

## High-pressure equation of state of magnesite: New data and a reappraisal

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### ABSTRACT

The room-temperature static compression of magnesite ( $\text{MgCO}_3$ ) has been measured by X-ray powder energy-dispersive diffraction in a diamond-anvil cell. Different pressure transmitting media and an internal pressure standard (gold) were used in order to differentiate the effects of stresses or pressure measurement errors in determining the isothermal bulk modulus  $K_0$  and first pressure derivative  $K'_0$ . A third order Eulerian equation of state accounts well for the sets of data obtained in different configurations and yields a bulk modulus  $K_0 = 115(1)$  GPa and an ambient unit-cell volume  $V_0 = 278.9(1) \text{ \AA}^3$  with a pressure derivative  $K'_0$  fixed to 4, consistent with recent measurements of Zhang et al. (1997) and Ross (1997). Measurements collected to 72 GPa allow us to have a reliable constraint on the first pressure derivative  $K'_0$ . The best fit to the data yields  $K_0 = 108(2)$  GPa,  $K'_0 = 4.6(2)$ , and an ambient unit-cell volume  $V_0 = 279.1(1) \text{ \AA}^3$ . The first pressure derivative  $K'_0$  would be 4.5(1) with a bulk modulus fixed to the value of 110 GPa derived from the ultrasonic measurement of Christensen (1972).

### INTRODUCTION

There has been considerable interest in the stability of carbonates under lower mantle pressure and temperature conditions, because they are potential hosts for oxidized carbon in the Earth's mantle (Berg 1986; Canil and Scarfe 1990; Kushiro et al. 1975; McGetchin and Besancon 1973; Wyllie and Huang 1976). Magnesite is reported to be the stable phase at pressures up to 50 GPa in the presence of silicates (Biellmann et al. 1993; Brey et al. 1983; Katsura et al. 1991), and retains its  $R\bar{3}c$  structure to 55 GPa under hydrostatic conditions (Katsura et al. 1991; Gillet 1993). However, whether magnesite is stable over the entire pressure and temperature range of the mantle or not remains unclear. Evaluation of stability requires information on the equation of state of this compound and its breakdown products (i.e., periclase and  $\text{CO}_2$ ).

Determinations of bulk modulus through high-pressure X-ray diffraction (XRD) studies are conflicting (Fiquet et al. 1994; Redfern et al. 1993; Ross 1997; Zhang et al. 1997). Discrepancies probably arise from the different experimental conditions used. Redfern et al. (1993) performed a powder XRD study on a mixture of magnesite and sodium chloride, loaded with a 4:1 mixture of methanol:ethanol as pressure transmitting medium in a diamond-anvil cell. The Decker NaCl equation of state (Decker 1971) was used for in situ pressure determination. Fiquet et al. (1994) studied a fine powder of magnesite compressed in a silicon oil (47V1000 from Prolabo) in a diamond-anvil cell, with pressures determined utilizing ruby fluorescence. Using a second-order Birch-Murnaghan equation of state ( $K'_0 = 4$ ),

Redfern et al. (1993) and Fiquet et al. (1994) obtained similar values for  $K_0$ , respectively, 142(9) and 138(3) GPa. These results are at variance with the single-crystal study by Ross (1997) in a mixture of methanol-ethanol up to 7 GPa, where a value  $K_0 = 111(1)$  GPa was obtained, with pressures measured from ruby fluorescence. Zhang et al. (1997) reported  $K_0 = 103(1)$ , using the SAM85 cubic-anvil apparatus and the NaCl equation of state. The latter two measurements are in better agreement with adiabatic bulk moduli ( $K_S$ ) of 112 and 113.8 GPa, determined from acoustic measurements (Christensen 1972; Humbert and Plicque 1972, respectively) than the diamond-anvil cell powder XRD experiments by Redfern et al. (1993) and Fiquet et al. (1994).

We investigate here the effects of different experimental conditions on the high-pressure behavior of magnesite. In particular, the non-hydrostaticity of the pressure transmitting medium, the stress state on the sample and/or pressure sensor, the pressure measurement and the different techniques involved in this determination are discussed. Finally, emphasis will be put on the determination and the level of confidence on the first pressure derivative  $K'_0$ , which is a crucial parameter when extrapolating an equation of state to the very high pressures relevant to the Earth's lower mantle.

### EXPERIMENTAL METHODS

A clear inclusion-free magnesite crystal was selected from a cleavage rhomb of Bahia magnesite, similar to those studied by Humbert and Plicque (1972) and Fiquet et al. (1994). The sample was powdered in an agate mortar, and loaded in a membrane diamond-anvil cell. Diamond anvils with culets 400  $\mu\text{m}$  in di-

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ameter, and 200  $\mu\text{m}$  holes drilled in pre-indented stainless steel gaskets were used. Because magnesite has a small X-ray scattering cross section, Fiquet et al. (1994) loaded rather large amounts of the sample into the gasket hole in order to increase the signal. Here we took care of loading smaller amounts, which did not exceed one-third of the sample chamber volume, in order to avoid bridging between the diamond culets at high pressure. Several pressure transmitting media were used, in combination with different pressure measurement techniques: (1) We collected 22 patterns in two independent series up to 39.7 GPa in dry argon, loaded cryogenically in the diamond-anvil cell and pressure was measured with the ruby fluorescence of 5 m chips of ruby, affixed to the edge of the stainless steel pressure chamber. Pressure values were cross-checked with the equation of state of Ar (Ross et al. 1986), using lattice parameters determined from recorded XRD at each experimental condition. (2) We recorded 12 patterns up to 24.9 GPa in a mixture 16:4:1 methanol-ethanol-water and 14 patterns up to 13 GPa in the same silicon oil as used in our previous study (Fiquet et al. 1994). Pressure was measured using the ruby fluorescence technique and was cross-checked with the diffraction of a pure gold very fine powder, intimately mixed with magnesite. The equation of state proposed by Anderson et al. (1989) and the elastic compliances and pressure derivatives given by Golding et al. (1967) were used for pressure and stress-state calculations. (3) Two measurements were made at 58 and 72.5 GPa on a mixture of powdered magnesite and very high-purity platinum, loaded without any pressure transmitting medium and uniformly laser-heated for several minutes with a continuous YAG-laser to about 2100–2300 K before the diffraction pattern acquisition. Pressure was calculated from the equation of state for Pt (Jamieson et al. 1982) and stress state inferred from the Pt elastic compliances reported in MacFarlane et al. (1965).

Diffraction patterns were recorded using the energy-dispersive set-up available at the station DW11 at LURE (Orsay, France). Acquisition time of the order of 60 to 90 min was needed to obtain reliable counting statistics up to 45 keV at a  $2^\circ$  angle of about  $12^\circ$ . Four to six diffraction lines, subsets of 104, 006, 113, 022, 116, and 122, were used for cell parameter refinements up to the highest pressure of 40 GPa. The lattice parameters were calculated through a least-square procedure with the assumption of a rhombohedral  $R\bar{3}c$  space group. Standard deviations were calculated for each parameter by adding a 30 eV ( $5 \times 10^{-3}$  Å) constant reading uncertainty and the standard deviation from least-squares gaussian fits of the peak positions. A third-order Eulerian finite-strain equation of state was then fitted to the pressure-volume measurements and the errors on  $K_0$  and its first pressure derivative  $K'_0$  were calculated using the uncertainties on both the volume and pressure measurements. Two additional measurements on laser-heated samples of magnesite and platinum were collected at beamstation ID9 (ESRF, Grenoble, France) using focused 0.4561 Å monochromatic X-ray radiation in association with imaging plates. Two-dimensional patterns were integrated after geometric corrections using the program Fit2d (Hammersley 1996) and treated with the program package GSAS. For these calculations, 16 reflections were used in the unit-cell determination.

## RESULTS AND DISCUSSION

The experimental results are in Table 1 and Figure 1, along with previous measurements. Equation of state parameters obtained from the different data sets are summarized in Table 2.

**TABLE 1.** Unit-cell parameters of magnesite as a function of pressure

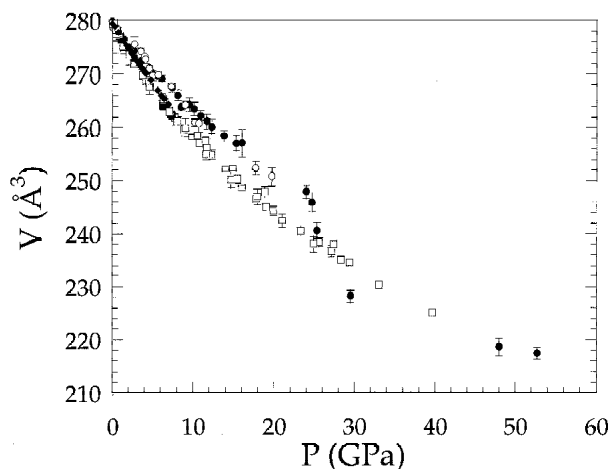
$P$ (GPa) <sup>R*</sup>	$P$ (GPa) <sup>†</sup>	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
<b>Argon series (1)</b>				
0.00		4.628(1)	15.055(9)	279.14(33)
1.90		4.615(1)	14.899(12)	274.85(31)
3.00		4.606(1)	14.791(14)	271.71(38)
4.20		4.595(1)	14.708(16)	268.90(37)
6.10		4.586(3)	14.583(33)	265.66(93)
7.70		4.567(6)	14.498(42)	261.90(145)
9.10		4.556(7)	14.399(36)	258.79(140)
9.90		4.555(3)	14.377(17)	258.27(64)
10.80		4.549(5)	14.342(22)	257.02(93)
12.30		4.549(6)	14.221(45)	254.91(153)
14.00		4.535(4)	14.159(26)	252.16(85)
16.00		4.520(4)	14.053(25)	248.68(89)
17.80		4.515(2)	13.964(13)	246.53(42)
19.00		4.508(5)	13.924(37)	245.05(121)
21.00		4.490(16)	13.891(74)	242.48(306)
23.30		4.491(8)	13.769(44)	240.53(161)
25.60		4.481(9)	13.708(47)	238.37(175)
27.10		4.467(9)	13.695(63)	236.68(209)
<b>Argon series (2)</b>				
15.40		4.522(4)	14.130(34)	250.25(102)
19.90		4.499(5)	13.938(47)	244.32(132)
28.30		4.463(1)	13.630(12)	235.12(31)
33.00		4.440(5)	13.495(30)	230.37(99)
39.70		4.421(4)	13.297(30)	225.07(89)
<b>Magnesite + platinum (no transmitting medium)</b>				
72.44‡		4.282(3)	12.726(21)	202.09(62)
58.01‡		4.321(2)	13.014(16)	210.39(45)
<b>Silicon oil</b>				
0.14	0.16	4.631(1)	15.043(6)	279.43(19)
0.78	0.69	4.631(2)	14.942(19)	277.53(55)
2.00	1.45	4.613(43)	14.895(36)	274.46(117)
3.30	2.69	4.603(4)	14.809(36)	271.73(116)
5.02	4.47	4.590(3)	14.724(22)	268.60(70)
7.20	6.28	4.574(3)	14.638(26)	265.23(86)
9.34	7.93	4.559(4)	14.499(37)	261.02(114)
9.60	8.10	4.564(5)	14.473(41)	261.10(129)
10.80	8.91	4.555(4)	14.452(33)	259.69(103)
14.00	11.61	4.540(7)	14.287(59)	254.99(186)
16.80	15.45	4.531(7)	14.076(46)	250.28(155)
19.90	18.85	4.515(6)	14.037(58)	247.83(170)
15.90	14.89	4.537(33)	14.156(23)	252.31(78)
13.00	11.54	4.563(2)	14.280(12)	257.46(40)
<b>16:4:2 methanol:ethanol:water</b>				
1.e-04	0.18	4.636(3)	15.004(15)	279.29(28)
0.81	0.82	4.625(7)	14.972(59)	277.39(99)
0.41	0.34	4.628(5)	14.997(39)	278.23(67)
1.28	1.42	4.607(2)	14.963(11)	275.08(166)
2.05	2.24	4.609(9)	14.871(98)	273.58(149)
3.74	3.84	4.604(5)	14.696(41)	269.75(65)
5.60	5.46	4.592(6)	14.651(76)	267.58(106)
7.03	7.41	4.574(4)	14.516(45)	263.05(64)
9.00	8.69	4.556(6)	14.455(90)	259.88(115)
11.70	11.01	4.545(5)	14.323(90)	256.21(110)
14.70	14.60	4.523(5)	14.124(88)	250.19(107)
18.90	18.95	4.514(7)	13.995(79)	246.93(109)
25.10	25.59	4.480(9)	13.697(89)	238.05(125)

Note: Standard deviations in parentheses. Uncertainty in  $P$  is estimated to be better than 3%.

\* Pressures measured with the ruby fluorescence technique.

† Pressure measurement based on gold diffraction peaks and the equation of state proposed by Anderson et al. (1989).

‡ Pressure measurement based on platinum diffraction peaks and the equation of state of Jamieson et al. (1982).



**FIGURE 1.** Molar volume of magnesite as a function of pressure. Open squares = Table 1. Open circles = Redfern et al (1993). Solid circles = Fiquet et al. (1994). Solid squares = Zhang et al. Solid diamonds = Ross (1997).

The results of Fiquet et al. (1994) and Redfern et al. (1993) disagree with the other studies, which appears to be a consequence of the non-hydrostaticity of the pressure transmitting medium and/or stresses developed in the sample, as proposed by Reynard et al. (1996) and Ross (1997). The consistency of our measurements with the most recent studies of Ross (1997) and Zhang et al. (1997) is apparent in Figure 2, where data points plot within 1 or 2 esd from one set to another. The internal consistency of our results using different pressure media is also obvious. Not surprisingly, we obtain a bulk modulus  $K_0 = 111(1)$  GPa with  $K'_0$  fixed at 4, when data recorded to 40 GPa are all fitted together. It is worth, however, analyzing the individual data sets in different pressure media on their own. Resulting EOS parameters are given in Table 2. In a hydrostatic environment (i.e., in the 16:4:1 mixture of methanol-ethanol-water below the solidification pressure of 11 GPa), pressures measured with ruby and gold are consistent within error. The calculated differential stresses are low even well above 11 GPa, being 0.06, 0.09, and 0.15 GPa at 14.7, 17.9, and 24.9 GPa,

respectively. In silicon oil, a systematic difference exists between the pressures measured with the ruby fluorescence and those inferred from the equation of state of Au. When the latter are used, a good agreement is reached with the measurements performed in Ar or in the methanol:ethanol:water mixture (see Table 2). In this run, the pressure measurements from the ruby scale were thus probably biased. This may arise from bridging of the ruby in the sample chamber or from non-hydrostatic stresses in silicon oil. The calculated differential stresses are relatively small (around 0.17 GPa), although uniformly present at all pressures in this run. Given the ambiguity in pressure measurement, these data points were discarded from further refinements. Two other data sets were obtained from measurements carried out in quasi-hydrostatic conditions in Ar up to 40 GPa. Because solid Ar shows several diffraction lines, no Au was added in these runs in order to avoid peak interference. The pressure determinations from the ruby fluorescence were cross-checked with the Ar equation of state from Ross et al. (1986). The measured volumes for Ar are consistent within 3% up to the highest pressure achieved with those by Ross et al. (1986), which may thus be regarded as a maximum uncertainty of the ruby fluorescence pressure measurement.

Magnesite compresses anisotropically (Fig. 3), which is typical of all rhombohedral carbonates, with the  $c$  axis being nearly three times as compressible as the  $a$  axis, at pressures below 25 GPa. These results are consistent with all previous studies. No phase transition could be observed at pressures near 25 GPa, and the rhombohedral form of magnesite was observed to the highest pressure of 72 GPa reached in this study. The phase transition proposed by Fiquet et al. (1994) thus appears to be an artifact. No change in the compression mechanism can be evidenced on the basis of these measurements and the effect observed in our previous study appears likely to be triggered by the non-hydrostatic conditions.

When data recorded in hydrostatic or quasi-hydrostatic conditions (i.e., only those collected in Ar and in the methanol:ethanol:water mixture) are fitted to a third order Birch-Murnaghan equation of state (see Table 2), results compare very well with the single-crystal study of Ross (1997), or with that interred from acoustic measurements (Christensen 1972;

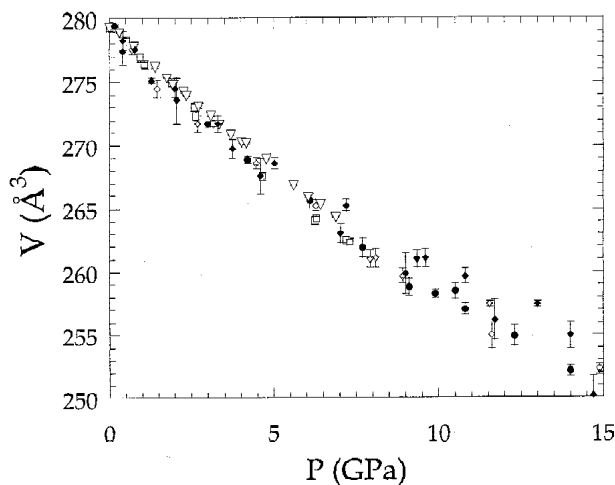
**TABLE 2.** Equation of state of magnesite

Method	$V_0(\text{Å}^3)$	$K_0$ (GPa)	$K'_0$	Reference
Acoustic		112*	—	Christensen (1972)
Acoustic		113.8*	—	Humbert and Plicque (1972)
X-ray: powder		142(9)	4	Redfern et al. (1993)
		151(7)	2.5	
X-ray: powder		138(3)	4	Fiquet et al. (1994)
		156	2.5(2)	
X-ray: powder		103(1)	4	Zhang et al. (1997)
		108(3)	2.3	
X-ray: single crystal		111(1)	4	Ross (1997)
		117(3)	2.3(7)	
X-ray: powder	279.5(3)	95(6)	6.8(1.3)	alcohol-water mixture <sup>†</sup>
	279.7(3)	92(8)	9.1(2.2)	silicon oil <sup>†</sup>
	279.2(2)	103(3)	5.4(4)	Ar (both series) <sup>†</sup>
	279.3(1)	102(3)	5.6(4)	argon + alcohol -water <sup>†</sup>
	278.9(1)	114(1)	4	argon + alcohol-water <sup>†</sup>
	279.1(1)	108(2)	4.6(2)	Ar + alcohol-water+2HP data <sup>†</sup>
		110 <sup>‡</sup>	4.5(1)	Ar + alcohol-water + 2HP <sup>†</sup>

\* Adiabatic bulk modulus  $K_S$ .

<sup>†</sup> This work.

<sup>‡</sup> Fixed to equal  $K_T$  from Christensen (1972).



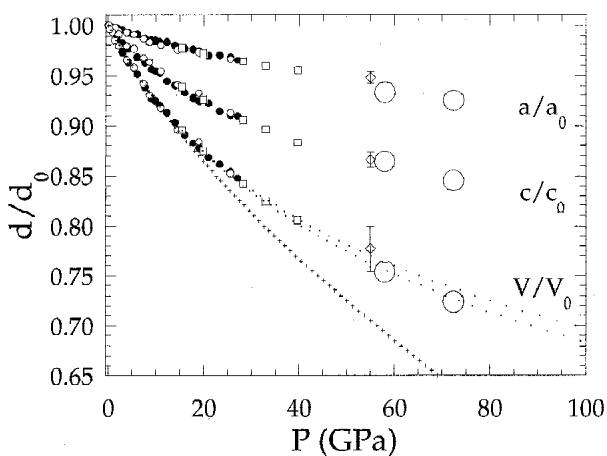
**FIGURE 2.** Detailed view of Figure 1. Data from Redfern et al. (1993) and Fiquet et al. (1994) not represented. Open squares = Zhang et al. (1997). Open triangles = Ross (1997). Other symbols are from this work using different pressure transmitting media. Solid circles = argon. Solid squares = methanol-ethanol-water mixture. Solid diamonds and open diamonds, silicon oil with pressure inferred from the equation of state for gold.

Humbert and Picque 1972). Our results are in reasonable agreement with the slightly lower value of 103 GPa obtained by Zhang et al. (1997). Non-hydrostatic stresses, which are critical for minerals that have large and anisotropic compressibilities such as carbonates, have been shown to be absent or low in these measurements and the present results differ from the previously overestimated  $K_0$  values. Large non-hydrostatic stresses in these studies were advocated to account for this overestimation (Reynard et al. 1996; Ross 1997). Our results show, however, that the nature of the pressure transmitting medium itself (silicon oil vs. liquid and solid alcohol mixture) does not significantly affect the magnitude of these stresses. Large stresses thus rather result from the loading of a large amount of sample relative to pressure transmitting medium, and subsequent bridging between the diamond culets at high pressure.

Our results are suitable for constraining the first pressure derivative  $K'_0$ , due to the large pressure interval. In the other studies, the presence of stresses or the limited pressure range investigated might lead to a large uncertainty in the determination of this parameter, which is crucial in the extrapolation of magnesite densities to lower mantle pressures. Generally, values of  $K'_0$  significantly lower than 4 have been inferred, around 2.5, in all experiments carried out so far. All sets of data presented here and taken individually yield  $K'_0$  higher than 4, in disagreement with previous studies. Figure 3 shows that a bulk modulus of 117 or 108 GPa combined with a  $K'_0$  value of 2.5 does not account for our experimental data above 25 GPa and certainly not for our highest pressure points at 58 and 72 GPa, for which the volumes are underestimated by 8 and 11%, respectively. Deviatoric stresses evaluated for these very high-pressure experiments carried out without any pressure transmitting medium drop from 1.2 to 0.3–0.4 GPa after the laser heating cycle, and are unlikely to account for such a large discrepancy. As shown in Figure 3, this increases the pressure

and volume error bars for these measurements but they still cannot be accounted for by the equation of state parameters  $K_0$  and  $K'_0$  reported by Ross (1977) or Zhang et al. (1997). The best fit to the combination of data points obtained in argon and alcohol only (see Table 2) is consistent with our highest pressure measurements and with the results reported in Katsura et al. (1991). A better constraint on the pressure derivative determination may be obtained from this extended pressure range than for experiments carried out to a few GPa only. Even when using the precise measurements of Ross (1997), this makes the previous determination of  $K_0$  around 2.5 very doubtful unless either higher-order derivatives are not negligible or the Birch-Murnaghan formulation is inadequate in such an anisotropic solid. As the classical trade-off between the bulk modulus  $K_0$  and its pressure derivative is observed even when the highest pressure points are included in the data set, we did not attempt to refine higher-order terms. Including the high-pressure experiments in the refinement only brings slight differences in the results, as shown in the last two entries of Table 2.

These results have important consequences for the calculation of the stability field of magnesite with respect to decarbonation reactions. Recent calculations (Matas et al., in preparation) show for instance that our preferred values would lead to a decomposition to periclase and  $\text{CO}_2$  in the lower mantle near 100 GPa, or even lower pressures if increasing the iron content of the carbonate, whereas the former values of  $K'_0$  implied no decarbonation over the whole lower mantle pressure range. These results thus have interesting consequences for the fate of carbonates buried in the deep mantle in subduction zones and for the global carbon cycle.



**FIGURE 3.** The variation of  $a/a_0$ ,  $c/c_0$ , and  $V/V_0$  as a function of pressure. The best fits to a Birch Murnaghan equation of state are shown (with quasi-hydrostatic experiments only. Dotted lines,  $V_0 = 279.3 \text{ \AA}^3$ ,  $K_0 = 102 \text{ GPa}$ , and  $K'_0 = 5.6$ ; and  $V_0 = 279.1 \text{ \AA}^3$ ,  $K_0 = 108 \text{ GPa}$ , and  $K'_0 = 4.6$  when taking into account the two additional high-pressure experiments). Crosses, that proposed by Ross (1997), i.e.,  $V_0 = 279.4 \text{ \AA}^3$ ,  $K_0 = 117 \text{ GPa}$ , and  $K'_0 = 2.3$ . Large open circles, monochromatic XRD of laser-heated samples. Open diamonds, data from Katsura et al. (1991). Solid circles and open squares, samples compressed in Ar. Small open circles, samples compressed in methanol: ethanol: water.

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