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# Effects of Fe/Mg on the Compressibility of Synthetic Wadsleyite: $\beta$-$(Mg_{1-x}Fe_x)_2SiO_4$ ($x \leq 0.25$)

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**Abstract.** Four crystals of synthetic wadsleyite, $\beta$-$(Mg,Fe)_2SiO_4$, were mounted together in one diamond-anvil cell for the determination of unit-cell parameters as a function of pressure. The Fe/(Fe+Mg) are 0.00, 0.08, 0.16, and 0.25 (the most iron-rich stable composition). Unit-cell refinements were made at 12 pressures up to 4.5 GPa. No phase transitions were observed and all crystals remained dimensionally orthorhombic. Of the three axes, **c** is the most compressible (0.000239(3) $GPa^{-1}$), whereas compressibilities of **a** and **b** are both about 30% less. The Fe content has no systematic effect on volume or linear compressibilities. Bulk moduli, based on a Birch-Murnaghan equation of state (K′ assumed to be 4.00) are 160(3), 169(3), 164(2), and 165(3) GPa for the four crystals in order of increasing Fe. Substitution of Fe for Mg, therefore, does not appear to have a systematic effect on bulk modulus. Other factors, especially $Fe^{3+}/Fe^{2+}$ and other deviations from the strict $Mg_2SiO_4-Fe_2SiO_4$ binary, may have a greater influence on compressibility.

## Introduction

Physical properties vary in important yet often subtle ways along solid solution series. The effects of Fe/Mg are of crucial importance in characterizing the properties of mantle silicates, because we must rely on indirect measurements of mantle properties to deduce the appropriate bulk and mineralogical composition of the earth's deep interior. Models of the composition, mineralogical layering, and dynamic state of the mantle thus depend critically on our ability to infer Fe/Mg through careful interpretation of the seismic record.

This study is one of the series of investigations on the effects of solid solution on oxide and silicate compressibility. Previous work on wüstites (Hazen 1981), feldspars (Angel et al. 1988), and pyroxene (McCormick et al. 1989), as well as work in progress on olivines and Ca–Fe–Mg garnets, establish the feasibility of comparing several compositionally related single crystals in a single high-pressure mount. In this method, the unit-cell volume refinements of different crystals are made at identical pressures, so pressure measurements do not contribute to resolving differences among compressibilities of several similar crystals. In conventional experiments with only one crystal per mount, pressure errors constitute the greatest source of uncertainty in calculating compressibilities. Reproduceability (precision) is typically $\pm 0.05$ GPa (i.e., 1% or greater) for ruby fluorescence pressure measurements below 5 GPa.

We report here on a suite of four synthetic wadsleyite samples ($\beta$-$(Mg,Fe)_2SiO_4$), synthesized as single crystals (Finger et al. 1990). This work is the first high-pressure, single-crystal diffraction study of this phase, and it provides the first compressibility data on iron-bearing members of the $\beta$-$(Mg,Fe)_2SiO_4$ solid solution series.

## Experimental

### *Sample Description*

The single crystals of $\beta$-$(Mg,Fe)_2SiO_4$ were synthesized using a 2000-ton uniaxial split-sphere apparatus (USSA-2000) at the High-Pressure Laboratory of the State University of New York at Stony Brook. Samples with compositions 0.00, 0.08, 0.16, and 0.25 Fe/(Fe+Mg) were produced at pressures of about 16 GPa. Synthesis temperature for the iron-free sample was 1400° C, while the iron-bearing crystals were grown at 1800° C.

All four of these crystals may deviate slightly from the ideal compositional binary, $Mg_2SiO_4-Fe_2SiO_4$. Mössbauer spectroscopy of the $Fe_{16}$ sample reveals 8% (atomic) of total iron is trivalent (Finger et al. in review). Furthermore, studies of other synthetic wadsleyite reveal small but significant amounts of bound $OH^-$ associated with the O1 site (Smyth 1987; see also Smyth and Bish 1988).

Subequant crystals approximately 0.1 mm maximum diameter were selected from each composition and were examined optically and by X-ray diffraction at room conditions. Crystal chemical details are reported by Finger et al. (in review), who observed that all specimens are orthorhombic, *Imma*, with silicon in tetrahedral coordination and Fe+Mg distributed among three symmetrically distinct octahedra. Iron and magnesium display significant partial

ordering among the three octahedral sites. Iron is slightly enriched on M3, the largest of the six-coordinated sites, whereas Fe is significantly depleted on M2. The sequence of iron ordering (M3 > M1 > M2) is the same as the site energy sequence reported by Smyth and Bish (1988).

### *High-Pressure Experiments*

Four single crystals of the different $\beta$-$(Mg,Fe)_2SiO_4$ samples were mounted together in a diamond anvil cell designed for single-crystal X-ray diffraction studies (Hazen and Finger 1982). An Inconel 750X gasket with 0.45 mm diameter hole was centered over one 1.0 mm diamond anvil, while the four crystals were affixed to the other 1.0 mm anvil face with a small dot of the alcohol insoluble fraction of vaseline petroleum jelly. Several 0.01 mm fragments of ruby were sprinkled near the crystals for internal pressure calibration. Special care was taken to ensure that the crystals were separated from each other by at least 0.04 mm, and that clearance of 0.1 mm was maintained between the crystals and gasket wall. These precautions prevent significant x-ray shadowing of any crystal by adjacent crystals or the gasket wall.

All x-ray measurements were performed with a Huber automated four-circle diffractometer with graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.7093$ Å). Unit-cell parameters for each crystal were measured with the procedure of King and Finger (1979), whereby several reflections are measured in eight equivalent orientations. This procedure minimizes errors associated with crystal centering and diffractometer alignment. All refinements, furthermore, relied on reflection centering procedures (Finger and Hadidiacos 1982) within a relatively narrow $2\Theta$ range, from 18 to 33°, in order to reduce systematic errors associated with measuring lattice parameters at different $2\Theta$ ranges (Swanson et al. 1985).

When comparing unit-cell parameters at several different pressures, it is important to employ the same set of reflections for each measurement. For example, cell parameters of the $Fe_{16}$ sample at all twelve pressures were determined with the same set of 16 reflections: 033, 231, 240, 004, 134, $\bar{1}34$, 204, 105, $\bar{1}05$, 341, $34\bar{1}$, 035, 244, 055, $41\bar{3}$, and $30\bar{5}$ (the sixteen Friedel pairs are also included by the 8-reflection centering routine). The $Fe_{00}$, $Fe_{08}$, and $Fe_{25}$ cell-parameter determinations relied on 14, 13, and 14 reflections, respectively. All reflections were selected from the classes noted above for $Fe_{16}$, plus the classes 053, 303, 154, 080, and 073.

Data were collected on all four crystals in the following sequence of pressures (GPa): 0.00, 0.60, 1.16, 1.86, 2.63, 3.11, 3.67, 4.17, 2.14, 1.35, 4.51, 0.00 (all $\pm 0.05$ GPa). Room-pressure parameters were measured on the crystals in the diamond-anvil cell before and after high-pressure experiments, and the pressure was cycled once during the experiments to detect any irreversible changes in the crystals.

## Results and Discussion

### *Linear Compressibilities*

Unit-cell parameters for the four synthetic wadsleyite crystals at 12 *P* are recorded in Tables 1–4. Room-pressure cell parameters for the three iron-bearing samples agree within one estimated standard deviation before and after the high-pressure experiments. The iron-free sample, however, displays a slight, possibly significant, decrease in *b* from 11.4406(8) to 11.4375(7) Å, and an increase in *a* from 5.681(3) to 5.686(3) Å.

Figures 1–3 illustrate the axial compressibilities for the four crystals. General trends are similar for these specimens. In each case the *c* axis is the most compressible. Average *c*-axis compressibilities between 0 and 4.5 GPa for all samples are consistent with $\beta = 0.00239 \pm 0.00003$ GPa$^{-1}$, and we observe no significant compositional effect. Both *a* and *b* axes display average compressibilities of 0.00168 GPa$^{-1}$, or about 30% less, for the four samples. A similar result was reported by Sawamoto et al. (1984), who reported single-crystal elastic moduli derived from Brillouin spectroscopy. The stiffness of *a* and *b* relative to *c* results from the pseudo-layering of the structure, with (Mg,Fe)-octahedral layers parallel to (001), and cross linking by $Si_2O_7$ tetrahedral pairs. Tsukimura et al. (1990) described the high-temperature crystal chemistry of $\beta$-$Mg_2SiO_4$. They observed similar anisotropy, with the *c* axis thermal expansion approximately twice that of *a* or *b*.

Small but significant differences occur in *a* and *b* compressibilities for the four compositions. The $Fe_{00}$ and $Fe_{25}$ crystals are significantly more compressible along *a* (0.00173(3) GPa$^{-1}$) than the $Fe_{08}$ and $Fe_{16}$ specimens (0.00162(3) GPa$^{-1}$). These differences are evident from the slopes in Fig. 1. Similarly, the $Fe_{00}$ and $Fe_{16}$ samples have *b*-axis compressibilities approximately 0.00173(3) GPa$^{-1}$, compared to 0.00160(3) GPa$^{-1}$ for the other two samples (compare slopes in Fig. 2).

**Table 1.** Unit-cell parameters of $\beta$-$(Mg_2SiO_4)$ at several pressures

| Pressure (GPa) | a(Å) | b(Å) | c(Å) | Vol(Å$^3$) |
|---|---|---|---|---|
| 0 | 5.6810 (28) | 11.4406 (8) | 8.2361 (7) | 535.30 (27) |
| 0.60 | 5.6796 (31) | 11.4267 (8) | 8.2264 (8) | 533.89 (30) |
| 1.16 | 5.6722 (35) | 11.4179 (9) | 8.2146 (9) | 532.01 (34) |
| 1.35 | 5.6709 (31) | 11.4122 (8) | 8.2095 (8) | 531.30 (29) |
| 1.86 | 5.6677 (38) | 11.4040 (10) | 8.1999 (9) | 530.00 (36) |
| 2.14 | 5.6626 (29) | 11.3990 (8) | 8.1935 (7) | 528.88 (28) |
| 2.63 | 5.6604 (47) | 11.3903 (12) | 8.1852 (12) | 527.73 (44) |
| 3.11 | 5.6539 (37) | 11.3783 (9) | 8.1739 (9) | 525.84 (34) |
| 3.67 | 5.6503 (35) | 11.3653 (9) | 8.1628 (9) | 524.19 (33) |
| 4.17 | 5.6409 (35) | 11.3570 (9) | 8.1537 (9) | 522.36 (33) |
| 4.51 | 5.6400 (33) | 11.3494 (9) | 8.1470 (8) | 521.49 (31) |
| 0 after | 5.6861 (25) | 11.4375 (7) | 8.2355 (6) | 535.60 (24) |

**Table 2.** Unit-cell parameters of $\beta$-$(Mg_{0.92}Fe_{0.08})_2$ $SiO_4$ versus pressure

| Pressure (GPa) | a(Å) | b(Å) | c(Å) | Vol(Å$^3$) |
|---|---|---|---|---|
| 0 | 5.6964 (19) | 11.4429 (19) | 8.2592 (15) | 538.36 (19) |
| 0.60 | 5.6921 (18) | 11.4307 (14) | 8.2496 (14) | 536.76 (18) |
| 1.16 | 5.6882 (18) | 11.4232 (14) | 8.2392 (14) | 535.36 (18) |
| 1.35 | 5.6873 (17) | 11.4177 (13) | 8.2315 (13) | 534.52 (17) |
| 1.86 | 5.6808 (20) | 11.4096 (16) | 8.2265 (16) | 533.21 (20) |
| 2.14 | 5.6772 (17) | 11.4062 (13) | 8.2163 (14) | 532.05 (17) |
| 2.63 | 5.6746 (18) | 11.3949 (14) | 8.2089 (14) | 530.80 (18) |
| 3.11 | 5.6675 (18) | 11.3858 (14) | 8.1988 (14) | 529.06 (18) |
| 3.67 | 5.6643 (23) | 11.3751 (18) | 8.1852 (18) | 527.39 (23) |
| 4.17 | 5.6583 (29) | 11.3681 (22) | 8.1774 (23) | 526.01 (29) |
| 5.51 | 5.6552 (23) | 11.3595 (15) | 8.1746 (15) | 525.14 (23) |
| 0 after | 5.6975 (19) | 11.4405 (15) | 8.2600 (15) | 538.41 (20) |

**Table 3.** Unit-cell parameters versus pressure for $\beta$-$(Mg_{0.84}Fe_{0.62})_2SiO_4$

| Pressure (GPa) | a(Å) | b(Å) | c(Å) | Vol(Å$^3$) |
|---|---|---|---|---|
| 0 | 5.7060 (12) | 11.4528 (23) | 8.2691 (9) | 540.38 (15) |
| 0.60 | 5.7020 (13) | 11.4463 (25) | 8.2590 (10) | 539.04 (16) |
| 1.16 | 5.6960 (11) | 11.4330 (21) | 8.2469 (8) | 537.06 (13) |
| 1.35 | 5.6924 (15) | 11.4307 (29) | 8.2431 (11) | 536.37 (19) |
| 1.86 | 5.6896 (13) | 11.4182 (24) | 8.2333 (10) | 534.88 (16) |
| 2.14 | 5.6858 (8) | 11.4159 (16) | 8.2268 (6) | 533.98 (10) |
| 2.63 | 5.6812 (10) | 11.4051 (20) | 8.2166 (8) | 532.40 (13) |
| 3.11 | 5.6765 (11) | 11.3910 (23) | 8.2059 (9) | 530.60 (15) |
| 3.67 | 5.6714 (10) | 11.3810 (19) | 8.1956 (7) | 529.00 (12) |
| 4.17 | 5.6686 (13) | 11.3700 (25) | 8.1881 (10) | 527.73 (16) |
| 4.51 | 5.6648 (11) | 11.3679 (22) | 8.1822 (9) | 526.91 (14) |
| 0 after | 5.7046 (14) | 11.4539 (23) | 8.2698 (9) | 540.35 (16) |

**Table 4.** Unit-cell parameters versus pressure for $\beta$-$(Mg_{0.75}Fe_{0.25})_2SiO_4$

| Pressure (GPa) | a(Å) | b(Å) | c(Å) | Vol(Å$^3$) |
|---|---|---|---|---|
| 0 | 5.7114 (14) | 11.4863 (22) | 8.2852 (10) | 543.53 (15) |
| 0.60 | 5.7066 (18) | 11.4755 (27) | 8.2757 (12) | 541.94 (19) |
| 1.16 | 5.7002 (16) | 11.4687 (24) | 8.2641 (11) | 540.25 (16) |
| 1.35 | 5.6995 (15) | 11.4651 (22) | 8.2604 (10) | 539.78 (15) |
| 1.86 | 5.6931 (13) | 11.4533 (19) | 8.2494 (9) | 537.90 (13) |
| 2.14 | 5.6920 (15) | 11.4495 (23) | 8.2447 10) | 537.31 (16) |
| 2.63 | 5.6831 (13) | 11.4418 (20) | 8.2335 (9) | 535.39 (13) |
| 3.11 | 5.6829 (17) | 11.4231 (27) | 8.2226 (12) | 533.78 (18) |
| 3.67 | 5.6746 (17) | 11.4156 (26) | 8.2134 (12) | 532.05 (18) |
| 4.17 | 5.6694 (14) | 11.4142 (21) | 8.2036 (10) | 530.88 (14) |
| 4.51 | 5.6691 (13) | 11.4036 (18) | 8.1999 (10) | 530.11 (14) |
| 0 after | 5.7113 (19) | 11.4861 (28) | 8.2857 (13) | 543.55 (19) |

The reasons for these subtle, but significant, differences remain puzzling. There is no correlation with the obvious compositional difference – Fe/(Fe+Mg). Under nonhydrostatic conditions, differences might arise from orientational effects: crystal directions perpendicular to the diamond anvil faces could show greater compressibility because of pressure medium stiffness. In the present experiments, however, no such correlation is observed. The $Fe_{00}$ sample was oriented with *a* almost perpendicular to the flat diamond faces (thus accounting for the relatively large *a*-axis errors in Table 1), whereas the *b* axis of the $Fe_{16}$ is in that orientation, yet both samples show relatively large *b*-axis compressibilities. The *a* axes of both $Fe_{08}$ and $Fe_{25}$ samples lie at approximately 45° to the anvil faces, yet the *a*-axis compressibilities of these two samples are significantly different.

### *Bulk Moduli*

Pressure-volume data for the four samples (Fig. 4 and Table 5) were fitted with program VOLFIT to a Birch-Murnaghan equation of state with 4 as the assumed pressure derivative (*K'*). Bulk moduli of the four samples, in order of increasing iron, are 160±3, 169±3, 164±2,

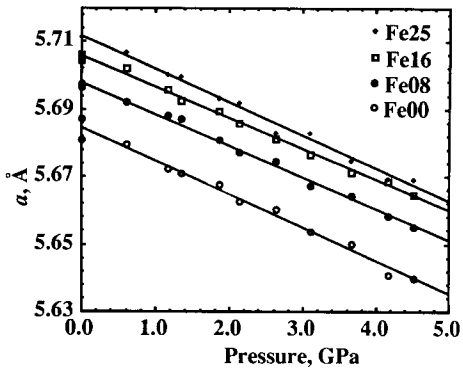


**Fig. 1.** Variation of *a* versus pressure for $\beta$-$(Mg,Fe)_2SiO_4$

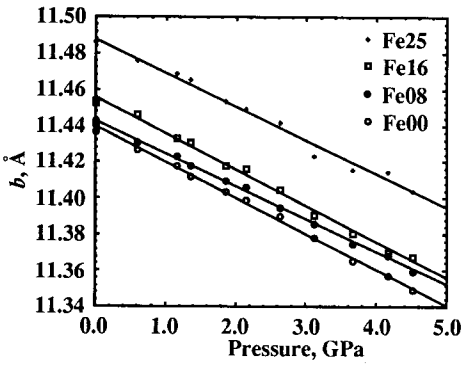


**Fig. 2.** Variation of *b* versus pressure for $\beta$-$(Mg,Fe)_2SiO_4$

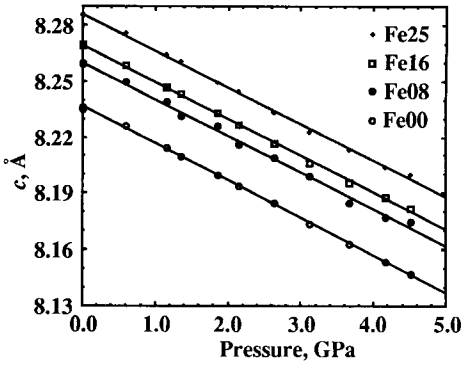


**Fig. 3.** Variation of *c* versus pressure for $\beta$-$(Mg,Fe)_2SiO_4$

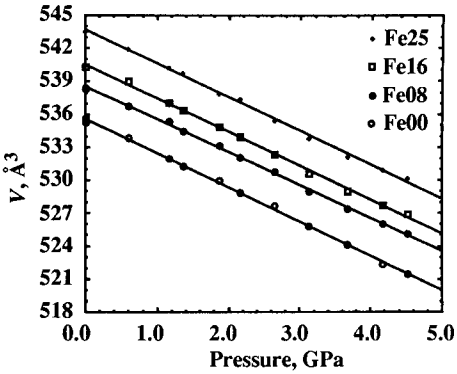


**Fig. 4.** Variation of *V* versus pressure for $\beta$-$(Mg,Fe)_2SiO_4$

**Table 5.** V/Vo for four modified spinel crystals versus pressure

| Pressure (GPa) | $Fe_{00}$ | $Fe_{08}$ | $Fe_{16}$ | $Fe_{25}$ |
|---|---|---|---|---|
| 0 | 0.99968 | 0.99995 | 1.00003 | 0.99998 |
| 0.60 | 0.99709 | 0.99698 | 0.99755 | 0.99706 |
| 1.16 | 0.99358 | 0.99438 | 0.99388 | 0.99395 |
| 1.35 | 0.99224 | 0.99282 | 0.99261 | 0.99308 |
| 1.86 | 0.98982 | 0.99039 | 0.98985 | 0.98962 |
| 2.14 | 0.98773 | 0.98823 | 0.98818 | 0.98854 |
| 2.63 | 0.98558 | 0.98591 | 0.98526 | 0.98501 |
| 3.11 | 0.98205 | 0.98268 | 0.98193 | 0.98204 |
| 3.67 | 0.97897 | 0.97958 | 0.97897 | 0.97886 |
| 4.17 | 0.97555 | 0.97702 | 0.97662 | 0.97671 |
| 4.51 | 0.97393 | 0.97540 | 0.97510 | 0.97529 |
| 0 after | 1.00028 | 1.00005 | 0.99997 | 1.00002 |

and $165 \pm 3$ GPa if $V_0$ is not constrained. Note, however, that these values are very sensitive to the assumed $K'$, as well as to constraints placed on $V_0$. For example, bulk moduli approximately 3 GPa larger result if $K'$ is assumed to be 3 instead of 4. Furthermore, calculated bulk moduli are almost 5 GPa larger if values of $V_0$ are constrained to the average of the two observed "0" values. ("0 GPa" values measured before and after high-pressure experiments are actually made at some pressure between 0.0 and 0.1 GPa because pressure fluid must be retained in the cell; otherwise surface tension of expanding air bubbles in the pressure chamber can push crystals out of orientation.)

Given these uncertainties, the average isothermal bulk modulus of about 165 GPa determined in this study is in reasonable agreement with the 174 GPa value recorded by Sawamoto et al. (1984) in their Brillouin spectroscopy study of $\beta$-$Mg_2SiO_4$. The small, but possibly significant, differences in bulk moduli of the four different Fe/(Fe+Mg) stem directly from the unexplained differences in *a*- and *b*-axis compressibilities. The $Fe_{00}$ sample, which has relatively compressible *a* and *b*, naturally has the lowest observed bulk modulus of the four. Similarly, $Fe_{08}$ with *a*- and *b*-axis compressibilities slightly less than average also has a larger than average bulk modulus.

## Conclusions

Substitution of ferrous iron for one quarter of the magnesium atoms in $\beta$-$Mg_2SiO_4$ has little systematic effect on wadsleyite compressibility. Within a few percent, all four samples studied show the same linear and volume compressibilities, bulk moduli agree with $\pm 3\%$ of 164 GPa. At this level of precision, therefore, iron substitution has no effect on compressibility.

There is, however, unexplained fine structure to the unit-cell versus pressure results. The small, but significant, differences in these four samples may reflect some as yet undescribed minor compositional or structural difference – ferric iron, $OH^-$, stacking faults in the layer-like structure, or other deviations from the ideal $\beta$-$(Mg,Fe)_2SiO_4$ phase. On the other hand, we cannot rule out an unknown source of systematic error that affects our measurements of *a*- and *b*-axis compressibilities, while producing uniform *c*-axis data. High-pressure structural studies of the four samples may clarify the subtle differences among these related crystals.

In either case – deviations from crystal ideality or systematic errors – it appears doubtful that equation-of-state variations will provide a useful means for remote determination of the Fe/(Fe+Mg) of $\beta$-$(Mg,Fe)_2SiO_4$ in the earth's mantle. The significant density effects of iron substitution must remain the best indicator of mantle iron content.

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