Internal Resistive Heating of an Almax-Boehler Diamond Anvil Cell

A Thesis Presented

by

Adairé Tuandé Heady

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Abstract of the Thesis

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A new internal resistively heated diamond anvil cell (DAC) for the investigation of Earth materials at simultaneous high pressure and temperature will be developed on base of the Almax-Boehler type DAC. Combining resistively heated strip heater with the large opening angle design of the Almax-Boehler DAC will be beneficial for *in situ* diffraction and spectroscopy experiments of the structure-property relationships in Earth materials at pressure and temperature conditions of the Earth's interior.

This new design will address some of the technical shortcomings of the laser heated DACs method, such as inhomogeneous temperature distribution and imprecise measurement of the temperature. Previous studies employing the internally resistive heating method have shown that the temperature quality is homogeneous and stable. An internal resistive heater has the potential to generate temperatures in the sample comparable to the laser heating method, thus preventing pressure and temperature restrictions and/or requiring additional equipment to

maintain functionality as with an external resistive heater. The goal in this work was to fabricate a strip heater for the Almax-Boehler type DAC, which is effective with diffraction studies at simultaneous high pressure and temperature. The new technique offers great promise, and future work with greater modifications of this high pressure-temperature device is plausible.

To Otis & Elizabeth Heady
Although you are not physically present,
I know you were here with me every step of the way.

Still I Rise

You may write me down in history
With your bitter, twisted lies,
You may tread me in the very dirt
But still, like dust, I'll rise.

Does my sassiness upset you?
Why are you beset with gloom?
'Cause I walk like I've got oil wells
Pumping in my living room.

Just like moons and like suns,
With the certainty of tides,
Just like hopes springing high,
Still I'll rise.

Did you want to see me broken?
Bowed head and lowered eyes?
Shoulders falling down like teardrops.
Weakened by my soulful cries.

Does my haughtiness offend you?
Don't you take it awful hard
'Cause I laugh like I've got gold mines
Diggin' in my own back yard.

You may shoot me with your words,
You may cut me with your eyes,
You may kill me with your hatefulness,
But still, like air, I'll rise.

Does my sexiness upset you?
Does it come as a surprise
That I dance like I've got diamonds
At the meeting of my thighs?

Out of the huts of history's shame, I rise
Up from a past that's rooted in pain, I rise
I'm a black ocean, leaping and wide,
Welling and swelling I bear in the tide.
Leaving behind nights of terror and fear, I rise
Into a daybreak that's wondrously clear, I rise
Bringing the gifts that my ancestors gave,
I am the dream and the hope of the slave.
I rise, I rise, I rise.

- Maya Angelou

May you all rest in eternal peace.

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Mentee. As an undergrad working for the Director of the Bridge to the Doctorate program, I remember being intrigued by the program and vowing to be a Fellow when I became a grad student. And, I know that it was not luck that brought me this opportunity. I am grateful to have been a graduate student with financial support, which allowed me to focus on my graduate career. And if at any time there seemed to be a problem, Kathryne and Angel came to the rescue. In addition, the social aspect of the CIE program made SBU tolerable. Thank you to the CIE family for making activities that were worthwhile. From individual to group bonding, I have made some lifelong friends, learned about the academic and career paths of those within the top administrative and academic ranks, and found enlightenment from the work of my peers.

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CHAPTER 1. INTRODUCTION

1.1 – Background

Our curiosity to understand the dynamics of the Earth's interior has sustained for centuries (Bass & Parise, 2008). However, due to limited physical access of the Earth, it is difficult to fathom the planet merely miles beneath our feet (Bass & Parise, 2008). The inability to directly observe deep Earth is a major limitation, which incites debate about the Earth. In addition, speculations emerge to explain this vast and diverse mass because of the countless unanswered questions. Nonetheless, some of the fascination with Earth science is discovering the answers to some probing questions so that we are conscious of potential discoveries and/or dangers. With our attempt to understand the formation, progression, and present constitution of the Earth, in addition to characterizing the origins of natural phenomena, we search to comprehend the mineralogical state and chemical composition of the Earth (Tarbuck, Lutgens, & Dennis, 2011).

A comprehensive illustration of the Earth's interior becomes available from various geophysical observations, particularly from mineral physics and seismology (Bass & Parise, 2008; Bass, Sinogeikin, & Li, 2008; Bassett, 1979). Such observations are interpreted through experimental and computational geophysics, whereby laboratory experiments attempt to reconstruct the pressure and temperature conditions that occur within the depths of the Earth, and to study the properties of the Earth materials under these extreme conditions (Bassett, 1979). The field of seismology supplied the initial source of information in regards to the dynamics within the Earth (Li & Liebermann, 2007). The identification of the Earth's internal structure –

crust, mantle, and core – was obtained from seismic studies generated by the velocity variations of compressional and shear waves propagating throughout the layers of the Earth (Winter, 2001). Dziewonski and Anderson established a compilation of global seismic data, including density and velocity profiles of the Earth that provides a standard to the Earth science community referred to as the Preliminary Reference Earth Model, PREM, shown in Figure 1.1.1 (Dziewonski & Anderson, 1981). Additional information is required from this given framework, however in order to interpret the seismological findings, the key is understand the properties of minerals (Bass et al., 2008).

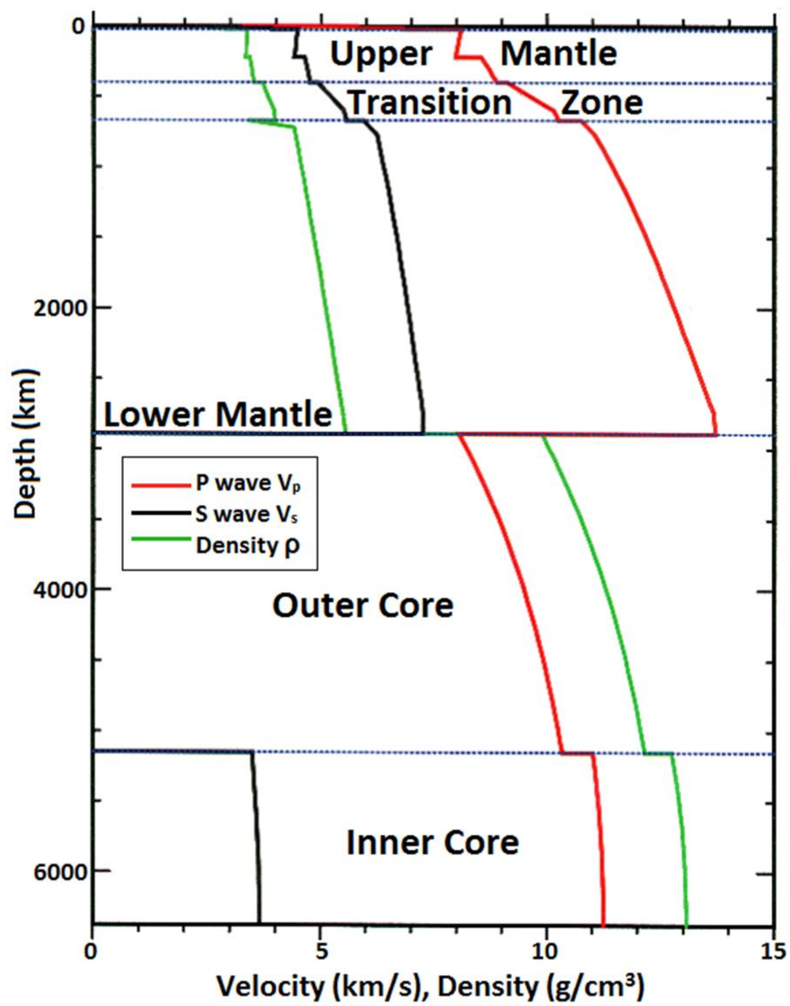

Figure 1.1.1. Dziewonski and Anderson's Preliminary Reference Earth Model, PREM (1981), which illustrates the subdivisions of the Earth separated by the discontinuities of the density and velocities of the P and S waves as a function of depth. (Dziewonski & Anderson, 1981)

For over a half century the motivation behind technological developments in high pressure research has been tailored to investigating the behavior of materials at simultaneous high pressure and temperature conditions; many of these developments involved individuals within the Earth science community because of their dedication to simulate deep Earth conditions in the laboratory (Liebermann, 2011). Today, geoscientists continue to develop various high pressure techniques that allow mineral physicists to measure a material's elastic properties and beyond, under conditions equivalent to that of deep Earth, to compare with geophysical observations (Bass & Parise, 2008; Bass et al., 2008).

The approaches to generate these conditions in the laboratory are dynamic and static compression, which are complementary although very different (Bassett, 1979; Evans et al., 2007). The dynamic approach of high pressure experimentation is the technique by which materials are altered by shock-wave compression, while the static approach implements a vessel to apply fixed pressure by one of two techniques: a multi-anvil apparatus (MAA) or a diamond anvil cell (DAC), see Figure 1.1.2 (Evans et al., 2007; Liebermann, 2011). Prior to the DAC, the dynamic approach was the sole method for investigating the pressure and temperature conditions of the Earth's deep interior (Bass et al., 2008). Shock-wave compression is restricted, however, to one pressure-temperature condition on the Hugoniot for melting and phase changes of a certain material, whereas the DAC offers *in situ* measurements for accurate determination of material properties (Boehler, 2000; Dubrovinsky, Dubrovinskaia, Prakapenka, & Abakumov, 2012a, 2012b). Nonetheless, the essential benefit of the DAC in comparison to dynamic compression is to provide stable constant pressure and temperature conditions for several hours; this time stability allows for a wide variety of analytical techniques (Boehler, 2000). The DAC is a compact and versatile apparatus making notable progress in static high pressure research, and with further development in DAC technology, improvements in anvils and/or design are possible (Bass et al., 2008; Dubrovinsky et al., 2012b).

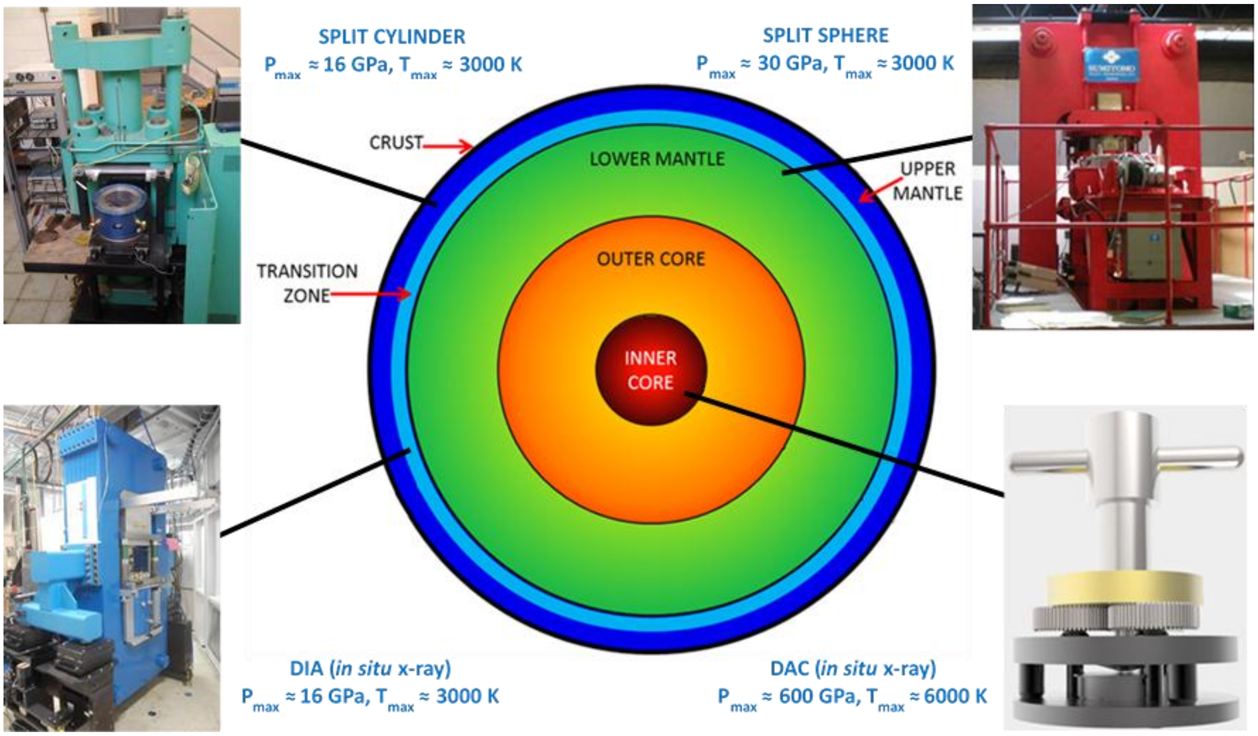

Figure 1.1.2. The following anvil devices are utilized for static compression: (top left) the Kennedy press, (top right) the Sumitomo press, (bottom left) BAM 11, and (bottom right) the Almax-Boehler DAC with gearbox. Each apparatus is capable of simulating pressure and temperature conditions within the given sections of the Earth (black lines).

1.2 – Motivation

Advancing technological developments in DACs have been successful in high temperatures at ultrahigh pressures (Du, Miyagi, Amulele, & Lee, 2013). But, a multitude of issues remain as it relates to high temperature with DACs, regardless of the heating method (Dubrovinskaia & Dubrovinsky, 2003). In particular, the motivation to study material properties at simultaneous pressure-temperature has become a great challenge due to temperature inhomogeneity (Du et al., 2013). Such studies, in conjunction with synchrotron radiation, commonly employ the laser-heated DAC (LHDAC), which imposes the highest temperature range (Zha et al., 2008). However, this technique creates steep temperature gradients, axially and radially, inside the sample (Miyagi et al., 2013). Additionally, temperature instabilities are considerable due to sample properties (Zha & Bassett, 2003). Other contributing factors, e.g., laser functionality, thermal pressure, etc. may exist with laser heating, resulting in unreliable and disputable data (Miyagi et al., 2013; Zha & Bassett, 2003). While some investigators are in search of improvements for laser heating, others are determined to modify the DAC with resistive heating.

This study proposes a new design for simulating realistic conditions in the Earth's interior via a resistive heated DAC. While not as effective as laser heating, internal resistive heating has existed almost as long (Zha & Bassett, 2003). Researchers have shown that an internal resistively heated DAC can be utilized for various types of DACs (Komabayashi, Fei, Meng, & Prakapenka, 2009). As seen in Figure 1.3.1 from the modified graph of Mao & Hemley, resistive heating displays a small pressure and temperature range to that of laser heating, and does not clearly indicate the types of resistive heating (H.-K. Mao & Hemley, 1998). This research will attempt to create a range specifically for internal resistively heated DAC systems by applying an improved "wire heating" technique (Zha & Bassett, 2003). The present work is a modified internal resistive heater derived from the strip heater created by Chang-Sheng Zha, to be developed for an Almax-Boehler DAC (Boehler, 2006; Zha & Bassett, 2003). The main objectives in this study is to expand the pressure and temperature range of internally heated Almax-Boehler DACs through design modifications, assemble the apparatus for synchrotron radiation *in situ* experiments, and make a replicable high P-T device capable of greater modifications.

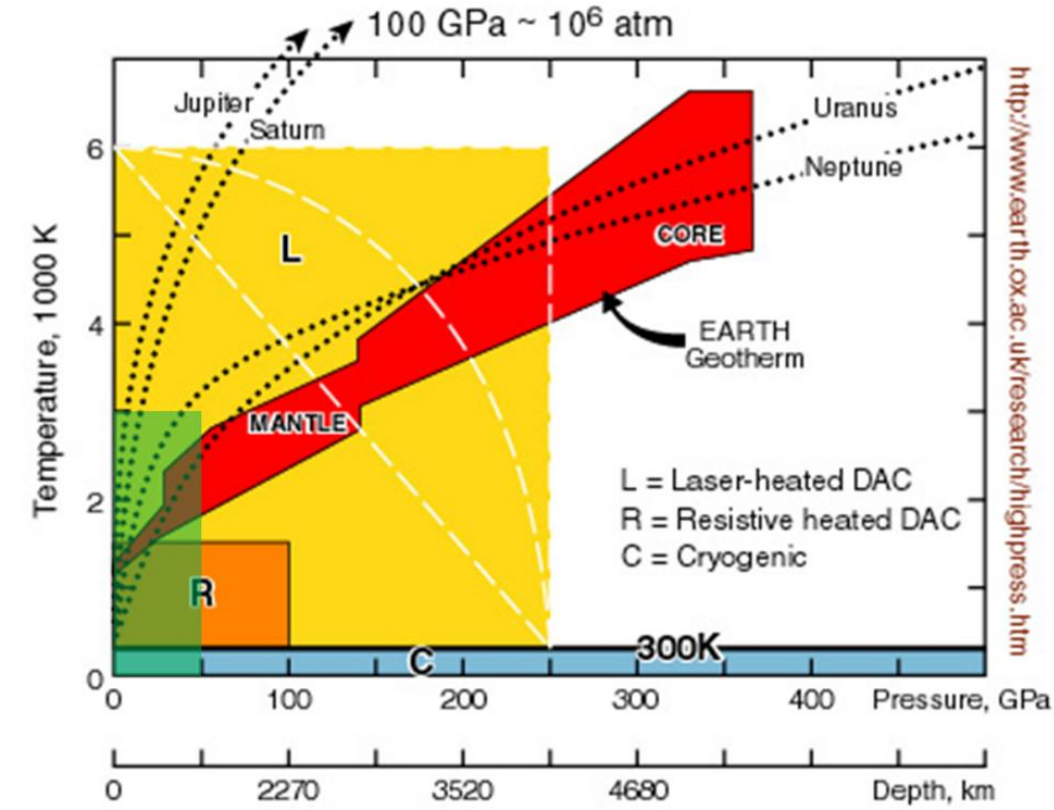

Figure 1.2.1. Temperature and pressure range of certain heating methods of a DAC along with the Earth's geotherm and other planetary bodies. This modified Mao & Hemley graphic includes the initial target pressure and temperature range of the internal resistive heater (green rectangle) for this study. (http://www.earth.ox.ac.uk/research/groups/ultra_high_pressure/introduction)

CHAPTER 2. DIAMOND ANVIL CELL

2.1 – History of the DAC

The 20th century saw remarkable advances in high pressure generation, as a result of the many contributing technological developments and scientific applications. Throughout the early 20th century, the ingenuity of Percy Williams Bridgman highly influenced high pressure science; during his era, he constructed devices such as the anvil-type and piston-cylinder apparatuses (Jayaraman, 1983). In his absence, developments with high pressure devices continued with the likes of Drickamer, Hall, Kawai, and others designing and/or modifying a new generation of apparatuses for particular experimental techniques (Jayaraman, 1986). However, by the mid-20th century, the work of Lawson and Tang of the University of Chicago introduced diamonds to high pressure research, with the fabrication of their split-diamond bomb (Bassett, 2009). In their failed attempt to build a metal cell for x-rays, diamonds were suggested citing, "the great strength of diamond would permit a much smaller pressure device with lower x-ray absorption" (Hazen, 1999). Although the split-diamond bomb took advantage of some of the diamond properties, the assemblage of the machinery restricted the pressure (Hazen, 1999). For several years following, the use of diamonds for high pressure research was abandoned and MAAs advanced progressively (Jayaraman, 1983; Liebermann, 2011).

By the late 1950s, two independent research groups, the University of Chicago and the National Bureau of Standards (NBS), had breakthroughs with their ideal high pressure diamond apparatuses simultaneously (Bassett, 2009). While pursuing different analytical techniques, both groups integrated Bridgman's approach of opposed anvils to design their devices (Hazen, 1999).

The University of Chicago group, now under the supervision of Jamieson and Lawson, engineered their DAC for use with x-ray diffraction (XRD) experiments, and thus x-rays travelled parallel to the flat diamond culets (Jayaraman, 1986). Whereas, Weir and his colleagues at the NBS machined their cell for spectroscopy studies, which required observing the sample, therefore the x-rays would pass normal to the culets (Hazen, 1999). These two significant developments produced notable capabilities, some never-before-seen, including: information on the sample strength and elastic properties, and direct observations of phase boundaries, recrystallization, birefringence, etc. (Bassett, 2009). However, the NBS design garnered the invention of the DAC due to their exploration of diamond's greater potential in high pressure research; although the DAC setup of Jamieson and Lawson ironically was later determined to be invaluable (Bassett, 2009; Hazen, 1999).

During the ensuing years, the DAC evolved tremendously, pioneered at the hands of the NBS high pressure group (Jayaraman, 1983). With improvements to the original DAC design, the NBS group extended DAC use for powder and single-crystal XRD (Barnett, Block, & Piermarini, 1973). In the case of powder or single-crystal materials, the solid sample would be contained within a closure of itself (Barnett et al., 1973). On the other hand, in order to study liquids, an enclosure needed to be implemented, thus initiating the metal gasket technique for hydrostatic pressure generation (Jayaraman, 1983). In addition, new pressure transmitting medium was established to sustain hydrostatic conditions at high pressures; hence, guidelines were implemented for numerous pressure transmitting fluids and direct comparisons of the media proved useful for DAC experiments (Jayaraman, 1986; Marchand, 2009).

With urgency from superiors to improve pressure calibration methods in the DAC, the high pressure group investigated numerous techniques to measure the pressure to no avail

(Piermarini & Block, 2001). In a general discussion among colleagues about this major obstacle, fluorescence spectroscopy was suggested, inspiring the study of pressure dependence of fluorescing materials (Piermarini & Block, 2001). Of the many materials examined, ruby exhibited optimal results, with intense R lines shifting linearly when excited by a laser under pressure (Jayaraman, 1983). Through calibrating the R line shifts of ruby with the Decker equation of state for NaCl, pressures were verified, and later progressed into a very accurate method of pressure measurement (Boehler, 2005; Piermarini, Block, Barnett, & Forman, 1975). This significant advancement of *in situ* pressure measurement, in 1972, together with the DAC invention, "stimulated the profound advances in high pressure research" (Barnett et al., 1973; Piermarini & Block, 2001). Even further, Mao and Bell revisited the ruby fluorescence method and modified the pressure gauge for quasi-hydrostatic and non-hydrostatic conditions, while also extending the pressures (Miletich, Allan, & Kuhs, 2000). Although secondary, this quick and simple technique has since seen many revisions, with a very recent correction to Mao's results, thanks in part to the improvement of lasers (Bassett, 2009; Liu Lei and Bi Yan and Xu, 2013).

The high pressure group at NBS continued to supply new innovations to the DAC, and some such as those mentioned above remain the fundamentals in studying samples under high pressure (Bassett, 1979). Since the initiation of the DAC, it remains to be one of the most common devices used in static high pressure research and the only device to reach pressures corresponding to Earth's core and beyond (Bass et al., 2008; Kantor et al., 2012).

2.2 – Principle

The simplicity and versatility of the DAC has made it an attractive apparatus for many fields of study (Bassett, 2009). The DAC concept can be understood by the pressure formula (eq. 2.1), defined as the force perpendicular to the area, whereby very large pressures can be generated with a moderate force between small culets (Bassett, 1979). Equation 2.2 shows the force required to achieve roughly 100 GPa of pressure with diamond culets of 300 µm diameter, which are used in this study.

$$P = \frac{F}{A} = \frac{mg}{\pi r^2} \quad (2.1)$$

$$100\text{ GPa} \approx \frac{71\text{ N}}{\pi(1.50 \times 10^{-4} m)^2} \quad (2.2)$$

The main components of the DAC are a pair of diamond anvils mounted into metal backing plates, a metal gasket indented to create a pressure chamber, and a force-generating device. The underlying principle of the DAC apparatus is that an alignment mechanism parallels and centers the opposing diamond anvils, and the sample held within the gasket is compressed between the culets by a driving force (Jayaraman, 1986).

2.3 – DAC Variations

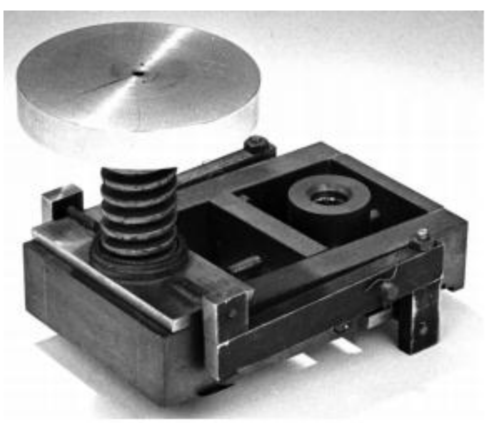

Figure 2.3.1. The original NBS first class lever DAC developed by Charles Weir, Alvin Van Valkenburg, Ellis R. Lippincott, and Elmer N. Bunting. (Bassett, 2009)

Following the creation of the NBS first class lever DAC as seen in Figure 2.3.1, an influx of laboratories engaged in modifications and enhancements of the DAC for certain experimental techniques (Bassett, 1979; Piermarini et al., 1975). The suggested technique among other factors such as size and geometry motivated the variety in DACs (Jayaraman, 1983; Kantor et al., 2012). Another important aspect is the mechanical characteristics of the DAC, namely the force application and the anvil alignment mechanism, which are the components to generate pressure and align the diamond anvils, respectively (Kantor et al., 2012).

The two main driving forces recognized for DACs are a screw type and a gas-membrane type (Kantor et al., 2012). Early DACs being of a screw type, required manual adjustment of a varied amount of screws/bolts and/or a lever-arm mechanism to apply a load to the diamond anvils (Dunstan & Spain, 1989; Kantor et al., 2012). Whereas, the gas-membrane type operates as a hydraulic or pneumatic driving mechanism, with a gas pressure or hydraulic fluid that acts on a membrane to alter the load on the diamonds, thus allowing automatic pressure adjustments (Dunstan & Spain, 1989; Miletich et al., 2000). With continual progress in DAC modifications, some researchers have developed driving forces that intertwine the two main types and other rare types such as oil hydraulic and piezo-driven types (Kantor et al., 2012; Smith Jr & Fang, 2009).

Furthermore, the diamond anvil alignment mechanism is vital to the operational success of the DAC (Kantor et al., 2012). This multifaceted apparatus entails a design and principles to perfectly align the diamonds (Dunstan & Spain, 1989). With the basic diamond anvil design remaining substantially consistent, traditionally, two main designs exist for diamond alignment: a piston-cylinder assembly and a plate-type assembly (Boehler & De Hantsetters, 2004; Kantor et al., 2012). Moreover, alignment principles can be incorporated for multiples types of adjustments to position the diamonds properly; such principles are rotating wedges, stand-off screws, a pair of hemi-cylindrical rockers, a rocking hemisphere, etc. (Dunstan & Spain, 1989; Miletich et al., 2000). Whether simple or complex, each component has its own advantages and disadvantages, therefore it is the needs and creativity of the researcher to find the precise driving force and alignment mechanism suitable for their particular experimental technique/s (Dunstan & Spain, 1989).

Many variations of DACs resulted from the numerous driving force and alignment mechanism combinations (Jayaraman, 1983). Table 1 from Smith provides a non-exhaustive list of some of the different types of DACs (Smith Jr & Fang, 2009). There are an array of DACs, which cover numerous analytical methods (Pippinger, Miletich, & Burchard, 2011). Although DAC technology has progressed immensely, many of the modern DACs are influenced by the originating models: the Bassett cell, the Merrill-Bassett cell, the NBS cells, the Syassen-Holzapfel cell, and the Mao-Bells cells (Bassett, 1979; Smith Jr & Fang, 2009).

Table 2.1. Diamond anvil cell types and their mechanical properties

Diamond anvil cell (DAC) Types	Force Application	Method	Translation	Rotation	Size
Bassett-Takahashi-Stook (Bassett) (1967)	Threaded gland piston	3 Screw	Upper plate	Lower hemisphere	Compact
Merrill-Bassett (1974)	Three-screw platen	3 Screw	Pre-aligned	Pre-aligned	Small
Piermarini-Block (1975)	Belleville spring washer lever arm	1 Screw	Upper plate	Lower hemisphere	Small
Syassen-Holzapfel (1977)	Thread-and-knee	1 Screw	Lower plate	Upper rocker	Large
Mao-Bell (1978)	Belleville spring washer lever arm	1 Screw	Upper WC rocke	Lower WC rocker	Large
Mao-Bell (1980)	Two-pairs of left/right hand bolts	2 Screw	Translation	None	Large
Letoullec-Pinceaux-Loubeyre (1988)	Membrane press	Membrane	Upper WC rocke	Lower WC rocker	Large
Dunstan (1988)	Single press, single anvil	3 Screw	None needed	None needed	Compact
Bassett-Shen-Bucknum-Chou (1993)	Belleville spring washer platen	3 Screw	Upper plate	Lower hemisphere	Large
Allan-Miletich-Angel (1996)	Four-screw platen	4 Screw	Lower plate	Upper hemisphere	Compact
Silvera (1999)	Single press, double anvil	Any	None needed	None needed	Large
Balzaretti (1999): internal heating	Modified Piermarini-block	1 Screw	Upper plate	Lower hemisphere	Compact
Zha-Bassett (2003): internal heating	Modified Bassett	3 Screw	Upper plate	Lower hemisphere	Large
Dubrovinskaia-Dubrovinsky (2003)	Modified Merrill-Bassett	3 Screw	Pre-aligned	Pre-aligned	Small
Burchard-Zaitev-Maresch (2003)	Hollow-screw structure	1 Screw	Upper seat	Lower hemisphere	Large
Evans (2007): dynamic pressure	Most screw type DACs	Piezoelectric actuators	n/a	n/a	Compact
Shinoda-Noguchi (2008): induction heating	Modified Merrill-Bassett	3 Screw	Upper WC rocke	Lower WC rocker	Small

(Smith Jr & Fang, 2009)

2.4 – Diamonds

"For the better part of a century scientists relied on the earth to learn how diamonds were made. Today, they rely on diamonds to learn how the earth was made" (Hazen, 1999). Diamonds have long been revered for their beauty as a gemstone, and, with great investigation into their material properties, have become quite beneficial for industrial and scientific applications (Klein, Dutrow, & Dana, 2008). Being a limited commodity in nature and an important resource in technology due to its exemplary properties, researchers have made breakthroughs in the synthetic diamond making process (Irifune & Hemley, 2012; Irifune, Kurio, Sakamoto, Inoue, & Sumiya, 2003). In academia, the current methods of synthesizing diamonds are high pressure high temperature (HPHT) and chemical vapor deposition (CVD), which are being enhanced through the geoscience community; making breakthroughs are the Geophysical Laboratory at Carnegie Institute of Washington, who grow single-crystal diamonds through microwave plasma CVD, while the Geodynamics Research Center at Ehime University conduct HPHT syntheses in MAAs to form nanopolycrystalline diamond (NPD) (Irifune & Hemley, 2012). Both forms of diamond have been implemented in DAC experiments, with developments into the next generation of high pressure apparatuses (Irifune & Hemley, 2012).

2.4.1 – Properties. The value of diamonds in high pressure research is strongly due to a variety of properties. As the hardest known material, diamond is the best anvil material (Miletich et al., 2000). Additionally, it has a low atomic number, therefore a very low absorption (Bassett, 2009). Furthermore, its strength gives the DAC the ability to attain and sustain high pressure (Boehler, 2000). Other properties such as its high chemical inertness increase the effectiveness of studying materials under high pressure and temperature conditions (Boehler, 2005). Diamond is acknowledged as the best thermal conductor, therefore accurate temperature measurements can be obtained with a thermocouple attachment (Bassett, 2009). The combination of good thermal conductivity and high electrical resistivity makes diamond suitable in resistive heating applications (Adams, Christy, & Norman, 1993). Finally, the transparency of diamond allows the direct visibility of the sample, diamond alignment, thereby preventing the destruction of the anvils, and visual observation to various analytical techniques, via a wide range of the electromagnetic spectrum, as shown in Figure 2.4.1 (Bassett, 2009).

2.4.2 – Limitations. Contrary to popular belief, diamond is in fact not forever. Under extreme pressure and temperature conditions, the functionality of a diamond can fail due to oxidation and/or graphitization (Miletich et al., 2000). Because of its high thermal conductivity, diamond can interfere with the heat absorption in the sample (Boehler, 2000). To rectify diamond failure, the implementation of a vacuum is a preventative measure (Miletich et al., 2000). It is inevitable that the diamonds will conduct heat away from the sample chamber, therefore a thermal insulation barrier has to be applied (Miletich et al., 2000).

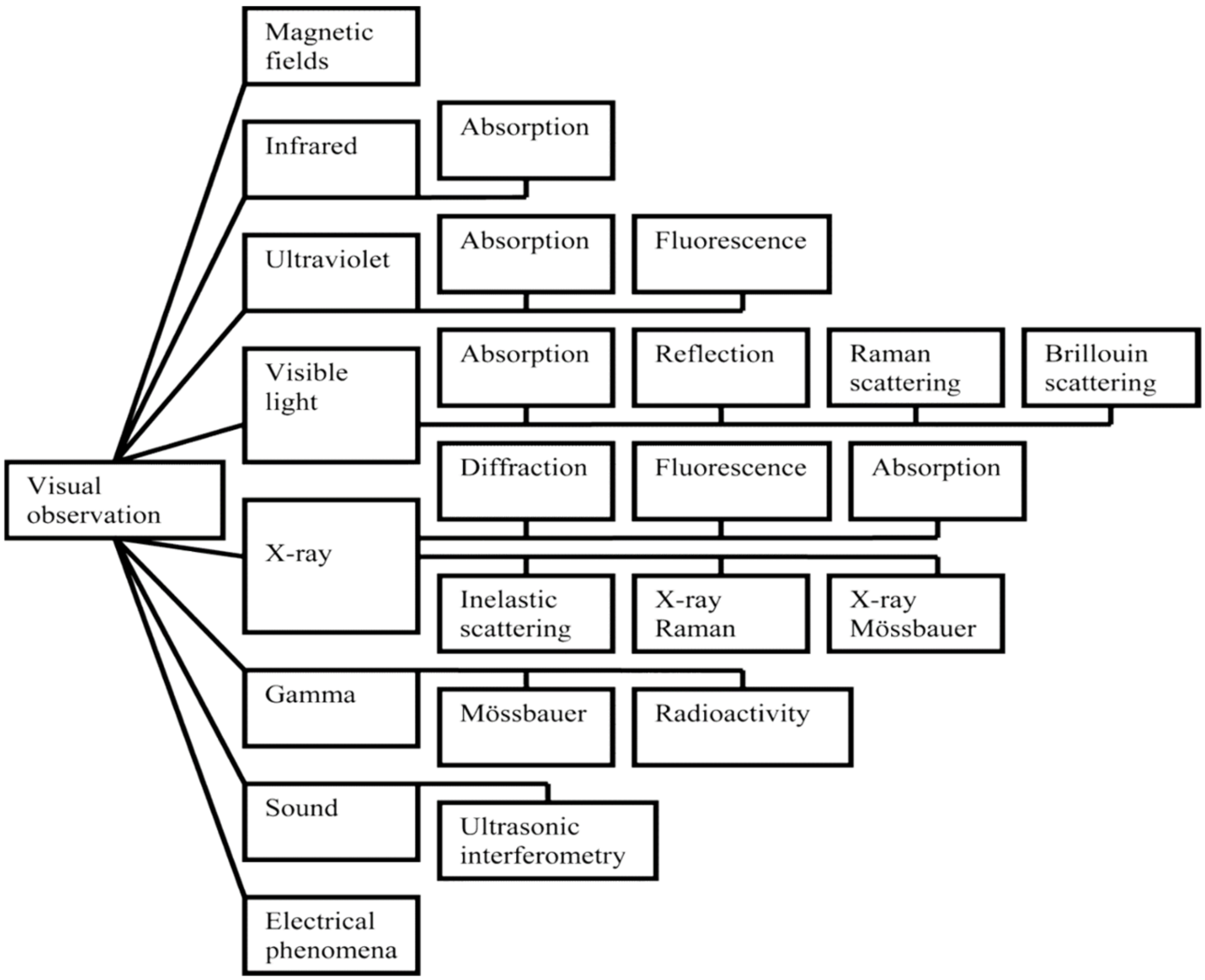

Figure 2.4.1. The analytical techniques associated with DAC experiments, due to the transparency of the diamond anvils, which allows many forms of radiation. (Bassett, 2009)

2.5 – Gaskets

A metal gasket was the vital source to hydrostatic pressure generation in a DAC, which has become a standard tool (Jayaraman, 1986; Miletich et al., 2000). The metal gasket, when compressed by the diamond anvils, extrudes between the diamonds creating an encapsulated chamber, thereby serving as a support for the diamonds and a chamber for the sample and/or pressure medium (Bassett, 2009; Miletich et al., 2000). The gasket is prepared from a metal foil, some of which are rhenium, tungsten, stainless steel, and their alloys, which is pre-indented between the anvils to the required thickness, followed by a hole drilled in the center of the indentation (Jayaraman, 1983).

When performing the indentation and drilling of the gasket, certain considerations need to be taken into account for the high pressure experiments (Miletich et al., 2000). The thickness, within the indented area of the gasket, has to be thin enough to prevent gasket deformation (Bassett, 2009). Also, the gasket hole has to be much smaller than the culet size of the anvil to keep the entire sample from leaking out of the chamber (Dunstan & Spain, 1989).

2.6 – Heating Methods

High temperatures in the DAC are applied through two main heating techniques, laser and resistive heating (Fan et al., 2010). The presence of temperature was one of the earliest additions to the DAC, made possible through the high pressure group at NBS and affiliated colleagues (Bassett, 2009). Through resistive heating, a sample can be heated externally or internally, while laser heating is solely internal (Jayaraman, 1983). In the following sections, a brief overview will be discussed about the given heating methods.

2.6.1 – Laser Heated DAC. Laser heating is the most commonly used technique for simultaneous high pressure and high temperature in a DAC in conjunction with synchrotron radiation (Zha et al., 2008). As seen in Figure 1.2.1, laser heating has a wide pressure-temperature field, with conditions exceeding the Earth's core (pressures greater than 360 GPa and temperatures above 6500 K) (Bassett & Brown, 1990). Temperature is measured with optical pyrometry rather than a thermocouple because the sample is well insulated from the anvils (Miletich et al., 2000; Zha & Bassett, 2003). In this simple laser heating assembly, sample preparation is quite simple, and diamond and mechanical failure due to temperature are void in the DAC, therefore pressure and temperature limitations do not exist (Dubrovinskaia & Dubrovinsky, 2003; Zha & Bassett, 2003).

While laser heating has the largest pressure and temperature range, this heating system creates very large temperature gradients in the radial and axial directions due to a small heating zone, which makes accurate characterization of the temperature distribution a challenge (Du et al., 2013; H.-K. Mao & Hemley, 1996; Shen, Mao, & Hemley, 1996). Sample thickness affects the heating efficiency, so thin samples are essential for uniformed heating; but with many samples, laser absorbing materials are added to supply an adequate absorption, which results in a thin sample reduced in value and increased in background noise (Shen et al., 1996; Zha & Bassett, 2003). Also, heating instabilities are initiated by the heterogeneous mixture of the sample and absorber (Andrault & Fiquet, 2001). Other laser heating problems exist due to the functionality of the laser, which also result in non-homogeneous temperatures and heat loss (Fukui et al., 2013; Komabayashi et al., 2009).

Significant advances have been ongoing to minimize temperature gradients in LHDACs (Bassett, 2009). Such improvements include double-sided lasers, multimode lasers, flat-top laser power distributions, and bean shaping optics (Du et al., 2013; Miyagi et al., 2013). With double-sided lasers, thicker samples are heated, with uniform temperature distribution (Shen et al., 1996). Most modern lasers achieve high stability in power and beam position to prevent minor variations, which can cause severe heating instabilities in a matter of seconds (Boehler, 2005; Boehler, 2006; Miletich et al., 2000). The small heating spot remains an inconvenience for some important geological applications, which leaves some invaluable information absent (Boehler, 2006; Du et al., 2013).

2.6.2 – Resistive Heating. Resistive heating covers a lower temperature range of approximately 300 K to over 3000 K (Fan et al., 2010). Similar to MAAs, resistive heating in a DAC creates a homogeneous temperatures in the pressure chamber (Du et al., 2013). Temperature measurement is convenient with the use of thermocouples (Fan et al., 2010). Resistive heating maintains temperature stability for several hours (Zha & Bassett, 2003).

2.6.2.1 – External Resistive Heating. External resistive heating was once standard practice in DAC heating (Jayaraman, 1986). With external heating, the stresses observed in laser heating are practically nonexistent (Dubrovinskaia & Dubrovinsky, 2003). More complex than laser heating, this heating method can have multiple assemblages, with the heater surrounding the DAC, the diamond supports, or the diamonds and gasket (Zha & Bassett, 2003). However, external heating has pressure and temperature limitations as a result of extreme heat exposure, thus creating functionality issues with the DAC: oxidation and graphitization of diamonds, softening and welding of the gaskets, distortion of DAC body, etc. (Dubrovinskaia & Dubrovinsky, 2003; Zha & Bassett, 2003). The latter affects the DAC sustaining constant pressure, and the thermal expansion of the different parts can lead to substantial pressure variations (Dubrovinskaia & Dubrovinsky, 2003). Consequently, supplementary equipment will be inserted into the system to avoid mechanical damage (Pasternak et al., 2008).

2.6.2.2 – Internal Resistively Heated DAC. An alternative internal heating method is "wire heating" in an internal resistively heated DAC developed by Liu and Bassett (Liu & Bassett, 1975; Zha & Bassett, 2003). This technique simply passes current through a metal wire in the sample chamber (H. K. Mao, Bell, & Hadidiacos, 1987). Similar to laser heating, the objective is to only heat the sample, while the DAC body remains at lower temperatures (Zha & Bassett, 2003). However, the "wire heating" temperature distribution within the heating zone is more constant, more uniform, and much larger than a LHDAC (Zha & Bassett, 2003). The temperatures achieved from an internal resistive heated DAC are greater than those from external resistive heating, while avoiding most of the pressure and temperature limitations (Komabayashi et al., 2009; Zha & Bassett, 2003). In addition, the internal resistively heated DAC provides exceptional time stability for investigating materials with *in situ* experiments (Zha & Bassett, 2003).

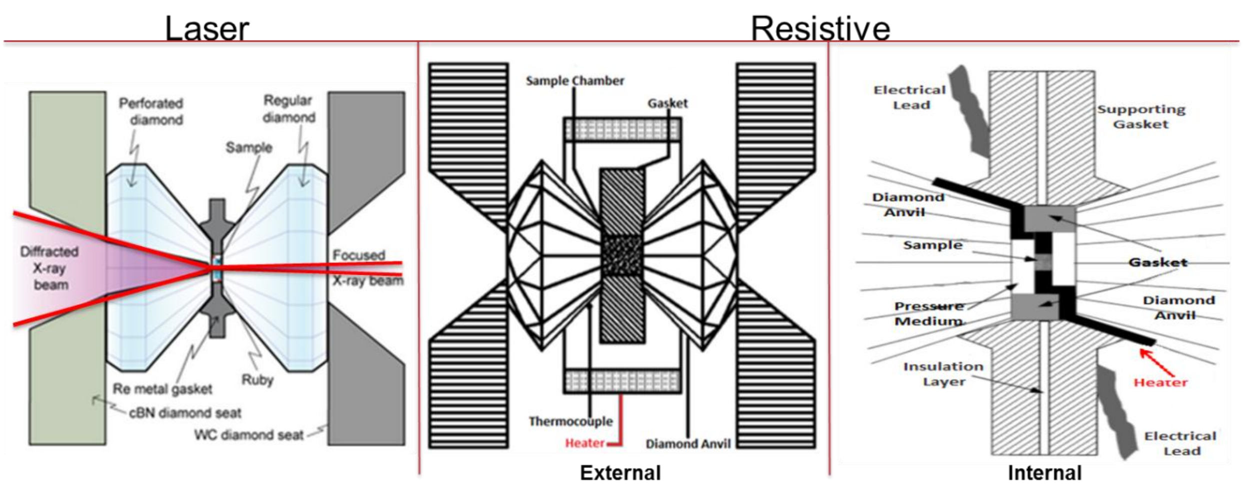

Figure 2.6.2. The two main heating methods for a DAC, laser and resistive. (From left to right) Laser heating is solely internal, while resistive can either be external or internal. The red indicates the heater for each method. (http://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/diamond_anvil.html#Intro) (Fan et al., 2010; Zha & Bassett, 2003)

CHAPTER 3. PROPOSED DESIGN

From previous experiments, we have found that an internal resistively heated DAC can provide temperatures in the range of a LHDAC, without most of the undesirable effects, and internal heating through "wire heating" can apply homogeneous temperature profiles like external heating. Our concept is that an internal heating system can be accommodated to the body of the Almax-Boehler cell, and the work of Zha offers a great starting point. The following section will give a description of the design we envisioned.

3.1 – Heater Design

The heater design in this system was based on the "wire heating" design of Zha (Zha & Bassett, 2003). Figure 3.1.1(a) shows a cross-section of the heating setup, in which a zig zag style wire heater is positioned such that the hot zone containing the sample is insulated by the pressure medium and diamond-MgO gasket, all of which is housed between diamond anvils and stainless steel support gaskets (Zha & Bassett, 2003). The intent of his work was to develop an internal resistive heating method, which supplied a homogeneous temperature profile and maintained time stability for the investigation of materials via *in situ* x-ray diffraction and Raman spectroscopy (Zha & Bassett, 2003).

In his heater-sample assemblage, a well-insulated sample chamber was formed, with a hot zone area of 200×80 μm reaching temperatures of 2800 K, while the diamond seat measured 470 K (Zha & Bassett, 2003). By the method of electrical resistance, which is inversely proportional to the cross-sectional area, Zha designed the rhenium heater so that the hot zone had the highest resistance (smallest cross-sectional area), and the larger ends of the heater had a lower resistance (Zha & Bassett, 2003). In addition, the ends of the heater were in contact with the support gaskets and diamonds, therefore the remaining body of the DAC was kept at a low temperature (Zha & Bassett, 2003). He used a direct current power supply to achieve stable and homogeneous temperature on the sample (Zha & Bassett, 2003). After cycling his heater-sample assemblage, he found a linear relationship offers insight to the internal heating system, which will be discussed later in Section 3.1.3 (Zha & Bassett, 2003). Pressures up to 10 GPa were achieved. Zha reported that the heater needed to be smaller, with a hot zone area less than 40 × 80 μm to achieve pressures greater than 50 GPa (Zha & Bassett, 2003). Through the course of experimentation, he amended some of the heating assembly and materials, to optimize pressure and temperature in the sample chamber, see Figure 3.1.1(b) (Zha et al., 2008). With these changes, he extended the pressure and temperature range to approximately 80 GPa and 2000 K, respectively (Zha et al., 2008).

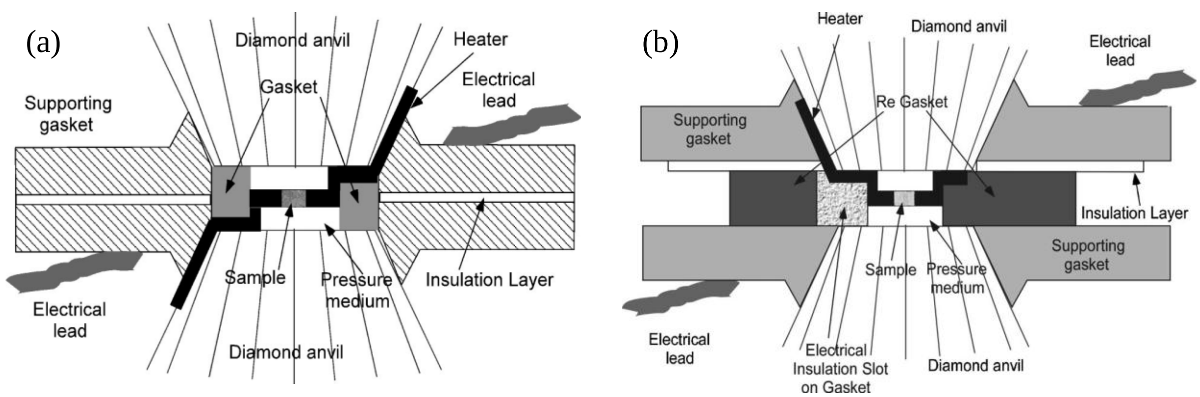

Figure 3.1.1. Diagram of Zha's internal resistive heating assembly. (a) A zig zag style strip heater, (b) The heater is simplified, gasket material modified, and an additional electrical insulation added. (Zha & Bassett, 2003; Zha et al., 2008)

3.1.1 – Dumb-bell Style Heater. With the heating assemblages of Zha acknowledged, we modeled our internal heater system similarly. We opted to use the dumb-bell style heater idea, which suits the resistance method. Rather than use a zig zag pattern, the thin strip of metal was kept flat. Our heater employs a stacking method of a dumb-bell style heater sandwiched between insulating gaskets, and supported by gaskets.

3.1.2 – Design Materials. While many heating devices are developed for Mao-Bell and/or Merrill-Bassett types of DACs, we chose to use the Almax-Boehler DAC, which is void of guide pins and/or other sliding parts (Boehler, 2006). Our dumb-bell strip heater will be made of molybdenum, a metal which has some of the characteristics of rhenium and has been modeled as a heater (Bassett, Shen, Bucknum, & Chou, 1993). Although commonly seen in a MAA setup, boron epoxy, which can be used as a compressing medium between anvils, can operate as a gasket for DACs (Liermann et al., 2009). Stainless steel will be the supporting gasket; it remained functionally sound during the Zha experiments (Zha & Bassett, 2003; Zha et al., 2008).

3.1.2.1 – Almax-Boehler DAC. The diamond anvil cell used in this heating system is the Almax-Boehler DAC (Boehler, 2006). It is a plate-type assembly with two steel plates elastically deformed by a screw-type force application, consisting of three outer (alignment) screws, three inner (set) screws, and three (fine-thread) middle screws, see Figure 3.1.2 (Boehler, 2006). Each set of screws is crucial to the pressure and/or alignment of the DAC. The latter is necessary to achieve high pressures without damaging the diamond anvils. Our Almax-Boehler DAC is equipped with 300 µm culets to generate high pressure, and has special conical seats to allow for up to 90° optical aperture along the windows of the anvil, thus offering large-angle x-ray diffraction (Boehler, 2006). Pressures are applied manually with a gearbox.

3.1.2.2 – Molybdenum Heater. Molybdenum is a transition metal with one of the higher melting points (~2896 K) of all elements. This metal has served as an external heater for low temperature DAC studies (Bassett et al., 1993). More recently, molybdenum wire was used as an external heater for a TAU-type cell, with temperatures tested to 1573 K in an inert atmosphere

(Ar+2% H_2) (Dubrovinskaia & Dubrovinsky, 2003). In Zha's internal heating system, the electrical leads to the power supply were welded to the stainless steel gaskets (Zha & Bassett, 2003; Zha et al., 2008). Whereas, in our heating system, the leads are directly connected to the dumb-bells of the heater.

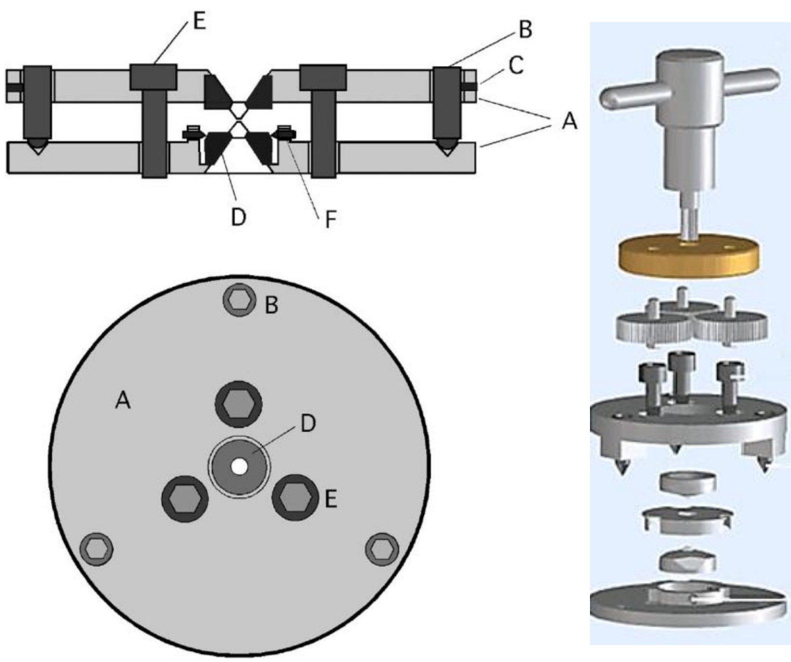

Figure 3.1.2 (top left) Cross-section of the Almax-Boehler DAC (A) steel plates, (B) outer screws, (C) set screws, (D) tungsten carbide supports, (E) middle screws, (F) inner screws. (bottom left) Aerial view of DAC. (right) Exploded view of DAC components with gearbox. (Boehler, 2006)

3.1.2.3 – Boron Epoxy Gaskets. A boron and epoxy mixture was grounded and molded into gaskets of variable thickness. Most often, these gaskets are used for radial diffraction experiments (Liermann et al., 2009). Boron epoxy gaskets have been utilized up to pressures of 50 GPa (Merkel & Yagi, 2005). Boron epoxy gaskets are a non-conducting and non-metallic material, which is also transparent to x-ray (Merkel & Yagi, 2005).

3.1.2.4 – Stainless Steel Gaskets. Since the advent of the gasket, stainless steel has been a standard, inexpensive gasket material (Chapman et al., 2010; Miletich et al., 2000). The gaskets were simply formed by a punch and die cutting various thicknesses ranging from 0.025 mm to 0.25 mm. Because it does not demonstrate pressure-induced deformation of the gasket below 10

GPa, stainless steel gaskets are capable of larger gasket holes and thicker pre-indentation (Chapman et al., 2010). It has exceptional properties, which make it suitable for DAC experiments (Jayaraman, 1986). Stainless steel gaskets usually have internal friction greater than the radial forces in the pressure chamber (Boehler, 2000). However, tests show that stainless steel does not prove to be apt for high pressure and temperature experiments (Dubrovinskaia & Dubrovinsky, 2003).

3.1.3 – Design Methods.

3.1.3.1 – DAC Preparation. While there are several steps to prepare the DAC, each one is crucial to the success of a high pressure experiment. Much of the work is performed under a microscope to ensure each process is accurate, and in case it is not corrections can be made accordingly. We began with a thorough cleaning of the DAC parts and soaking the diamonds in acetone to remove any dirt or debris, and checked for any residual dirt or damage. The diamonds were fixed onto the tungsten carbide supports with a high temperature epoxy compound. These diamond anvil seat units are then secured into the steel backing plates; the upper seat is press fitted into the plate, while the bottom seat is fixed with three set screws, which also performs to laterally align the diamond anvil unit.

In addition to the lateral alignment, the diamond culet faces have to be paralleled, to avoid the destruction of the diamonds during experimentation. Parallelism of the diamonds occurred when the each of the three adjustment screws were altered, followed by the diamonds carefully being brought into contact with each other to observe the interference colors and fringes. Contact between the diamonds are a result of the three fine-thread screws being turned simultaneously with a gearbox, which seemed to be a daunting task because it required strength and caution to turn the gearbox to make sure the diamonds touched gently. This process was carried out until the diamonds were perfectly aligned, which is known when there is a solid gray color instead of colors and fringes.

3.1.3.2 – Heater Fabrication. With a framework of our heater for the Almax-Boehler DAC, we began cutting out dumb-bell shaped heaters from 100 × 100 mm stainless steel foil with a thickness of 0.25 mm. The goal was to physically cut the smallest width to 1 mm and the ends a width of 5 mm. However, achieving these widths became difficult because the strips of wire were shaped using shears and a paper cutter, which created some limitations and caused the thin wire to curve. The length of the heater would eventually need to be defined, so we considered lengths less than the diameter of the DAC, which is approximately 49 mm, but due to our methods of cutting the length was longer. However, we continued with the use of the strips, while considering other shapes that would be electrically sound with the tools that we could access.

Although, we did not finalize the dimensions of heater, we seek to establish a style of heater with dimensions suitable for molybdenum. The assumed heater would follow the proportions outlined by Zha in Table 3.1, which would be achieved by laser cutting. Our original thickness for molybdenum was the same thickness as the stainless steel employed. However, with a limited gap between the diamonds, the heater would need to be thinner to make room for the gasket.

3.1.3.3 – Boron Epoxy Synthesis. In consideration of a gasket, we wanted a material non-metallic and capable of performing as an insulator. Our supporting gasket was stainless steel, therefore we did not want to experience issues resulting from metal on metal contact. In addition, a well-insulated gasket would keep the diamonds from conducting away the heat produced, while also protecting the diamonds from extreme temperatures in the sample chamber.

We chose a boron epoxy, which can be easily made and molded into a gasket. A mixture of boron, epoxy part A, and epoxy part B with a ratio 2:0.2:0.02 in grams was mixed and finely ground in acetone for nearly 30 minutes. Before being pressed and molded, the boron epoxy dried in air for an hour to evaporate the acetone. The material was placed in a jig and gaskets were prepared in thicknesses ranging from 0.1 to 1mm. We found that gaskets less than 0.5 mm crumbled upon removal from the jig. The remaining gaskets were cured in a vacuum oven at approximately °C for 30 minutes. Gaskets less than 1mm were brittle and cracked to the touch. Such a large gasket thickness created uncertainty for the setup, and because of its brittleness the execution of drilling a hole would be a challenge.

Table 3.1. Diamond anvil cell and internal heating system comparisons

Internal Heating System		Zha (2003)	Zha (2008)	This work	Comments
DAC Type		Bassett	Bassett	Almax-Boehler	The Almax-Boehler DAC is void of guide pins and other sliding parts. In addition, the position of the diamond anvils sitting in the backing plates, make it desirable for large-angle x-ray diffraction due to its optical aperture of up to 90°.
Heater Style		Zig zag	Simplified zig zag	Straight dumb-bell	The dumb-bell style follows the principle of resistance according to the dimensions. Thus, the center hole would have the highest resistance in all styles, but the ends of the heater are different with the dumb-bell.
Heater Material		Rhenium ribbon	Rhenium ribbon	Molybdenum	Molybdenum is a transition metal similar to rhenium. Although molybdenum (2896 K) has a lower melting point than rhenium (3459 K), it is less expensive.
Heater Dimensions	Heating Area	200 x 80 μm	-	< 40 x 80 μm	Zha suggested a heating area of less than 40 x 80 μm to achieve pressures greater than 50 GPa.
	Thickness	20 μm	12 μm	12 μm	According to the power vs. temperature graph, the smaller heater reaches the same temperatures as the large heater, but with less power. Therefore, dimensions less than Zha (2003) will be more attractive as a smaller heater.
	Width	80 μm	-	< 80 μm	
	Cross-section	20 x 80 μm	-	-	
	Central Hole	25 μm	20 μm	20 μm	
Supporting Gasket		Stainless steel	Stainless steel	Stainless steel	Stainless steel is a standard gasket, suitable for DAC experiments.
Insulation Layer		Mica	-	Boron-Epoxy (Insulating gasket)	Boron-epoxy is non-conducting and non-metallic material, which can be simply produced and fabricated into a gasket. It has the ability acts as an insulating material and gasket.
Gasket		Diamond-MgO powder	Rhenium		
Pressure Medium		SiO_2 glass	SiO_2 glass	NaCl	
Pressure Standard		Au	MgO/Pt	Any	The pressure standards used for x-ray diffraction are Pt, Au, MgO, NaCl, KCl, or C, while ruby can be applied for spectroscopy.

3.2– Power vs. Temperature Curve

The work of Mao showed the linear relationship between temperature and electrical power (H. K. Mao et al., 1987). However, the graph by Zha was very insightful, in that it shows a direct proportional relationship of heater size to power (Zha & Bassett, 2003). In Figure 3.1.3, both heaters show the characteristic linear relationship, however the slopes are different (Zha & Bassett, 2003). The small heater, indicated by the squares, uses much less power to achieve the same temperatures as the large heater (circles) (Zha & Bassett, 2003).

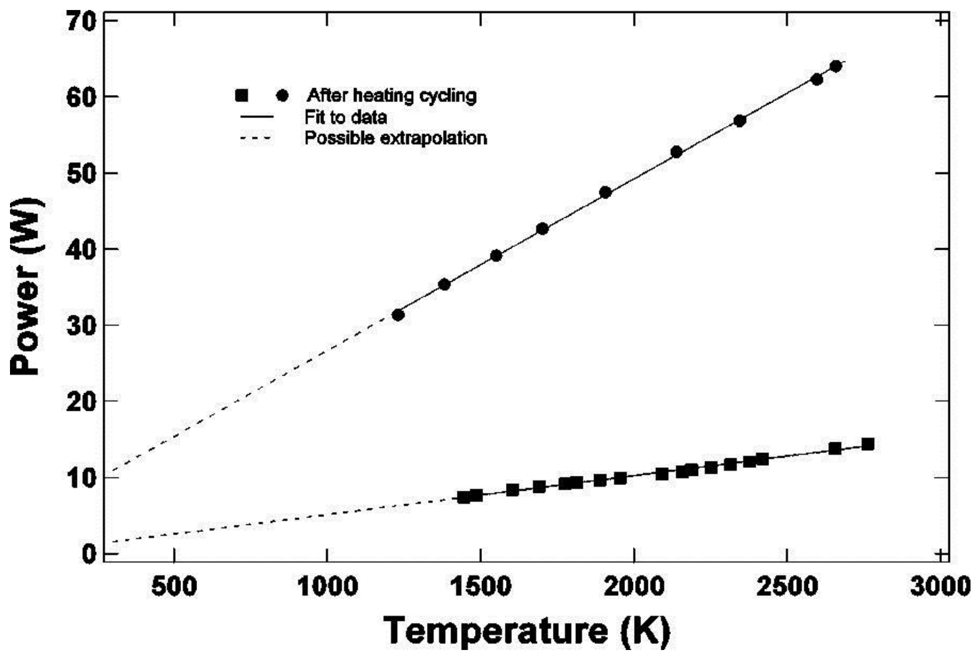

Figure 3.1.3 A graph of the linear relationship of power and temperature. The small heater (squares) requires less power to achieve the same temperature as the large heater (circles). (Zha & Bassett, 2003)

In physics, power is recognized as the product of current and voltage (eq. 3.1). By deriving the equation, we can find the relationship of resistance in electric power.

$$P = I \cdot V = I(I \cdot R) = I^2 \cdot R = \frac{V^2}{R} \cdots\cdots\cdots\cdots\cdots\cdots \text{(3.1)}$$

If we use this equation to calculate for current, knowing the constant voltage control mode (2 mV) given from the experiments and extrapolating the power for a given temperature for both heaters, it can be said that the ratio of large heater current to small heater current is 6:1 for the same temperature; and the amount of current drawn depends on the resistance, therefore the more current the less resistance and vice versa (Zha & Bassett, 2003).

In Section 3.1, the need for a small heater was discussed to achieve greater pressures. The temperature vs. power curve further proved that a small heater is required for less power, thus less current. Power also has a correlation to heat; its units are watts, which is joules per second, where joules is the heat.

$$Watts = \frac{Joules}{second} \rightarrow Joules \ = Watts \ \times second \quad \cdots\cdots (3.2)$$

From (3.2), it can be inferred that with the small heater will have less heat over time than the large heater. The large heater would require an inert atmosphere to avoid functionality issues within the DAC, due extreme heat exposure as we discussed earlier (Zha & Bassett, 2003). When operating electrical power, there is the danger of electrical hazards, so by minimizing the power, it can provide safer work conditions.

3.3 – Resistivity of Molybdenum Heater

According to the electrical resistance method, the resistance of the heater will be the highest at the smallest cross-sectional area, thereby distinguishing the "hot zone" (Zha & Bassett, 2003). In order to quantify the resistance, R, of a wire, we use Pouillet's law, which can be expressed as

$$\mathrm{R} \ = \rho \frac{L}{A} \quad \cdots\cdots (3.3)$$

Therefore, the law can be applied to this work, where in our case, $\rho = 5.34 \times 10^{-8}$ Ωm the resistivity coefficient of molybdenum at standard temperature, L is the length of the heater, and A is the cross-sectional area of the heater. (Eq. 3.3) can be re-written as

$$\mathrm{R} = 5.34 \times 10^{-8}\Omega\mathrm{m} \cdot \frac{8.13 \times 10^{-4}\mathrm{m}}{A}$$

$$\mathrm{R} = \frac{43.41 \times 10^{-12}\Omega\mathrm{m}^2}{A} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \text{(3.3a)}$$

However, our goal is simultaneous high pressure and temperature conditions, thus the resistance can change with temperature. Such values of resistance of must be determined by another formula.

$$\mathrm{R} = \mathrm{R_0}[1 + \alpha(\mathrm{T} - \mathrm{T_0})] \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \text{(3.4)}$$

For molybdenum's temperature coefficient, $\alpha = 4.579 \times 10^{-3}$ /°C at the standard temperature of 20°C (293 K), the equation can be written as

$$\mathrm{R} = \mathrm{R_0}[1 + 4.579 \times 10^{-3}/°\mathrm{C} \cdot (\mathrm{T} - 20°\mathrm{C})]$$

$$= \mathrm{R_0}[1 + 4.579 \times 10^{-3}/°\mathrm{C} \cdot (727°\mathrm{C} - 20°\mathrm{C})]$$

$$= \mathrm{R_0}[1 + 4.579 \times 10^{-3}/°\mathrm{C} \cdot (707°\mathrm{C})]$$

$$= \mathrm{R_0}[1 + 4.579 \times 10^{-3}]$$

$$= \mathrm{R_0}[1 + 3.237]$$

$$\mathrm{R} = \mathrm{R_0}[4.237] \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \text{(3.4a)}$$

From (eq. 3.4a), it can be seen that the resistance of molybdenum rises by over a factor of four as temperature increases from 20°C (293 K) to 727°C (1000 K).

Evidence of the resistance method is found with the above equations for our heater at both ambient temperature (top) and 1000 K (bottom). If we use the dimensions suggested by Zha, Figure 3.3.1 shows us that moderately low resistivity are achieved at low temperature, even across the smallest cross-sectional area, while the heater at 1000 K displays a wide range of resistivity, with the largest cross-sectional area having low resistivity and the smallest cross-sectional area a much higher resistivity.

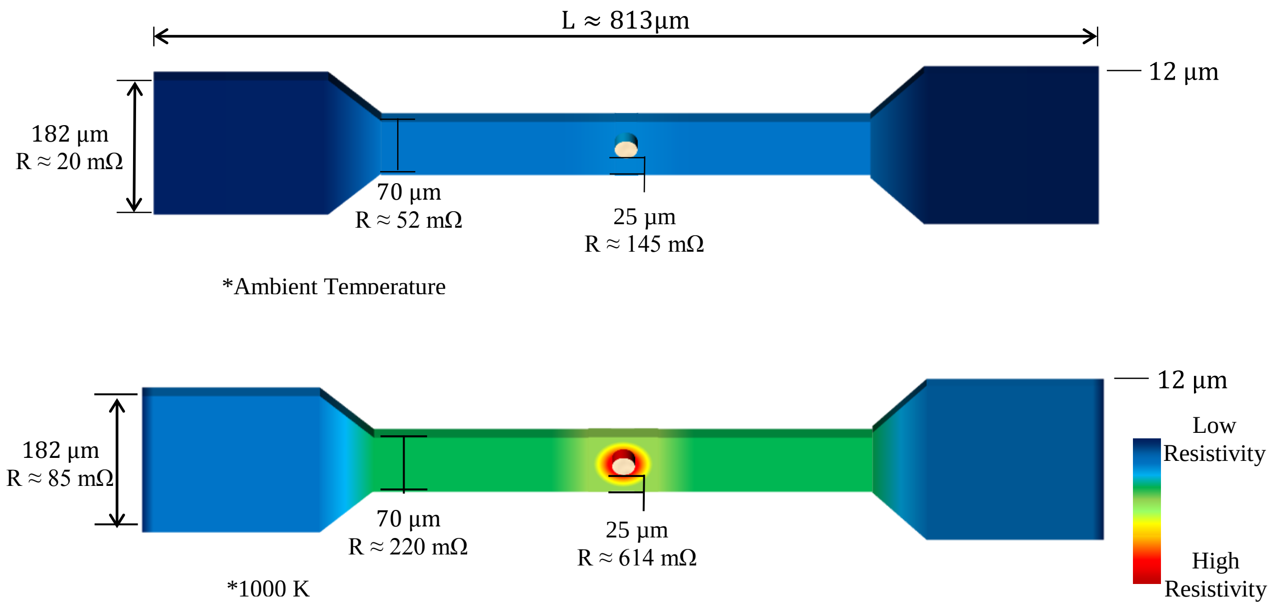

Figure 3.3.1. The schematic shows the ideal dumb-bell style heater with dimensions suggested by Zha used for resistance calculations. The top heater at ambient temperature shows moderately low resistivity, while the bottom heater at 1000 K shows a variety of resistivity.

3.4 – Heater Gasket Unit

The internal heating system of the dumb-bell style heater was to be in a stacking method. The boron epoxy creates the first layer of sandwiched material around the heater, followed by the stainless steel gasket. Figure 3.2.1 shows a schematic of the internal heating setup. However, this setup was very delicate, from the thin heater to the fragile boron epoxy. Applying pressure to close the DAC, would ruin the internal heating system. In previous experiments, boron epoxy was confined by a kapton ring to avoid deformation (Merkel & Yagi, 2005). The boron gasket, due to its brittle nature, crumbles to the touch, therefore another material is required or it needs to be confined. The smallest cross-section of the heater, after being drilled with a hole, was as small as a piece of filament on both sides. It definitely had the highest resistance, but any pressure to that area would snap the heater. The internal heating setup was mechanically and electrically flawed, however other styles of heater have been suggested that seem plausible.

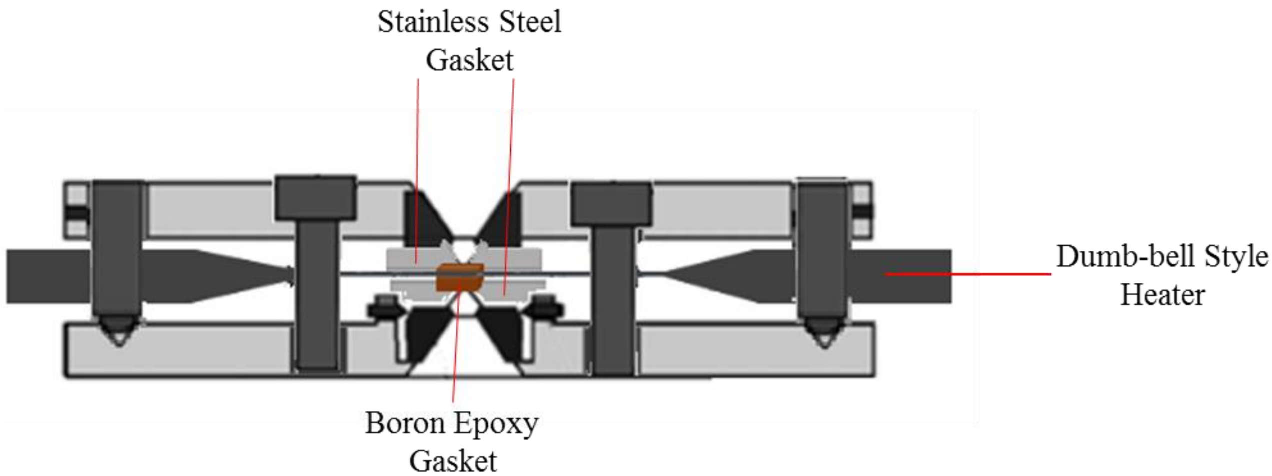

Figure 3.2.1 Schematic of the Almax-Boehler cell with the newly designed internal resistive heating system. (Boehler, 2006)

CHAPTER 4. SUMMARY AND OUTLOOK

The concept outlined in this thesis promotes further experimental study of an internal resistive heating system for an Almax-Boehler DAC. Different heating setups have acknowledged the breakthroughs and issues for this heating method. However, the intricate details of the heating assembly for each device has to be tailored to the design materials and sample, which makes this method difficult to implement and use. Prior to performing high pressure experiments, researchers found undesirable parts of the heating assembly, which in turn produced adverse effects. Therefore, in brainstorming the crucial components of the heating system, e.g., the pressure medium, gasket, heater, insulator, and sample, multiple options for the materials and assembly have to be thoroughly investigated for the successful execution of the internal heating system and experiments.

The new "strip heater" was proposed in order to take advantage of the large angle aperture of 90° of the Almax-Boehler DAC, which is the DAC of choice for our studies and it complements the experimental setups at our synchrotron facilities; employ molybdenum, a metal known for its high melting point, and has been used in a prior study, therefore some knowledge has already been incited; and improve upon previous internal heating designs by Zha, although for a different DAC. Our hope is that this proposed design can be rectified and assembled, with progression towards a new internal resistively heated DAC for simultaneous high pressure and temperature conditions, in conjunction with synchrotron radiation, which will overlap the laser heated DAC and shock wave methods. With this current proposal, the next phase is to finish the heating assembly and execute test heating runs.

REFERENCES

Adams, D. M., Christy, A. G., & Norman, A. J. (1993). Optimization of diamond anvil cell performance by finite element analysis. *Measurement Science and Technology, 4*(3), 422.

Andrault, D., & Fiquet, G. (2001). Synchrotron radiation and laser heating in a diamond anvil cell. *Review of Scientific Instruments, 72*(2), 1283-1288.

Barnett, J. D., Block, S., & Piermarini, G. J. (1973). An Optical Fluorescence System for Quantitative Pressure Measurement in the Diamond-Anvil Cell. *Review of Scientific Instruments, 44*(1), 1-9.

Bass, J. D., & Parise, J. B. (2008). Deep Earth and Recent Developments in Mineral Physics. *Elements, 4*(3), 157-163.

Bass, J. D., Sinogeikin, S. V., & Li, B. (2008). Elastic Properties of Minerals: A Key for Understanding the Composition and Temperature of Earth's Interior. *Elements, 4*(3), 165-170.

Bassett, W. A. (1979). The Diamond Cell and the Nature of the Earth's Mantle. *Annual Review of Earth and Planetary Sciences, 7*, 357-384.

Bassett, W. A. (2009). Diamond anvil cell, 50th birthday. *High Pressure Research, 29*(2), 163-186.

Bassett, W. A., & Brown, J., G. E. (1990). Synchrotron Radiation: Applications in the Earth Sciences. *Annual Review of Earth and Planetary Sciences, 18*, 387-447.

Bassett, W. A., Shen, A. H., Bucknum, M., & Chou, I. M. (1993). A new diamond anvil cell for hydrothermal studies to 2.5 GPa and from −190 to 1200 °C. *Review of Scientific Instruments, 64*(8), 2340-2345.

Boehler, R. (2000). High-pressure experiments and the phase diagram of lower mantle and core materials. *Reviews of Geophysics, 38*(2), 221-245.

Boehler, R. (2005). Diamond cells and new materials. *Materials Today, 8*(11), 34-42.

Boehler, R. (2006). New diamond cell for single-crystal x-ray diffraction. *Review of Scientific Instruments, 77*(11), 115103.

Boehler, R., & De Hantsetters, K. (2004). New anvil designs in diamond-cells. *High Pressure Research, 24*(3), 391-396.

Chapman, K. W., Chupas, P. J., Halder, G. J., Hriljac, J. A., Kurtz, C., Greve, B. K., Wilkinson, A. P. (2010). Optimizing high-pressure pair distribution function measurements in diamond anvil cells. *Journal of Applied Crystallography, 43*(2), 297-307.

Du, Z., Miyagi, L., Amulele, G., & Lee, K. K. M. (2013). Efficient graphite ring heater suitable for diamond-anvil cells to 1300 K. *Review of Scientific Instruments, 84*(2), 024502.

Dubrovinskaia, N., & Dubrovinsky, L. (2003). Whole-cell heater for the diamond anvil cell. *Review of Scientific Instruments, 74*(7), 3433-3437.

Dubrovinsky, L., Dubrovinskaia, N., Prakapenka, V. B., & Abakumov, A. M. (2012a). Implementation of micro-ball nanodiamond anvils for high-pressure studies above 6 Mbar. *Nat Commun, 3*, 1163.

Dunstan, D. J., & Spain, I. L. (1989). Technology of diamond anvil high-pressure cells: I. Principles, design and construction. *Journal of Physics E: Scientific Instruments, 22*(11), 913.

Dziewonski, A. M., & Anderson, D. L. (1981). Preliminary reference Earth model. *Physics of the Earth and Planetary Interiors, 25*(4), 297-356.

Evans, W. J., Yoo, C.-S., Lee, G. W., Cynn, H., Lipp, M. J., & Visbeck, K. (2007). Dynamic diamond anvil cell (dDAC): A novel device for studying the dynamic-pressure properties of materials. *Review of Scientific Instruments, 78*(7), 073904.

Fan, D., Zhou, W., Wei, S., Liu, Y., Ma, M., & Xie, H. (2010). A simple external resistance heating diamond anvil cell and its application for synchrotron radiation x-ray diffraction. *Review of Scientific Instruments, 81*(5), 053903.

Fukui, H., Sakai, T., Sakamaki, T., Kamada, S., Takahashi, S., Ohtani, E., & Baron, A. Q. R. (2013). A compact system for generating extreme pressures and temperatures: An application of laser-heated diamond anvil cell to inelastic X-ray scattering. *Review of Scientific Instruments, 84*(11), 113902.

Hazen, R. M. (1999). *The Diamond Makers*: Cambridge University Press.

Irifune, T., & Hemley, R. J. (2012). Synthetic diamond opens windows into the deep Earth. *Eos, Transactions American Geophysical Union, 93*(7), 65-66.

Irifune, T., Kurio, A., Sakamoto, S., Inoue, T., & Sumiya, H. (2003). Materials: Ultrahard polycrystalline diamond from graphite. *Nature, 421*(6923), 599-600.

Jayaraman, A. (1983). Diamond anvil cell and high-pressure physical investigations. *Reviews of Modern Physics, 55*(1), 65-108.

Jayaraman, A. (1986). Ultrahigh pressures. *Review of Scientific Instruments, 57*(6), 1013-1031.

Kantor, I., Prakapenka, V., Kantor, A., Dera, P., Kurnosov, A., Sinogeikin, S., Dubrovinsky, L. (2012). BX90: A new diamond anvil cell design for X-ray diffraction and optical measurements. *Review of Scientific Instruments, 83*(12), 125102.

Klein, C., Dutrow, B., & Dana, J. D. (2008). *The 23rd edition of the manual of mineral science: (after James D. Dana)*: John Wiley & Sons, Inc.

Komabayashi, T., Fei, Y., Meng, Y., & Prakapenka, V. (2009). In-situ X-ray diffraction measurements of the γ-ε transition boundary of iron in an internally-heated diamond anvil cell. *Earth and Planetary Science Letters*, *282*(1–4), 252-257.

Li, B., & Liebermann, R. C. (2007). Indoor seismology by probing the Earth's interior by using sound velocity measurements at high pressures and temperatures. *Proceedings of the National Academy of Sciences of the United States of America, 104*(22), 9145-9150.

Liebermann, R. C. (2011). Multi-anvil, high pressure apparatus: a half-century of development and progress. *High Pressure Research, 31*(4), 493-532.

Liermann, H.-P., Merkel, S., Miyagi, L., Wenk, H.-R., Shen, G., Cynn, H., & Evans, W. J. (2009). Experimental method for in situ determination of material textures at simultaneous high pressure and high temperature by means of radial diffraction in the diamond anvil cell. *Review of Scientific Instruments, 80*(10), 104501.

Liu, L.-G., & Bassett, W. A. (1975). The melting of iron up to 200 kbar. *Journal of Geophysical Research, 80*(26), 3777-3782.

Liu Lei and Bi Yan and Xu, J.-A. (2013). Ruby fluorescence pressure scale: Revisited. *Chinese Physics B, 22*(5), 056201.

Mao, H.-K., & Hemley, R. J. (1996). Experimental Studies of Earth's Deep Interior: Accuracy and Versatility of Diamond-Anvil Cells. *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences, 354*(1711), 1315-1332.

Mao, H.-K., & Hemley, R. J. (1998). New windows on the Earth's deep interior. *Reviews in Mineralogy and Geochemistry, 37*(1), 1-32.

Mao, H. K., Bell, P. M., & Hadidiacos, C. (1987). Experimental Phase Relations of Iron to 360 Kbar, 1400°C, Determined in an Internally Heated Diamond-Anvil Apparatus. In M. H. Manghnani & Y. Syono (Eds.), *High-Pressure Research in Mineral Physics: A Volume in Honor of Syun-iti Akimoto* (pp. 135-138). Washington, DC: American Geophysical Union.

Merkel, S., & Yagi, T. (2005). X-ray transparent gasket for diamond anvil cell high pressure experiments. *Review of Scientific Instruments, 76*(4), -.

Miletich, R., Allan, D. R., & Kuhs, W. F. (2000). High-Pressure Single-Crystal Techniques. *Reviews in Mineralogy and Geochemistry, 41*(1), 445-519.

Miyagi, L., Kanitpanyacharoen, W., Raju, S. V., Kaercher, P., Knight, J., MacDowell, A., Alarcon, E. Z. (2013). Combined resistive and laser heating technique for in situ radial X-ray diffraction in the diamond anvil cell at high pressure and temperature. *Review of Scientific Instruments, 84*(2), 025118.

Pasternak, S., Aquilanti, G., Pascarelli, S., Poloni, R., Canny, B., Coulet, M.-V., & Zhang, L. (2008). A diamond anvil cell with resistive heating for high pressure and high temperature x-ray diffraction and absorption studies. *Review of Scientific Instruments, 79*(8), 085103.

Piermarini, G. J., & Block, S. (2001). The Diamond Anvil Pressure Cell. In D. R. Lide (Ed.), *A Century of Excellence in Measurements, Standards, and Technology: A Chronicle of Selected NBS/NIST Publications, 1901-2000* (Vol. 958, pp. 395): National Institute of Standards and Technology.

Piermarini, G. J., Block, S., Barnett, J. D., & Forman, R. A. (1975). Calibration of the pressure dependence of the R1 ruby fluorescence line to 195 kbar. *Journal of Applied Physics, 46*(6), 2774-2780.

Pippinger, T., Miletich, R., & Burchard, M. (2011). Multipurpose high-pressure high-temperature diamond-anvil cell with a novel high-precision guiding system and a dual-mode pressurization device. *Review of Scientific Instruments, 82*(9), 095108.

Shen, G., Mao, H.-k., & Hemley, R. J. (1996). Laser-heated diamond anvil cell technique: double-sided heating with multimode Nd: YAG laser. *Computer, 1*, L2.

Smith Jr, R. L., & Fang, Z. (2009). Techniques, applications and future prospects of diamond anvil cells for studying supercritical water systems. *The Journal of Supercritical Fluids, 47*(3), 431-446.

Tarbuck, E. J., Lutgens, F. K., & Dennis, T. (2011). *Earth: An Introduction to Physical Geology*: Prentice Hall PTR.

Winter, J. D. N. (2001). *An Introduction to Igneous and Metamorphic Petrology*: Prentice Hall PTR.

Zha, C.-S., & Bassett, W. A. (2003). Internal resistive heating in diamond anvil cell for in situ x-ray diffraction and Raman scattering. *Review of Scientific Instruments, 74*(3), 1255-1262.

Zha, C.-S., Mibe, K., Bassett, W. A., Tschauner, O., Mao, H.-K., & Hemley, R. J. (2008). P-V-T equation of state of platinum to 80 GPa and 1900 K from internal resistive heating/x-ray diffraction measurements. *Journal of Applied Physics, 103*(5), 054908.