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Equations-of-state for close-packed materials at high pressures: geophysical evidence

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Abstract. The Earth's lower mantle and outer core are identified by seismology as regions that are homogeneous in composition and mineral structure over wide pressure ranges. Variations with pressure, P , of bulk modulus, K , density, ρ , and, for the lower mantle, rigidity modulus, μ , are reported in seismic models with much greater resolution than is achieved over similar pressure ranges by laboratory methods. These data are an under-utilized resource for high pressure equation-of-state studies. The lower mantle data are particularly useful for two reasons: (1) the minerals believed to be present can be obtained in metastable equilibrium at low pressure for laboratory examination, (2) a linear relationship between μ , K and P allows extrapolation to infinite pressure, giving a direct estimate of $K'_\infty \equiv (\partial K_s/\partial P)_s(P \rightarrow \infty) = 1.425(10)$. The core equation-of-state is less well constrained, but two independent approaches give $K'_\infty = 3.0(2)$. Although not always recognized K'_∞ is a parameter of every equation-of-state, but none of the usual equations gives values compatible with terrestrial data. A new approach is proposed, representing $K' \equiv dK/dP$ as a function of P/K , since at infinite pressure $(P/K)_\infty = 1/K'_\infty$ and the endpoint of the equation-of-state is precisely determined. Two equations that fit all of the observations are suggested. This use of K'_∞ is particularly relevant to estimates of thermodynamic properties at high pressure because it constrains the dimensionless derivatives K' and KK'' on which these estimates depend.

1. Introduction

High pressure mineral physics is now placing increasingly stringent demands on equations-of-state for the Earth's deep interior. Identification of plausible compositions by extrapolation of P - ρ relationships is still of interest, but is not very demanding of the equations-of-state that are assumed and, as a consequence, provides a poor test of their validity. Attention is turning to higher derivative properties, $K' = dK/dP$ and $K'' = d^2K/dP^2$, which are needed for the estimation of thermal properties. Among these the temperature dependences of elastic moduli are of particular current interest in connection with small lateral variations in seismic velocities that are seen to be superimposed on the strong pressure-driven radial variations. Standard finite strain theory, which to most geophysicists means the theory due primarily to Birch [1], is inadequate for the task. While some other empirical relationships may fare somewhat better, the present study is motivated by the need for a new approach that makes more effective use of existing data.

Rigidity modulus, μ , generally receives little attention in equation-of-state studies. In many situations it is more difficult to measure at high pressure than is bulk modulus, K

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(usually termed incompressibility in geophysical literature), and it does not appear in the thermodynamic identities that link K to other thermoelastic properties. In seismology μ is as well observed as is K , and it is more sensitive to effects such as thermal anomalies and especially partial melting, but, although there have been attempts to incorporate it in finite strain theory, it has had only a minor role in equation-of-state studies. The following section draws attention to a new use of rigidity data in the determination of K'_∞ . This is a parameter of every finite strain theory, but has not been considered experimentally accessible and is rarely even mentioned. Keane [2] recognized its significance and proposed a finite strain equation that incorporated it, but only as a parameter to be fitted to compression data. Elsasser [3] and, more recently, Holzapfel [4] suggested that all finite strain theories should approach the infinite pressure limit $K'_\infty = 5/3$, appropriate for an electron gas in the Thomas–Fermi limit, but this is in conflict with observations on both the Earth's lower mantle and core. Neither Keane's equation nor Holzapfel's equation H12 (which he reports [5] 'can fit all the available data for individual low-or high-pressure phases of any element . . .') gives a satisfactory fit to the Earth's lower mantle.

In the Earth we are not dealing with single elements or, in the case of the mantle, even with simple compounds but with composite materials. This requires a little care in the interpretation of observed elastic moduli [6]. In fitting mineral elasticity data, I have found that the Hill average [7] of Voigt and Reuss limits is as good as any other averaging method [8]. The procedure for averaging derivative properties is given by Stacey [9]. This requires recognition that, when a composite is compressed, the least compressible component becomes an increasing volume fraction of the whole. There is therefore a component of dK/dP additional to that due to the intrinsic increase in K for each constituent. In the case of the lower mantle minerals the values of dK/dP are all quite similar, but because the values of K differ the composite dK/dP is higher than for the individual minerals. This does not affect the lower mantle data directly, but it is important to the zero pressure extrapolation, which is here constrained to the value $K'_0 = 4.21$ [9] in fitting equations-of-state, this being derived from laboratory observations on lower mantle minerals.

A proviso should be noted concerning the new equations that are presented here. They are derived specifically for use with close-packed structures (which may include liquids where rigidity is not considered) at high pressures, such that bond-angle rigidity is unimportant. In this approximation atomic forces are effectively central. Bond angles may be distorted away from their 'preferred' (low pressure) values to accommodate the close-packing and any bond-angle rigidity becomes indistinguishable from central forces between the atoms that are bonded. This approximation is found to be extremely well satisfied in the lower mantle. It probably does not apply to the more open crystal structures of the upper mantle, but a rigorous test is precluded by the limited pressure ranges of mineralogical homogeneity.

2. The μ - K - P equation and K'_∞

In a close-packed structure with central forces and nearest neighbour interactions dominating, all elastic moduli must be explained as derivatives of the same bond potential, $\phi(r)$, as a function of atomic spacing r . At arbitrary pressure, $P \propto -\phi'/r^2$ and, by a second differentiation with respect to volume, $K \propto (1/3)(\phi''/r - 2\phi'/r^2)$ where primes indicate differentiation with respect to r . It follows that $(K - 2/3P) \propto \phi''$. This is an example of what Falzone and Stacey [10] called second order elasticity theory because to calculate strain energy at arbitrary pressure in terms of changes in bond length, Δr , these changes must be calculated to second order in strain. Applying the same principle to shear [10] each of the shear moduli, and a weighted average of them is also seen to be a linear function of ϕ''/r and ϕ'/r^2 or ϕ''/r and P .

In this circumstance there is a linear relationship between μ , K , and P [11, pp 264–7]

$$\mu = AK - BP \quad (1)$$

where both A and B are necessarily positive. This was first pointed out as an explanation for the high Poisson's ratio (0.445) of the Earth's inner core [10] and subsequently [11] to indicate that $\mu/K \rightarrow 0$ as $P \rightarrow \infty$ and that $(P/K)_\infty = 1/K'_\infty$. This is conveniently expressed [12] by rewriting equation (1) to make the physical significance of the constants A and B more obvious

$$\frac{\mu}{K} = \left(\frac{\mu}{K}\right)_0 (1 - K'_\infty P/K). \quad (2)$$

Fitting equation (2) to the lower mantle tabulation in PREM (preliminary reference Earth model [13]) we obtain [11] $(\mu/K)_0 = 0.631(1)$ and $K'_\infty = 1.425(10)$. This fit is surprisingly good bearing in mind the uncertainties in PREM and the long extrapolation to $(\mu/K) = 0$. The reason is evidently that in PREM the P- and S-wave velocities and density are all modelled as third order polynomials in radius over the lower mantle range, and although this parametrization imposes a distortion on derivative properties such as K' , μ and K are affected by the parametrization in exactly the same way and their ratio is unaffected. The remarkable result is that we have a more precise value of K'_∞ than we have of K' at any other pressure.

3. Fitting equations-of-state to the lower mantle

Two new equations constrained to the observed K'_∞ as well as to $K'_0 = 4.21$ [9] are discussed below. Ten other equations have been tried for comparison, but without the K'_∞ constraint, since only one of them meets this fitting criterion. Details of the fitting procedure are given in [9]. The 'successful' equations are the Morse potential, the Rydberg potential, and the Birch fourth order theory (third order theory in the nomenclature of Holzapfel [4], but fourth order according to Birch [1] because Helmholtz free energy is written as a fourth order polynomial in generalized strain). The finite strain equation derived from the Rydberg potential has been strongly advocated by Vinet *et al* [14] and others [15] with no obvious reference to its original derivation in 1932 [16] or subsequent use as an equation-of-state for solids (e.g., [17]). Holzapfel's equations [4, 5] were not included in the reported tests but his equation H12 has since been added to the list of equations that are incompatible with homogeneity of the lower mantle.

In view of the range of apparently quite different equations that fit the lower mantle equally well ($\pm 0.15\%$ in density over the pressure range 28.3–127 GPa), it is evident that such fitting is no indication of an equation's validity (although a misfit is evidence of invalidity). We are dealing with alternative equations that all happen to have the correct form over the tested range. However plotted, the curvature of an equation-of-state is slight and it is fairly easy to find an empirical match to a data set, without a physical basis for it. But the curvature is subtly different for each of the equations and the thermodynamic implications of higher derivative properties, K' and especially K'' , cannot be trusted without more information. This is where the K'_∞ constraint becomes important. It exerts a fine control on the curvature of a $P(\rho)$ or $K(\rho)$ equation, especially at the high pressure end of a tested pressure range. Values of K'_∞ for the three well-fitted equations are $2/3$ for the Morse and Rydberg potentials and $11/3$ for the Birch equation, compared with 1.425 for the lower mantle itself. The curvature of the Birch equation is very serious, for the other two less so, but the case for developing an equation that matches the observed K'_∞ is strong.

In fitting higher derivative equations to the lower mantle tabulation of the Earth model [13] we are effectively limited to a very restricted data set because the manner of model

parametrization effectively imposes its own equation-of-state on the data. The result is curvature of a K' versus P/K plot that is unphysical and simply a figment of the parametrization [9]. However, there is little doubt that the average K' over the lower mantle is reliable. Volume averages for the lower mantle are $K' = 3.369$ at $P/K = 0.1457$. Then, with the two end points, $K'_0 = 4.21$ at $P/K = 0$ and $K'_\infty = 1.425$ at $(P/K)_\infty = 0.702$, it is apparent that a graph of K' versus P/K is only moderately curved and a quadratic equation is an obvious first try

$$K' = K'_0 + K_0 K''_0 \frac{P}{K} + \frac{1}{2} K_0^2 K'''_0 \left(\frac{P}{K} \right)^2 \quad (3)$$

where

$$\frac{1}{2} K_0^2 K'''_0 = K'^3_\infty - K'_0 K'^2_\infty - K_0 K''_0 K'_\infty. \quad (4)$$

We may suppose that equation (3) is the beginning of a convergent series but have insufficient reliable data to evaluate higher coefficients. With the fixed end points and the mean lower mantle values as the third constraint, $K_0 K''_0 = -6.245$, $\frac{1}{2} K_0^2 K'''_0 = 3.243$. Thus, if equation (3) is taken to be the beginning of a series, it looks like the expansion of an exponential

$$K' = K'_0 \exp \left(\frac{K_0 K''_0 P}{K'_0 K} \right) \quad (5)$$

where

$$K_0 K''_0 = K'_0 K'_\infty \ln(K'_\infty / K'_0) \quad (6)$$

so that a more useful form of equation (5) is

$$K' = K'_0 (K'_\infty / K'_0)^{K'_\infty P / K}. \quad (7)$$

Equation (7) has the advantage of requiring one fewer fitted constant than does equation (3). Indeed, it is specified entirely by K'_0 and K'_∞ without requiring a mantle value of K' , which is, paradoxically, the least certain of the parameters used to fit equation (3).

Both equations (3) and (7) fit the lower mantle tabulations of ρ and K very well [9], making a total of five equations that do so. In this circumstance the logical preference is for equation (7). It matches the (K, ρ, P) tabulation to $\pm 0.13\%$ in ρ and 0.6% in K [9] over the whole range, without requiring the problematic selection of a lower mantle value of K' , and the K'_∞ fit ensures that higher derivatives, at least to K'' , are reliable. Since the lower mantle is believed to be close to adiabatic, the fitted equation-of-state is an adiabat, that is $K \equiv K_S = \rho(\partial P / \partial \rho)_S$ and $K'_S \equiv (\partial K_S / \partial P)_S$, where S is entropy.

If equations (3), (5), or (7) have analytical solutions they have yet to be found, but numerical treatment is straightforward and for integration in equal increments in $P/K = x$ we can write

$$\ln \left(\frac{\rho}{\rho_0} \right) = \int_0^x \frac{dx}{1 - x K'} \quad (8)$$

$$\ln \left(\frac{K}{K_0} \right) = \int_0^x \frac{K' dx}{1 - x K'}. \quad (9)$$

Equations (8) and (9) are quite general. For the special case of equations (5) or (7) there is a relationship between these integrals, giving

$$\frac{K}{K_0} \left(\frac{\rho}{\rho_0} \right)^b = \frac{K'}{K'_0} \left/ \left(1 - K' \frac{P}{K} \right) \right. = \frac{K K''}{K_0 K''_0} \quad (10)$$

where $b = K_0 K''_0 / K'_0$ as in equations (5) and (6).

4. Thermal properties

Equation (7) gives K' directly in terms of P/K . ρ/ρ_0 , K/K_0 and KK'' are obtained from equations (8), (9) and (10). The connection between these quantities and thermal properties is made via the thermodynamic Grüneisen parameter

$$\gamma = \frac{\alpha K_T}{\rho C_V} = \frac{\alpha K_S}{\rho C_P} \quad (11)$$

α being volume expansion coefficient and C is specific heat at either constant volume or constant pressure. For many purposes (such as calculation of adiabatic temperature gradients) knowledge of γ suffices, but where specific values of α are required they are obtained from γ by equation (11) with the assumption that C_V is known, the temperature being everywhere well above the Debye temperature. In the case of the silicate mantle this means $C_V = 3R = 24.9 \text{ J K}^{-1} \text{ mol}^{-1}$ with a small anharmonic correction [18]. Thus virtually all geophysical calculations of thermal properties have relied on one or other of the rival formulae relating γ to the pressure dependences of elastic moduli. There are two survivors from the original wider field, the acoustic gamma and the modified free volume gamma. Numerically they agree reasonably on the variation of γ with depth in the lower mantle (table 1), but the fact that there are still two different formulae with strong proponents is an admission that this is not an unambiguously resolved problem.

Table 1. Grüneisen parameter in the Earth's lower mantle: a comparison of two theories.

Radius (km)	Pressure P (GPa)	Bulk modulus K (GPa)	Acoustic γ	Modified FV γ
Zero pressure reference	0	203.2	1.355	1.366
5600	28.29	313.3	1.225	1.225
5200	46.49	380.3	1.181	1.161
4800	65.52	444.8	1.148	1.114
4400	85.43	508.5	1.119	1.078
4000	106.39	574.4	1.097	1.051
3630	126.97	641.2	1.080	1.031

The acoustic γ derives from the original Grüneisen definition of a mode γ , $\gamma_i = -(\partial \ln v_i / \partial \ln V)_T$ for an identified lattice mode of frequency v_i by supposing that all modes are either compressional or shear acoustic modes and that one simply sums the γ_i for the two mode types in proportions 1/3 and 2/3, giving

$$\gamma_A = \frac{1}{6} \frac{K}{K + \frac{4}{3}\mu} \frac{dK}{dP} + \frac{1}{3} \frac{K + 2\mu}{K + \frac{4}{3}\mu} \frac{K}{\mu} \frac{d\mu}{dP} - \frac{1}{6}. \quad (12)$$

This has seemed attractive because it appeals directly to the seismically observed elasticities and so is immediately calculable from an Earth model. The lower mantle K' variation by equation (7) with corresponding μ by equation (2) gives the values in table 1. Dispersion of mode frequencies is no problem because it is the logarithmic derivative that is needed, but, apart from the neglect of optic modes, the assumption that all acoustic modes are appropriately averaged by the two available moduli is not easy to assess. For many materials equation (12) gives reasonable values, but doubt is raised by the fact that it gives a positive γ for a simple, central force harmonic lattice, for which γ should be negative.

The free volume γ does not appeal to the existence of modes, but can be derived by considering the motions of individual atoms in the force fields of their neighbours. It takes its

name from a derivation by free volume theory [19] but has been derived by two other quite different methods [20, 21]

$$\gamma_{FV} = \frac{\frac{1}{2} \frac{dK}{dP} - \frac{5}{6} + \frac{2}{9} \frac{P}{K}}{1 - \frac{4}{3} \frac{P}{K}}. \quad (13)$$

The coincidence of three derivations appeared persuasive, but a molecular dynamical calculation [22] revealed a flaw. All of the derivations assumed either explicitly or implicitly that the thermal motions of neighbouring atoms were uncorrelated, but this is not what is observed. Motions of neighbours are positively correlated, more so for motion in the direction of the bond joining them than transversely. More recently a higher anharmonic (high temperature) correction factor, h , has been added [18], resulting in what I now refer to as the modified free volume γ

$$\gamma_{MFV} = h \frac{\frac{1}{2} \frac{dK}{dP} - \frac{1}{6} - \frac{f}{3} \left(1 - \frac{1}{3} \frac{P}{K}\right)}{1 - \frac{2}{3} f \frac{P}{K}} \quad (14)$$

where

$$h = 1 + \frac{m}{2} (K' - 1) \frac{\Delta\rho}{\rho}. \quad (15)$$

Here m is a numerical factor depending on the differing atomic masses (unity for a monatomic lattice but about 1.45 for lower mantle minerals) and $(-\Delta\rho/\rho)$ is the total thermal dilation at the specified pressure. For this purpose the expansion coefficient is obtained from γ itself by equation (11) but assumed to vary with temperature in the manner of a Debye function. At $P = 0$ the effective Debye temperature is $\theta_D \approx 950$ K and the potential temperature $T \simeq 1725$ K [9] with T/θ_D taken as constant over the adiabatic temperature profile. The factor f in equation (14) accounts for the correlations in atomic motion. If the correlation in instantaneous (thermal) displacements of a pair of neighbouring atoms from their equilibrium positions were the same for motions in the direction of the bond joining them and transversely to it, then f would be 2. This corresponds to γ_{FV} (equation (13)). But the transverse correlation is always smaller and $f > 2$ (see [12]). f is not an absolute constant, but for monatomic lattices $f \approx 2.35$ and for typical minerals $f \simeq 2.27$. For a hypothetical harmonic lattice ($K'_0 = 1$), equation (14) gives negative γ_0 , as expected ($\gamma_0 \approx -0.45$). Partly for this reason I favour the use of equation (14) rather than equation (12).

Given a function $K'(P/K)$ carefully matched to seismic observations (equation (7)) and $\gamma(K', P/K)$ by equation (14) one can immediately calculate two other thermal parameters, α and $q = (\partial \ln \gamma / \partial \ln \rho)_T$. Then using a thermodynamic identity we obtain the temperature dependence of K_S

$$-\frac{1}{\alpha K_S} \left(\frac{\partial K_S}{\partial T} \right)_P \equiv \delta_S = K'_S - 1 - \gamma + q - (\partial \ln C_V / \partial \ln V)_S \quad (16)$$

where the last term is neglected at deep earth temperatures. (This is particularly easy to justify for an adiabatic variation of C_V because the variation of Debye temperature, θ , is similar to the adiabatic variation of temperature, that is T/θ is almost constant and the material stays at almost the same point on the characteristic Debye curve.) Geophysical applications of these parameters are discussed elsewhere (e.g., [9, 11]) but the principles are general and apply to any high pressure situation.

In geophysics the adiabatic bulk modulus K_S and its pressure and temperature derivatives are emphasized. This is inevitable because seismic waves involve adiabatic compressions and because temperature gradients in the Earth are believed to be close to adiabatic, being controlled by convection. Corresponding isothermal properties that are generally considered in theoretical

studies can be quite different, notably $\delta_T = -1/(\alpha K_T)(\partial K_T/\partial T)_P = (\partial \ln \alpha/\partial \ln V)_T$ is much bigger than δ_S (equation (16)) (by a factor exceeding 1.5 in the lower mantle) and care is required not to confuse them. Compact summaries of identities that relate these parameters in a notation convenient for geophysical applications are given in [11], appendix E, for first derivative identities and [12] for an extension to second derivatives.

5. Liquid iron and the Earth's core

An equation-of-state for the Earth's core is necessarily less precise than for the lower mantle, but nevertheless some useful general conclusions emerge. The limitations arise from two difficulties (1) Most of the core (the outer core) is liquid, precluding application of equation (2). The solid inner core is small and although a reliable average value of μ is obtained, shear waves are not directly observed and $d\mu/dP$ cannot be taken directly from seismology [12]. (2) Assuming the validity of the available data, laboratory liquid iron, or alloys, and the liquid outer core cannot be fitted to a common $K(P)$ relationship, apparently because in the intervening pressure range there are structural changes in the liquid corresponding to phase transitions in solid iron.

The second point may be seen by comparing zero pressure parameters for laboratory liquid iron at its melting point [23], $K_0 = 109.7 \pm 0.7$ GPa, $K'_0 = 4.661 \pm 0.040$, with values at the top of the outer core ($P = 135.75$ GPa), $K = 644.1$ GPa, $K' = 3.58$. If we assume that $(\partial(\partial K_S/\partial P)_S/\partial T)_P \approx 0$, as for deep mantle silicates [18], then we may integrate either equation (5), equation (3) neglecting the final term or any similar equation to estimate K/K_0 and, by assuming the core value of K , obtain $K_0 = 119$ to 122 GPa depending on which equation is assumed to apply. In all cases K_0 is much greater than for laboratory liquid iron, whereas the calculated value should be much less since it corresponds to a higher temperature, that is the foot of the core adiabat. In principle the disagreement could be avoided by assuming that K'_0 is more strongly temperature dependent than appears reasonable. There is no other evidence for this, so the equation-of-state for the core cannot be extrapolated reliably to zero pressure laboratory iron. This means that the constraints on it are much weaker than in the case of the lower mantle.

Nevertheless we can restrict the value of K'_∞ for the core to a very limited range by two independent arguments because the extrapolation is a much smaller one than in the case of the lower mantle. Assuming the laboratory value of K'_0 , and fitting equation (5) to the core data gives $K'_\infty = 3.12$. Alternatively if we appeal to the inner core value of $\mu/K = 0.12$ at $P/K = 0.25$, then any reasonable value of $(\mu/K)_0$, say $(\mu/K)_0 = 0.6$, gives $(P/K)_\infty \approx 0.3125$ at $(\mu/K) = 0$ and therefore $K'_\infty = 1/(P/K)_\infty = 3.2$. In both cases there is little scope for uncertainty because the extrapolation is very short, but if the effect of anelasticity on μ is allowed for, K'_∞ for the core may be as low as 2.8 [18]. Thus we can put $K'_\infty = 3.0 \pm 0.2$ with some confidence. It is certainly quite different from the lower mantle value and from the Elsasser–Holzapfel limit (5/3) based on Thomas–Fermi theory.

6. Conclusions

Recognition that K'_∞ offers the possibility of a powerful constraint on high pressure equations-of-state has a long history [2–5, 11, 12] but a method of obtaining realistic values is recent [9, 11, 12]. It has little value as a parameter to be constrained by $P - \rho$ data-fitting [2] and there is no justification for the supposition [3–5] that it should approach the free-electron (Thomas–Fermi) limit of 5/3. The two terrestrial materials for which seismological observations provide

measured values (lower mantle silicate, $K'_{\infty} = 1.425 \pm 0.010$, and core alloy, $K'_{\infty} = 3.0 \pm 0.2$) are clearly very different and disallow the supposition that is made explicit in some theories [3–5] and is implicit in many others [1, 14, 15, 17] that K'_{∞} is a universal constant. Indeed it may be a physically meaningful parameter only for close-packed materials at high pressure, such as those considered here. In any case, we cannot suppose that it necessarily has the same value for different phases or crystallographic structures of the same material. In spite of being metallic, iron at 130–360 GPa (the Earth's core) is not at all like the free-electron gas that it is presumed to convert to in the Thomas–Fermi limit of extreme compression. It is a completely different phase and its equation-of-state does not extrapolate to that limit. K'_{∞} is a parameter describing the behaviour of a material in its observed state and cannot be carried through the phase transitions that it would undergo on the way to the infinite pressure limit.

The most important reason for wanting to know K'_{∞} is that it provides a close control on the curvature of a plot of K' versus P/K and therefore on the thermodynamic parameters that can be inferred from such a plot. In the case of the Earth it is obvious that these parameters are not obtainable in any other way. The relationships outlined in section 4 are used in studying the thermodynamics of the Earth [9, 11, 12, 24], but are general and can be used for any material for which the equation-of-state is sufficiently well defined.

The essential significance of K'_{∞} is that it is the reciprocal of $(P/K)_{P \rightarrow \infty}$, so that a graph of K' versus P/K has a fixed end point corresponding to the infinite pressure extrapolation. Of course observations of K' are more difficult and uncertain than variations in ρ or K with P , but if they can be obtained they define an equation-of-state much better. It is very convenient that, as in the case of the deep Earth, K'_{∞} itself can be obtained without any observations of K' if rigidity, μ , can be measured and fitted to equation (2). It may not be easy to achieve this in laboratory measurements with the precision of seismological observations of the Earth's interior but the reward will be much better equations-of-state constraints than are generally obtained.

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