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August 3, 2005

High Pressure Research

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# **HYBRID BRIDGMAN ANVIL DESIGN: AN OPTICAL WINDOW FOR *IN-SITU* SPECTROSCOPY IN LARGE VOLUME PRESSES**

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**The absence of in-situ optical probes for large volume presses often limits their application to high-pressure materials research. In this paper, we present a unique anvil/optical window-design for use in large volume presses, which consists of an inverted diamond anvil seated in a Bridgman type anvil. A small cylindrical aperture through the Bridgman anvil ending at the back of diamond anvil allows optical access to the sample chamber and permits direct optical spectroscopy measurements, such as ruby fluorescence (*in-situ* pressure) or Raman spectroscopy. This performance of this anvil-design has been demonstrated by loading KBr to a pressure of 14.5 GPa.**

*Keywords:* Large Volume Press; Diamond Anvil; Paris-Edinburgh Cell

## **INTRODUCTION**

One of the significant features of the diamond-anvil cell (DAC) for high-pressure materials research is the fact that diamond is transparent to a wide-range of electromagnetic radiation, extending from the far infrared to high energy x-rays, thus permitting *in-situ* microscopic and spectroscopic investigations of samples in highly compressed states. In fact, the initial revolutionary advances and impact of diamond-anvil cell research was in part stimulated

by the development of the ruby fluorescence pressure-scale, which permitted *in situ* evaluation of the pressure by measuring the shift of the R-line luminescence [1,2]. Since then, a large number of optical and x-ray spectroscopic probes have been employed in DAC research to reveal a wide-range of physical, chemical and electronic properties at high pressures. In contrast, a typical large volume press (LVP) uses an opaque tungsten carbide (WC) or sintered diamond anvil, severely restricting *in-situ* optical and spectroscopic investigations of samples under pressures. Large diamonds of several 10s of carats for use in a LVP are prohibitively expensive, though efforts are underway to develop such materials for research purposes [3]. As a result, *in-situ* measurements in LVPs have largely been limited to x-ray, neutron, and electrical conductivity measurements, even for more compact LVP-designs like the Paris-Edinburgh Cell (PEC).

There have been numerous attempts made to incorporate optical access into various LVPs. For example, Drickamer [4] used Bridgman-type anvils surrounded by a steel belt-type sample container with a sequence of NaCl window plugs. The sample was then observed through a small NaCl-filled window in the lateral direction. Pressure was calibrated by testing different samples under load and watching for their previously determined phase transitions. The sample itself (on the order of up to 1 mm<sup>3</sup> for the Drickamer cell I which could reach ~ 5 GPa) is also embedded in the NaCl medium. Another design (Drickamer cell II) could reach a maximum pressure of ~ 16 GPa (6 ° cone, 2.4 mm flat) but very few data were recorded beyond 14 GPa. At the highest pressures the center thickness for this cell (II) was on the order of 100 μm.

Eremets [5] used an optical fiber to gain optical access to the sample in a LVP in order to excite and collect ruby fluorescence. In this approach, a quartz optical fiber was fixed into a ceramic tube with molten glass. This tube was inserted axially into the central depression of a toroidal anvil. Using this configuration, he was able to achieve and measure a pressure of 5.6 GPa. However, large deformations of the anvil and cracks appearing in the fiber during pressure

release proved to be difficult challenges. Secco *et al.* [6] also evaluated the potential of metal or ceramic tube encased optical fibers for use with a multi-anvil apparatus but found that the viable pressure range for this approach was limited to slightly more than 1 GPa.

Daniels [7] developed the Sapphire Ball Cell (SBC) as an alternative to the DAC and further modified this device to accommodate large sapphire balls, 0.5” or 1” in diameter, thereby achieving the large amount of sample necessary for neutron scattering experiments. However, the performance of the sapphire limits this approach to a pressure range of ~1 GPa.

Recently, Goncharenko [8] reported neutron scattering from samples compressed by specially designed large synthetic sapphire anvils with diameters of ~ 1 cm and culet sizes ranging from 1.5 to 8 mm. They were capable of reaching pressures of 15 GPa while maintaining sample volumes of up to 0.01 mm<sup>3</sup> (10 GPa with 0.1 mm<sup>3</sup>). Strictly speaking, however, those devices were pressure cells and microscopic samples, not generally considered large volume presses.

Unusual or highly specialized probes, such as neutron or synchrotron x-ray sources, can permit *in-situ* studies of samples in a LVP, but access to these resources is limited and not always readily available. The inability to easily measure the pressure on a sample in a LVP in a laboratory setting, on the other hand, leads to large uncertainties and lingering questions regarding materials’ properties and processes at high pressures. For example, a reliable *post mortem* evaluation of the pressure achieved in a LVP is typically difficult. One can use the formula  $p \sim m \cdot F/A$  for the pressure ( $p$ ) in the sample under a load ( $F$ ) and the measured dimension of the contact area ( $A$ ) after pressure release. If one assumes a parabolic pressure distribution, then  $m = 2$  which may not be correct. We found, through experimentation, that this approximation works only moderately well for Bridgman-type anvils and fails for toroidal anvils. The pressure multiplication at the center of a sample under compression by Bridgman type

anvils depends on quite a few factors like radius and thickness of the gasket, as well as the diameter of the sample region [4,9]. A direct determination of the pressure  $p$  in a LVP sample, *e.g.*, by ruby fluorescence or other optical technique, would therefore be extremely useful for diagnosing LVP performance characteristics.

Another benefit of optical access to a LVP sample under pressure is demonstrated by the observation that optical radiation can lower the onset pressure of a material's chemical/physical transformation. For example, in our recent studies of CO [10,11], we have shown that CO polymerizes at  $\sim 5$  GPa in the absence of illumination, but at  $\sim 3$  GPa the transformation can be photo-catalyzed by irradiating with 514 nm laser light [12] and the transformation pressure can be reduced to even lower pressures when the sample is exposed to x-rays [13]. Similar observations have been made for the photo-induced ring opening of benzene under pressure [14]. Since lower transition pressures permit larger sample volumes, the advantage of optical access is extremely attractive for materials research as well as industrial scale-up synthesis approaches for advanced material technology development and applications.

From the preceding discussion it is clear that several attempts have been made in the past to address the lack of optical access to a LVP sample under compression, by using flat diamond windows, sapphire balls, and sapphire anvils of Bridgman-type design. However, none of these efforts succeeded to the desired level of performance; that is, to reach  $\sim 10$  GPa with a macroscopic sample, several mm in diameter. We attribute this limitation to the lack of adequate mechanical strength in sapphire or an unsupported diamond window. In this paper, we describe our recent development which incorporates a diamond anvil as a pressure window and has achieved an unprecedented level of success in ease of implementation and delivering optical access.

## APPARATUS

The large volume press used in the present study was a Paris-Edinburgh Cell (PEC), model V7, a modification of the more popular and smaller V3 [15,16]. Nevertheless, the method described below is applicable more generally to large-volume presses that use opaque WC or sintered-diamond anvils. Furthermore, the loads required to carry out these experiments are relatively low (of order several tons) and thus, could even be performed in an enlarged gem anvil cell. The sample assembly itself was of a hybrid design, combining a conventional Bridgman anvil and our modified “windowed” Bridgman anvil. The piston anvil was a Bridgman type truncated cone of WC with a 9 mm flat described in Ref. [10]. The opposing top anvil (breech) was replaced by a WC-diamond anvil assembly. The WC anvil (grade H10) had an access hole in the shape of a funnel drilled through its center. The funnel merged into a straight bore of 0.7 mm diameter before opening up into an inverted cone that had been precisely cut to accept a diamond anvil with a table diameter of 3.8 mm. A diamond anvil (0.7mm flat tip, 2.6 mm height of Almax design) was placed upside down (large table facing outward toward sample area) into the opening, cushioned by an extruded piece of steel foil and fixed in place by epoxy (2850 Stycast). Figure 1 shows a schematic of the sample anvil assembly. Both anvils were supported by maraging steel binding rings and experienced several tons of compressive force in the radial direction. A load of ~20 tons was necessary to seat the anvils into the binding rings.

A stainless steel gasket with a hole diameter of 2.5 mm (initial thickness of 0.5 mm) and an outer diameter of ~12 mm contained the sample, which consisted of KBr salt with ruby chips dispersed within the salt matrix. The central part of the sample (~0.7 mm diameter) could be imaged using a relay lens system and a long working distance microscope objective (working distance of 150 mm and magnification of 3) through the access hole. A laser and spectrometer were coupled to the optical system for laser spectroscopy measurements such as Raman and

ruby-fluorescence pressure measurements.

## APPLICATION

An important aspect of the experimental setup was to use components similar to those used for our standard PEC experiments. In this way we could evaluate the operation ease and viability of our design for LVP applications, including cryogenic conditions. Optical access and imaging of the sample region was accomplished through the bore of the breech (diameter of 6 mm) and the diamond window by a relay-lens system and a microscope objective. Our optical system imaged the central sample region with a spatial resolution of better than 10  $\mu\text{m}$ . We incorporated a video camera to display and monitor the image of the sample region. We integrated the laser into the system with a tunable chip mirror that permitted the laser beam to be selectively focused on different parts of the sample containing items of interest, such as ruby chips. A knife-edge assembly in the path of the collected light spatially filtered the signal for selective measurement in the spectrometer, i.e., spatially resolved ruby-fluorescence pressure determinations.

Figure 2 shows a succession of ruby R-line luminescence signals that were measured. At 12.0 GPa the pressure varied by 0.3-0.4 GPa when moving the laser beam 200  $\mu\text{m}$  from the sample center. Increase of the load beyond 14.5 GPa resulted in chips fracturing off of the inner surface of the WC anvil access hole. These chips fell onto the diamond window and obscured the view of the sample. This fracturing was accompanied by a loss of pressure on the sample of about 2 GPa. After removing the load and doing a *post mortem* examination it was found that the sample hole had increased from 2.5 mm to a diameter of almost 4 mm with a thickness of  $\sim$  200  $\mu\text{m}$ . Furthermore, the gasket had ruptured radially with an associated loss of material. The diamond anvil itself was not damaged. This result is not unexpected, considering that the WC

anvils typically fail at pressures of ~10 GPa.

Figure 3 shows the correlation of the load with the pressure, as determined by the ruby fluorescence method. If one takes the area  $A$  under compression to be that of the table of the diamond and calculates the ratio,  $F/A$ , one determines the pressure multiplication ( $m$ ) to be ~3, i.e. the ratio  $F/A$  has to be multiplied with  $m = 3$  to obtain the value for the maximum pressure at the center of the sample. This is in stark contrast to estimates based on the assumption of a parabolic pressure profile.

## **DISCUSSION**

Although we only achieved a pressure of ~14 GPa in these experiments, we feel our approach holds great promise. Anvils, such as sintered diamond or a stronger grade of WC that can sustain higher loads should be able to generate even higher pressures. We postulate that the chips breaking off from the inner wall at the highest pressure are generated at the relatively sharp corner between straight and cone-shaped sections. Chamfering this corner to remove the sharp corner should improve the pressure performance.

The inverted diamond acts as a window into the center of the sample region under pressure. The geometry of the anvil assembly allows us to apply the principle of unsupported area<sup>17</sup> to determine the pressure between the sides of the diamond window and the anvil wall. Since the central 0.7 mm of the inverted anvil (the diamond flat tip) are unsupported, one finds a pressure between diamond and WC anvil in the steel foil that is about 4 percent larger than the value of  $F/A$  (assuming the pressure in the foil does not change with distance from the hole center). Moreover, although our test took place in a PEC-LVP the concept of the inverted diamond anvil window should work just as well or even better on a smaller scale. Further optimization of parameters and materials is warranted, but the success of the current effort

demonstrates that the inverted diamond anvil window principle makes it possible to image large samples under pressure. To this end we are currently constructing a cell where two diamond anvils are in the inverted configuration, with the hope of imaging large LVP-sized samples at pressures of several 10s of GPa.

## **CONCLUSION**

The goal of our experiments was to develop an anvil design that allows the use of optically transparent windows that permit *in situ* optical characterizations of samples under pressure. The capability of illuminating the pressurized sample allows direct spectroscopic pressure measurements and might also assist in potential transformations of the sample material (e.g. by laser heating and photo-catalysis). Moreover, our optical system permits high quality imaging of the central part of the sample under pressure. We have shown that pressures higher than 14 GPa can be reached for large macroscopic samples of several mm diameter. We are confident that even higher pressures can be achieved, by using stronger materials, such as sintered diamond, as the anvil material. The optically transparent breech anvil also makes the sample region accessible to the broad range of modern optical diagnostic techniques, such as *in-situ* laser-heating and Raman spectroscopy. Further development attempts are under way to develop and test a similar design for toroidal sintered diamond anvils.

## ***Acknowledgments***

The authors gratefully acknowledge the assistance of Ken Visbeck in design and fabrication of components used in this project. This work was performed under the auspices of U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng.-48.

## Figure Captions:

- Figure 1** Schematic of the sample assembly using an opposed diamond anvil as an optical window. A type-Ia diamond (~1/3 carat, 0.7 mm flat, 3.8 mm table) was used in an opposed configuration; the sample was loaded in a 2.5 mm hole drilled through a 0.5 mm-thick stainless steel gasket. The lower pavillion of the diamond anvil was supported by the WC anvil with a thin layer of steel serving as a stress cushion. The top of the diamond anvil was truncated to a 0.7 mm flat for optical window.
- Figure 2** Ruby R-line fluorescence obtained from ruby chips in a KBr sample during pressure loading. Note that the R-line rapidly broadens with increasing pressure owing to a large strain developed within the sample.
- Figure 3** Correlation of load on the sample (kN) and pressure at the sample center (GPa), showing an approximately linear relationship.

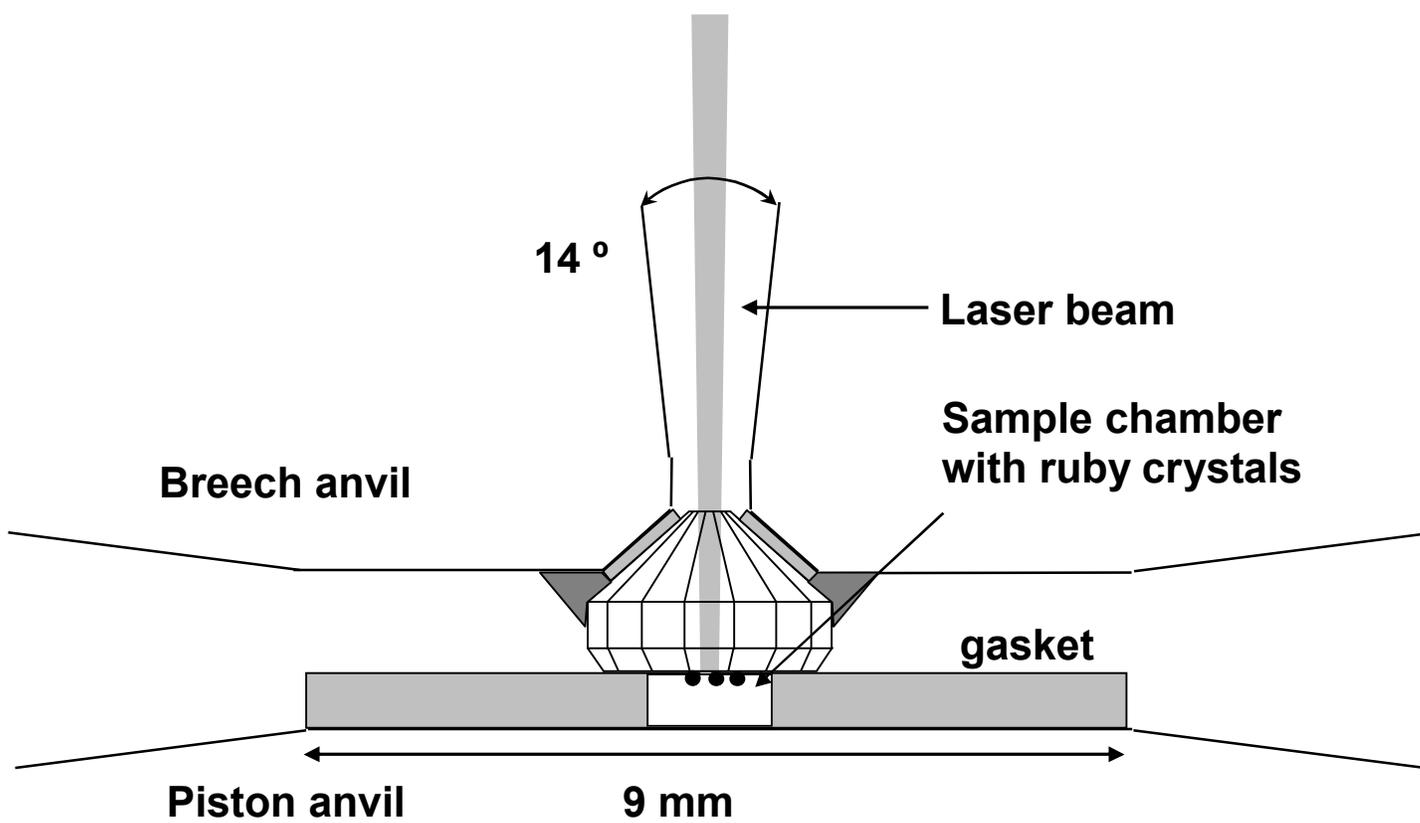


FIGURE 1

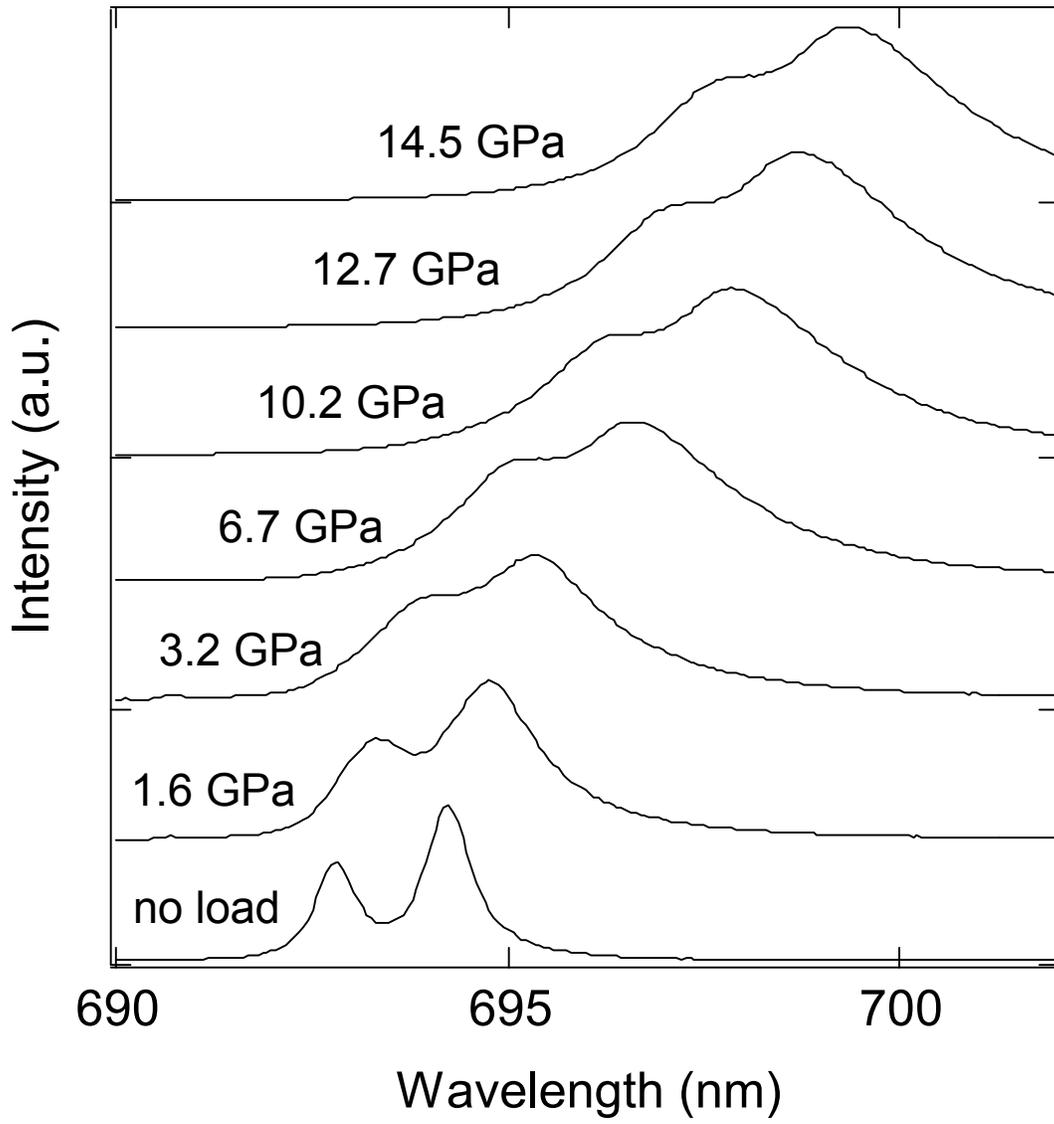
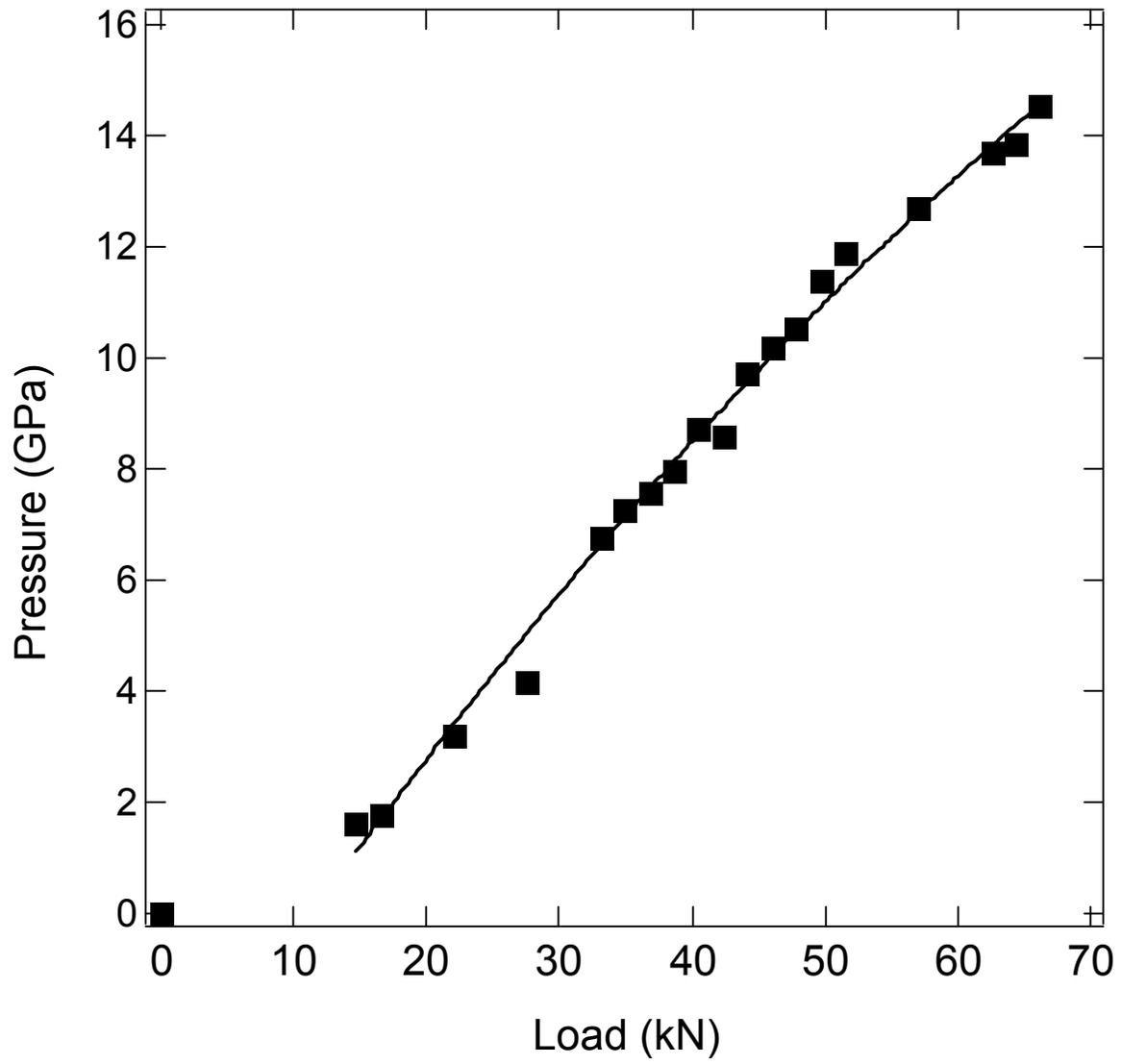


FIGURE 2



**FIGURE 3**

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