Reports

Synthesis and Equation of State of (Mg,Fe)SiO₃ Perovskite to Over 100 Gigapascals

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Silicate perovskite of composition $(Mg_{0.88}Fe_{0.12})SiO_3$ has been synthesized in a laserheated diamond-anvil cell to a pressure of 127 gigapascals at temperatures exceeding 2000 K. The perovskite phase was identified and its unit-cell dimensions measured by in situ x-ray diffraction at elevated pressure and room temperature. An analysis of these data yields the first high-precision equation of state for this mineral, with values of the zero-pressure isothermal bulk modulus and its pressure derivative being $K_{0T} =$ 266 ± 6 gigapascals and $K'_{0T} = 3.9 \pm 0.4$. In addition, the orthorhombic distortion of the silicate-perovskite structure away from ideal cubic symmetry remains constant with pressure: the lattice parameter ratios are $b/a = 1.032 \pm 0.002$ and $c/a = 1.444 \pm$ 0.006. These results, which prove that silicate perovskite is stable to ultrahigh pressures, demonstrate that perovskite can exist throughout the pressure range of the lower mantle and that it is therefore likely to be the most abundant mineral in Earth.

UMEROUS HIGH-PRESSURE PHASEequilibrium experiments carried out over the past 10 years have shown that the dominant minerals of the earth's upper mantle, olivine [(Mg,Fe)₂ SiO₄], pyroxene [(Mg,Fe)SiO₃], and garnet [(Mg,Fe,Ca)₃Al₂Si₃O₁₂], all transform to a dense, perovskite-structured high-pressure phase coexisting with minor oxides at the conditions of the earth's lower mantle (>24 GPa, ≥ 2000 K) (1, 2). Although silicate perovskite is believed to be an important mineral component of the mantle, no studies of its physical properties have yet been carried out at pressures above 40 GPa. Indeed, measurements of the detailed structure, bulk modulus, thermal expansion, and mid-infrared and Raman spectra have all used perovskite samples quenched from high pressures and temperature to ambient conditions (1, 3). Therefore, the purpose of the present study was to investigate the stability and structure of (Mg,Fe)SiO₃ perovskite in situ over a pressure range representative of the entire lower mantle: 24 to 136 GPa (4).

In this study, perovskite was synthesized from a natural orthopyroxene of composition (Mg_{0.88}Fe_{0.12})SiO₃ (Table 1). A gasketted Mao–Bell type diamond cell was used (5), and three to five small ruby chips were placed over each sample to allow us to measure the pressure by the ruby fluorescence method (6). Once the desired pressure had been obtained, the orthopyroxene in each run was converted to perovskite by heating with a CW Nd:YAG (yttrium-aluminum-garnet) laser (7). After conversion to perovskite, the samples were x-rayed in the diamond-anvil cell without lowering the pressure (ϑ). Results were obtained for five samples synthesized at pressures ranging from 25 to 127 GPa, as summarized in Table 2. We found no evidence for the presence of any phase other than the perovskite.

After the high-pressure diffraction patterns were obtained, the samples were xrayed at zero pressure in a conventional 57.3-mm Debye-Scherrer camera. The zero-pressure lattice parameters were calculated based on 12 to 20 diffraction lines,



Fig. 1. Room-temperature static-compression data (closed circles) for $(Mg_{0.88}Fe_{0.12})SiO_3$ perovskite. The compression measurements (open circles) below 10 GPa are from Yagi *et al.* (10). The solid line through the data is the isotherm calculated on the basis of the Birch-Murnaghan equation of state derived from an Eulerian finite-strain formalism. Error bars show the standard deviation.

yielding $a = 478.3 \pm 0.7$ picometers (pm), $b = 493.5 \pm 0.8$ pm, and $c = 689.6 \pm 0.7$ pm, and a zero-pressure density of $4.254 \pm 0.002 \times 10^6$ g m⁻³. These values are in accord with previous measurements (1, 3), thus supporting our conclusion that no phase other than perovskite was synthesized: partitioning of iron and magnesium with respect to another phase would be expected to alter the lattice parameters of perovskite (1, 2).

As indicated from the data in Table 2, the ratios of lattice parameters are equivalent at each pressure to the values obtained for perovskite quenched to zero pressure: b/a = 1.032 and c/a = 1.444. Thus, we observe no change in the degree of distortion for this orthorhombic structure over the pressure range of the mantle (9). This result is in accord with the earlier measurement of Yagi *et al.* to 8.5 GPa (10). One theoretical prediction that the distortion of the silicate-perovskite structure increases with pressure is not supported by our data, but more recent calculations appear to be consistent with our measurements (11).

The room-temperature isotherm for $(Mg_{0.88}Fe_{0.12})SiO_3$ perovskite is plotted in Fig. 1, and the room-temperature staticcompression data of Yagi *et al.* (10) are shown for comparison. The solid line represents the isotherm calculated with the use of a Birch-Murnaghan (Eulerian) finite-strain equation of state (12). The bulk modulus and its pressure derivative, for use in the equation of state, are determined by calculating Birch's normalized stress and strain variables from the pressure-volume data (12). In this formalism, the strain is:

$$f = \frac{1}{2} \left[(V/V_0)^{\frac{-2}{3}} - 1 \right]$$
(1)

where V/V_0 is the ratio of the high-pressure to zero-pressure volume. Also, defining the normalized pressure

$$F = \frac{P}{3f(1+2f)^{\frac{5}{2}}}$$
(2)

where P is pressure, we obtain a polynomial expansion:

$$F(f) = K_{0T} \left[1 + \left(\frac{3}{2} K'_{0T} - 6 \right) f + \dots \right] (3)$$

Here, K_{0T} is the isothermal bulk modulus at zero pressure, and K'_{0T} is its pressure derivative. Because our data do not resolve higher order terms in the expansion, we derive values of K_{0T} and K'_{0T} by a linear least-squares fit as shown in Fig. 2. A fit to all of the static-compression data, including those of Yagi *et al.* (10), yields

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Table 1. Composition of orthopyroxene starting material.*

Constituent	Fraction (%)
MgO	34.22 (0.69)†
TiŎ	0.03 (0.05)
MnO	0.05 (0.03)
NiO	0.05 (0.15)
SiO ₂	56.19 (0.59)
FeO	8.54 (0.14)
CaO	0.29 (0.04)
Al_2O_3	0.05 (0.03)
Total	99.38
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Fig. 2. The five new static-compression data points (closed circles) and the data from Yagi *et al.* (10) (open circles) plotted as Eulerian strain (f) versus the normalized pressure (F). Error bars show the standard deviation.

*Electron microprobe analysis; sample from Bamble, Norway. †Values in percent by weight with standard deviations given in parentheses.

Table 2. Compression data for (Mg_{0.88}Fe_{0.12})SiO₃ perovskite*

Run number	Pressure† before heating (GPa)	Pressure after heating (GPa)	X-ray diffraction data		Lattice			
			hkl	<i>d</i> -spacing (pm)	parameters (pm)	V/V ₀	b/a	c/a
121985	86 (10)	77.8 (1.2)	$112 \\ 211 \\ 113 \\ 004 + 220 \\ 132 + 024 \\ 312$	$\begin{array}{c} 227.3 \ (0.7) \\ 192.7 \ (0.6) \\ 178.1 \ (0.3) \\ 161.3 \ (0.2) \\ 132.2 \ (0.5) \\ 129.3 \ (0.3) \end{array}$	a = 446.5 (1.4) b = 461.7 (1.4) c = 645.2 (2.0)	0.817 (0.003)	$1.034 \\ (0.005)$	1.445 (0.006)
020686	112 (16)	101.7 (2.3)	$ \begin{array}{r} 112 \\ 211 \\ 022 \\ 004 + 220 \end{array} $	$\begin{array}{c} 225.2 \ (1.4) \\ 189.2 \ (0.4) \\ 184.4 \ (0.6) \\ 157.9 \ (0.3) \end{array}$	a = 440.2 (1.4) b = 454.8 (1.5) c = 635.9 (2.0)	0.782 (0.004)	1.033 (0.005)	1.445 (0.007)
041586	127 (10)	111.9 (3.0)	$002 \\ 110 \\ 112 \\ 211 \\ 004 + 220$	318.8 (1.7) 315.7 (1.1) 223.8 (0.3) 189.7 (0.7) 159.0 (0.3)	a = 439.8 (1.5) b = 454.1 (1.6) c = 635.7 (2.2)	0.780 (0.003)	$1.032 \\ (0.005)$	1.445 (0.007)
042886	53 (6)	47.0 (3.3)	112113122004 + 220131132 + 024312	$\begin{array}{c} 232.7 \ (0.5) \\ 182.9 \ (0.4) \\ 177.4 \ (0.3) \\ 164.1 \ (0.2) \\ 145.6 \ (0.1) \\ 135.4 \ (0.2) \\ 132.4 \ (0.3) \end{array}$	$ a = 457.6 \ (1.3) \\ b = 471.5 \ (1.3) \\ c = 660.4 \ (1.4) $	0.875 (0.003)	1.030 (0.005)	1.450 (0.005)
063086	25 (5)	20.8 (2.3)	$112 \\ 211 \\ 122 \\ 004 + 220 \\ 132 + 024 \\ 312$	$\begin{array}{c} 238.1 \ (0.5) \\ 200.7 \ (0.5) \\ 180.9 \ (0.4) \\ 168.2 \ (0.6) \\ 138.5 \ (0.3) \\ 135.5 \ (0.3) \end{array}$	a = 466.5 (1.7) b = 481.7 (1.8) c = 676.5 (2.1)	$\begin{array}{c} 0.934 \\ (0.004) \end{array}$	$1.033 \\ (0.005)$	1.450 (0.007)

*Uncertainties in parentheses are standard deviations. †For a detailed explanation of the difference between the pressure columns, see (7).

 $K_{0T} = 266 \pm 6$ GPa and $K'_{0T} = 3.9 \pm 0.4$. Our new values are in good agreement with those of Yagi *et al.* based on the lowpressure data, but the tenfold increase in the pressure range of the data obtained in this study provides tighter constraints on the equation of state than is possible from the low pressure data alone (13). As has been emphasized in numerous studies, such equation-of-state data play a central role in evaluating the constitution of the earth's deep interior (14).

In summary, we have demonstrated that the high-pressure perovskite phase of $(Mg,Fe)SiO_3$ is stable over essentially the entire range of conditions existing in the earth's lower mantle. Moreover, we find that the detailed structural distortion of this phase is remarkably stable over the broad range of pressures and temperatures so far investigated. Altogether, our experiments provide direct evidence that silicate perovskite is likely to be the most abundant mineral constituent of the planet.

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- study. 8. A MoK_{α} x-ray beam from a Rigaku rotating-anode x-ray generator is collimated to approximately 50 μ m and directed along the axis of applied force through the diamond cell.

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- 15. Work supported by the National Science Foundation.

17 October 1986; accepted 19 December 1986

Lysosphingolipids Inhibit Protein Kinase C: **Implications for the Sphingolipidoses**

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Lysosphingolipids potently and reversibly inhibited protein kinase C activity and binding of phorbol dibutyrate in vitro and in human platelets. As with activation of protein kinase C by phosphatidylserine and sn-1,2-diacylglycerol, inhibition was subject to surface dilution. Accordingly, inhibition in mixed micelle assays was dependent on the molar percentage of lysosphingolipids rather than the bulk concentration. Lysosphingolipids inhibited protein kinase C activity at molar percentages similar to those required for activation by phosphatidylserine and sn-1,2-diacylglycerol. Since lysosphingolipids accumulate in Krabbe's disease, Gaucher's disease, and other sphingolipidoses, the hypothesis that lysosphingolipid inhibition of protein kinase C represents the missing functional link between the accumulation of sphingolipids and the pathogenesis of these disorders appears to unify existing data. The accumulation of lysosphingolipids would cause progressive dysfunction of signal transduction mechanisms vital for neural transmission, differentiation, development, and proliferation and would eventually lead to cell death.

ROTEIN KINASE C PLAYS IMPORTANT roles in signal transduction, cellular differentiation, and tumor promotion. The interaction of extracellular signals with their receptors leads to the phospholipase C-dependent hydrolysis of inositol phospholipids, especially phosphatidylinositol-4,5-bis-phosphate, resulting in the formation of two second messengers, inositol tris-phosphate (IP_3) and diacylglycerol



Fig. 1. Structure of lysosphingolipids. Lysosphingolipids are derivatives of the long-chain base sphingosine where the 1-hydroxyl is substituted by different head groups. With the exception of lysosphingomyelin (sphingosylphosphorylcholine) where the linkage is through a phosphodiesteric bond, lysosphingolipids have a glycosidic bond at C-1.

(DAG) (1). IP₃ mobilizes Ca^{2+} from intracellular stores (2). DAG activates protein kinase C (1). Phorbol diesters, which are potent tumor promoters, also bind to and activate protein kinase C (3, 4).

Protein kinase C is found in highest concentrations in the mammalian central nervous system (5) where it appears to participate in transduction of neurotransmitter and other signals, receptor regulation (1, 6), and neuronal differentiation. Phorbol diester receptors are associated with fetal brain cells that are actively elaborating neurites (7). Protein kinase C activity in rat brain rises during the first month of postnatal development (8); it also changes in primary neuronal cultures with age (9). Localization of protein kinase C by specific antisera to the perinuclear and presynaptic areas (10) is consistent with a role in neuronal differentiation and function. Although the precise role of this enzyme in neural development is unknown, the correlations noted suggest that alterations in its level or activity during critical periods in neural development could result in functional and pathologic changes.

Sphingosine was discovered in our laboratory to be a potent and reversible inhibitor of protein kinase C activity and of phorbol diester binding in mixed micellar assays, and

also in human platelets, neutrophils, and HL-60 cells (11). The critical structural features of sphingosine required for inhibition of protein kinase C were the primary amine and a hydrophobic character (11). Since inhibition still occurred when the 1hydroxyl was substituted, the question of whether lysosphingolipids (Fig. 1) would inhibit protein kinase C arose. This question is of interest for at least two reasons: (i) naturally occurring inhibitors of protein kinase C could be of importance in the regulation of signal transduction; and (ii) lysosphingolipid inhibition of protein kinase C might have functional consequences in the sphingolipidoses.

The sphingolipidoses are a group of diseases that arise as a consequence of inborn errors of sphingolipid metabolism (see Fig. 4). These diseases have their onset most commonly in the neonatal period of early childhood with affected patients exhibiting organomegaly or progressive mental and neurologic dysfunction (12). Usually there is a deficiency of a lysosomal enzyme involved in the catabolism of a particular sphingolipid, resulting in the accumulation of lipid molecules proximal to the enzymatic lesion. Progressive accumulation of sphingolipids occurs predominantly in the lysosomes of the tissues where synthesis or catabolism (or both) is most active. The lipid-storing cells, specific for each disease, are scattered throughout the involved tissues such as spleen, liver, lung, lymph nodes, bone marrow, and central nervous system. In patients with neurologic disease there is, in addition, neuronal degeneration, loss of cells from the cerebral and cerebellar cortexes, brain atrophy, gliosis, and demyelination. The excessive accumulation of sphingolipids, which are normal cellular lipid constituents, is thought to result in the formation of the lipid-storing cells. However, the molecular basis linking sphingolipid accumulation, the histopathology, and the severe neurodegenerative disease has remained a mystery.

We now report that lysosphingolipids (Fig. 1) are potent inhibitors of protein kinase C activity and of phorbol-diester binding, both in vitro and in human platelets. We propose that lysosphingolipids represent the functional missing link between the accumulation of sphingolipids and the pathogenesis of the sphingolipidoses.

Lysosphingolipids differ from their respective parental sphingolipids by not hav-

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