A critical evaluation of pressure scales at high temperatures by in situ X-ray diffraction measurements

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Abstract

We conducted multi-anvil experiments at simultaneous high pressures and temperatures using multiple internal pressure standards including Au, Pt, MgO, W, Mo, Pd, and Ag. Extensive synchrotron X-ray diffraction data for Au, Pt, and MgO were collected at pressures up to 28 GPa and temperatures between 300 and 2173 K. We compare pressures calculated from different pressure scales and demonstrate large discrepancies in pressure determination using different pressure standards or different thermal equations of state for the same standard. The comparison allows us to quantitatively determine the differences in pressure using different pressure scales in the high P–T experiments. Using the MgO scale of [J. Geophys. Res. 106 (2001) 515] as a reference pressure scale, new Au and Pt scales are presented that are consistent with the MgO scale. We further examined the validity of the assumption of constant q value (volume dependence of the Grüneisen parameter in the Mie–Grüneisen relation) for the calculations of thermal pressures, and show that an expression of q as a function of temperature and pressure may be necessary to best fit the simultaneous high P–T data.
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1. Introduction

A correct pressure scale is fundamentally important for interpreting geophysical observations using laboratory experimental data obtained at high pressure and temperature. It also allows us to make comparisons of high-pressure results produced in different laboratories using different experimental and analytical

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techniques. Metals such as Au, Pt, W, Mo, Pd, Ag, and Cu, whose equations of state are established based on shock compression experiments and thermodynamic data, are commonly used as pressure standards in high-pressure experiments. Commonly used non-metal pressure standards include MgO and NaCl. At room temperature, the ruby fluorescence pressure gauge is extensively used in diamond-anvil experiments. The ruby gauge was calibrated by simultaneously measuring the shift of ruby R_1 luminescent line and specific volume of metal standards (Cu, Mo, Pd, and Ag) as a function of pressure. The established calibration curve based on equations of state of metal standards (Mao et al., 1986) has proven to be accurate, confirmed by direct measurements of pressure by combining Brillouin scattering and X-ray diffraction techniques (Zha et al., 2000).

Accurate determination of pressure at high temperature is more difficult because of large uncertainty in calculating the thermal pressure. Gold (Au) has been extensively used as an internal pressure standard in high-pressure and high-temperature experiments. However, there are at least four different thermal equations of state of gold that predict significantly different pressures at high temperature for a measured specific volume (Jamieson et al., 1982; Heinz and Jeanloz, 1984; Anderson et al., 1989; Shim et al., 2002). The difference in calculated pressures can be as large as 2.5 GPa at 25 GPa and 2000 K (e.g., Hirose et al., 2001a,b; Ono et al., 2001; Hirose, 2002).

Another common internal pressure standard is MgO whose thermal equation of state has been studied extensively by shock and static compression experiments (e.g., Jamieson et al., 1982; Duffy and Ahrens, 1995; Utsumi et al., 1998a; Fei, 1999; Hama and Suito, 1999; Dewaele et al., 2000; Speziale et al., 2001) and by theoretical calculations (e.g., Inbar and Cohen, 1995; Karki et al., 1999; Matsui et al., 2000). At 25 GPa and 2000 K, the MgO pressure scale proposed in the early study of Jamieson et al. (1982) yields a pressure about 2 GPa below the recent scale proposed by Speziale et al. (2001). The thermal equation of state for MgO proposed by Matsui et al. (2000) is in general agreement with the results of Speziale et al. (2001) over a wide pressure and temperature range. It yields pressures about 0.5 GPa lower than those of Speziale et al. (2001) at pressure and temperature conditions near the 660 km seismic discontinuity.

Fig. 1 illustrates the discrepancy in pressure determination using different thermal equations of state of Au and MgO based on the same X-ray diffraction data. Such a large discrepancy could lead to serious geophysical consequence in understanding the nature of the 660 km seismic discontinuity in the Earth's mantle.

Decker's NaCl pressure scale (Decker, 1971) is widely used in synchrotron based multi-anvil experiments prior to 1998, when pressure generation was limited to less than 20 GPa. Brown (1999) recently revised the pressure scale and found pressure differences at high temperatures (>700 K) generally below 0.3 GPa.

The Pt pressure scales proposed by different authors (Jamieson et al., 1982; Holmes et al., 1989) are in general agreement. The differences in pressure at high temperatures are less than 0.5 GPa. However, these scales were developed based on shock wave data only, and have not been critically evaluated by comparing static high P–T data.

Establishment of a reliable pressure scale is severely hindered by lack of consensus within one pressure standard, regarding the thermal equation of state. The differences are largely due to reliance by some on shock wave data and by others on independently derived thermodynamic parameters. The equations of state for Au by Jamieson et al. (1982) and Anderson et al. (1989) show two end-member cases. Jamieson et al. (1982) relied on the shock wave data alone for the development of the Au scale, whereas Anderson et al. (1989) relied heavily on thermodynamic parameters consistent with high-temperature elasticity measurements at ambient pressure.

The discrepancies within each pressure standard make consistency between different pressure standards at high temperatures even more problematic. In some cases, the calculated pressures based on different standards could differ as much as 4 GPa (Fig. 1). To address these issues, we performed high P–T experiments using a multi-anvil apparatus installed at the SPring-8 synchrotron beamline. X-ray diffraction data for multiple internal pressure standards (Au, Pt, MgO, W, Mo, Pd, Ag) were obtained under simultaneous high P–T conditions up to 28 GPa and 2173 K. These data were used to evaluate pressure scales based on the existing equations of state of Au, Pt, MgO, W, Mo, Pd, and Ag. A set of equations of state is proposed to produce mutually consistent
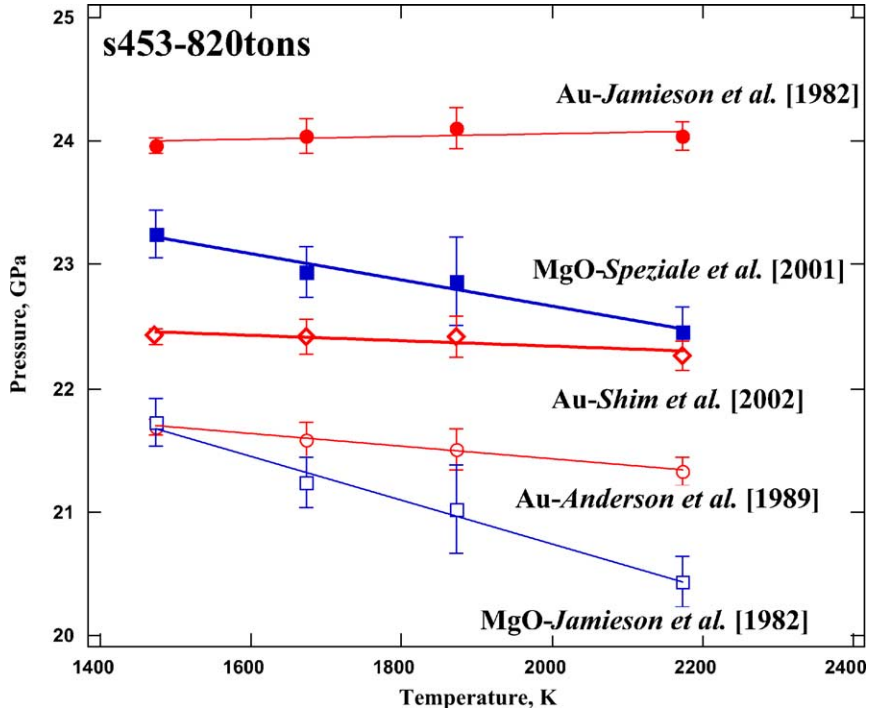
Fig. 1. Calculated pressures using MgO and Au pressure scales at high temperatures. Solid circles, open diamonds, and open circles represent pressures calculated from Au scales by Jamieson et al. (1982), Shim et al. (2002), and Anderson et al. (1989), respectively. Solid and open squares represent pressure from MgO scales by Speziale et al. (2001) and Jamieson et al. (1982), respectively.

results using different internal pressure standards at high pressures and temperatures.

2. Experimental procedures

The experiments were conducted at the BL04B1 high-pressure and high-temperature beam line in the SPring-8 synchrotron facility (Japan). A 1500 t hydraulic press with an MA8 double-stage system was used to generate pressures. The second-stage assembly consists of eight corner-truncated tungsten carbide (WC) cubes that form an octahedral cavity for the cell assembly. The synchrotron X-ray is accessed through the gap between the WC cubes. A detailed description of the facility was given by Utsumi et al. (1998b). The cell assembly used in this study is similar to the 8/3 (octahedron edge length/truncated edge length) assembly described by Bertka and Fei (1997). It contains a cylindrical Re heater with a wall thickness of

25 μm and a fitted $LaCrO_3$ sleeve outside the heater as thermal insulator. Along the X-ray path, $LaCrO_3$ was replaced with either MgO or Al_2O_3 to maximize the X-ray flux through the sample chamber. Sample temperature was measured with an axially introduced W5%Re–W26%Re (Type C) thermocouple. Reported temperatures were not corrected for the effect of pressure on emf. The selected pressure standards were placed next to the contact point of the thermocouple wires. Fig. 2 shows a back-scattered electron image of the sample chamber. The sample chamber was divided into two compartments separated by MgO powder. Each compartment was loaded with one metal standard mixed with powdered MgO. The temperature gradient in this assembly is about 30 °C/500 μm (Bertka and Fei, 1997; van Westrenen et al., 2003). We limited the total length of the sample chamber to about 250 μm to avoid a large temperature gradient.

The internal pressure standards used in this study include Au, Pt, Pd, Mo, W, Ag, and MgO. All metal
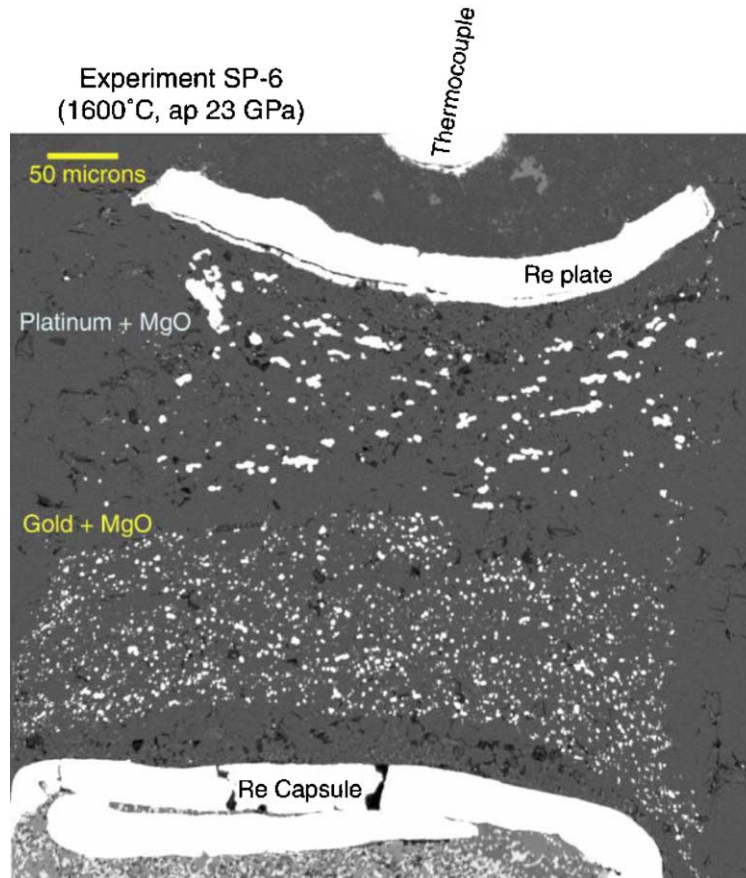
Fig. 2. A representative back-scattered electron image of the sample chamber quenched from 23 GPa and 1873 K. The sample chamber contains multiple internal pressure standards, Au, Pt, and MgO.

standards were mixed with ultra pure MgO powder to minimize re-crystallization of metal standards at high temperature. The weight ratio of MgO to metal is about 4:1. The mixtures were loaded into a MgO capsule. In each experiment, a Au–MgO mixture was loaded into one of the two sample compartments and another metal–MgO mixture occupies the other compartment. The two compartments were separated by MgO powder to avoid metal alloying. Extensive X-ray diffraction data on Au, MgO, and Pt were collected under the same P–T conditions.

An energy-dispersive diffraction technique was used for unit-cell volume determination, using polychromatic (white) synchrotron radiation. The diffraction data were collected with a single-element (Ge) solid-state detector, at a fixed 2θ angle. The energy-channel number relationship is determined by measuring the energies of well-determined X-ray emission lines (Kα and Kβ) of Cu, Mo, Ag, Ta, Pt, Au, Pb, Ba, ^{109}Cd, ^{152}Eu, and ^{57}Co. The 2θ angle is calibrated by measuring the energies of diffraction peaks, corresponding to the known interplanar spacings $d_{h\,k\,l}$, of solids, such as gold and platinum, at ambient conditions. Typical beam size is $50\,\mu\mathrm{m} \times 100\,\mu\mathrm{m}$. Typical time for collecting a diffraction pattern is about 300 s.

3. Experimental results

Over 60 X-ray diffraction data points were collected at pressures up to 28 GPa and temperatures ranging from 300 to 2173 K. Because all pressure standards

Table 1
Measured unit cell parameters of MgO and Au at high pressures and temperatures

Run no.	T (K)	a_{MgO} (Å)	P_{MgO} (GPa)[a]	a_{Au} (Å)	P_{Au} (GPa)[b]	P_{Au} (GPa)[c]	P_{Au} (GPa)[d]
s456003	1273	4.1337(10)	16.14(15)	4.0152(4)	15.33(6)	15.76	15.86
s701014	1473	4.2011(10)	8.64(11)	4.0779(3)	8.45(4)	8.46	8.46
s456004	1473	4.1490(7)	15.28(10)	4.0281(9)	14.78(13)	15.22	15.32
s454003	1473	4.0991(11)	22.88(18)	3.9861(17)	21.30(30)	22.01	22.18
s453001	1473	4.0968(12)	23.25(19)	3.9838(4)	21.69(7)	22.42	22.61
s457002	1473	4.0963(3)	23.34(7)	3.9799(2)	22.36(4)	23.11	23.31
s451011	1473	4.0889(8)	24.58(13)	3.9743(4)	23.36(7)	24.14	24.33
s693017	1673	4.1235(1)	20.36(2)	4.0036(10)	19.73(16)	20.48	20.65
s453003	1673	4.1071(13)	22.94(20)	3.9920(8)	21.59(14)	22.42	22.62
s454006	1673	4.1046(11)	23.34(17)	3.9911(8)	21.74(13)	22.58	22.77
s460005	1673	4.1041(18)	23.43(25)	3.9902(12)	21.89(20)	22.73	22.93
s695007	1673	4.0972(9)	24.56(15)	3.9823(7)	23.22(13)	24.11	24.33
s456005	1873	4.1674(1)	15.45(2)	4.0513(6)	14.41(8)	14.77	14.84
s693019	1873	4.1299(4)	20.74(6)	4.0114(10)	19.85(16)	20.65	20.83
s455007	1873	4.1208(15)	22.13(22)	4.0050(3)	20.83(5)	21.68	21.87
s457010	1873	4.1190(38)	22.41(59)	4.0013(9)	21.39(15)	22.29	22.49
s696009	1873	4.1174(10)	22.66(15)	4.0044(15)	20.91(23)	21.78	21.97
s454008	1873	4.1164(7)	22.82(11)	4.0031(1)	21.11(2)	21.99	22.19
s453004	1873	4.1161(24)	22.87(36)	4.0005(10)	21.51(16)	22.42	22.62
s451013	1873	4.0995(27)	25.56(43)	3.9830(6)	24.35(10)	25.42	25.67
s454009	2023	4.1244(6)	22.60(9)	4.0101(14)	21.03(22)	21.93	22.13
s700010	2023	4.1218(10)	23.00(15)	4.0058(22)	21.68(34)	22.63	22.83
s693021	2073	4.1411(5)	20.43(7)	4.0211(10)	19.77(16)	20.57	20.74
s459002	2173	4.1380(20)	21.56(28)	4.0177(6)	20.91(9)	21.81	22.00
s453005	2173	4.1320(15)	22.46(21)	4.0148(7)	21.33(11)	22.26	22.46
s694007	2173	4.1296(26)	22.82(37)	4.0138(8)	21.47(13)	22.42	22.62

$a_0 = 4.2118(5)$ for MgO. $a_0 = 4.0786(2)$ for Au.

[a] Pressures were calculated using the MgO scale of Speziale et al. (2001).
[b] Pressures were calculated using the Au scale of Anderson et al. (1989).
[c] Pressures were calculated using the Au scale of Shim et al. (2002).
[d] Pressures were calculated using the Au scale of this study.

are of cubic symmetry, the diffraction patterns are relatively simple with well-resolved diffraction peaks. Tables 1 and 2 list experimental conditions, measured unit cell parameters of internal pressure standards, and calculated pressures. The unit cell parameters for MgO, Au, and Pt were derived from at least three observed diffraction lines. Typical uncertainty for unit cell parameter measurements is about 0.0015 Å (cf. Tables 1 and 2). The calculated pressures based on Au as the internal standard vary widely, depending on the choice of Au pressure scales. The differences are illustrated in Fig. 1 and also discussed in recent literature (e.g., Hirose et al., 2001a,b; Ono et al., 2001; Hirose, 2002; Shim et al., 2002; Matsui and Nishiyama, 2002; Fei et al., 2004). The emphasis of this study is to compare different internal standards

and quantitatively determine the differences in calculated pressures using the different standards. We have obtained extensive data for Au, MgO, and Pt over a wide pressure and temperature range. These data allow us to evaluate the differences and develop equations of state that produce mutually consistent results in pressure determination at high temperatures. Limited data were also obtained for W, Mo, Pd, and Ag.

3.1. MgO–Au

For the experiments in which both MgO and Au were used as the internal standards, we calculated the pressures using the existing equations of state for MgO and Au. Fig. 1 shows the calculated pressures as temperature increased from 1473 to 2173 K in one

Table 2
Measured unit cell parameters of Au and Pt at high pressures and temperatures

Run no.	T (K)	a_{Au} (Å)	P_{Au} (GPa)[a]	P_{Au} (GPa)[b]	a_{Pt} (Å)	P_{Pt} (GPa)[c]	P_{Pt} (GPa)[d]
s424056/7	300	4.0502(16)	3.70(23)	3.70	3.9065(9)	3.58(20)	3.63
s424054/5	300	4.0309(7)	6.48(11)	6.45	3.8962(6)	5.90(14)	5.97
s424052/3	300	4.0015(16)	11.17(28)	11.04	3.8757(8)	10.85(20)	10.92
s424050/1	300	3.9842(15)	14.19(27)	14.00	3.8646(5)	13.73(13)	13.77
s424048/9	300	3.9713(12)	16.60(23)	16.33	3.8541(13)	16.59(36)	16.58
s424046/7	300	3.9571(6)	19.39(12)	19.03	3.8445(11)	19.32(31)	19.24
s424042/3	300	3.9471(9)	21.46(18)	21.02	3.8370(4)	21.54(12)	21.39
s376004	1473	4.0390(8)	13.26(11)	13.70	3.9022(5)	12.68(10)	13.37
s377002	1473	4.0122(9)	17.10(14)	17.79	3.8866(8)	16.31(19)	17.06
s381006	1473	3.9988(10)	19.19(15)	20.00	3.8743(10)	19.35(25)	20.13
s379003	1473	3.9837(5)	21.71(9)	22.62	3.8632(15)	22.25(40)	23.03
s380008	1473	3.9769(7)	22.90(13)	23.85	3.8616(11)	22.68(30)	23.46
s383004	1473	3.9539(3)	27.17(5)	28.24	3.8437(1)	27.70(3)	28.43
s375014	1673	4.0552(8)	12.55(10)	12.86	3.9104(16)	12.26(34)	13.01
s377003	1673	4.0236(10)	16.75(15)	17.45	3.8909(11)	16.67(27)	17.53
s381007	1673	4.0107(5)	18.64(7)	19.49	3.8833(10)	18.50(25)	19.39
s378006	1673	4.0005(12)	20.22(18)	21.17	3.8741(8)	20.79(21)	21.70
s379005	1673	3.9940(7)	21.25(11)	22.27	3.8722(20)	21.28(51)	22.19
s380009	1673	3.9879(6)	22.26(11)	23.34	3.8695(13)	21.98(32)	22.89
s383005	1673	3.9634(10)	26.58(18)	27.85	3.8532(9)	26.38(25)	27.28
s376012	1873	4.0684(10)	12.38(12)	12.54	3.9168(13)	12.28(26)	13.10
s376013	1873	4.0683(5)	12.38(6)	12.55	3.9156(10)	12.54(20)	13.36
s375016	1873	4.0657(9)	12.69(11)	12.89	3.9174(9)	12.16(18)	12.96
s376006/7	1873	4.0635(6)	12.94(7)	13.18	3.9116(12)	13.39(24)	14.24
s382009	1873	4.0575(6)	13.65(7)	13.99	3.9100(20)	13.73(43)	14.60
s382006/7	1873	4.0546(7)	14.00(9)	14.38	3.9098(11)	13.78(24)	14.64
s377007	1873	4.0373(9)	16.21(12)	16.84	3.8992(23)	16.13(53)	17.07
s377005	1873	4.0370(6)	16.25(8)	16.88	3.8983(6)	16.34(13)	17.28
s377006	1873	4.0368(11)	16.28(15)	16.91	3.8989(28)	16.20(66)	17.14
s377004	1873	4.0348(3)	16.54(4)	17.21	3.8998(6)	16.00(13)	16.93
s381016	1873	4.0213(1)	18.41(1)	19.26	3.8887(25)	18.58(60)	19.57
s378008	1873	4.0138(11)	19.50(16)	20.44	3.8830(10)	19.96(25)	20.98
s378010	1873	4.0138(9)	19.50(13)	20.44	3.8825(2)	20.08(5)	21.10
s378011	1873	4.0137(7)	19.48(10)	20.46	3.8828(12)	20.01(29)	21.03
s379009	1873	4.0056(14)	20.73(21)	21.77	3.8803(5)	20.62(12)	21.65
s379007	1873	4.0047(4)	20.86(7)	21.92	3.8821(18)	20.18(44)	21.20
s379011	1873	4.0042(10)	20.95(16)	22.01	3.8781(17)	21.17(42)	22.20
s379018	1873	4.0040(19)	20.98(29)	22.04	3.8770(1)	21.45(3)	22.48
s380018/9	1873	3.9989(7)	21.76(11)	22.89	3.8750(13)	21.95(32)	22.99
s380012/3	1873	3.9969(6)	22.08(10)	23.23	3.8756(7)	21.80(17)	22.84
s380010	1873	3.9960(4)	22.23(7)	23.39	3.8759(8)	21.72(21)	22.76
s383010	1873	3.9721(10)	26.23(19)	27.66	3.8600(7)	25.89(19)	26.95

$a_0 = 3.9231(5)$ for Pt. $a_0 = 4.0786(2)$ for Au.

[a] Pressures were calculated using the Au scale of Anderson et al. (1989).
[b] Pressures were calculated using the Au scale of this study.
[c] Pressures were calculated using the Pt scale of Holmes et al. (1989).
[d] Pressures were calculated using the Pt scale of this study.

experiment at constant load oil pressure. The MgO scale of Jamieson et al. (1982) predicts the lowest pressures over this temperature range, whereas the Au scale of Jamieson et al. (1982) gives the highest

pressures. The pressures calculated from the MgO scale of Speziale et al. (2001) are about 1.5 GPa higher than those from the Au scale of Anderson et al. (1989). Matsui and Nishiyama (2002) reported similar

discrepancy between the Au and MgO scales. The difference in the calculated pressures between the MgO scale of Speziale et al. (2001) and the revised Au scale of Shim et al. (2002) is relatively small (<0.5 GPa) at 25 GPa and 1873 K.

The MgO scale of Speziale et al. (2001) was developed by taking all available experimental data (static and shock wave) into account. The model with variable q parameter (logarithmic volume derivative of the Grüneisen parameter) can reproduce the experimental data over a wide pressure and temperature range. The proposed thermal equation of state is also in general agreement with results from molecular dynamics simulation (Matsui et al., 2000). The first primary pressure scale (extended to ultra-high pressure) at room temperature was established based on simultaneous measurements of elasticity and volume of MgO at high pressure (Zha et al., 2000). At the present time, we are lacking a practical pressure scale at high temperature that can be utilized to compare high P–T data collected by different laboratories. We are in favor of using the MgO scale of Speziale et al. (2001) as the pressure scale for consistency and inter-laboratory comparison. Of course, the MgO scale of Speziale et al. (2001) needs to be further verified by redundant equation-of-state measurements (e.g., simultaneous X-ray diffraction and acoustic measurements).

Using the MgO scale of Speziale et al. (2001) as a reference, we plotted our new compression data of Au over the temperature range of 1473–2173 K (Fig. 3). Shim et al. (2002) used the hydrostatic compression data at room temperature (Takemura, 2001) and shock wave Hugoniot data as constraints to derive the thermal equation of state for Au. Their equation of state misfits our data by about 0.5 GPa. We can fit our data by adjusting the q value. The best-fitted q values are 0.15, 0.27, 0.41, and 0.81 for the data at 1473, 1673, 1873, and 2127 K, respectively, assuming that all the other parameters are the same as those of Shim et al. (2002). The q value of 1.0 appears to fit best to the Hugoniot data (Shim et al., 2002). Our data indicate a q value of less than 1.0 with some temperature dependence. Within the uncertainties of the experimental data, a q value of 0.7 (±0.3) gave reasonable representation of both static and shock wave data.
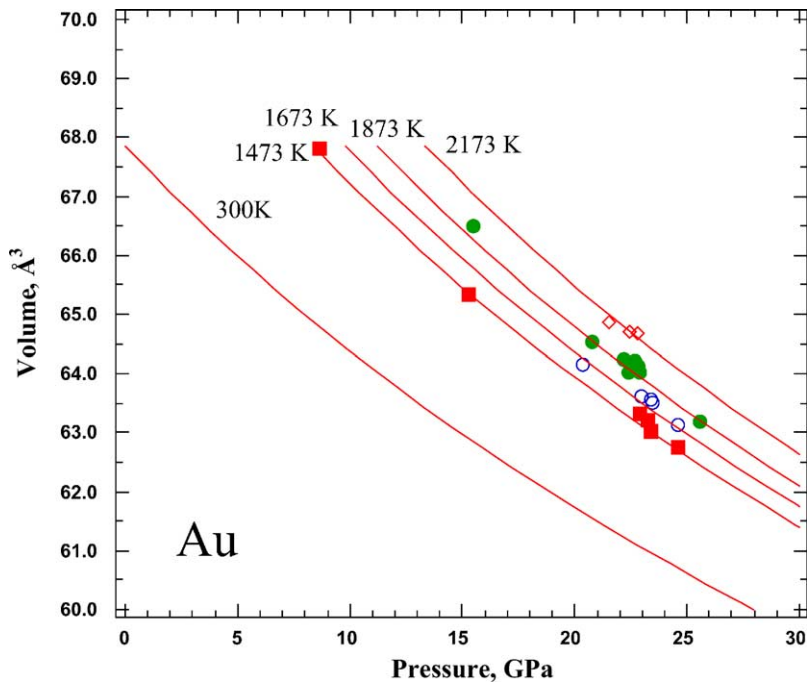

Fig. 3. Calculated isotherms for Au at 300, 1473, 1673, 1873, and 2173 K. Solid squares, open circles, solid circles, and open diamonds represents experimental data collected at 1473, 1673, 1873, and 2173 K, respectively.

3.2. Au–Pt

We designed experiments to compare pressure determination using Au and Pt as the internal standards. There are two proposed thermal equations of state for Pt (Jamieson et al., 1982; Holmes et al., 1989). Both were derived from shock wave data, but Jamieson et al. (1982) gave consistently lower pressures. For example, the difference in the calculated pressures between the two studies is about 0.5 GPa at 25 GPa and 2273 K. All discussions in this paper regarding Pt will be based on the equation proposed by Holmes et al. (1989).

Before we evaluate the Pt pressure scale at high temperature, it is important to examine the bulk modulus of Pt at room temperature. Fig. 4 shows our compression data of Pt at 300 K. These data were collected during decompression at room temperature, after the sample was annealed at 227 K and 25 GPa. A least-squares fit to the hkl d-spacings indicates no measurable deviatoric stress. The pressures were calculated using the equation of state of Au derived from the hydrostatic compression data at room temperature (Takemura, 2001). A least-squares fit to the compression data of Pt yielded a 300 K isothermal bulk modulus $K_{OT} = 290 \pm 10$ GPa and its pressure

derivative $K'_{OT} = 2.7 \pm 0.9$. However, the compression range is too small to give a reliable K'_{OT} value. Other studies indicated the K'_{OT} value close to 5. Simultaneously fitting the 300 K and high-T data yielded a higher value of $K'_{OT} = 4.8$ with bulk modulus $K_{OT} = 273 \pm 3$ GPa (see below).

Because of the possible effect of deviatoric stress at low temperature, we collected X-ray diffraction data of Au and Pt only at temperatures above 1473 K. The maximum pressure of this study is about 28 GPa. The Pt scale of Holmes et al. (1989) and the Au scale of Anderson et al. (1989) predicted similar pressures at temperatures between 1473 and 1873 K. As discussed above, the Au scale of Anderson et al. (1989) gives lower pressures than the revised Au scale of Shim et al. (2002) over the P–T range of this study. We further refined the Au scale of Shim et al. (2002) to produce mutually consistent pressures with the MgO scale of Speziale et al. (2001). In order to establish a Pt scale that is consistent with our Au scale as well as the MgO scale of Speziale et al. (2001), we re-determined the thermal parameters for the equation of state of Pt by fitting to the compression data at 300, 1473, 1673, and 1873 K. The optimized parameters are $K_{OT} = 273$ GPa, $K'_{OT} = 4.8$, $\theta_0 = 230$ K,
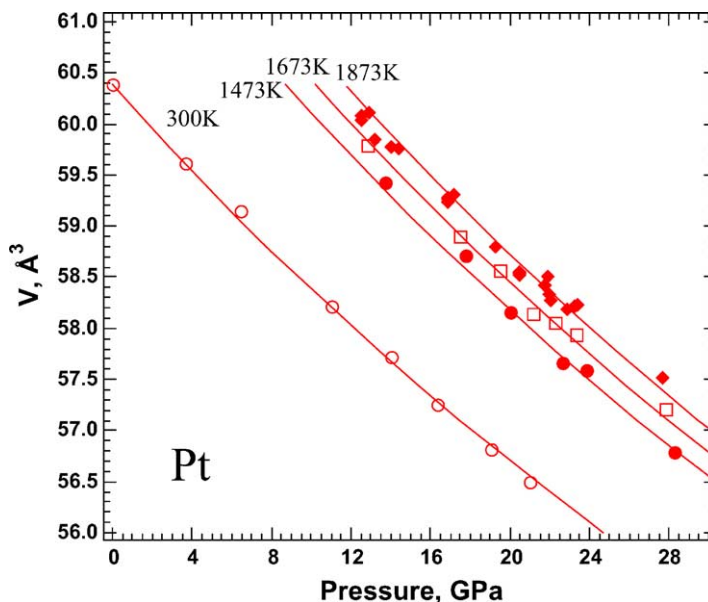

Fig. 4. Calculated isotherms for Pt at 300, 1473, 1673, and 1873 K. Open circles, solid circles, solid circles, open squares, and solid diamonds represents experimental data collected at 300, 1473, 1673, and 1873, respectively.

Table 3
Model parameters for the equations of state of MgO, Au, and Pt

Parameters	MgO[a]	Au[b]	Pt[c]
V_0 (Å^3)	74.71(1)	67.850(4)	60.38(1)
K_{OT} (GPa)	160.2(2)	167(3)	273(3)
K'_{OT}	3.99(1)	5.0(2)	4.8(3)
θ_0 (K)	773	170	230
γ_0	1.524(25)	2.97(3)	2.69(3)
q_0	1.65(40)	0.7(3)	0.5(5)
q_1	11.8(2)	0	0
$3R$ (J/g K)	0.12664	0.12500	0.12786

[a] All parameters are from Speziale et al. (2001) ($q = q_0(V/V_0)^q_1$).
[b] All parameters except q value are from Shim et al. (2002).
[c] This study.

$\gamma_0 = 2.69$, and $q = 0.5$. Fig. 4 shows the experimental and calculated isotherms of Pt. Table 3 summarizes the thermodynamic parameters of MgO, Au, and Pt that produce mutually consistent pressures at high temperatures.

3.3. Other pressure standards, W, Mo, Pd, and Ag

In addition to the evaluation of consistency among the MgO, Au and Pt pressure standards, we also conducted several experiments using W, Mo, Pd, and Ag as the internal standards. We chose these metals as the pressure standards because they are of simple cubic structure and some of them were used for establishing the ruby pressure scale. However, they are not ideal pressure standard materials at high temperature because they are chemically reactive and easily oxidized under high oxygen fugacity conditions. We only collected a few useful data points at temperatures below 1473 K. Fig. 5 shows a comparison of the calculated pressures from the different standards. The pressures were calculated using the equations of state by Hixson and Fritz (1992) for W and Mo, and by Carter et al. (1971) for Ag and Pd. All metal standards underestimate pressures relative to the MgO scale of Speziale et al. (2001) at high temperatures. The Pd scale gives the lowest pressures.
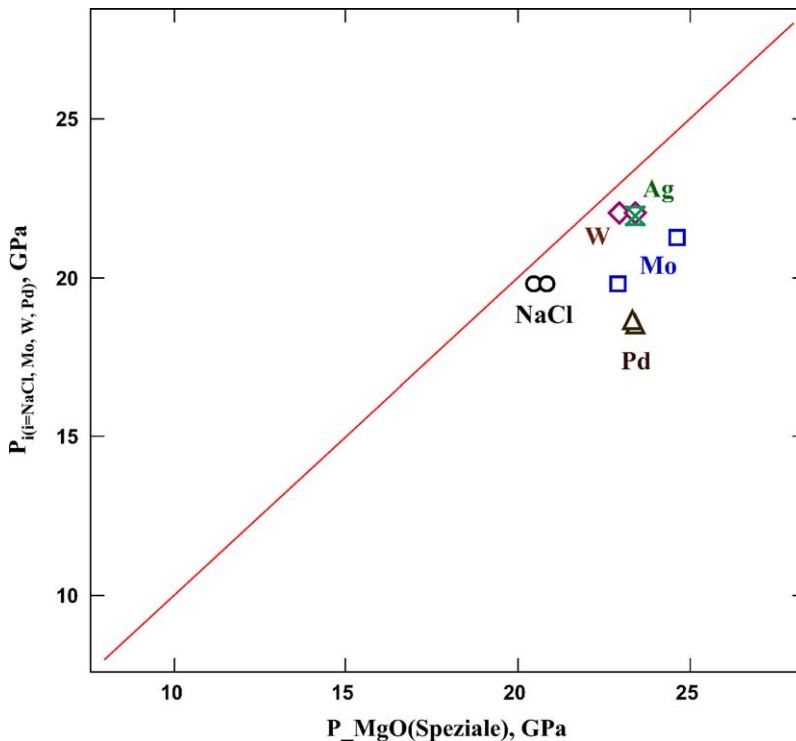

Fig. 5. Calculated pressures from the MgO scale of Speziale et al. (2001) compare to the pressures calculated from different internal pressure standards (W, open diamonds; Mo, open squares; Pd, open triangles; Ag, double triangles; and NaCl, open circles) at 1473 K.

More experimental data are needed to further constrain the thermal equations of state for W, Mo, Pd, and Ag.

4. Discussion

4.1. Comparison of internal pressure standards

The existing thermal equations of state of pressure standards such as Au, MgO, and Pt, predict a range of pressures at high temperatures for samples under the same pressure and temperature conditions. The maximum differences in the calculated pressures could be as large as 3 GPa at *P–T* conditions corresponding to the boundary between the transition zone and the lower mantle (cf. Fig. 1). The MgO scale of Jamieson et al. (1982), who adopted the thermodynamic parameters given by Carter et al. (1971), predicted the lowest pressure relative to the other pressure scales. This equation of state for MgO does not reproduce more recent static and shock wave data (e.g., Duffy and Ahrens, 1995; Fei, 1999) and should not be used for pressure calculations at high temperatures. Speziale et al. (2001) proposed an equation of state for MgO based on analysis of all available static and shock wave data. The new MgO scale predicts pressures between those of the Au scales of Anderson et al. (1989) and Jamieson et al. (1982), and in general agreement with the results from molecular dynamic simulation of the equation of state of MgO (Matsui et al., 2000). Recently, Shim et al. (2002) pointed out that Anderson et al. (1989) equation of state did not reproduce the shock wave data and Jamieson et al. (1982) used a value for the Grüneisen parameter that is too high. The revised Au scale by Shim et al. (2002) and the MgO scale of Speziale et al. (2001) predict similar pressures at high temperatures. The differences in the calculated pressures by the two pressure scales are about 0.5 GPa at 25 GPa and 2000 K. Using the MgO scale of Speziale et al. (2001) as a practical scale for consistency, we further refine the Au scale of Shim et al. (2002) using our new high *P–T* data. We can adjust the 0.5 GPa difference by either increasing the Grüneisen parameter γ_0 or decreasing the *q* value. Shim et al. (2002) used a *q* value of 1.0 to fit the shock compression data up to 580 GPa. The shock wave data below 200 GPa seem to indicate a

q value of less than 1.0 that gives better fit to our static high *P–T* data. Our modified Au scale, with a *q* value of 0.7, gives pressures that are consistent with those calculated from the MgO scale of Speziale et al. (2001).

Pressures calculated from the Pt scale of Holmes et al. (1989) and the Au scale of Anderson et al. (1989) give similar pressures at high temperatures. Because pressures calculated from the Au scale of Anderson et al. (1989) are about 1.0 GPa lower than those of Shim et al. (2002) and about 1.5 GPa lower than those from the MgO scale of Speziale et al. (2001) at conditions corresponding to the 660 km discontinuity, the Pt scale underestimates pressures relative to the Au scale of Shim et al. (2002) and the MgO scale of Speziale et al. (2001). Our new thermal equation of state for Pt is consistent with our modified Au scale and the MgO scale of Speziale et al. (2001) as well.

4.2. Thermal equation of state

The Mie–Grüneisen relation is commonly used to calculate the thermal pressure in shock wave studies. Static compression data at room temperature are often compared to the reduced shock wave Hugoniot data. In the Hugoniot calculations, the Grüneisen parameter is a function of volume ($\gamma = \gamma_0 (V/V_0)^q$), assuming a constant *q* value. The *q* value is usually assumed to be 1 in shock wave data reduction. Recent study of MgO demonstrates that variable *q* is required to satisfy the high *P–T* static and shock wave data (Speziale et al., 2001). First-principles theoretical calculations (Inbar and Cohen, 1995) and thermodynamic analysis (Anderson et al., 1993) also indicate that the *q* value is a function of pressure. Our high *P–T* data on Au are best fitted with a *q* value that varies as a function of temperature. Shock wave data lie along a high *P–T* trajectory. A constant *q* value may be sufficient to describe the high *P–T* shock wave data because of the trade-off between the pressure and temperature effects. The difficulty of simultaneously fitting the static high *P–T* and shock wave data may indicate inadequacy of the formulation of the Mie–Grüneisen relation with a constant *q* value. With more static high *P–T* data available, the assumption of constant *q* value should be further examined.

4.3. Practical pressure scale versus absolute pressure scale

Pressure determinations at high temperature rely on $P–V–T$ equations of state of pressure standards such as Au, Pt, MgO, and NaCl. These thermal equations of state are derived from shock wave and thermodynamic data. With recent advances in synchrotron radiation and high-pressure and high-temperature techniques, static high $P–T$ data have accumulated at an increasingly fast rate. It is essential to ensure consistency in pressure determination at high temperature if different pressure standards were used in high $P–T$ experiments. We have demonstrated that calculated pressures using the existing equations of state of pressure standards could differ by as much as 3 GPa at pressure and temperature conditions corresponding to upper parts of the Earth's lower mantle. The thermal equation of state of MgO is the least controversial one from recent theoretical and experimental studies. We are in favor of using the MgO scale of Speziale et al. (2001) as a reference pressure scale for consistency and inter-laboratory comparison. We further established thermal equations of state for Au and Pt that are consistent with the MgO scale of Speziale et al. (2001).

This study provides us with a means to compare high $P–T$ data obtained using different pressure standards such as MgO, Au, and Pt. The ultimate goal for pressure calibration is to establish an absolute pressure scale. Such a goal can be achieved by redundant equation-of-state measurements, i.e. simultaneous density and elasticity determination at high pressure and temperature. MgO is an ideal material for the attempt of redundant equation-of-state measurements (e.g., simultaneous X-ray diffraction and acoustic measurements). Zha et al. (2000) successfully measured the volume and elasticity simultaneously at room temperature by combining Brillouin scattering and X-ray diffraction techniques. Extending these measurements to high temperatures would provide a direct check for the MgO scale of Speziale et al. (2001).

5. Concluding remarks

The existing thermal equations of state for pressure standards such as Au, MgO, and Pt, predict a range of pressures at high temperatures for samples under the same pressure and temperature conditions. For high $P–T$ experiments, especially at synchrotron facilities, there is an urgent need to establish a reliable and self-consistent pressure scale at high temperature. We evaluated different pressure scales in a series of high $P–T$ experiments with multiple internal pressure standards and concluded that the use of a single practical pressure scale such as the MgO scale of Speziale et al. (2001) would be beneficial for consistency check and data comparison. We determined the relative differences among different pressure scales and established new Au and Pt scales that are consistent with the MgO scale of Speziale et al. (2001). These scales allow us to compare high $P–T$ data that were collected using different internal pressure standards.

Speziale et al. (2001) and also this study showed that it is often difficult to reconcile the static high $P–T$ data or thermal expansion data at ambient pressure with the shock wave Hugoniot data using the Mie–Grüneisen relation with a constant volume dependence q value. The temperature and pressure dependence of the q value may not be easily delineated from the Hugoniot data because Hugoniot are in a high $P–T$ trajectory. Isothermal compression data over a wide pressure and temperature range should provide tight constraints on the q value and its possible temperature and pressure dependence. Further experimental data at simultaneous high pressure and temperature are required to determine the q value as a function of pressure and temperature.

Acknowledgements

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