Optimal equations of state for mantle minerals from simultaneous non-linear inversion of multiple datasets

B.L.N. Kennett, Ian Jackson*

Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia

A fully non-linear inversion scheme is introduced for the determination of the parameters controlling the equation of state of mineral phases using the thermodynamically consistent formulation introduced recently by Stixrude and Lithgow-Bertelloni. The formulation is based on a directed search in an eight-dimensional parameter space using the neighbourhood algorithm developed by Sambridge to search for the minimum of an objective function derived from the misfit to multiple data sets that constrain different aspects of the mineral behaviour. No derivatives are employed. The progress towards the minimum builds on the accumulated information on the character of the parameter space acquired as the inversion progresses. When only a limited range of experimental information is available there is a strong possibility of multiple minima in the objective function, which can pose problems for conventional iterative least-squares or other gradient methods. The addition of many different styles of data tends to produce a better defined minimum. The non-linear inversion works directly with experimental measurements and the parameter values are controlled by the full set of data rather than derived from individual data sets. The influence of different data types can be readily assessed by allowing differential weighting.

The new procedure is illustrated by application to MgO, for which extensive experimental data are available. These include the variation of relative volume $V$ with temperature $T$ and pressure $P$ from both static and shock-compression experiments, acoustic measurements of compressional and shear (and hence bulk) moduli, and calorimetric determinations of entropy as a function of temperature at atmospheric pressure. Preliminary neighbourhood algorithm inversions highlighted tensions between marginally incompatible subsets of data. We have therefore excluded one-atmosphere $V(T)$ data for $T > 1800$ K for which the quasi-harmonic approximation is inadequate, along with elastic moduli derived from Brillouin spectroscopy under conditions ($P > 14$ GPa) where significant departures from hydrostatic conditions are expected. With these limited exclusions based on sound physical principles, the neighbourhood algorithm search identified a compact family of models that provide a good fit to the diverse experimental data and a measure of the covariance between key model parameters. The optimum model also provides a good fit to shock wave data that were not employed in the inversion.

Comparison of alternative models for the thermoelasticity of MgO, evaluated under appropriate $P-T$ conditions, suggests that residual uncertainties in the values of key thermoelastic parameters may continue to preclude definitive answers concerning the chemical composition and temperature of the Earth’s lower mantle. A particular issue is sensitivity to pressure calibration and an alternative NA inversion provides a model that is independent of any empirical pressure scale.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

A thermodynamically consistent formulation for the equation of state of mineral systems has been presented by Stixrude and Lithgow-Bertelloni (2005) that can be specified in terms of nine distinct variables. The ambient volume can normally be determined precisely by X-ray diffraction studies, leaving eight physically significant parameters that can be constrained by different sets of experimental results (or ab initio computations). A characteristic feature of mineral physics is the wide variety of methods that can be brought to bear on the properties of a material at different conditions of temperature and pressure. The different data sets have varying intrinsic reliability and constrain different aspects of the behaviour, and need to be used together to provide a description of the material properties through an equation of state. The merit of the formulation developed by Stixrude and Lithgow-Bertelloni, building on the earlier work of Davies (1974), is that it
is possible to represent all the different styles of available data sets through the same set of parameters.

Stixrude and Lithgow-Bertelloni (2005) advocate an iterative approach to the determination of the eight free variables in their formulation of the equation of state. They use particular data sets to constrain certain parameters and then employ these values in further optimisations to determine the remaining quantities. Such an approach can cope with unavailable data sets by extrapolation from mineral systems for which properties are better known. However, there is a very real possibility of error propagation through the iterative process, so that the later parameters to be extracted will carry a strong imprint from the earlier.

We here adopt a rather different strategy. We view the equation of state as a representation of the material parameters and seek to find the set of parameters which best allow an appropriate fit to all available data sets. To this end we use a direct search method for inversion in the eight-dimensional physical parameter space, exploiting the properties of the very effective neighbourhood algorithm (NA) of Sambridge (1999), which has been used with considerable success in a wide variety of problems (e.g., earthquake location, receiver function inversion, oil-field production). The neighbourhood algorithm uses stochastic sampling of the eight-dimensional parameter space, to search for combinations of parameters with acceptable fit to the different classes of data. Considerable flexibility is allowed in the choice of misfit measure because no differentiation is needed.

At each stage the eight-dimensional parameter space is partitioned into a series of convex polygons called Voronoi cells. Each cell surrounds a previously generated model (specified by the eight different parameters) for which the fit to the data has been determined. As the algorithm proceeds new models are randomly generated in the neighbourhood of those models that have smaller data misfit. In this way all previous models guide the search, and the more promising regions of parameter space are preferentially sampled.

We demonstrate the application of this fully non-linear inversion procedure for the parameters controlling the equation of state by application to MgO. We employ both a restricted data set and a compilation of the full range of available data. In each case the neighbourhood algorithm technique is highly effective at both determining the best fitting set of model parameters, and also in providing insight into the nature of the potential trade-offs between different classes of parameters. The exploration of the eight-parameter space demonstrates that there is potential for multiple minima in the misfit criterion that would pose considerable dangers for a conventional iterative least-squares procedure.

The optimal model fitted to the full range of experimental data is inevitably a compromise among the various constraints. The residual uncertainties relating, for example, to the issue of pressure calibration are sufficient to lead to noticeable variations in extrapolation to lower-mantle conditions. The variability poses questions as to the application of the equation of state results to the interpretation of chemical composition and temperatures at depth.

2. Determination of equation of state parameters

2.1. Non-linear inversion

The conventional approach to parameter estimation for mineral physics data sets is to use a least-squares formulation in an iterative inversion, with linearisation around successive model estimates. Such a process requires the calculation of the derivatives of the observed quantities with respect to the parameters describing the equation of state. The calculation of such derivatives normally requires multiple numerical evaluations since analytical formula-tions are rarely available. Because local linearisation is applied, the results can be quite sensitive to the assumed starting point and although convergence may occur to a minimum, it is by no means guaranteed to represent the best fit to data.

With the advent of faster computers it is now feasible to calculate the estimates of the observed quantities afresh for each postulated set of parameters rather than rely on linearisation and so avoid any differentiation. This more flexible formulation allows us to use more general representations of the misfit functions, e.g., robust measures that can reduce the significance of outliers.

In this paper we introduce the NA for the representation of the properties of minerals through the determination of the parameters specifying an equation of state. We employ the Stixrude and Lithgow-Bertelloni (2005) formulation that can be described through eight different parameters related to the thermodynamic properties of the material. The NA procedure exploits all previous information in the inversion procedure to focus in on those parts of parameter space where the current misfit measure is least (Sambridge, 1999). For the equation-of-state problem the NA algorithm in the form we have used undertakes a broad search in eight-dimensional space and exploits the character of the misfit behaviour to focus attention on those models which have the best fit to data.

The non-linear inversion works directly with experimental results. The influence of the various datasets can be readily assessed by employing different weighting for individual data sets.

2.1.1. The use of a neighbourhood algorithm

The neighbourhood algorithm is a derivative-free method for searching a multidimensional parameter space for models of acceptable data fit. It is based on some simple geometrical concepts, involves two tunable parameters, and makes use of randomised, or stochastic, sampling of parameter space. We outline the approach below. Full details can be found in Sambridge (1999).

The central idea behind the neighbourhood algorithm is the use of Voronoi cells to guide the search in parameter space. Voronoi cells are simply nearest neighbour regions, as defined by a suitable distance norm (e.g., Okabe et al., 1992). Here we use the \( L_2 \)-norm with a sum over each of the distinct data sets constraining the mineral properties. Fig. 1 shows examples of Voronoi cells, defined about an irregular set of points in the plane. Each cell is a convex polygon about its defining point. Note that the sides of each cell are formed from the perpendicular bisectors between neighbouring pairs of points. Voronoi cells have many useful properties and have found applications in a number of fields (see Okabe et al., 1992 for a review). From Fig. 1 we see that the size and shape of Voronoi cells automatically adapts to the density and distribution of the defining points. This is the property which is exploited in the search algorithm. We see from Fig. 1 that the Voronoi cell defines a neighbourhood about each point.

The main consideration for the neighbourhood algorithm inversion is to set a search space by specifying bounds on the variations of the individual equation-of-state parameters. Such bounds can be quite coarse, and indeed it is advantageous not to choose too narrow a span so that the algorithm can determine the large-scale properties of the eight-dimensional space before focussing on the finer details. An initial population of \( n_s \) models is generated, with each specified by the eight physical parameters. Usually this initial population is chosen to follow a uniform random distribution within the bounds on the parameter space. At each iteration, the current \( n_s \) models with lowest data misfit are determined and a new set of \( n_r \) models are uniformly distributed inside their Voronoi cells, that is, \( n_r/n_s \) in each cell. Subsequent iterations are repeated in a similar manner, with the \( n_r \) best models and their Voronoi cells being updated at each iteration. The number of models per iteration \( n_r \) and the number of Voronoi cells to be occupied are the
two tuning parameters of the NA procedure. For each model tested, we calculate the associated set of observable quantities for each of the different data sets and use this to generate the appropriate composite misfit measure.

The algorithm only uses the composite misfit measure to rank the goodness of fit of the different models; the actual value of the misfit is not used directly. The use of a rank measure to drive the algorithm allows considerable freedom in controlling the way in which the data influence the NA search. For the equation-of-state problem we have summed a misfit function for each type of data, using a specification of relative data error as the primary means of determining the relative weight to be applied to each data set. Fig. 1 shows an example of the neighbourhood algorithm (used for a four-parameter problem) at iterations 1, 5, 10, and 20, with \( n_s = 9 \) and \( n_r = 2 \). Notice how the Voronoi cells adapt to the sampling and quickly focus in the south eastern part of the domain. The precise details of the sampling method are described in Sambridge (1999). It turns out that the book-keeping calculations are surprisingly straightforward and may be handled very efficiently.

The behaviour of the search algorithm depends on the two control parameters, \( n_s \) and \( n_r \). As can be seen in Fig. 1, for small values of \( n_s \), the NA procedure takes on the character of a contracting irregular grid, and can efficiently optimize a function. The power of the NA approach is due to the fact that at each iteration the sampling is driven by the size and distribution of the Voronoi cells, and these are controlled automatically by all previous samples.

In the application to the equation of state we have used \( n_s = 15 \) and \( n_r = 5 \), which allows for a broader sampling of the parameter space. As we note below we have found examples where there can be distinct local minima in the misfit function, and such situations are best handled when the neighbourhood algorithm can explore the parameter space rather than be tuned to rapid convergence.

2.1.2. Inversion assessment

We have found that the results from the neighbourhood algorithm for the equation-of-state problem are very robust provided we use a sufficient number of iterations. We have used 500 iterations so that in all, 7500 different combinations of model parameters are tested in each inversion. The way in which the algorithm determines the minimum in misfit depends on the initial distribution of sampling in eight-dimensional space, which is controlled by the “seed” provided to the random number generator. The values of the parameters at the location in eight-dimensional parameter space with the best fit to data hardly vary when runs are made with different seeds, and there is a very clear delineation of the region of best fit.

Even with a conservative strategy for parameter space sampling, convergence is achieved within the set of 7500 trials. With 3000 models (200 iterations) the character of the final configuration becomes apparent, but the extra testing refines the parameter estimates and confirms the validity of the global minimum of the misfit. The Strixrude and Lithgow-Bertelloni formulation allows a compact scheme for computing the various observable quantities, so that rapid calculations can be made for each set of parameters. With a full set of 14 datasets of many different types for MgO the computation time for 7500 models and the manipulations needed for the NA inversion is of the order of 140 s on a Sun Blade 200, which is not a particularly fast workstation. This relatively quick computation means that it is entirely feasible to undertake a number of inversions with different specifications.
The neighbourhood algorithm is much more effective than a simple random Monte Carlo sampling of the same region of eight-dimensional parameter space. Based on a number of tests we would estimate that at least 300,000 trials would be required to ensure that the misfit would approach the level achieved with the NA technique.

We have combined the misfit information for the different classes of dataset by simple addition of suitable measures for each type of data. The relative significance of the different types of information is primarily controlled by the assumptions made about the relative errors for that class of data. We have also included the possibility of differential weighting between data sets and so, by adjusting the weights, we can examine the influence of individual data sets or types of data.

The neighbourhood algorithm is able to track several patches of apparently good fit simultaneously (Sambridge, 1998) and so converge to the true global minimum. The search space is determined by the specified set of bounds on the values of the parameters. If the bounds are set too narrowly for a particular parameter the algorithm will not be stopped but will tend to a solution and the extreme of the range for that parameter.

3. Applications to equation-of-state inversion

The Stixrude and Lithgow-Bertelloni (2005) formulation of the equation of state is based on a finite strain expansion with a vibrational density of states approximated by the Debye model. This Birch–Murnaghan–Mie–Grüneisen–Debye representation depends on a finite strain expansion with a vibrational density of states approximated by the Debye model. This equation of state is based on a finite strain expansion with a vibrational density of states approximated by the Debye model. This equation of state is based on a finite strain expansion with a vibrational density of states approximated by the Debye model. This equation of state is based on a finite strain expansion with a vibrational density of states approximated by the Debye model.

The remaining eight parameters have to be determined from the different physical properties of the mineral as a function of temperature and pressure. A group of parameters describes the elastic moduli and their variation with pressure; these are the isothermal bulk and shear moduli at zero pressure and temperature $K_{00}$, $G_{00}$ and their pressure derivatives under the same conditions $K_{00}'$, $G_{00}'$. The remaining parameters are related to the thermal characteristics of the material: $\theta_0$ is the effective Debye temperature—a summary quantity for the vibrational contributions in the quasi-harmonic approximation, $\gamma_0$ is the Grüneisen parameter, $q_0$ represents the logarithmic derivative of $\gamma_0$ with respect to volume and $\eta_0$ is the shear-strain derivative of $\gamma_0$.

The temperature derivative at constant pressure for a quantity $M$ such as an elastic modulus can be expressed as a combination of an intrinsic part associated with the temperature dependence at constant volume and the extrinsic part induced by thermal expansion:

$$
\left( \frac{\partial M}{\partial T} \right)_p = \left( \frac{\partial M}{\partial T} \right)_V - \alpha T \left( \frac{\partial M}{\partial P} \right)_T,
$$

where $\alpha$ is the thermal expansion coefficient. The quantities appearing in (1) can be evaluated from the Stixrude and Lithgow-Bertelloni formulation in an internally consistent manner for specified conditions of temperature and pressure. The intrinsic temperature dependence of the isothermal bulk modulus is given approximately by

$$
\left( \frac{\partial K}{\partial T} \right)_V \approx -\alpha K_T (q - 1)
$$

and the extrinsic part by $-\alpha K_T K_T'$. The relative proportions of intrinsic and extrinsic contributions are thus controlled by the ratio of $(q - 1)$ to $K_T$. The corresponding approximation for the intrinsic temperature dependence of the shear modulus is

$$
\left( \frac{\partial G}{\partial T} \right)_V \approx -\alpha K_T \frac{\eta}{\gamma}
$$

and now the balance between intrinsic and extrinsic contributions for the shear modulus depends on the ratio between $\eta_0/\gamma$ and $G_T'$. We will make use of these dependencies in the presentation of the results of the inversion for the eight physical parameters.

3.1. Parameterisation and misfit function

We should note that the eight parameters that control the equation-of-state are of very different physical dimensions and further that the available data sets cover very different physical characteristics. Internally the inversion algorithm works with quantities scaled by the specified bounds so that the effective parameters used are non-dimensional.

We specify a relative error $\sigma_i^{\text{ref}}$ for each dataset and build the overall objective function representing the overall misfit as a sum of $L_2$ contributions from each of the $N$ datasets:

$$
\mathcal{F} = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{m(i)} \left( \frac{d_i^{(j)} - c_i^{(j)}}{\sigma_i^{(j)}} \right)^2,
$$

where $m(i)$ is the number of data points in the $i$th dataset. For each dataset $d_i^{(j)}$ is the experimental quantity and $c_i^{(j)}$ is the corresponding quantity calculated from the equation of state using the current set of parameter values. Once again we are working with non-dimensional contributions so we are able to combine the misfits for the different data sets. The weighting term $w_i^{(j)}$ allows us to vary the influence of the individual data sets and so determine the sensitivity of the inversion to particular types of data.

As noted above the neighbourhood algorithm works by ranking the values of the objective function for the different parameter sets. The minimum of $\mathcal{F}$ is not sought directly, but instead the smallest value of $\mathcal{F}$ encountered during the directed search in the eight-dimensional parameter space is returned. The full set of values of $\mathcal{F}$ are kept in a database and so we can undertake retrospective assessment of the quality of the solution, with associated displays of the co-variation of different combinations of pairs of parameters.

3.2. Restricted data set for MgO

Our first illustration of the application of the neighbourhood algorithm approach is with just four different datasets:

(a) Entropy $S$ as a function of temperature $T$ at a pressure of 0.1 MPa from calorimetry as tabulated by Robie and Hemingway (1995);
(b) Thermal expansion $V(T)$ data from the dilatometric measurements of Suzuki (1975);
(c) Shear modulus and bulk modulus as a function of temperature $T$ at 0.1 MPa from the single-crystal resonance measurements of Isaak et al. (1989);
(d) Compressional and shear wave speeds as a function of relative volume $V/V_0$ and temperature $T$ from the high pressure ultrasonic transfer-function measurements of Kono et al. (2007, 2009).

In this inversion we have set $V_0$ to 11.244 cm$^3$ mol$^{-1}$ (Smyth and McCormick, 1995) and the relative errors for entropy $\sigma(S)/S$ as $10^{-2}$, for the thermal expansion $\sigma_T$ is $10^{-3}$ and for the elastic moduli and wave speed measurements we have used $\sigma_v$ as $10^{-2}$. The bounds on the parameters used in the directed search are shown in Table 1. As can be seen the ranges for the parameters are broadly drawn so as to encompass a spread beyond the expected values.
Fig. 2. Display of the sampling of eight-parameter space in the course of the inversion for the restricted set of information for MgO (four datasets). The symbols are colour coded by misfit. Large misfits are indicated by open symbols, but once the misfit is below a threshold colour is introduced with a progression from light to darker tones as misfit decreases. The group of models with closest misfit to the optimum are shown in black. The crossplots are designed to illustrate the dependencies of the elastic moduli and their derivatives, the relationship of the thermal variables, and the comparative behaviour of the intrinsic and extrinsic parts of the moduli.

Fig. 2 represents the outcome of the inversion through a sequence of crossplots of various parameters. In the first row we use the parameters relating to the elastic moduli and their derivatives, in the second the thermodynamic parameters. The final row compares the contributions from the intrinsic and extrinsic components of the bulk and shear modulus. In this plot we display all the 7500 parameter sets tested during the neighbourhood inversion with the points coded by the level of data misfit ($F$). For misfits above a certain threshold all points are plotted with open symbols, tone is then introduced in a progression to darker symbols. The immediate neighbourhood of the minimum is represented through black points to allow an assessment of the control on the parameter set.

The displays allow us to see some of the trade-offs that occur between different parameters as the minimum misfit is approached. Thus, for example, the relative variation in $\gamma_0$ is much greater than in $\theta_0$ for the better fitting models. Nevertheless the actual minimum when found is tightly defined. The plot of the $K_T$ trials against those for $K'_T$ shows clear evidence for dual regions of good fit, whereas this is not evident for the shear modulus. Such multiple minima can have a major impact on methods relying on iterative linearisation to solve the non-linear problem. Yet, as can be seen for Fig. 2, the directed search of the neighbourhood algorithm is able to exploit all the information on the character of the misfit dependence in eight-dimensional space to find a clear global minimum.

The progress to the global minimum samples a broad range of parameter values, but quite rapidly the algorithm delineates the main regions of better fit and then concentrates attention in this area. For this case it is possible to achieve more rapid convergence to the global minimum by reducing $n_r$ so that new sampling is concentrated near the best current point. Nevertheless we favour a broader sampling strategy to cope with potential inconsistencies between datasets that can contribute to the presence of local minima.

### Table 1
Ranges allowed for the eight parameters in the inversion.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{T0}$</td>
<td>158 GPa</td>
<td>164 GPa</td>
</tr>
<tr>
<td>$K'_T$</td>
<td>3.7</td>
<td>4.5</td>
</tr>
<tr>
<td>$G_{T0}$</td>
<td>127 GPa</td>
<td>133 GPa</td>
</tr>
<tr>
<td>$G'_T$</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>763 K</td>
<td>783 K</td>
</tr>
<tr>
<td>$\theta_0$</td>
<td>1.35</td>
<td>1.65</td>
</tr>
<tr>
<td>$\delta_0$</td>
<td>0.5</td>
<td>1.7</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>2.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

3.3. Inversion with a broad range of data sets

Building on the success of the restricted inversion in the previous section we now assemble a comprehensive set of mineral physics data for the properties of MgO and undertake an inversion for the eight parameters controlling the equation of state with constraints from 14 different data sets. We supplement the data employed previously with:

- $V(T)$ data from X-ray diffraction to 3000 K from Dubrovinsky and Saxena (1997), $\sigma_r(V/V_0) = 0.002$;
Wavespeeds \( V_p, V_s \) as functions of temperature, for a polycrystalline specimen from ultrasonic interferometry measurements in a liquid pressure medium from Jackson and Niesler (1982), \( \sigma(M) = 0.002; \)

Wavespeeds \( V_p, V_s \) as a function of relative volume, for a polycrystalline specimen from ultrasonic transfer-function measurements from Li et al. (2006), \( \sigma(V_p, V_s) = 0.001; \)

Relative volume as a function of pressure from Speziali et al. (2001), \( \sigma(V/V_0) = 0.0015; \)

Relative volume as a function of temperature and pressure from Dewaele et al. (2000), \( \sigma(V/V_0) = 0.005; \)

Shock compression \( \rho(P) \) data from Marsh (1980), Vassiliou and Ahrens (1981), Svendsen and Ahrens (1987) and Duffy and Ahrens (1995), \( \sigma(\rho) = 0.01. \)

We have normally employed the relative errors suggested for the particular experimental datasets, with some slight adjustments to achieve balancing of the different datasets. Thus, e.g., we have decreased the relative error for entropy from that used in the restricted inversion to \( 7 \times 10^{-3} \), and used \( \sigma(V/V_0) = 2 \times 10^{-4} \) for the thermal expansion data of Suzuki (1975).

Initially we used pressure as the dependent variable for the static compression data and for the shock-wave results. Although it was possible to get satisfactory results in the inversion, we needed to assign rather high relative errors to balance these data classes against the rest. We therefore switched to volume as the dependent variable and were able to get a much more effective balance. The change required slightly more complex coding, but the rate of convergence of the inversion was improved.

Some tensions amongst marginally incompatible datasets were identified from preliminary NA inversions of the expanded dataset. For example, \( V(T) \) for \( T > 1800 \) K (Dubrovinsky and Saxena, 1997; Fiquet et al., 1999) was substantially over-predicted by the optimal model indicating a strong preference of these data for \( q_0 \sim 0.7 \), substantially lower than that of the final optimal model (Table 2). Similarly, the Sinogeikin and Bass \( M(P) \) data from Brillouin scattering were systematically overestimated by the optimal model—implying the need for lower values of \( K_f \) and \( G_f \). However, these imperatives for lower \( q_0 \) and \( K_f \) are opposed by the influence of the \( M(T) (M = K_f, L) \) data of Isaaq et al. (1989) and Jackson (unpublished data) where the underestimation of \( \frac{\partial K_f}{\partial T} \) by the optimal model would favour somewhat larger values of \( K_f \) and/or \( q_0 \).

Wu et al. (2008) have recently assessed the realm of validity, in \( P-T \) space, of the quasiharmonic approximation inherent in the Stixrude and Lithgow-Bertelloni formulation being used in the present study. They concluded that an empirical correction for the intrinsic temperature dependence (at constant volume) of the lattice vibrational frequencies for MgO becomes significant for temperatures beyond a pressure-dependent threshold rising from \( \sim 1500 \) K at \( 0.1 \) MPa to \( \sim 4500 \) K at \( 200 \) GPa. We have accordingly chosen to exclude one-atmosphere thermal expansion data for \( T > 1800 \) K from our final inversion. We have also excluded the Brillouin scattering \( M(P) \) data of Sinogeikin and Bass (2000) for \( P > 14 \) GPa on the grounds that the frozen methanol–ethanol–water pressure medium supports non-hydrostatic stress that may significantly perturb the measured pressure dependence of elastic moduli. The Brillouin scattered data of Zha et al. (2000) for \( P > 20 \) GPa, obtained with a He medium, have also been excluded because of much greater curvature in the \( G(P) \) trajectory than is compatible with the third-order principal isotherm.

In the fully non-linear inversion for the equation of state parameters we make use of the information contained in all the different datasets simultaneously and thereby aim for an optimal representation of the overall behaviour. As can be seen from Fig. 3, the zone of best fit for this composite data set, indicated in black, is very tightly defined. As a result we have well-controlled values for the equation of state parameters for MgO that are presented in Table 2. We note that the shape of the zone of best fit indicates some slight trade-offs between different equation-of-state parameters.

We have used the same style of display in Fig. 3 as in Fig. 2. It is immediately apparent that the requirements of the larger group of datasets force much more stringent requirements on the parameter set if good fit to all the data is to be achieved. We summarise the outcomes for the parameters in Table 2. The estimates of the likely deviations are based on multiple inversions with differences in both weighting of datasets and the random seeds used in the inversion. As can be seen in Fig. 3 there are some trade-off trends between different parameters that need to be recognised, and so the deviations cannot be considered to be entirely uncorrelated. Some trade-offs also appear between the intrinsic and extrinsic parts of the moduli as the misfit diminishes, with some residue remaining in the shape of the region of best fit in parameter space. The values of \( q_0 \) and \( \gamma_0 \) are more tightly controlled than the derivatives \( \eta_0 \) and \( \eta_0 \).

In the inversion we endeavour to exploit the dependence of each data set on the full set of eight parameters, and so we can find that the multiple data constraints pull the parameter set in different directions. Nevertheless the optimal model derived from the inversion of the full range of data sets provides a excellent overall fit (\( \chi^2 = 0.57 \)) as well as a satisfactory fit to each of the individual datasets as illustrated in Fig. 4. We can note some specific trends in the level of fit that can be associated with the tensions introduced by the requirements imposed by the many different constraints on the material behaviour.

The values obtained from the inversion are quite similar to those deduced by Stixrude and Lithgow-Bertelloni (2005) using a sequential iterative least-squares procedure on a much more limited set of information. By treating all the available constraints on material behaviour in a single inversion we avoid over dependence on any particular dataset. Further the non-linear inversion provides additional insight into the character of the parameter distribution through the mapping of the misfit function in terms of different sets of parameters.

The predictions of the optimal model are closely consistent with the individual subsets of data as illustrated in Fig. 4. The optimal model achieved by the fully non-linear guided search with the neighbourhood algorithm thus represents an excellent overall fit to a very diverse dataset concerning the thermoelastic properties of MgO. We wish to emphasise that the assimilation of diverse ther-
Fig. 3. Display of the sampling of eight-parameter space in the course of the inversion for the full set of information for MgO (14 datasets). The symbols are colour coded by misfit. Large misfits are indicated by open symbols, but once the misfit is below a threshold colour is introduced with a progression from light to darker tones as misfit decreases. The group of models with closest misfit to the optimum are shown in black. The crossplots are designed to illustrate the dependencies of the elastic moduli and their derivatives, the relationship of the thermal variables, and the comparative behaviour of the intrinsic and extrinsic parts of the moduli.

moelastic data into the framework provided by the Stixrude and Lithgow-Bertelloni (2005) finite-strain formulation has the major advantage of internal consistency. For example, the extrinsic part of the temperature sensitivity $|\partial M/\partial T|_P$ of the elastic moduli $M$, given by $-\alpha K'_T M'$, is consistent with the isothermal compression through the values of $K_T$ and $M'$.

The ultrasonic data of Kono et al. (2007, 2009) for polycrystalline MgO show a modest systematic deviation from the optimal model—being somewhat lower in modulus for $V/V_0 \sim 1$ and more strongly volume (pressure) dependent. Thus an optimal fit to these data alone would require lower $K_{T0}$ and $G_0$ along with higher $K'_T$ and $G'_T$—possibly the result of minor porosity in the polycrystalline specimen that may have been reduced by further sintering at the highest temperatures and pressures. For $V/V_0 < 0.97$, the $T(V/V_0)$ data of Li et al. (2006) for polycrystalline MgO are greater than those predicted by the optimal model by as much as 1% (again favouring a higher value of $K_{T0}$) in contradiction to the constraints from the more precise single-crystal $K(T)$ data. Such trends amongst data for polycrystals suggest a future variant of our current approach in which relative variations in modulus (i.e., $SM/M_0$) caused by changing pressure and temperature are modelled instead of the absolute values of $M$.

The optimal NA model systematically overestimates the density of shock-compressed material by an average 0.5%, increasing to 1.3% for $P > 100$ GPa. This dataset alone would accordingly favour somewhat higher values of $K'$ and $\gamma$ (through higher $\gamma_0$ and/or lower $q_0$). For example, the combination $K'_{T0} = 4.15$, $\gamma_0 = 1.54$ and $q_0 = 1.0$ (Jackson and Niesler, 1982) reduces the average misfit of the shock densities to 0.21% (0.33% for $P > 100$ GPa)– but at the cost of a poorer overall fit – especially to the $V(T)/V_0$ and $K_S(P)$ data.

3.4. Comparison of the predictions of the model with shock compression data

3.4.1. Hugoniot equation-of-state measurements

As part of the NA inversion, the model density $\rho$ or volume $V$ corresponding to each experimental Hugoniot pressure $P_H$ is found by interpolation amongst $(V, P_H)$ pairs calculated from

$$P_H(V) = P_{T0}(V) - \gamma(V) \Delta U_{T0}(V)/V$$

$$\Delta U_{T0}(V) = \int_{V_0}^V dV [\alpha K_T T - P_{T0}],$$

where the change in internal energy on isothermal compression from $V_0$ to $V$ at $T_0$ is given by

with $P$, $\alpha$ and $K_T$ as functions of $V$ at $T_0$, and $\gamma(V)$ evaluated from the Stixrude and Lithgow-Bertelloni model. In this approach, the Hugoniot energy $E_H = 0.5 P_H(V_0 - V)$ is partitioned between isothermal compression at $T_0$ and heating at constant $V$, but the temperature is not explicitly calculated.
Fig. 4. Plots of the fit of the optimal model from the neighbourhood algorithm inversion, indicated by solid lines, to the various data sets on the properties of MgO whose points are denoted by different classes of symbols.
3.4.2. Comparison of the optimal model with shock temperature measurements

In order to compare the predictions of our optimal NA model with the shock temperatures measured by Svendsen and Ahrens (1987, revised by Duffy and Ahrens, 1993), we need to relate the thermal energy increase beyond $T_0$ during shock compression

$$\Delta E_{\text{th}}(V) = E_{\text{th}}(V) - E_{\text{th}}(V_0)$$

to temperature through the specific heat. The model temperature corresponding to each experimental $(P, V)$ pair is found by interpolation amongst $(V, T, \Delta E_{\text{th}}(V, T))$ pairs calculated from the Stixrude and Lithgow-Bertelloni model at the experimentally determined volume $V$. The temperatures thus inferred from the model for shock pressures of 169–196 GPa are consistent with the measured shock temperatures of 3081–3663 K, within the experimental uncertainties (Fig. 5 a).

3.4.3. Comparison of the optimal model with shock measurements of compressional wave speed

Predictions of the optimal model have also been compared with the compressional wave speeds measured under conditions of shock compression by Duffy and Ahrens (1995) as follows. The volume $V$ of the shock-compressed material at each reported Hugoniot pressure was first estimated by interpolation amongst $(V, P, V)$ pairs calculated from the model as outlined above. The associated value of $T$ was then estimated as above by interpola-

Fig. 5. Comparison of the predictions from the optimal NA model with shock temperature and compressional wavespeed data that were not employed in the inversion.

Fig. 6. Sensitivity of the model Hugoniot to variation of key parameters of the model. The shock compression data represented by the plotting symbols are compared with the prediction of the optimal NA model of the present study (middle curve, as in Fig. 4) and alternatives labelled ‘JN’ involving the substitution $K_0' = 4.15$, $\gamma_0 = 1.54$ and $q_0 = 1.0$ (Jackson and Niesler, 1982) and ‘SLB’ corresponding to the model of Stixrude and Lithgow-Bertelloni (2005).

tion amongst $(V, \Delta E_{\text{th}}(V, T))$ pairs calculated from the model at the inferred shock volume $V$. Finally, $V_p$ was calculated from the model values of $K_S$ and $C$ for the $(V, T)$ conditions. These predictions are also in reasonable accord with the experimental data (Fig. 5b).

3.5. Comparisons with previous analyses

The optimal NA model of the present study is broadly consistent with that fitted by iterative least-squares to a more limited MgO dataset by Stixrude and Lithgow-Bertelloni (2005, Table 2). The most significant differences are the somewhat higher values of $M_0'$ of the NA model resulting from our exclusion of the $P > 14$ GPa Brillouin scattering data of Sinogeikin and Bass (2000), and the correspondingly lower values of $q_0$ and $\gamma_0$. These apparently minor differences have profound implications for the behaviour at very high pressure and temperature. As anticipated from the discussion of Section 3.3, the significantly lower value of $K_0'$ (3.9) in the Stixrude and Lithgow-Bertelloni (2005) model results in serious systematic overestimation of the shock densities, by an average 0.9% increasing to 1.7% for $P > 100$ GPa (Fig. 6).

Wu et al. (2008) have constructed an equation of state for MgO for use in pressure calibration at high temperature by combining the results of ab initio quasiharmonic calculations with low-pressure experimental data. In so doing, they found that it was necessary to introduce an empirical correction for the intrinsic temperature dependence of the frequencies of lattice vibration—in accord with a previous analysis by Jacobs and de Jong (2003). The latter authors also investigated the use of the Kieffer parameterisation of the vibrational density of states as a more elaborate and physically realistic alternative to the Debye model. However, the Kieffer model, constrained by additional spectroscopic measurements under conditions of high pressure and temperature, and the Debye model were each found to provide an adequate description of the thermoelectricity of MgO, provided that intrinsic anharmonicity was taken into account.

4. Discussion and conclusions

The neighbourhood algorithm has been demonstrated to be a powerful tool for the multi-parameter and multi-dataset inversion
needed to extract the eight parameters that describe the equation of state of a mineral. All the different classes of data are used together, rather than in an iterative sequential approach as advocated by Stixrude and Lithgow-Bertelloni (2005). In particular experimental data over the full available ranges of pressure and temperature are used together. The advantage is that the full range of information that is available to determine the optimum parameter set is brought to bear at once and that there is no influence from prior assumptions. We regard the parameterised form of the equation of state as a representation of the multiple datasets that have been used in the inversion. This representation of all the available data should then represent the best current form in which to make extrapolations to the conditions of high pressure and temperature prevailing in the Earth’s interior.

The fully non-linear approach can be used, if necessary, in a more restricted mode where one or more parameters are fixed by setting identical upper and lower bounds for these parameters. In this way inferences from cognate materials could be used to supplement limited available experimental (or ab initio) results.

The unusually wide range of available thermoelastic data for MgO provides an excellent opportunity for testing the NA inversion strategy. MgO, unlike most minerals, undergoes no shock-induced phase transformation (for \( P \leq 200 \) GPa) so that the extensive set of Hugoniot data are presumed representative of the compression of the B1-structured phase. Moreover, the recent studies by Li et al. (2006) and Kono et al. (2007) combining transfer-function ultrasonics with X-ray diffraction provide measurements of \( V_p \) and \( V_S \), as functions of volume, which like shock-wave data, are independent of any potentially uncertain empirical pressure scale.

However, as is evident from Section 3, even this extensive dataset has its complications and requires very careful evaluation. For example, measurements of \( V_p \) and \( V_S \) have been conducted in recent years to progressively higher pressures and temperatures within diamond-anvil and multi-anvil apparatus, but with Brillouin scattering and transfer-function ultrasonics – acoustic techniques of substantially lower precision (10−3) than ultrasonic interferometry (10−3). Thus the gain in constraining the values of \( M' \) (\( M = K_S, G \)) anticipated from the broadened range of (sometimes non-hydrostatic) pressure may be offset by the reduced precision and absolute accuracy of the measurements. The single-crystal ultrasonic interferometry of Jackson and Niesler to 3 GPa in a liquid pressure medium constrains \( K_{IS} \) to 4.15 ± 0.09, closely compatible with shock compression data (Fig. 6), whereas a value of 3.9, seriously inconsistent with the shock-compression data, is indicated by the diamond-anvil Brillouin-scattering data of Sinogeikin and Bass (2000) and Zha et al. (2000) to 20 and 55 GPa, respectively.

A major effort in the mineral physics community is currently directed towards minimising the impact of uncertainties in pressure calibration (e.g. Zha et al., 2000; Li et al., 2006; Kono et al., 2007, 2009). We have therefore undertaken an alternative inversion using the 9 of the 14 datasets that are independent of an empirical pressure scale. Some of the tensions among different data sets are thereby relieved. The results are tabulated in Table 3; we see that the only significant differences lie in an increase in \( K_{IS} \) and a decrease in \( q_0 \). As a result the fits to the Hugoniot data and the data of Kono et al. (2007, 2009) are markedly improved, with minor changes to the other datasets.

The difficulties in finding a model that fits all of the available data, even for a material as thoroughly studied as MgO, have significant implications for the interpretation of seismological models. This is well illustrated by the evaluation of the models from the Stixrude and Lithgow-Bertelloni (2005) and present NA studies at the representative deep-mantle conditions \( P = 120 \) GPa and \( T = 2300 \) K (e.g., Jackson, 1998). For the NA-derived model based on the 14 datasets, the density, compressional and shear wavespeeds differ by −0.7%, +2.8% and +3.7%, respectively, from those for the Stixrude and Lithgow-Bertelloni model. Interpreted in terms of the quasi-harmonic influence of temperature, this difference in density would require a temperature increase of around 560 K, whereas the substantial positive differences in wavespeeds would require lower temperatures by 1600 to > 2000 K. The inescapable conclusion is that residual uncertainties in the values of key equation-of-state parameters will continue to frustrate analyses seeking definitive answers concerning the chemical composition and temperature profile of the Earth’s lower mantle.

### Acknowledgement

We thank Dr. Kono and his colleagues for access to their unpublished ultrasonic data.

### References


---

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Likely deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_0 )</td>
<td>11.244</td>
<td>( - \text{cm}^2 \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>( K_0 )</td>
<td>160.34</td>
<td>0.05 GPa</td>
</tr>
<tr>
<td>( K_I )</td>
<td>4.34</td>
<td>0.04</td>
</tr>
<tr>
<td>( G_0 )</td>
<td>130.6</td>
<td>0.05 GPa</td>
</tr>
<tr>
<td>( G_I )</td>
<td>2.29</td>
<td>0.03</td>
</tr>
<tr>
<td>( \theta_0 )</td>
<td>768.5</td>
<td>0.2 K</td>
</tr>
<tr>
<td>( \eta_0 )</td>
<td>1.47</td>
<td>0.02</td>
</tr>
<tr>
<td>( \eta_0 )</td>
<td>0.98</td>
<td>0.05</td>
</tr>
<tr>
<td>( M_0 )</td>
<td>2.21</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Overall misfit 0.52 (nine datasets)