

1 Thermal Pressure in the Laser Heated Diamond Anvil Cell: A Quantitative  
2 Study and Implications for the Density vs. Mineralogy Correlation of the  
3 Mantle

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12 **Keypoints:** laser-heated diamond anvil cell, thermal pressure, density – mineralogy correlation

13

14 **Plain Language Summary:**

15 The primary window into the interior of the Earth below ~10 km are earthquake waves that give us a 3-  
16 dimensional elasticity/density image of the planet. In order to translate this into a geological model of  
17 the Earth, we need to know the physical and chemical response of rocks with the composition of the  
18 Earth's interior at increased pressure and temperature. This is achieved by experiments in which  
19 samples are subjected to the high pressure and temperatures of the deep Earth using laser heated  
20 diamond anvil cells. A long standing problem of such experiments is a hard to quantify pressure term  
21 caused by the heating of the sample. This paper quantifies the thermal pressure distribution in a typical  
22 experiment for the first time and explores the effect of its incomplete knowledge on the possible  
23 mineralogical composition of the Earth.

24

25 **Abstract:**

26 We present the first quantitative measurements of the magnitude and gradient of thermal  
27 pressure in a laser heated diamond anvil cell (LHDAC). The observed thermal pressure is strongly  
28 localized and follows the distribution of the laser hotspot. The magnitude of the thermal pressure is of  
29 the order of the thermodynamic thermal pressure ( $\alpha K_T dT$ ) with gradients between 0.5 – 1.0 GPa/10  
30  $\mu\text{m}$ . This poses constraints on pressure determinations during PVT equation of state measurements  
31 when using a LHDAC. We show that an incomplete account of thermal pressure in PVT experiments can  
32 lead to distortions of the coveted depth versus mineralogy correlation. However, the ability to spatially  
33 resolve thermal pressure in a LHDAC opens avenues to measure thermodynamic derivative properties,  
34 which are important for comprehensive thermodynamic descriptions of the interior of planets.

35 

## 1 Introduction

36 Over the past ~ 25 years, laser heated diamond anvil cells have played an important role in  
37 experimentally accessing the conditions of the interior of the Earth and Earth-sized planets (e.g.  
38 *Williams et al.* [1991]; *Guillaume Fiquet et al.* [1998]; *W Mao et al.* [2004]; *Ismailova et al.* [2016];  
39 *Bassett* [2016]). The technique allows experimental simulation of pressures and temperatures relevant  
40 to the interior of the Earth, while allowing in-situ probing of structural and thermo-elastic properties of  
41 samples using a large portion of the electromagnetic spectrum (e.g. *Shen and Mao* [2016]; *Mezouar et*  
42 *al.* [2017]). Despite the maturity of this technique, there persist remarkable discrepancies between  
43 results reported from different experiments (e.g. *Komabayashi and Fei* [2010]), and also between  
44 experiments and theory (e.g. *Dorogokupets et al.* [2015]).

45 From an experimental angle, the sources of discrepancies in a LHDAC experiment are often  
46 associated with difficulties in measuring the pressure and temperature of the sample chamber. A second  
47 source of experimental uncertainty stems from the difficulty in positioning the probe (e.g. an X-ray  
48 beam) at a position of well-defined pressure and temperature within a sample volume with high thermal  
49 gradients ( $\sim 10^4$  K/mm) (e.g. *Panero and Jeanloz* [2001]; *Abby Kavner and Nugent* [2008]) and non-  
50 hydrostatic stress conditions (e.g. *Meng et al.* [1993]). Differences in sample preparation cause  
51 additional elements of limited reproducibility (e.g. *Marquardt and Marquardt* [2012]), as does  
52 unrecognized contamination (e.g. *Morard et al.* [2017]). An additional, and largely experimentally  
53 uncharacterized, contribution to measurement uncertainties in P-V-T experiments is the increase in  
54 pressure during the heating event due to quasi-isochoric conditions and the concomitant pressure  
55 increase and gradients induced by local heating. This effect is commonly referred to as thermal pressure  
56 ( $P_{th}$ ); it is unrecorded in experimental set-ups where pressure is determined before and/or after the  
57 laser-heating event by using, for example, ruby fluorescence spectrometry. The combination of the laser  
58 heated material's finite shear strength and the temperature gradient produced by the focused laser spot  
59 produces a spatial gradient in thermal pressure which again is of the same order as the size of the  
60 probe.

61 The possible role of thermal pressure in laser-heated diamond cell experiments has long been  
62 recognized, but virtually no experiments have been conducted that measured the variation in thermal  
63 pressure *in situ* across a sample. In fact, the treatment of thermal pressure has been examined largely  
64 from a theoretical perspective. *Heinz* [1990] was the first to quantitatively address this issue from such a  
65 theoretical point of view. He estimated a  $P_{th}$  of  $\sim 2 - 10$  GPa for a spherical Gaussian hot spot with  $T_{max} =$   
66 2000 K, a thermal expansivity  $\alpha = 4 \times 10^{-5}/K$ , Poisson's ratio  $\nu = 0.25$ , and Young's modulus  $E = 200$  GPa.  
67 These calculations were done for various ratios of hot-spot to sample size for two scenarios: the case of  
68 a free surface boundary condition (which implies constant pressure at the surface), and the case of a  
69 constant volume. Calculated values for  $P_{th}$  ( $\sim 4$  to 5 GPa) for small hot spot sizes were very similar in  
70 both scenarios, indicating a local nature of  $P_{th}$  with high pressure gradients associated with the laser-  
71 heated spot. This result implies that most of the thermal pressure is maintained via the shear strength of  
72 the heated material, rather than through the constant volume restriction provided by the metal gasket.

73 *Dewaele et al.* [1998] performed finite element modeling – also based on solving the  
74 thermoelastic equations – for a realistic LHDAC model assembly consisting of samples (stishovite and

75 coesite) sandwiched between an argon pressure medium. Their analysis included the effects of the  
76 thermal conductivity of the sample and pressure medium on the temperature distribution, as well as the  
77 effects of the bulk and shear moduli parameterized as Lamé constants. For both coesite and stishovite,  
78 they differentiated between a model with solid and liquid argon as the pressure medium. Their results  
79 for a solid pressure medium compare well with the results cited by *Heinz* [1990] – a thermal pressure  
80 increase of ~30 % of the ‘cold’ pressure. Interestingly, they found only a small dependence of the  
81 thermal pressure on the relative amount of solid argon used as pressure medium. Their second model,  
82 assuming a completely molten pressure medium, reduced the expected thermal pressure by about 50  
83 %. This model approached the free-surface model of *Heinz* [1990].

84 *G Fiquet et al.* [1996], for the first time, reported direct observations of thermal pressure in a  
85 LHDAC while measuring P-V-T data of MgO periclase using a CO<sub>2</sub> laser. *Andrault et al.* [1998]  
86 experimentally determined the pressure increase induced by laser heating in a LHDAC using the phase  
87 transitions in the Mg<sub>2</sub>SiO<sub>4</sub> and SiO<sub>2</sub> systems. They found that the observed increase relative to the  
88 perfectly isochoric ‘thermodynamic’ limit is sample dependent, correlating positively with the product of  
89 the thermal expansion and bulk modulus,  $\alpha K_T$  (in accord with the ideal thermodynamic definition of  
90 thermal pressure as equal to  $\alpha K_T dT$ ), rather than with the shear modulus.

91 In this work, we experimentally quantify the distribution of thermal pressure created in a  
92 diamond anvil cell by a laser focus spot of 30  $\mu\text{m}$  FWHM – a typical diameter of an experimental laser  
93 heating spot – and compare it with previously published models as well as a simple model based on the  
94 assumption of isochoric conditions. We then use an idealized example to quantify the effect of not fully  
95 taking into account the thermal pressure on thermoelastic properties of a mantle-like material  
96 (Mg<sub>0.88</sub>Fe<sub>0.12</sub>SiO<sub>3</sub> bridgmanite) extracted from a LHDAC experiment, and explore the implications for the  
97 resultant inferred mineralogy versus depth correlation.

## 98 2 Methods

99 We combine spatially resolved synchrotron X-ray powder diffraction [*Kunz et al.*, 2005; *Laugier and*  
100 *Bochu*, 2002; *Prescher and Prakapenka*, 2015] at distributed points along a BX90 [*Kantor et al.*, 2012]  
101 DAC’s sample chamber’s diameter with a 2-dimensional temperature map [*Kiefer and Duffy*, 2005; *Kunz*  
102 *et al.*, 2018; *Manga and Jeanloz*, 1996; *Rainey and Kavner*, 2014] of the sample chamber through  
103 pressure-volume-temperature (PVT) Murnaghan equation of states (EOS) [*Anderson*, 1997; *Angel et al.*,  
104 2014; *Birch*, 1952; *Helfrich and Connolly*, 2009; *Murnaghan*, 1951] on samples of Agl [*Chauhan and*  
105 *Singh*, 2007; *Hull and Keen*, 1999] and San Carlos olivine [*Liu et al.*, 2005; *Liu and Li*, 2006] to determine  
106 the pressure distribution across the laser heated hotspot. By comparing these pressure values with the  
107 pressures measured at the same positions before the heating event [*H Mao et al.*, 1986], we obtain a  
108 distribution of the thermal pressure ( $P_{\text{th}}$ ) produced by the heating event. More details on the sample  
109 and X-ray diffraction techniques, as well as on the laser heating and temperature mapping are given in  
110 the Supporting Information, Section 1.

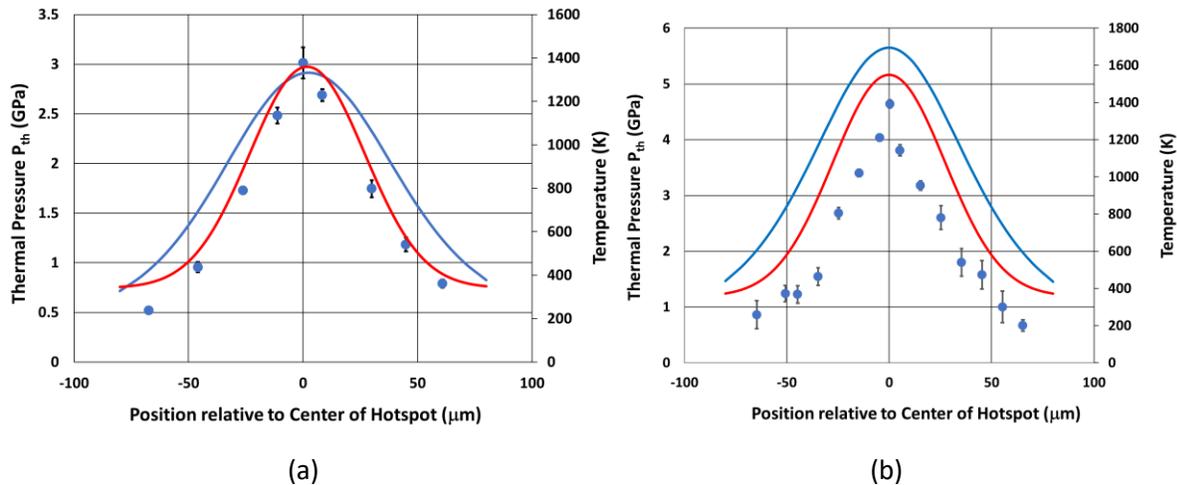
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## 3 Results

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### 3.1 Temperature profiles

113 Figure 1 shows the temperature profile (red) across the hot spots in Agl and San Carlos olivine. The hot-  
 114 spots can be fit with a Gaussian function (S.I. Table 1), and have approximately the width of the laser  
 115 spot. These are in agreement with the Gaussian intensity distribution of the IR fiber laser, and indicate  
 116 that the coupling of the samples with the laser is not markedly temperature dependent. Both  
 117 temperature curves decrease to basically room temperature at the sample/gasket interface. This  
 118 confirms the highly local nature of the temperature distribution in laser-heated samples within a DAC. It  
 119 is therefore justified to assume that the cold gasket does not suffer any temperature-induced  
 120 deformation: indeed, no irreversible deformation, as manifested by a shift in sample diameter, was  
 121 observed following heating. The heating process of the entire sample volume is thus, to a first  
 122 approximation, isochoric. To second order, it is possible that localized heating of the anvils may produce  
 123 a slight contraction in the axial direction of the sample (even while the radial direction remains  
 124 unchanged): the trade-off between the elastic response of the anvil to the thermal pressure within the  
 125 sample and the thermal pressure induced by localized heating is difficult to characterize, but this effect  
 126 is likely to be small.



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129 **Figure 1:** Observed beam temperature across the hotspot (red) and observed (blue symbols) and modeled (blue line) thermal  
 130 pressure in Agl (a) and San Carlos olivine (b). The position of the pressure peak coincides with the hotspot peak as is expected  
 131 for a thermal pressure-induced increase.

132 

### 3.2 Pressure profiles

133 Figure 1 also shows the observed thermal pressure distribution (blue dots) across the laser heated  
 134 hotspot (red line) as deduced from the procedure described above and in Supporting Information using  
 135 the thermoelastic constants given in S.I. Table 1.

136 In both samples, a significant pressure peak, that is at the same location as the peak of the hotspot, is  
 137 observed. In Agl, we observe a maximum thermal pressure of ~3 GPa at the center of the hotspot  
 138 (~1400 K). It decreases to 0.5 GPa within about 70 μm. At the steepest part of the slope, about 20 μm  
 139 from the center, the pressure drops by about 0.4 GPa per 10 μm. In San Carlos olivine, the situation is  
 140 similar. A pronounced pressure maximum of ~4.5 GPa above the room-temperature value is measured

141 at the center of the hotspot (~1600 K). The thermal gradient is somewhat larger than in AgI, ~1 GPa/10  
142  $\mu\text{m}$ : this difference likely reflects the marked difference in strength between the two materials. It is  
143 notable, however, that even within a weak solid like AgI, the thermal pressure remains localized and  
144 does not fully re-equilibrate through viscous relaxation across the sample over the multi-minute course  
145 of the experiment.

146 Indeed, in both materials the thermal pressure distribution closely traces the temperature distribution,  
147 giving testament to the local nature of thermal pressure as predicted by *Dewaele et al.* [1998] and *Heinz*  
148 [1990]. Nevertheless, an effect that is plausibly associated with material strength can be experimentally  
149 discerned: the peak thermal pressure in AgI is slightly lower and the pressure distribution is wider than  
150 is observed in olivine.

## 151 4 Discussion

152 This is – to the best of our knowledge – the first documented experimental determination of the spatial  
153 distribution of thermal pressure across a laser heated spot within the diamond anvil cell. The general  
154 magnitude of the values reported here correspond quite well to the thermodynamic thermal pressure  
155 ( $\alpha K_0 dT$ ) and also agree well with values predicted by *Heinz* [1990] for his constant volume model. That  
156 model corresponds closely to our experimental arrangement where a sample is loaded without pressure  
157 medium into a DAC and heated locally with a hot spot smaller than the sample volume. As expected, our  
158 values are somewhat higher (when adjusted for the hotspot's peak temperature) than the thermal  
159 pressures predicted by *Dewaele et al.* [1998] using finite element modeling. This is due to the fact that  
160 their modelling set-up included solid or liquid argon surrounding the sample as a pressure transmitting  
161 medium: such rare gas media are expected to be weak at high pressures (and temperatures), although  
162 argon can maintain substantial pressure gradients above ~20 GPa at 300 K [*Klotz et al.*, 2009].

163 The local nature of the observed thermal pressure is due to the finite shear strength of the expanding  
164 sample in a constrained volume. If the heated sample were a liquid or melt with no shear strength, the  
165 thermal pressure would equilibrate over the entire gasket hole. For the material, the size of the heated  
166 spot and sample, and the peak temperatures considered in this study, the equilibrated thermal pressure  
167 would amount to a homogeneous ~1.25 – 1.5 GPa increase across the entire sample volume. The  
168 observed gradients in thermal pressure therefore confirm that the temperatures attained were well  
169 below the melting point: however, even within a material that is expected to be relatively weak (AgI),  
170 thermal pressure-induced pressure increases of several GPa are observed.

171 To simulate the observed localized pressure increases within our samples, our model uses the non-zero  
172 shear strengths of the heated samples as a volumetric shielding mechanism between the colder material  
173 located radially outward from the hot spot, and the thermal expansion of the material within the hot  
174 spot (See Supporting Information Section 2). The volume of the heated material is therefore constrained  
175 to be smaller than the size of the gasket hole. We quantified this simple model by partitioning the  
176 sample volume with radial differential elements centered to the hot-spot. The temperature function was  
177 then derived from a Gaussian approximation of the experimental temperature maps. At a fixed radial  
178 distance, the thermal pressure is determined by assuming a rigid boundary at that fixed radial distance  
179 where the thermal expansion of the nested interior region is allowed to aggregate to a thermal pressure  
180 vector directed radially outwards. The fully rigid boundary construction assumed in our model is akin to

181 an infinite shear strength analogy that completely shields the colder exterior side of the shell from the  
182 hotter interior side. The model thus represents an upper bound on the expected thermal pressure  
183 increase. A detailed description of the model calculations is given in the Supporting Information, Section  
184 2. The predicted pressure distributions of this simple model (blue curve) are compared with the  
185 experimental data (blue dots) in Figure 1. For AgI, the model predicts the peak pressure accurately, but  
186 under-estimates the pressure gradient. In the case of San Carlos olivine, the model predicts a pressure  
187 distribution that is shifted upward from the observed values by about 1 GPa (at an observed peak  
188 pressure of  $\sim 4.5$  GPa). We attribute this discrepancy to the pressure gradient being too steep to be  
189 resolved with a  $10\ \mu\text{m}$  sized X-ray spot thus biasing the measured pressures towards lower values. This  
190 is consistent with the fact that the model matches the measured values much better for AgI where the  
191 lower shear strength allows for a flatter pressure gradient, which is better matched to the  $10\ \mu\text{m}$  X-ray  
192 spot size used. We therefore expect the real pressure increase to be sharper and to lie between the  
193 measured spots and the values given by the model.

194 Our measurements demonstrate that even for soft materials at temperatures close to their melting line,  
195 a significant pressure increase coupled with a pressure gradient around the localized hot spot is  
196 maintained in laser-heated diamond anvil cells. Given the steepness of the observed pressure gradient,  
197 this thermally-induced pressure increase and gradient is also expected to be significant in samples that  
198 are embedded in 'soft' pressure media such as Ne or He where their shear strength at high pressures  
199 becomes sufficient to contain the thermal pressure within the embedded sample (e.g. *Klotz et al.*  
200 [2009]). The shear strengths of the media consequently negate the full pressure-equilibrating effect  
201 expected in hydrostatic media for the pressure generated locally in the sample through local heating.  
202 These findings have ramifications for the design and interpretation of in-situ high-pressure high-  
203 temperature diffraction studies aimed at determining PVT equations of state of Earth materials and  
204 consequently for the mineralogical interpretation of geophysical density profiles based on LHDAC  
205 results.

206 *Ramifications for LHDAC experimental designs:*

- 207 (1) If, during a LHDAC experiment pressure is measured before and after the heating event,  
208 pressure can be significantly underestimated in the center of the hotspot (i.e. where the X-rays usually  
209 probe the sample) during the heating event: such localized, thermally-induced pressurization has not  
210 been previously characterized (e.g. *Andrault et al.* [1998]; *A Kavner and Duffy* [2001] ).
- 211 (2) Pressure measurements using the diffraction lines of a temperature-insulating pressure medium  
212 (i.e. Ne, Ar, He) may similarly underestimate the pressure within the hot sample given the steep  
213 pressure gradients we observed within the hotspot. The underestimation of the pressure derived from  
214 the lattice parameters of a solid, non-laser-absorbing pressure medium (such as NaCl or MgO) could be  
215 larger if the pressure medium simultaneously also acts as a thermal insulation material shielding the  
216 diamonds from the laser hot spot. In that case, it is possible that a significant portion of the diffracting  
217 volume within the pressure medium is also at a temperature significantly below the peak temperature.
- 218 (3) As a consequence of (1) and (2), the most reliable pressure determination in a laser heated  
219 diamond anvil cell is likely generated by a pressure standard that is intimately mixed with the sample,  
220 monitored in situ at simultaneous high temperature and pressure, and which differs from the material  
221 used to thermally insulate the diamonds from the sample. Ideally, such an internal calibrant (often Pt)  
222 would also be chemically inert at extreme conditions in order to avoid unwanted chemical reaction or  
223 alloying with the sample. Such a mixed phase geometry can be particularly effective when deployed in

224 instances where the calibrant itself is used as the laser-absorber within the sample (e.g. *Tateno et al.*  
225 [2019]).

226 (4) The observed steep gradients in thermal pressure demonstrate that a straightforward means of  
227 experimental optimization, in terms of sampling a spot at well-constrained pressure and temperature, is  
228 to combine a large uniform hot spot (which can be generated using beam shaping optics, such as a Pi  
229 shaper) with the smallest possible X-ray probe. Naturally, a small X-ray beam has the inherent problem  
230 of reduced data quality due to a decrease in powder statistics. This is especially true at high  
231 temperatures where recrystallization and grain growth are often observed (e.g. [*Irifune et al.*, 2005] ,  
232 [*Shen et al.*, 1998]). While poor powder diffraction statistics might still allow extraction of reliable  
233 volumetric data, other approaches could involve dispensing with monochromatic powder diffraction for  
234 PVT equation of state determinations based on diffraction. Single crystal and multigrain diffraction  
235 techniques are obvious alternatives that are commonly deployed at ambient temperatures, but are  
236 difficult (although not in principle impossible) to combine with laser heating, due to the requirement  
237 that the sample be rotated relative to the X-ray beam [*Dubrovinsky et al.*, 2010]. X-ray Laue  
238 microdiffraction can be a useful tool in cases where a sample cannot easily be rotated as required on a  
239 monochromatic single crystal diffractometer (e.g. *Barkov et al.* [2019]; *Tamura et al.* [2002]). However,  
240 in the absence of energy resolving area detectors, the application of Laue microdiffraction to PVT  
241 equation of state studies is not practical. A potentially viable technique that can be deployed using  
242 commonly available equipment is energy resolved Laue diffraction, which can use a scanning  
243 monochromator rather than an energy resolving detector. To make this approach feasible in the  
244 traditional transmission geometry employed in laser heating set-ups (e.g. *Kunz et al.* [2018], *Shen et al.*  
245 [2001]) requires a large energy range ( $\sim 15 \text{ keV} < E < 50 \text{ keV}$ ) to be covered in order to overcome the low  
246 density in reciprocal space coverage at low diffraction angles (e.g. *Kunz et al.* [2009]). Alternatively, a  
247 set-up where the laser heating is in the axial direction through the diamonds, but the detector is  
248 positioned at 90 degrees (i.e. signal through X-ray transparent gasket) could be envisaged.

249  
250 The key point here is that the sharply peaked pressure distributions that we document within laser-  
251 heated spots motivate either smaller X-ray probes (and larger heated spots) than have previously been  
252 deployed, or alternate diffraction techniques to enhance the spatial resolution of the X-ray probe itself.

253 *Ramifications for geophysical models derived based on LHDA experiments:*

254 A systematic off-set in the assumed pressures for PVT equation of states, as would occur if part of the  
255 induced thermal pressure is not recognized, has consequences for the geophysical conclusions deduced  
256 from such experiments. As an example, we tested the effect on a hypothetical experiment on  
257 bridgmanite ( $\text{Mg}_{(1-x)}\text{Fe}_x\text{SiO}_3$  ( $x = 0.12$ )). We created a synthetic PVT dataset with pre-heated pressures  
258 between  $\sim 25$  and 100 GPa and 3 different mantle relevant temperatures (2000, 2500 and 3000 K), with  
259 imposed thermoelastic parameters ( $V_0$ ,  $K_0$ ,  $K'$ , Anderson-Grüneisen  $\delta$ ,  $\alpha_0$ ,  $d\alpha/dP$ ) derived from the  
260 literature and tabulated in Table 1. We add to the pre-heated pressure a thermal pressure of  $\alpha K \Delta T$  (8.4,  
261 10.9, 13.3 GPa), assuming an  $\alpha K \sim 5 \times 10^{-3} \text{ GPa/K}$  in accordance with our measurements. We then use  
262 these synthetic  $V/V_0 - T$  data to fit a Murnaghan equation of state by assuming pressures that  
263 underestimated the total pressure by 2 GPa. This process yields a set of thermoelastic properties that  
264 are biased through the neglect of this thermal pressure (Table 1). As can be seen from Table 1, both the  
265 Anderson-Grüneisen parameter  $\delta$  ( $dK/dT$ ) and  $d\alpha/dP$  refine towards values that predict a density vs  
266 pressure curve that is shifted positively (to higher densities) relative to the true values (Figure 2). If such

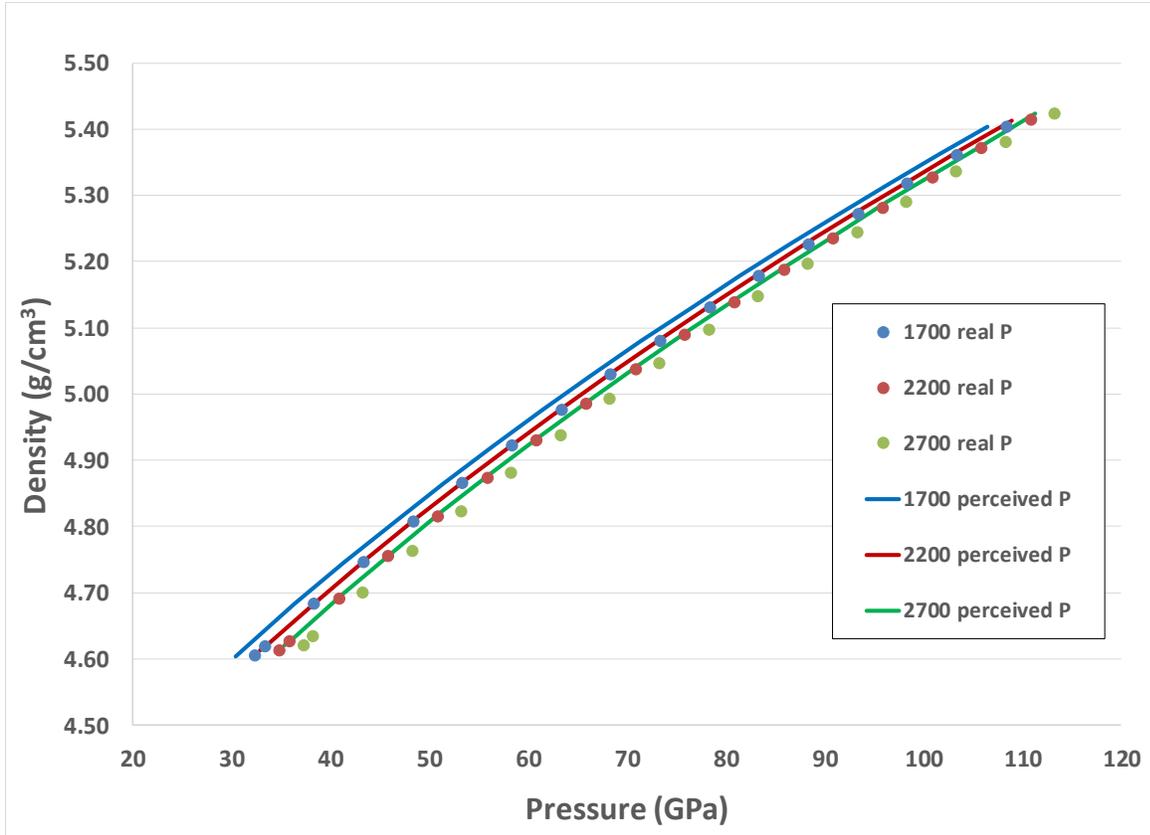
267 a slightly overestimated density vs depth (i.e. P and T) profile were compared with seismic data to  
 268 estimate the Fe content in bridgmanite in the Earth's mantle, this density difference would lead to an  
 269 underestimate of the Fe content in the mantle. For our model parameters, the sensitivity of the system  
 270 is such that even this small neglect of thermal pressure would generate an underestimate of the deep  
 271 mantle's inferred Fe number (based on a too-dense EOS) of  $\sim 0.03$ .

	"Synthetic" values	Refined values
$V_0$	163.7 <sup>1)</sup>	Not refined
$K_0$	246.7 <sup>1)</sup>	230.2(5)
$K'$	4.03 <sup>1)</sup>	4.40(1)
Anderson-Grüneisen $\delta$	3.25 <sup>2)</sup>	1.74(6)
$\alpha_0$	$2.0 \times 10^{-5}$ <sup>3)</sup>	$1.63(2) \times 10^{-5}$
$d\alpha/dP$	$-1.0 \times 10^{-7}$ <sup>3)</sup>	$-1.01(2) \times 10^{-7}$

272

273 **Table 1: Thermoelastic parameters for the "synthetic" Bridgmanite that were used to create ideal  $V/V_0(P,T)$  values together**  
 274 **with the corresponding values obtained from fitting a Murnaghan equation against the same  $V/V_0$  and T but P points**  
 275 **underestimated by 2 GPa. See text for more details. 1) *Shukla et al.* [2016]; 2) The 'synthetic'  $\delta$  is estimated by equating  $K(0)$**   
 276  **$+ dK/dT \times \Delta T = K_0 \times [1 + \alpha(P) \times \Delta(T)]^{-6}$  and solving for  $\delta$ . A  $dK/dT$  of  $\sim -0.01$  is assumed for this [*Shukla et al.*, 2016]],  $\alpha(P)$  is**  
 277 **assumed to be  $\sim 1.6 \times 10^{-7}$  for this (*Wang et al.* [1994]. 3) *Utsumi et al.* [1995]**

278



279

280 **Figure 2: Density versus pressure values for synthetic ideal  $(\text{Mg}_{0.88}\text{Fe}_{0.12})\text{SiO}_3$  bridgmanite at three different temperatures**  
 281 **with thermal pressure contributions corresponding to  $\alpha K_T dT$ ; and curves derived from thermoelastic properties as obtained**  
 282 **from a PVT data set that underestimates the thermal pressure by 2 GPa (“perceived P”). This difference can for example lead**  
 283 **to a wrong estimation of the Fe content of the phase considered (see text).**

284 We note also that the local character of the thermal pressure elevations that we observe (Figure 1)  
 285 suggests possible experimental avenues to measure difficult-to-characterize thermodynamic derivative  
 286 properties. In particular, the sample translation techniques that we have documented can be deployed  
 287 to measure the thermal pressure distributions within specially designed sample configurations. In  
 288 particular, as shown in the Supporting Information Section 3, for a sample suspended in a medium that  
 289 is of extremely high rigidity (e.g. diamond), the change in thermal pressure should reflect the  
 290 thermodynamic value of  $\alpha K_T dT$ . As such, if the thermal pressure can be assessed at two (or more)  
 291 different pressures at high temperatures, the thermodynamic relation of  $\alpha K_T$  (at  $P, T$ ) -  $\alpha K_T$  (at  $P_0, T$ )  
 292 being equal to the volumetric integral of  $(\delta_T - K'_T)d\ln V$  can be deployed to provide a direct measure  
 293 (assuming  $K'$  is constrained from equation of state measurements) of the Anderson-Grüneisen  
 294 parameter at extreme conditions (e.g. *Anderson and Isaak [1993]; Jackson and Rigden [1996]*). The  
 295 Anderson-Grüneisen parameter, which dictates the volume dependence of thermal expansion, is  
 296 difficult to constrain at high pressures: it is inferred to decrease with compression, but its pressure  
 297 dependence is not well known (*Anderson and Isaak [1993]*). In passing, we note that the other end-  
 298 member, measurement of thermal pressure within a medium with zero strength (and high gasket  
 299 strength), could also be deployed to constrain the pressure dependence of thermal pressure. In this  
 300 instance, an accurate characterization of both the volume of the heated sample and of the sample  
 301 chamber as a whole would be required to accurately interpret the sample-wide thermal pressure

302 increase. Hence, our present measurements demonstrate that, with appropriate experimental designs,  
303 accurate constraints on the pressure-dependence of the Anderson-Grüneisen parameter could be  
304 generated.

## 305 5 Conclusion:

306 We present the first quantitative experimental characterization of the pressure gradients caused  
307 by thermal pressures induced by temperature gradients in the laser-heated diamond anvil cell. The  
308 observed pressure increases correspond in magnitude to previously published theoretical and modeled  
309 values, and are also in accord with the thermodynamically expected value: the dominant parameter that  
310 governs the magnitude of thermal pressure is, unsurprisingly, the product of thermal expansion and the  
311 bulk modulus. Our results indicate that there is a nuanced effect on thermal pressure associated with  
312 material strength, thus showing that some diffusion of the stress field occurs within the samples. In  
313 particular, our results on AgI are both lower in their peak thermal pressure and have smaller spatial  
314 gradients of pressure with distance, which is consistent with AgI being weaker than olivine. Our simple  
315 modeling overestimates the thermal pressures accessed by olivine. We attribute this to the fact that the  
316 model provides an upper limit on the thermal pressure, combined with the fact that our X-ray probe is  
317 relatively large (10  $\mu\text{m}$ ) compared to the steepness of the pressure gradient (this is especially acute in  
318 olivine, where the observed pressure gradients are  $\sim 1 \text{ GPa}/10 \mu\text{m}$ ).

319 From an overarching perspective, our results clearly demonstrate that thermal pressures within  
320 laser-heated spots can be substantial and, even within relatively weak materials (AgI), remain localized  
321 around the laser-heated hot spot. As such, high-pressure/high-temperature measurements of  
322 (particularly) derivative parameters, such as thermal expansion at high pressures, likely require either  
323 multiple internal standards and/or a liquid medium to ensure that thermal expansions at extreme  
324 conditions are not underestimated. We also show that only a partial neglect of the thermal pressure can  
325 result in errors of the derived thermos-elastic properties that lead towards higher density at given P and  
326 T conditions. This in turns will cause significant errors on the correlation between density and  
327 mineralogy. Finally, our experimental design for measuring the spatial variations of thermal pressure  
328 could be deployed to quantitatively measure the pressure dependence of thermal pressure, and hence  
329 provide a direct constraint on the variation in the Anderson-Grüneisen parameter at deep planetary  
330 conditions.

## 331 Acknowledgments:

332 All raw data and analysis (diffraction images, temperature maps, pressure calculations, and density vs  
333 pressure analysis) are deposited in Dryad data repository (<https://doi.org/10.7941/D1F63W>).

334 X-ray diffraction experiments were performed at the Advanced Light Source (ALS) beamline 12.2.2. The  
335 ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences  
336 Division, of the US Department of Energy under Contract No. DE-AC03-76SF00098 at the Lawrence  
337 Berkeley National Laboratory and the University of California, Berkeley. Sample preparation benefitted  
338 from the ALS laser mill purchased by the Consortium for Materials Properties Research in Earth Sciences;

339 COMPRES supported this project under the NSF Cooperative Agreement EAR 16-49658. QW is supported  
340 by NSF EAR-1620423. EY was supported by a private fund (Yen-Zantua).

341 Discussions with Dion Heinz greatly improved this manuscript and are warmly acknowledged. A special  
342 thanks is owed to Howard Padmore who not only helped fund this project, but also acted as a mentor  
343 and source of inspiration.

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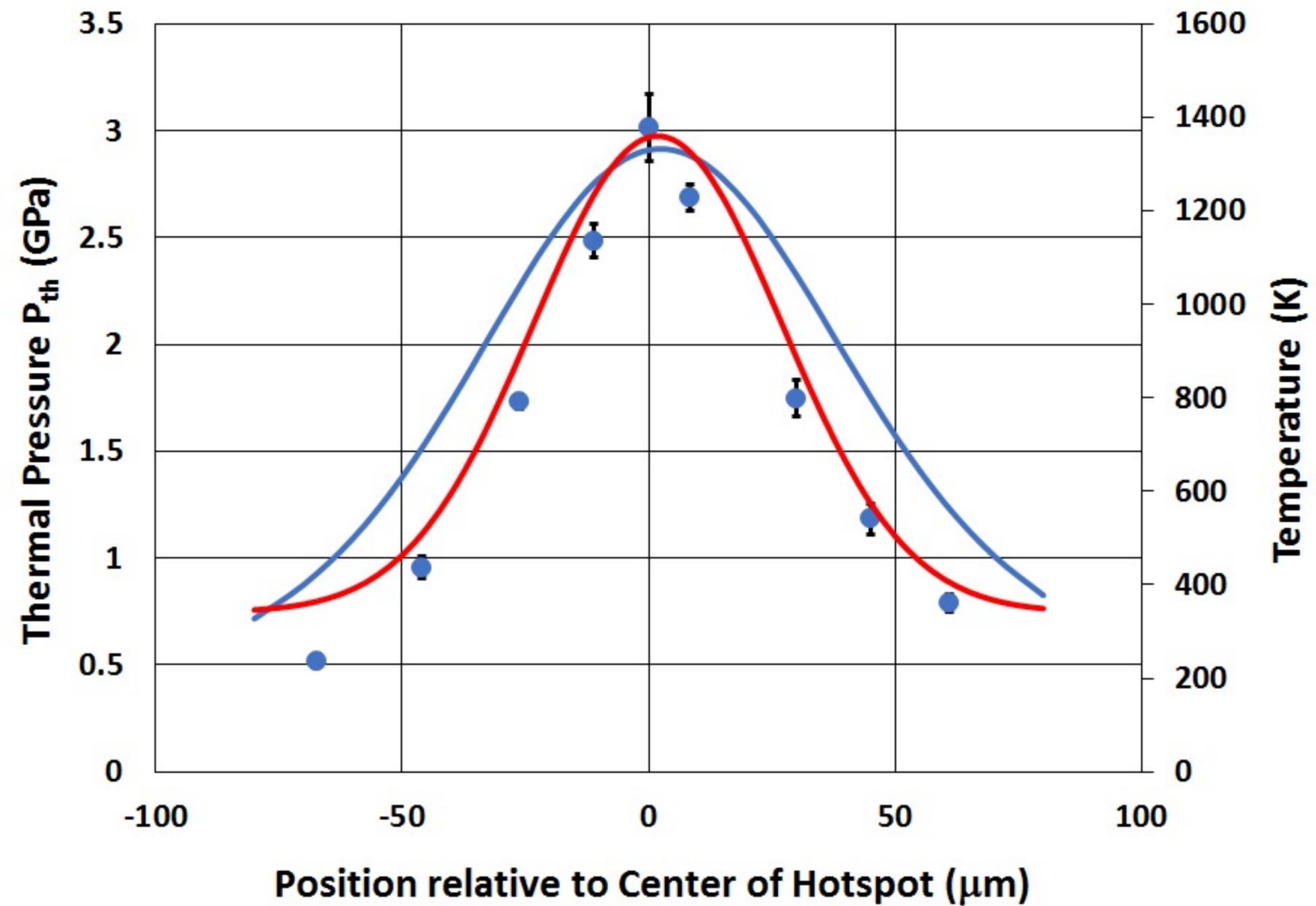
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Figure 1a.



**Figure 1b.**

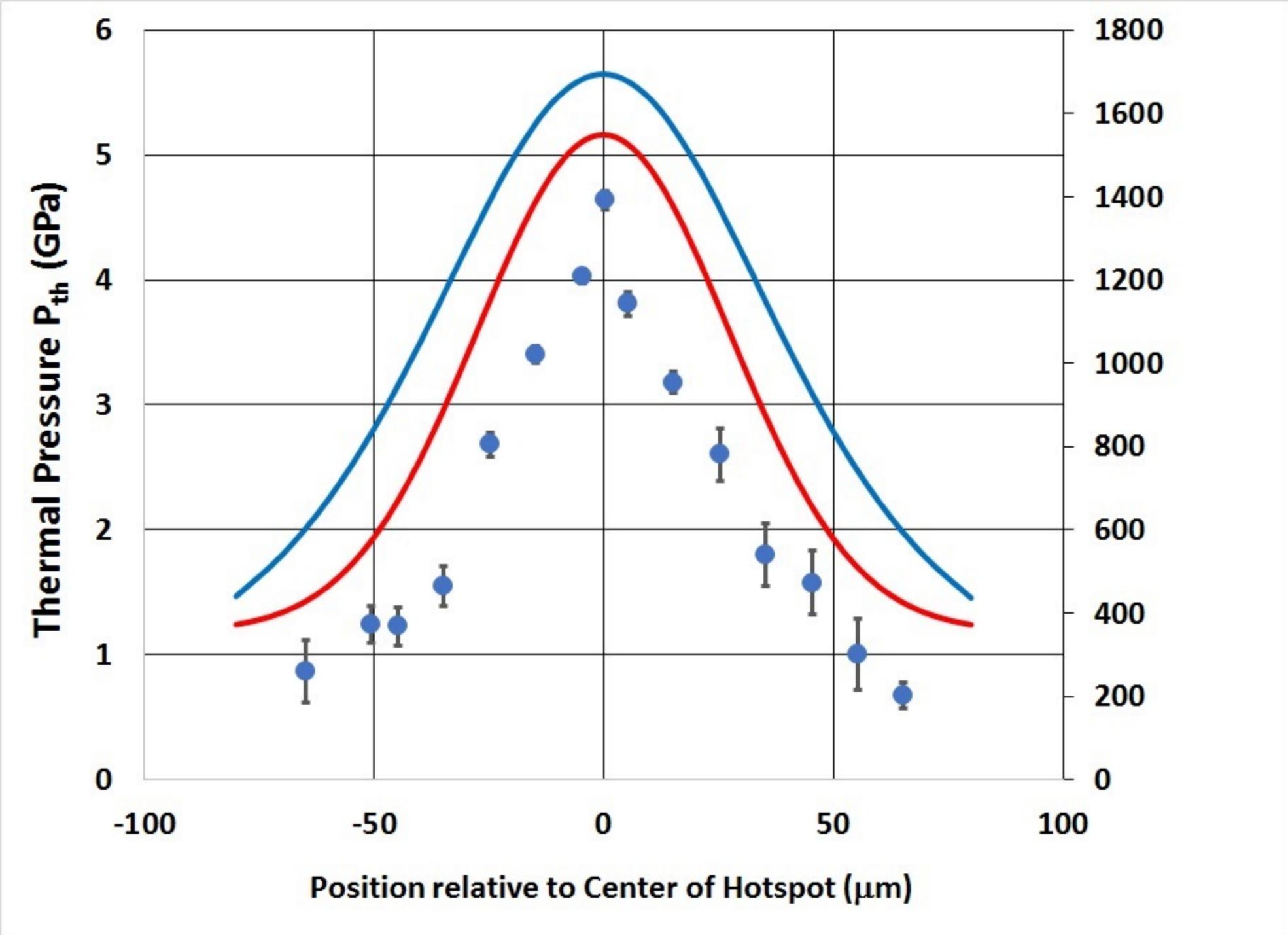


Figure 2.

