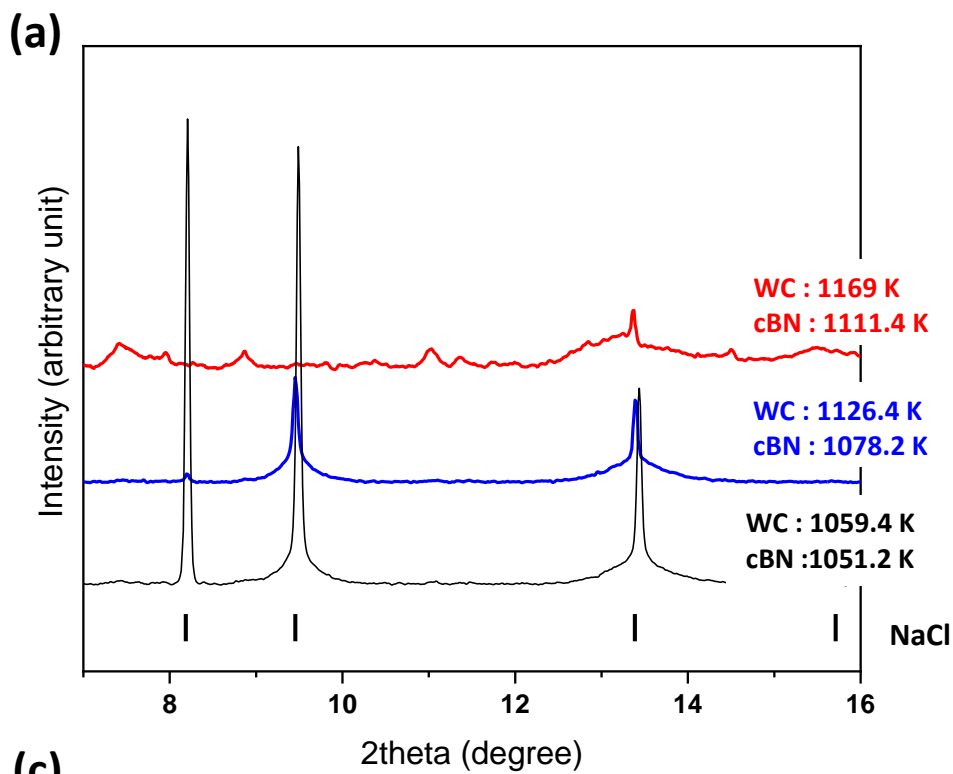
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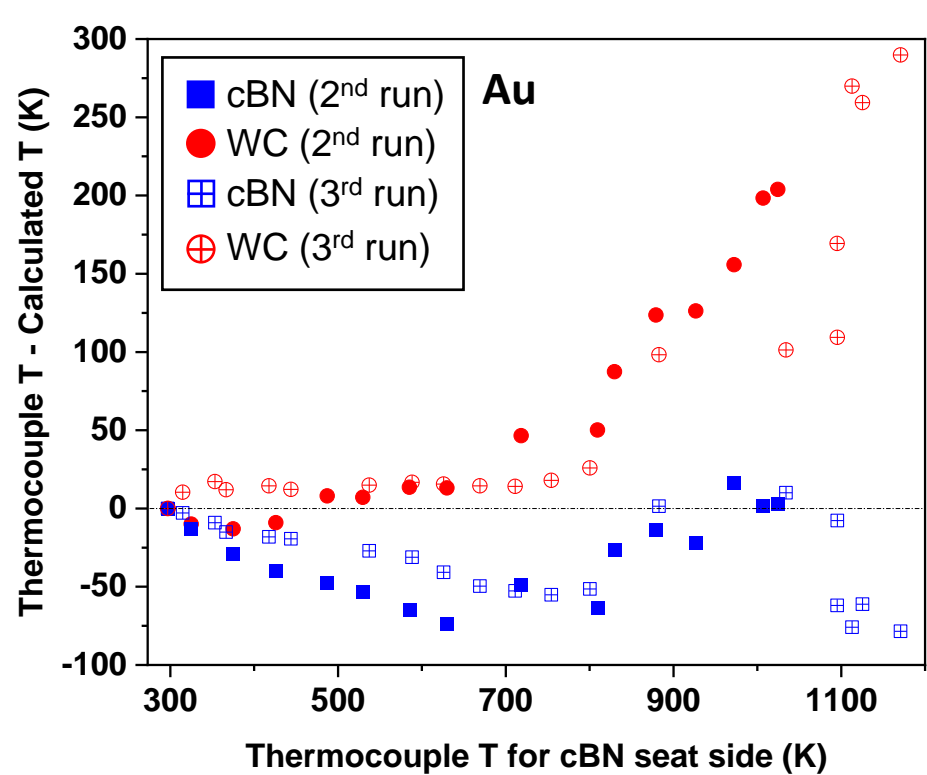
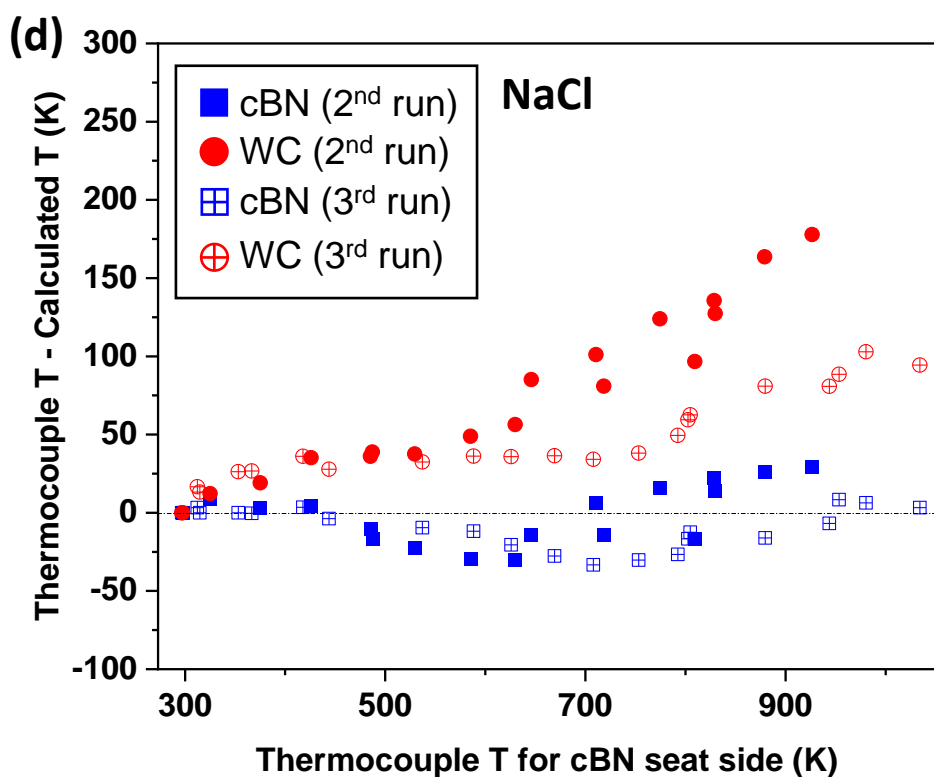
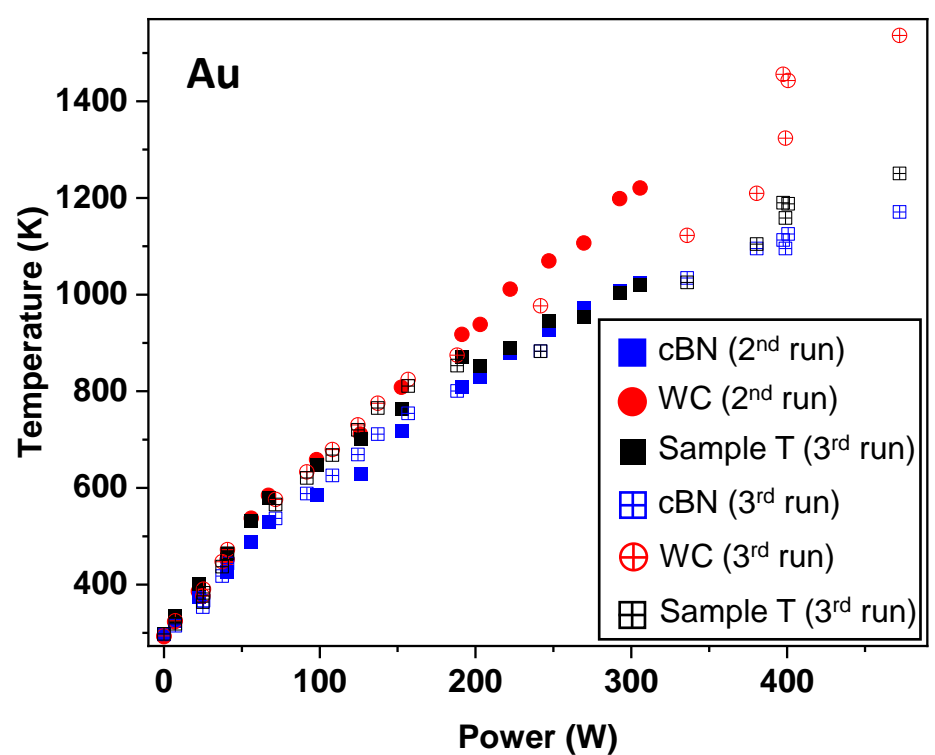
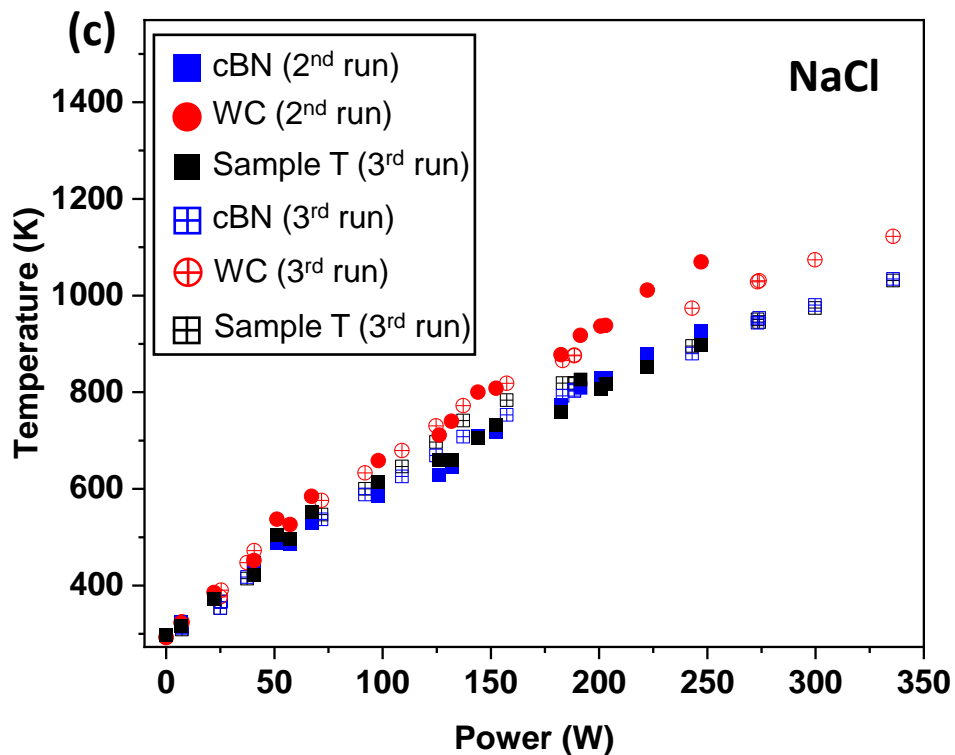
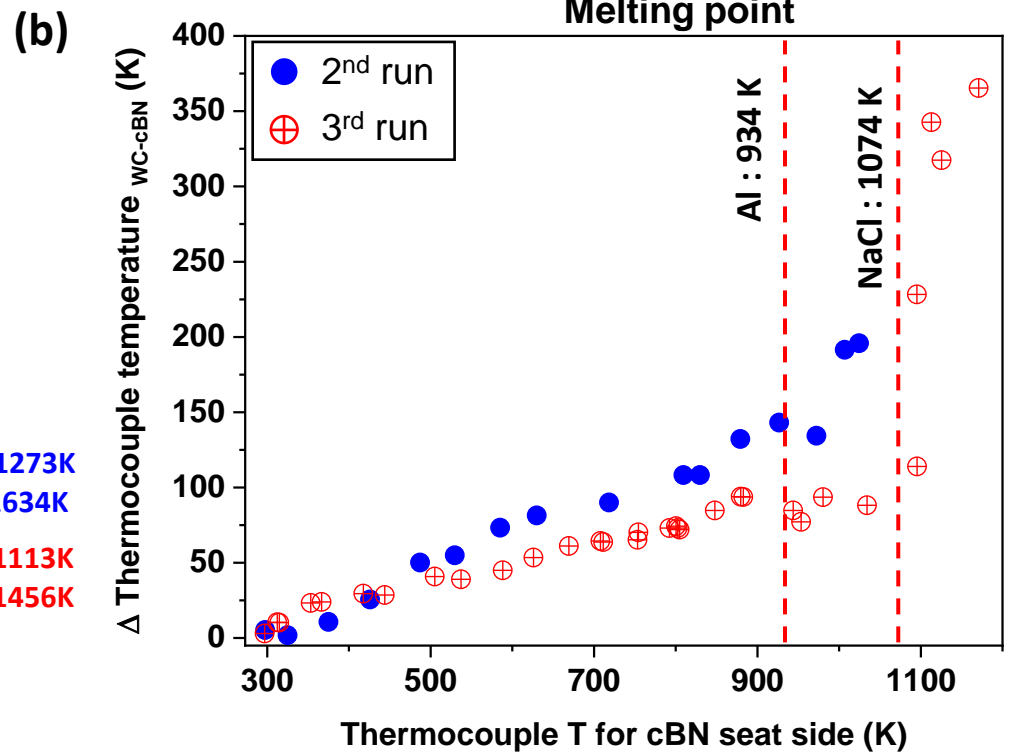
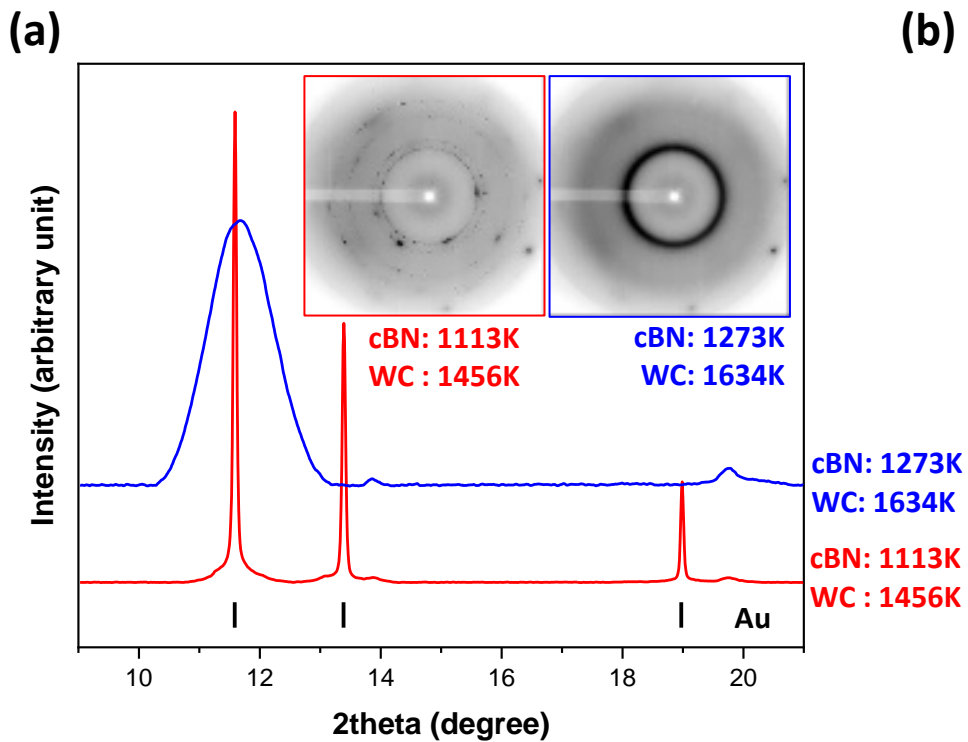


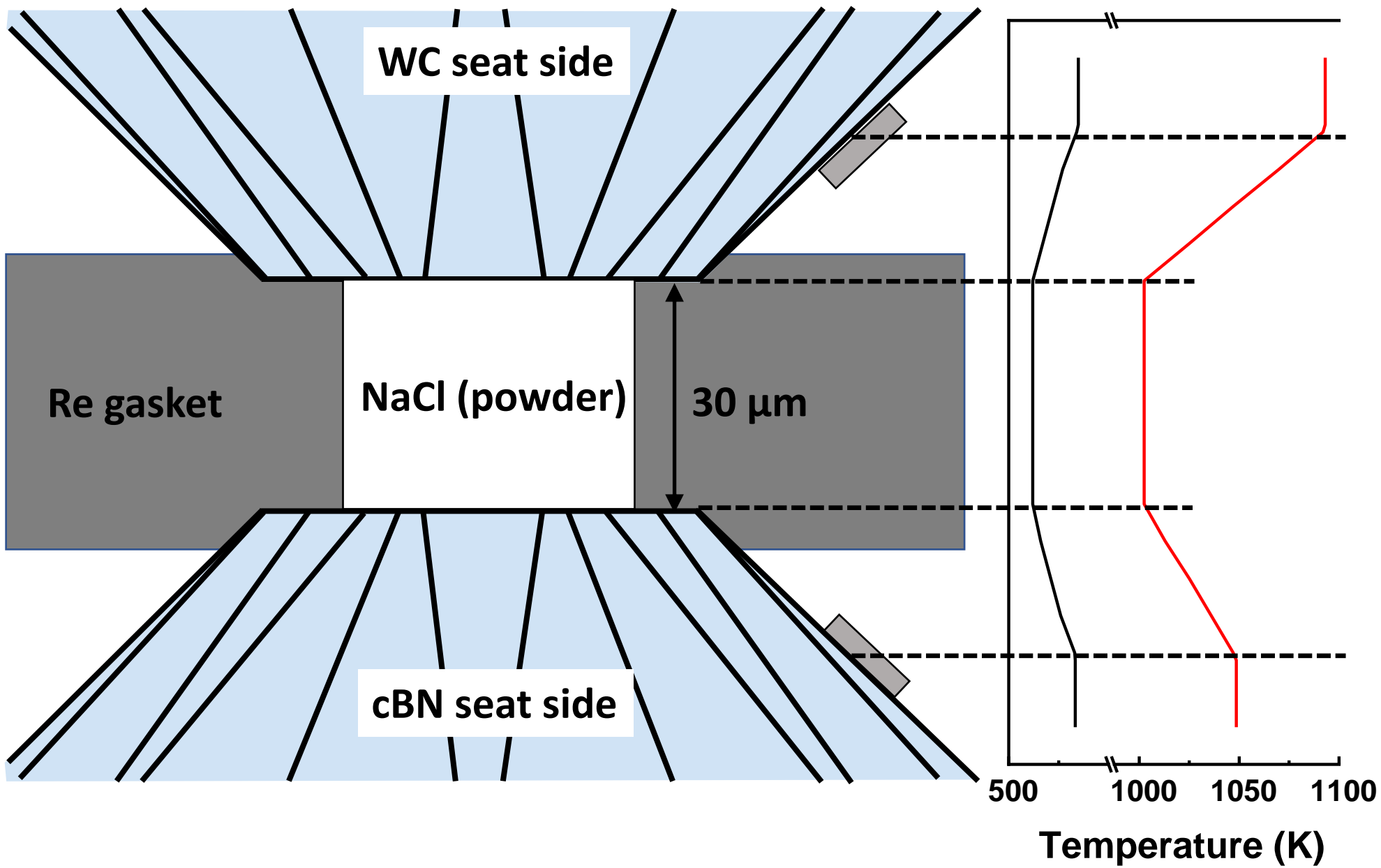
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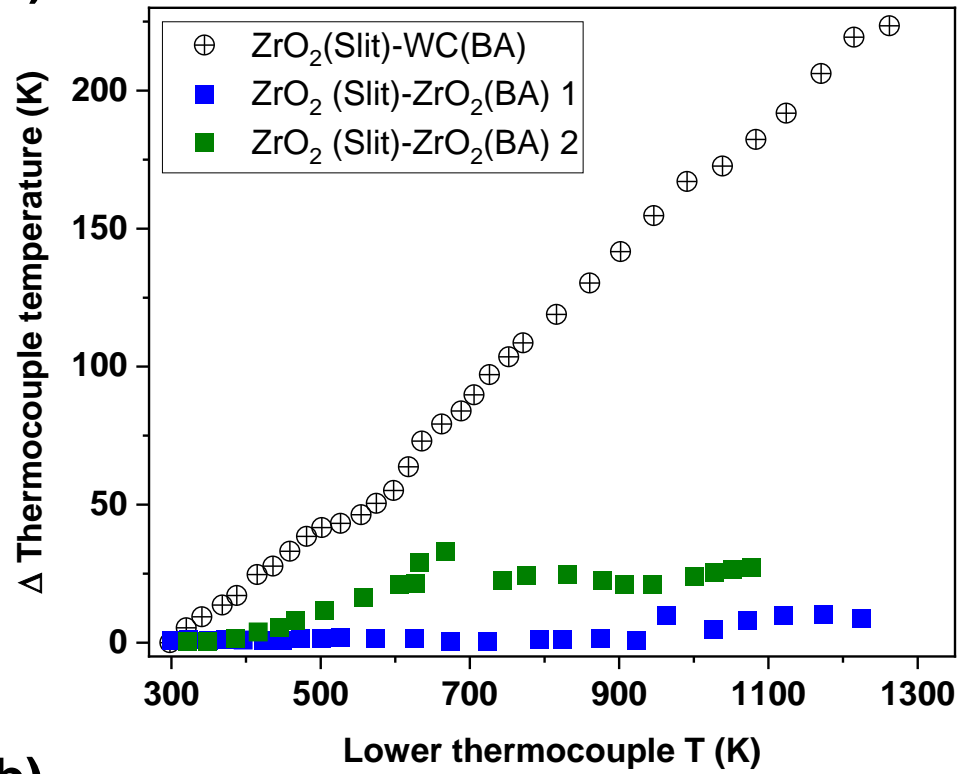




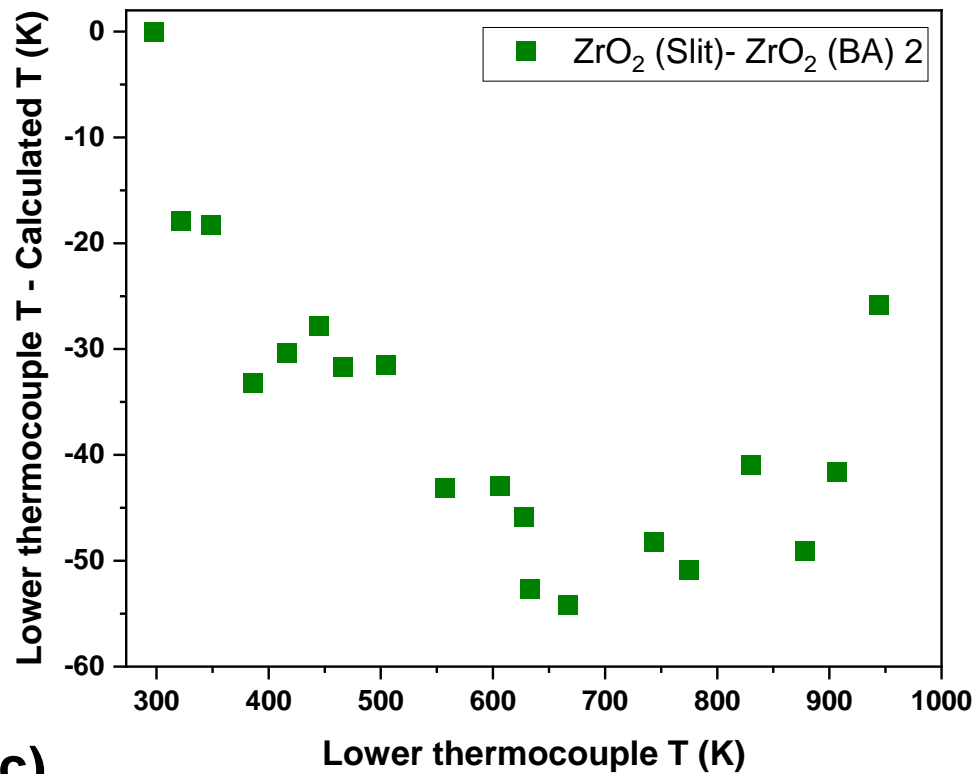




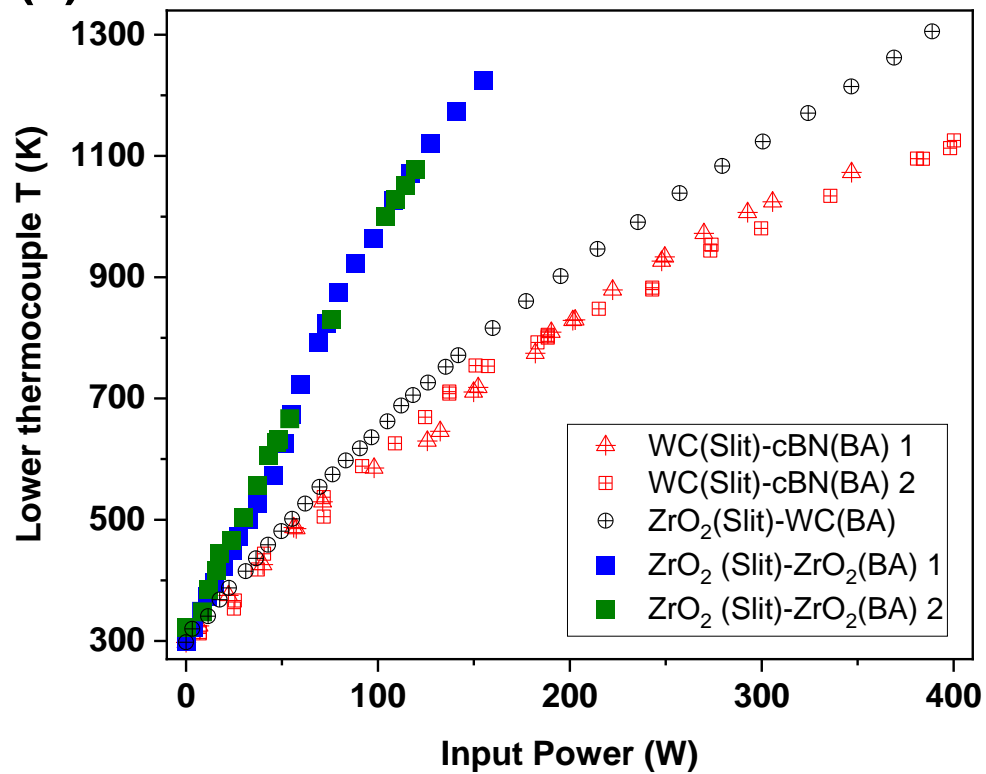
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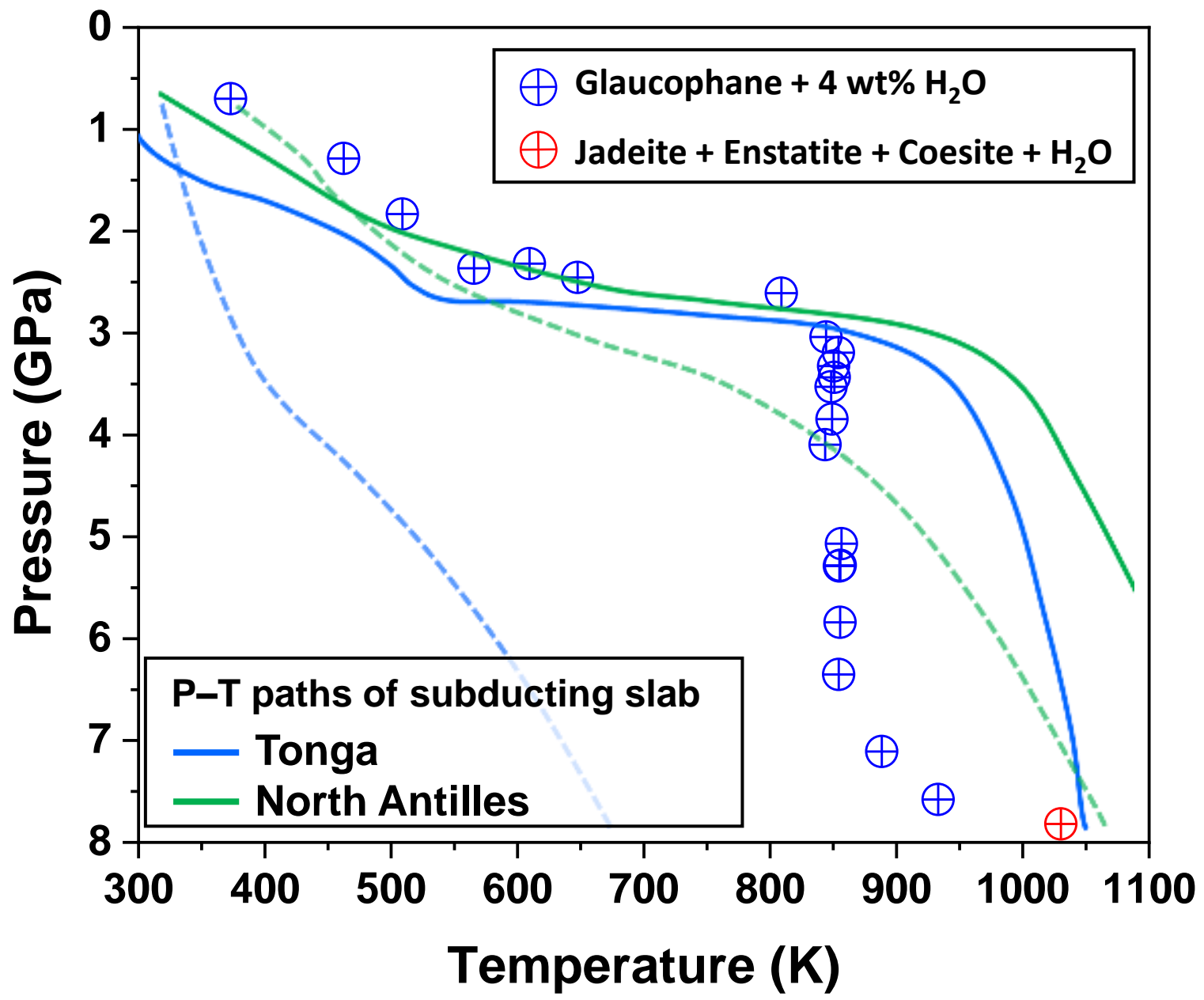


(b)



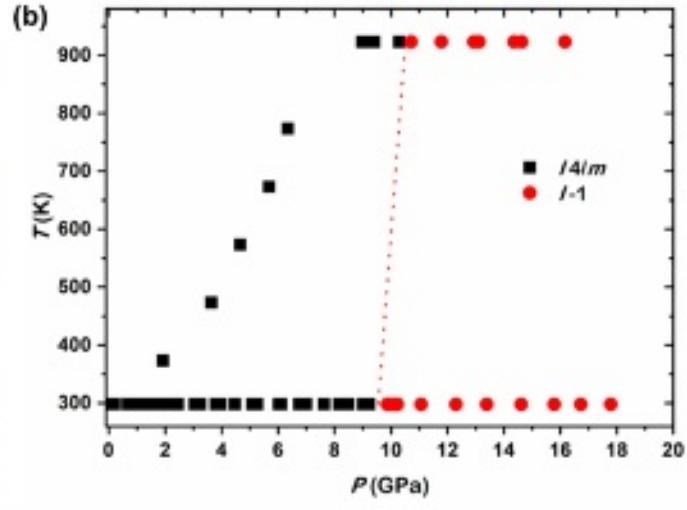
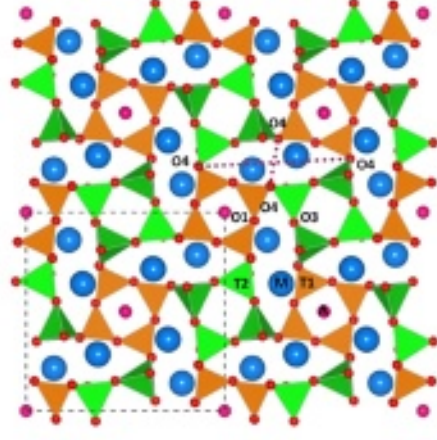
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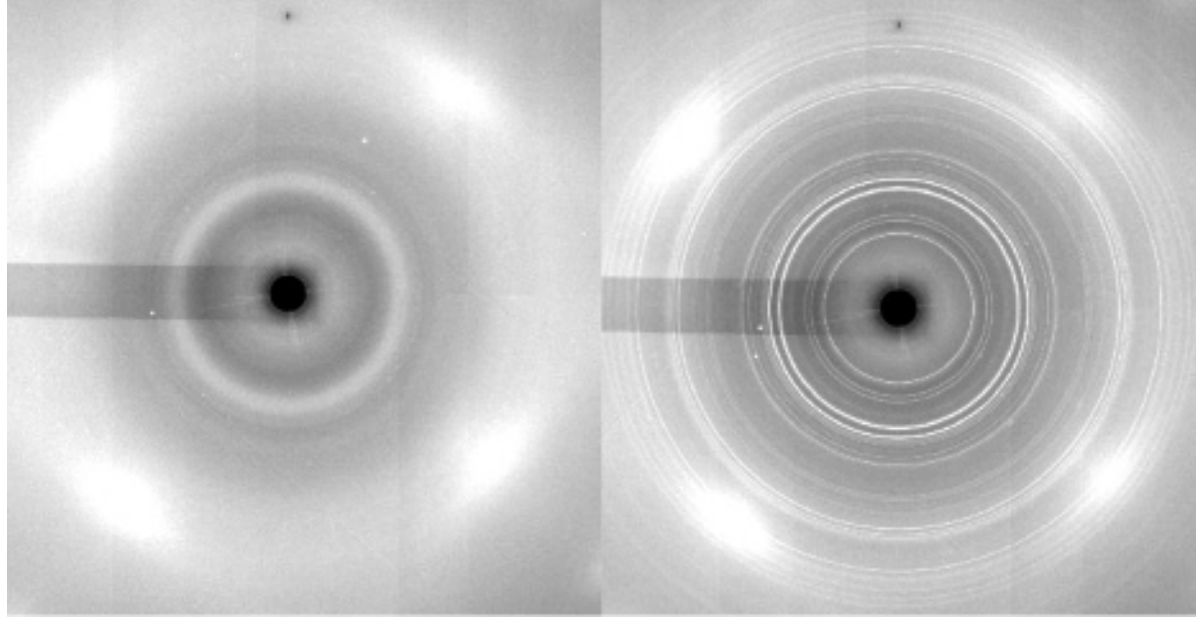




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