Table 2
Estimated values of K_S and $(\partial K_S/\partial p)$ for spinels in the $Mg_2SiO_4-Fe_2SiO_4$ system.

Mg/(Mg+Fe) ratio, mole %	ρ (g/cm^3)	K_S (Mb)	from eq. (3) $(\partial K_S/\partial p)$	from table 1 $(\partial K_S/\partial p)$
100	3.556	1.86	4.1	4.4
95	3.620	1.87	4.2	4.4
90	3.683	1.87	4.2	4.5
85	3.750	1.88	4.3	4.5
80	3.815	1.89	4.4	4.6
50	4.209	1.93	4.8	4.8
0	4.849	1.96	5.5	5.1

Table 3
Elastic properties and equation-of-state parameters of spinels in the (Mg,Fe) Al_2O_4 system.

Composition	ρ (g/cm^3)	V_p (km/sec)	V_S	μ (Mb)	K_S	$\left(\frac{\partial K_S}{\partial p}\right)_T$	Ref.
$MgAl_2O_4$ (p) *	3.581	9.761	5.492	1.080	1.972	4.30(±0.25)	[15]
$MgAl_2O_4$ (s)	3.581	9.764	5.492	1.080	1.974	3.76(±0.04)	[17]
$MgAl_2O_4$ (s)	3.581	9.712	5.465	1.072	1.950	–	[16]
Mg(2.6) Al_2O_4 (s)	3.619	9.914	5.642	1.154	2.020	4.18(±0.09) ***	[18]
Mg(2.6) Al_2O_4 (s)	3.619	9.914	5.642	1.154	2.020	3.76(±0.04) ***	[17]
Mg(3.5) Al_2O_4 (s)	3.630	9.928	5.660	1.164	2.026	–	[33]
Pleonaste ** (s)	3.826	9.265	5.043	0.973	1.987	4.90(±0.25)	[19]

* (p) stands for polycrystalline samples and (s) stands for single-crystal samples.

** This pleonaste has a "[(0.75)Mg(0.36)Fe] $Al_{1.90}O_4$ composition" [19].

*** This apparent difference in the $(\partial K_S/\partial p)$ values measured on the same sample, but by different investigators, seems to indicate the present inaccuracies in the attempt to characterize this important equation-of-state parameter of mantle minerals.

3. Equations of state

The forms of solid equations of state most often used in geophysics are those of Murnaghan and Birch. The Murnaghan equation of state [20], derived from the theory of finite strain, is an approximation in which the instantaneous bulk modulus is assumed to be a linear function of pressure. O.L. Anderson [21, 22], following Ryabinin [23], demonstrated with fifteen substances an applicability of the Murnaghan equation for predicting the compression curve of a solid; however, a perusal of the theory of the Murnaghan equation of state indicates that the Murnaghan equation should not be used for a solid in a pressure range above 0.5K. As stated by Chung et al. [24], use of the Murnaghan equation of state would lead to overestimates of the density and the seismic parameter ϕ at high pressures. The reasoning here is associated not only with the Murnaghan assumption of a linear variation of the bulk modulus with pressure but also with an inadequacy of the functional form of the equation itself. In his review, Macdonald [25, 26] presented several other limitations for the use of the Murnaghan equation of state at high pressures; he concluded from thermodynamics that the Murnaghan equation yields a finite negative pressure at which the density approached a finite value which is an unacceptable result. Therefore, we use the Birch equation in our discussion of equations of state for the olivine-transformed spinels.

While the Murnaghan equation of state was found by integrating a Taylor expansion of the bulk modulus in pressure, the Birch equation of state is based on the Taylor expansion of the strain energy with respect to the Eulerian strain components. Thus, the Birch equation of state is a phenomenological equation based on the rapidly converging Taylor expansion of the interatomic potential; the equation was derived from the finite strain theory of Murnaghan with the cubic and quadratic terms of the strain retained in the expression for Helmholtz free energy [27, 28]:

$$p = (3K_0/2)(y^7 - y^5)\,[1 + \tfrac{3}{4}(m-4)(y^2-1)] \qquad (4)$$

where $y = (V_0/V)^{\frac{1}{3}} = (\rho/\rho_0)^{\frac{1}{3}}$. K_0 and m are material parameters corresponding to the isothermal bulk modulus and its first pressure derivative evaluated at zero pressure. (If eq. (4) is used in an adiabatic form, K_0 and m are respectively the adiabatic bulk modulus and the adiabatic pressure derivative of the adiabatic bulk modulus).

Therefore, we propose the following equations of state for the olivine-transformed spinels in the $(Mg_xFe_{1-x})_2\,SiO_4$ system:

$$\begin{aligned}
&\text{For } \beta\text{–}Mg_2SiO_4\text{–spinel}: p(\text{in Mb}) = 2.79\,(y^7 - y^5)\,[1.3(y^2-1)]\\
&\text{For } \beta\text{–}(Mg_{0.9}Fe_{0.1})_2SiO_4: p(\text{in Mb}) = 2.81\,(y^7 - y^5)\,[1.4(y^2-1)]\\
&\text{For } (Mg_{0.8}Fe_{0.2})_2SiO_4: p(\text{in Mb}) = 2.84\,(y^7 - y^5)\,[1.5(y^2-1)]\\
&\text{For } (Mg_{0.5}Fe_{0.5})_2SiO_4: p(\text{in Mb}) = 2.89\,(y^7 - y^5)\,[1.6(y^2-1)]\\
&\text{For } Fe_2SiO_4\text{ (spinel)}: p(\text{in Mb}) = 2.94\,(y^7 - y^5)\,[1.8(y^2-1)]
\end{aligned} \qquad (5)$$

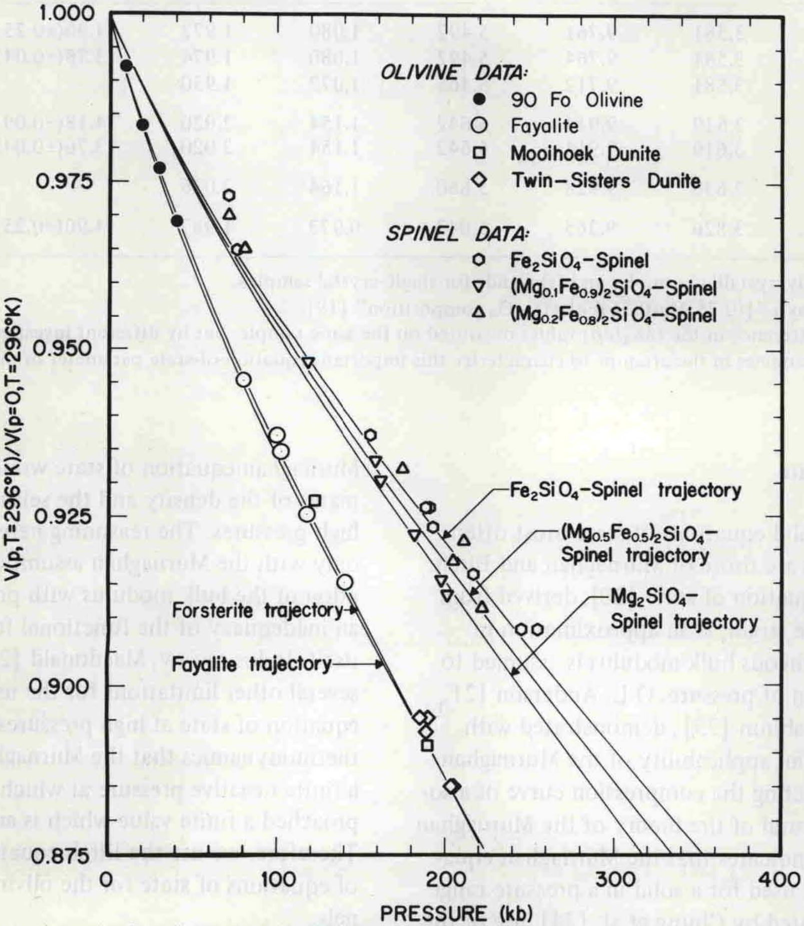

Fig. 5. Volume-pressure trajectories for olivines and the olivine-transformed spinels; comparison with isothermal compression data due to ref. [12]. The solid lines are from the present work, and they are independent of the compression data points.