

Assessment of temperature gradients in multianvil assemblies using spinel layer growth kinetics

Wim van Westrenen

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015, USA

Now at Institut für Mineralogie und Petrographie, ETH Zürich, Sonneggstrasse 5, ETH Zentrum, CH 8092, Zürich, Switzerland (willem.vanwestrenen@erdw.ethz.ch)

James A. Van Orman

Geophysical Laboratory and Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road NW, Washington, DC 20015, USA

Now at Department of Geological Sciences, Case Western Reserve University, 112 AW Smith Building, Cleveland, Ohio 44106, USA (jav12@cwru.edu)

Heather Watson

Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180, USA (watsoh@rpi.edu)

Yingwei Fei

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015, USA (fei@gl.ciw.edu)

E. Bruce Watson

Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180, USA (watsoe@rpi.edu)

[1] We present an empirical equation to link the thickness of a MgAl₂O₄ spinel layer growing at the interface between MgO and Al₂O₃ multianvil high-pressure assembly pieces to pressure (*P*), temperature (*T*), and time (*t*), extending the recent study of *Watson et al.* [2002] to the pressure range 6–16 GPa and temperature range 1673–2273 K. For the spinel thickness ΔX we obtain

$$\Delta X(\mu m) = \sqrt{(5.3 \pm 0.3) \cdot 10^8 \cdot \exp\left(-\frac{(33200 \pm 2118) + (1424 \pm 75) \cdot P(\text{GPa})}{T(\text{K})}\right) \cdot t(\text{s})}.$$

This equation can be used to assess the thermal gradient in any multianvil assembly where MgO and Al_2O_3 filler pieces are in contact at *P-T* conditions within the MgAl₂O₄ spinel stability field. As an illustration, we show that the central hot spot, in which temperatures can be considered constant, is close to 1 mm long in a common octahedral multianvil assembly with 8 mm edge length and rhenium furnace, while it extends to 3 mm long in an octahedron with 18 mm edge length using a straight graphite heating element. In addition, we present the results of a spinel growth experiment performed at 2273 K and 15 GPa with ¹⁸O enriched MgO, which shows that oxygen is mobile at a length scale exceeding that of the spinel layer. This finding raises the possibility that under some circumstances growth of spinel (and of reaction-product layers in other oxide systems) might be accomplished by concurrent fluxes of oxygen and cations. This "mobile oxygen" model differs from the more conventional Mg-Al exchange model proposed by *Watson and Price*



[2002] for the lower-pressure experiments and might explain the observed differences in systematics between the high- and low-pressure data sets.

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1. Introduction

[2] One of the biggest limitations in solid-media high-pressure, high-temperature research stems from the fact that large thermal gradients are unavoidable in the large majority of experimental set-ups. Samples are generally contained in small (millimeter to centimeter scale) pressure media, which can be heated to temperatures that can exceed 2700 K at high pressure, while in direct contact with large volume (centimeter to meter scale) presses that remain essentially at room temperature. The omnipresence of thermal gradients makes it critical to obtain accurate measurements of the thermal structure of any high-pressure assembly, particularly of the dimensions of the central hot zone termed "hot spot" in which temperatures are constant. The size of this hot spot in turn provides constraints on the maximum attainable sample volume, considering most studies require experiments to be done at one constant temperature.

[3] One common way of studying the spatial distribution of temperatures in high-pressure assemblies is through comparison of run product compositions with pre-determined temperaturedependent phase equilibria. These types of experiments are often cumbersome, limited in attainable pressure-temperature range, and subject to kinetic problems.

[4] Recently, *Watson et al.* [2002] presented an alternative assembly thermometer, based upon the study of *Watson and Price* [2002] on the rate of MgAl₂O₄ spinel growth at the contact between

MgO (periclase) and Al₂O₃ (corundum), the two most widely used refractory filler materials in highpressure assemblies. *Watson et al.* [2002] derived an empirical equation for the thickness ΔX of the MgAl₂O₄ spinel layer as a function of pressure (*P*), temperature (*T*), and experimental duration (*t*). Their equation, based on 43 piston cylinder experiments at *P* up to 4 GPa and *T* up to 2250 K, can be inverted to calculate the temperature in different parts of high-pressure assemblies if *P*, *t* and ΔX are known.

[5] In this study, we use multianvil experiments to significantly extend the P-T range of this parameterization to 16 GPa and 2273 K, close to the maximum pressure stability of MgAl₂O₄ spinel [Akaogi et al., 1999]. As an illustration of the usefulness of our parameterization, we determine the hot spot size for two common octahedral multianvil assemblies. In addition, we present results of a spinel growth experiment at 15 GPa and 2273 K, performed with ¹⁸O-enriched MgO, which shows conclusively that oxygen is mobile on the timescales of our experiments. Watson and Price [2002] concluded from the lower P-T experiments that spinel growth kinetics was most likely controlled by interdiffusion of Mg and Al ions. Our oxygen diffusion data suggest that at the high Pand T of this study, this may not be the case.

2. Experimental and Analytical Methods

[6] We used 800 ton and 1500 ton Walker-style multianvil presses at the Geophysical Laboratory





Figure 1. High-pressure assemblies used in this study, and photomicrographs of typical run products. (a) 18/11 assembly used at 6 GPa, and overview of experiment M-683. Inset shows location of element maps in Figures 2a and 2b. (b) 8/3 assembly used at 13-16 GPa, and overview of experiment L-236, with inset showing position of axial spinel thickness profile shown in Figure 2c. (c) 10/5 assembly used at 10 GPa.

for experiments at 6-10 and 13-16 GPa respectively. Three common octahedral pressure assemblies were used (Figure 1). For the experiments at 6 GPa, octahedra were cast with an edge length of 18 mm using Ceramacast[©] 584 (Aremco Products Inc.). A cylindrical central hole with a diameter of 4.70 mm was lined with a straight (untapered) graphite furnace, with Mo leads at either end to

ensure good electrical contact. Concentric cylinders of MgO and Al_2O_3 (99% pure, Vesuvius McDanel) ceramic were packed tightly inside the heater (Figure 1a). The cast octahedra, including fins to serve as gaskets, were inserted in the center of eight 25.4 mm long Toshiba Grade F tungsten carbide cubes, with an 11 mm truncation edge length. No experiments were performed with this

assembly at P > 6 GPa because of graphite furnaces transforming into diamond at the high temperatures needed in this study.

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[7] For the 10-16 GPa experiments, Cr-doped MgO octahedra of 10 and 8 mm edge length (obtained from Japan Ceramic Engineering Company, Inc.) were used as a basis. A rhenium foil heater of thickness 0.064 mm was inserted in a LaCrO₃ (Figure 1b) or ZrO₂ (Figure 1c) insulating sleeve. The 10 GPa experiments consisted of an outer MgO sleeve encapsulating Al₂O₃ rods. For experiments at 13-16 GPa, either MgO powder (99.95% pure, Alfa Aesar) or an MgO densified rod was encapsulated in Al₂O₃ sleeves and end caps. In one experiment at 15 GPa (L-243) ¹⁸Oenriched MgO powder was used, to determine the mobility of oxygen through the growing spinel layer. Details on the synthesis of this powder can be found elsewhere [Van Orman et al., 2003]. Pyrophyllite gaskets were used to separate the Toshiba tungsten carbide cubes, which in this case had a 5 or 3 mm long truncated edge. Temperatures were measured using a W5%Re-W26%Re thermocouple, with wires of 0.01 inch thickness in the 18/11 and 10/5 assemblies, and 0.005 inch thickness in the 8/3 assembly. In all cases, thermocouple wires were inserted axially into the center of the assembly through 4-bore alumina rods. Pressure for the 18/11 assembly was calibrated at 1473 K using SiO₂ quartz-coesite, coesite-stishovite, Fe₂SiO₄ fayalite-spinel, and CaGeO₃ garnetperovskite transitions. For the 10/5 assembly, pressure was calibrated at high temperature using the quartz-coesite, $Mg_2SiO_4 \alpha \rightarrow \beta$, and $MgSiO_3$ pyroxene $\rightarrow \beta$ + stishovite transitions [*Bertka and* Fei, 1997]. High-pressure calibration for the 8/3 assembly was based on experimental brackets of $Mg_2SiO_4 \beta \rightarrow \gamma$ and $MgSiO_3$ ilmenite-perovskite transitions at 2023 K.

[8] Experiments were pressurized at room T, then heated at the target pressure, and terminated by cutting off the power to the furnaces. Because of the relatively small volumes involved, quench times are less than 2 s for all experiments. After the runs, assemblies were cut and polished to expose an axial section. Because the interfaces in most experiments were cylindrical, care had to be

Experiment	Assembly	P, GPa	Т, К	Time, s	Spinel Layer Thickness, µm
M-692	18/11	6	1673	86400	44.1
M-683	18/11	6	2123	7200	99
M-685	18/11	6	2173	3600	114
M-722	10/5	10	1673	172800	8
M-729	10/5	10	1773	7380	11
M-728	10/5	10	1873	50400	16
M-732	10/5	10	1873	86400	19
L-230	8/3	13	1973	50100	8.6
L-236	8/3	14	~ 2248	8400	13.7
L-243 ^a	8/3	15	2273	34200	23
L-265	8/3	16	2273	24360	19.2

 Table 1. Experimental Conditions and Measured

 Spinel Layer Thicknesses in Assembly Hot Spot

 $^{\rm a}{\rm Experiment}$ using $^{18}{\rm O}{\rm -enriched}$ MgO as starting material (see Table 2).

taken to expose truly planar sections. As in the previous study by *Watson et al.* [2002], assembly centers were identified through the presence of thermocouple junctions in the section.

[9] A JEOL 8900 electron probe was used to produce high-resolution X-ray maps of the interface region between MgO and Al₂O₃, and digitized images of these maps were used to determine spinel layer thicknesses. In addition, in selected experiments quantitative measurements of periclase, corundum, and spinel compositions were obtained under operating conditions of 15 kV, 15 nA, using a spot diameter of approximately 1 μ m. Oxygen isotope ratios in the run product of experiment L-243 were measured using a Cameca 6f ion microprobe at the Department of Terrestrial Magnetism. Analytical details are given by *Van Orman et al.* [2003].

[10] Experimental conditions, together with measured spinel layer thicknesses in the hot spot of the assemblies, are given in Table 1. Oxygen isotope analyses for experiment L-243 are given as a function of distance from the periclase-spinel boundary in Table 2.

3. Spinel Layer Thicknesses

[11] Figure 1 shows examples of experimental charges after cutting and polishing. Figures 2a and 2b show digitized high-resolution X-ray maps

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Relative position, ^a µm	$^{18}O/(^{18}O + ^{16}O)$	Phase
-83	0.229	Periclase
-78	0.229	Periclase
-70	0.229	Periclase
-66	0.228	Periclase
-59	0.221	Periclase
-44	0.190	Periclase
-38	0.166	Periclase
-30	0.141	Periclase
-26	0.140	Periclase
-8	0.091	Periclase
+7	0.085	Spinel
+13	0.083	Spinel
+16	0.081	Spinel
+41	0.073	Corundum

Table 2. Oxygen Isotope Measurements Across MgO-Spinel-Al2O3 Interface in Experiment L-243

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 a Spinel layer in this experiment is 23 μm wide. On the relative position scale layer extends from 0 to +23 $\mu m.$

for Mg and Al for one section of experiment M-683 (detailed in Figure 1a), with MgAl₂O₄ spinel growth evident along MgO-Al₂O₃ interfaces. As observed by *Watson et al.* [2002] contacts between spinel and adjoining phases are slightly irregular as all phases are polycrystalline, but spinel thicknesses in a given assembly region are consistent. As a result of temperature gradients, spinel layers do vary measurably in thickness as a function of capsule position: away from a central hot spot, in which thicknesses are near-constant, layers thin rapidly toward the ends of the pressure assemblies. This is illustrated for experiment L-236 in Figure 2c.

[12] Watson et al. [2002] show that at constant high pressure and temperature, spinel layer thickness in assembly hot spots shows a parabolic dependence on time, as observed in earlier 1 atm studies. This dependence points to a diffusion-controlled growth of spinel [Watson and Price, 2002]. Following Watson et al. [2002], derived from the original work by Tamman [1920], we define a reaction rate constant, $k = \Delta X^2/2t$, which has the unit of diffusivity. Watson and Price [2002] have shown that k varies log linearly with inverse temperature at pressures of 1–4 GPa. Figure 3 shows our new data are at least qualitatively consistent with lowerpressure work: for both the 6 and 10 GPa experiments, k decreases log linearly with 1/T, and at any given temperature, k decreases with increasing pressure.

[13] Watson et al. [2002] made several attempts at finding a relationship between ΔX , pressure *P*, temperature *T* and time *t*, to be used to determine temperature distributions in high-pressure assemblies. Their preferred global model, applicable in the calibration range 1–4 GPa, 1473–2273 K gives

$$\Delta X(\mu m) = \sqrt{8.58 \cdot 10^{11} \exp\left(-\frac{48865}{T(K)} - 2.08\sqrt{P(GPa)}\right)}t(s)$$
(1)

Figure 4 shows that equation (1) does a very good job at reproducing spinel layer thicknesses within the calibration range (squares in Figure 4). However, crosses in Figure 4 show that equation (1) does not predict spinel layer thicknesses in our multianvil experiments very well in all cases: ΔX at 6 GPa is underestimated by up to a factor of 2, while ΔX at 13–16 GPa is overestimated by up to a factor of 3.

[14] Unfortunately the number of experiments at high pressure is not large compared to the 43 data points used in deriving equation (1). Therefore attempts at refitting the new and published data simultaneously were biased toward lower-pressure results, and resulting agreement between measured and predicted ΔX at high pressures (P > 4 GPa) remained poor. Instead, we refitted the high-pressure data (Table 1) only. We found that for the high-pressure data, fits using the functional form of equation (1) were not significantly better than fits using the normal kinetic and thermodynamic functional form (i.e., with a pressure term in the numerator of the temperature term). We therefore preferred to use the latter form. Our best-fit equation to describe spinel layer growth between pressures of 6 and 16 GPa and temperatures between 1673 and 2273 K, with associated 1σ errors in the fit parameters, is

 $\Delta X(\mu m)$

$$= \sqrt{(5.3 \pm 0.3) \cdot 10^8 \cdot \exp\left(-\frac{(33200 \pm 2118) + (1424 \pm 75) \cdot P(\text{GPa})}{T(\text{K})}\right) \cdot t(\text{s})}$$
(2)



Figure 2. High-resolution element maps showing qualitative concentrations of (a) Mg and (b) Al in one area of experiment M-683 (see Figure 1a and Table 1 for details). Although some of the run product was plucked out during polishing, the U-shaped spinel layer is clearly visible, with Al_2O_3 on the inside and MgO on the outside. Note that spinel rim is slightly thicker on the right side of the U-shaped layer, indicating a small radial thermal gradient in this assembly. (c) Variation in spinel thickness along the axis of experiment L-236 (see Figure 1b for exact profile location).

Figure 4 shows the resulting good agreement between measured and calculated ΔX for our multianvil experiments.

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[15] As observed by *Watson and Price* [2002], MgO periclase near the interface with spinel contains appreciable amounts of Al at high temperatures. Figures 5a and 5b show complete Al diffusion profiles in experiment M-685, starting at the MgO-MgAl₂O₄ interface, with an Al₂O₃ concentration of up to 8 wt% right next to spinel. No other cations besides Mg and Al were observed in our microprobe analyses, so Al cations must be charge-balanced by defects in MgO. As shown in Figure 5b, the maximum Al content of MgO decreases away from assembly hot spots, i.e., with decreasing temperature. This is consistent with the data plotted in Figure 5c, which shows the maximum Al/(Al + Mg) content of MgO at assembly



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Figure 3. Reaction constant $k = \Delta X^2/2t$ (ΔX in µm, t in s) shows a log linear dependence on inverse temperature for experiments performed at 1 and 2.5 GPa in the piston cylinder (data from *Watson et al.* [2002] (W2002)) and 6–16 GPa in the multianvil press (this study). At constant T, k decreases as a function of pressure. Lines are least squares fits through isobaric data sets.

hot spots as a function of T and P. As was the case for the lower-pressure data of *Watson et al.* [2002], the maximum Al content of periclase tends to increase with increasing temperature for any given pressure. Figure 5c also shows that at constant temperature, the maximum Al content of MgO



Figure 4. Measured versus predicted spinel layer thicknesses. Predicted values obtained using equations (1) and (2). Note that equation (1), based on experiments done at 1-4 GPa, does not predict high-pressure (6–16 GPa) experimental results from this study very accurately.



Figure 5. (a) High-resolution element maps showing qualitatively concentrations of Mg and Al in MgO in hot spot of experiment M-685. Edge of spinel layer visible at top right edge of both maps. Note Al concentration decreasing away from the spinel-MgO contact. Inset shows approximate location of Al concentration profile in (b). (b) Concentration (symbols) of Al₂O₃ in MgO as a function of distance from the spinel-MgO interface in hot and cold parts of experiment M-685. (c) Al/(Al + Mg) in MgO adjacent to spinel in assembly hot spots as a function of temperature for experiments at 2.5 GPa (data from Watson and Price [2002]) and 6-16 GPa (This study). Line is exponential fit through 2.5 GPa data points. Note that for a given temperature, the alumina content of MgO tends to decrease with increasing pressure.

decreases significantly with increasing pressure. This observation was not made by *Watson and Price* [2002], probably because of the limited pressure range of their study.

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[16] The large majority (36 out of 43) of experiments reported by Watson et al. [2002] and Watson and Price [2002] were performed at T < 1873 K. It is conceivable that the generally higher Al contents in the MgO in our runs lead to a slightly quicker spinel formation reaction, which could explain part of the underestimation of ΔX by equation (1) for our hot 6 GPa runs. However, this would not explain the underestimation of ΔX for experiment M-692 (6 GPa, 1673 K), which contains very little Al in MgO. Additionally, equation (1)'s overestimation of ΔX for the highest-pressure runs could conceivably be caused by a general slowing down of spinel formation as the boundary of the spinel stability field is approached. Both these terms are implicitly incorporated in equation (2).

4. What Controls Spinel Growth Kinetics?

[17] The reaction between periclase and corundum has been extensively studied at high temperatures and low pressures (for a summary, see *Watson and Price* [2002]). Although spinel growth control by diffusion is generally accepted, the controlling diffusion processes are still unclear. As noted by *Watson and Price* [2002], most studies ascribe spinel growth control to lattice or grain boundary diffusion of Al, Mg, or both. *Watson and Price* [2002] themselves also attribute growth control to interdiffusion of Mg and Al. These studies assume, implicitly or explicitly, that oxygen is effectively immobile during spinel growth.

[18] Results of our 15 GPa, 2273 K experiment L-243 (Table 2), in which ¹⁸O-enriched MgO was used as a starting material, provide strong evidence for significant mobility of oxygen during spinel growth at these conditions (Figure 6). The substantially disturbed initial oxygen isotope profile shows that significant oxygen interdiffusion took place through the periclase, the growing spinel layer, and the corundum. The profile shown in Figure 6 is estimated to extend at least



Figure 6. Ion microprobe measurements of oxygen isotope ratios across the periclase-spinel-corundum interfaces in experiment L-243 (data taken from Table 2). Initial profile shown with dotted lines, extent of spinel layer denoted by gray field. Amount of oxygen that moved across the periclase-spinel interface during the experiment is proportional to the hatched area A. C1 and C2 are oxygen isotope ratios at the periclase-spinel and spinel-corundum interfaces respectively. See text for interpretation.

100 μ m into the corundum. This suggests that, at this high *P* and *T* at least, spinel growth may not be controlled by the movement of Mg and Al cations only, as suggested, among others, by *Watson and Price* [2002] for the lower pressure experiments. This could be an explanation for the fact that, as discussed above, spinel rim growth systematics for piston cylinder and multianvil experiments cannot be fitted to one single model.

[19] Based on the results shown in Table 2 and Figure 6, we calculated the diffusion coefficient for oxygen through the spinel layer. Although this is strictly speaking a moving boundary problem, we made a rough estimate by considering the spinel layer to be of fixed width, and assuming a steady state flux across the spinel layer. The total amount of oxygen transported from the periclase to the spinel and corundum layers is proportional to the cross-hatched area A in Figure 6. Assuming a steady state oxygen flux $J_{\rm O}$ across the spinel layer,

$$J_{\rm O} = \frac{A}{t} \approx 1.7 \cdot 10^{-10} \,\frac{\rm m}{\rm s}.\tag{3}$$



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Figure 7. Axial temperature distributions in two multianvil assemblies shown in Figure 1. (a) 18/11 assembly, (b) 8/3 assembly. Approximate length of hot spot shown by arrows.

Noting the near-linear variation of oxygen isotope ratios with relative position through the spinel layer,

$$D_{\rm O} = \frac{J_{\rm O} \cdot l}{(C_1 - C_2)} \approx 4.6 \cdot 10^{-13} \,\frac{\rm m^2}{\rm s},\tag{4}$$

with *l* equal to the thickness of the spinel layer (23 μ m, Table 1), and C_1 and C_2 the values of ${}^{18}\text{O}/({}^{18}\text{O} + {}^{16}\text{O})$ at the periclase-spinel and spinelcorundum interfaces respectively (Figure 6). Oxygen lattice diffusion under these conditions [*Reddy and Cooper*, 1981] is orders of magnitude slower than this estimated value of D_{O} , which suggests a substantial part of the calculated flux was transported along grain boundaries. The grain size *d* in experiment L-243 was around 10 μ m, and therefore the product of oxygen grain boundary diffusivity D_{gb} and grain boundary width δ ,

$$\delta \cdot D_{gb} = D_0 \cdot d \approx 4.6 \cdot 10^{-18} \frac{m^3}{s}.$$
 (5)

This value for $\delta \cdot D_{gb}$ is in good agreement with measured values in polycrystalline MgO at similar *P*-*T* conditions $(3.8 \cdot 10^{-8} \text{ m}^3 \text{s}^{-1} [Van Orman et al., 2003]).$

[20] Our estimated O diffusivity through spinel at 15 GPa and 2273 K can also be compared with Mg lattice diffusivity in spinel [Sheng et al., 1992]. Using the elastic model discussed by Van Orman et al. [2003], the activation volume for Mg diffusion in spinel, needed to extrapolate the 1 atmosphere data of Sheng et al. [1992] to a pressure of 15 GPa, was estimated at 5.6 $\text{cm}^3\text{mol}^{-1}$. This leads to a predicted Mg lattice diffusivity in spinel at 15 GPa and 2273 K of $1.3 \cdot 10^{-13} \text{ m}^3 \text{s}^{-1}$, which is very close to our estimated O diffusivity at the same P-T conditions. No diffusion data exist for Al. However, results from experiments in the piston cylinder using Pt foil markers to delineate the position of the MgO-Al₂O₃ interface at the start of experiments [Watson and Price, 2002], generally seem to point toward growth of spinel into corundum. Taken at face value this suggests that Al is slower than both Mg and O, and that therefore either Mg or O could be rate-limiting, depending on which ion moves slower through the spinel layer at these P and T conditions.

5. Application: Thermal Gradients in Multianvil Assemblies

[21] Our equation (2), which as discussed above deviates slightly from the *Watson et al.* [2002] lower-pressure parameterization, can be used to assess thermal gradients in multianvil assemblies over the *P* range 6–16 GPa and *T* range 1673–2273 K. Given *P*, *t*, and ΔX (through measurements as shown in Figure 2), equation (2) can be inverted to extract *T* for any assembly in which MgO and Al₂O₃ are used adjacent to each other. As an illustration of this, axial *T* distributions are shown in Figure 7 for the 18/11 and 8/3 assemblies used in this study (as depicted in Figure 1). At 6 GPa and

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2123 K, axial *T* in the 18/11 assembly with straight graphite heater remains constant (within 20 K) over a length of approximately 3 mm (Figure 7a), virtually independent of desired experimental *T*. The radial gradient (not shown in Figure 7a, but discussed in the caption of Figure 2) is small (on the order of 25 K/mm distance from the assembly center). At 13–16 GPa in the 8/3 assembly with a rhenium foil heater, the hot spot is around 0.8–1 mm in length (Figure 7b). *T* gradients outside hot spots are large: just outside the hot spot, *T* decreases by around 150 K within around 0.2 mm.

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[22] Equations such as equations (1) and (2) should find wide applicability in experimental petrology. They provide a simple means of determining the temperature distribution in high-pressure assemblies, and a means of quantitatively testing new experimental assembly designs aimed at enlarging hot spots (e.g., by using stepped furnaces).

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