

# An Equation of State for Serpentine

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## Abstract

We present here the constants needed by the Analytic Equation of State (ANEOS) [1] package to model serpentine. The data used comes from varied sources with the most important data being shock experiments performed on samples of serpentine by Tyburczy *et al.* [2]. The importance of serpentine in planetary physics is its close resemblance to carbonaceous chondritic material. Since we do not have any equation of state information on carbonaceous chondrites we can use, to a first approximation serpentine.

## 1 Introduction

Pure Serpentine comes in three polymorphs Chrysotile, Antigorite and Lizardite. The formula for Serpentine is  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . Naturally occurring serpentine is a mixture of all three plus other impurities so it is more correctly called *serpentinite*.

Table 1 compares the elements (by weight) found in serpentinite (from Canada) with that of carbonaceous chondrites. The obvious differences between the two are that serpentinite is devoid of FeS (and Carbon) and has considerably more MgO than carbonaceous chondrites. The variation of composition of carbonaceous chondrites though does suggest that serpentinite is a reasonable fit.

## 2 Shock Data

When constructing an equation of state for a particular material the main source of information for the material is the shock data. The shock data is a series of experiments in which the material of interest is hit with a projectile at ever increasing velocities. For each impact the shock velocity and particle

Component	Serpentinite	Carbonaceous Chondrite
FeS	–	6.5–18.4
SiO <sub>2</sub>	37.5–43.4	22.5–33.4
TiO <sub>2</sub>	–	0.07–0.12
Al <sub>2</sub> O <sub>3</sub>	0.38–4.68	1.65–2.93
MnO	0.00–0.27	0.19–0.23
FeO	0.00–9.24	9.45–25.43
MgO	39.3–40.0	15.8–24.0
CaO	0.12–0.32	1.22–2.64
Na <sub>2</sub> O	0.09–0.28	0.22–.75
K <sub>2</sub> O	0.00–0.28	0.04–0.14
P <sub>2</sub> O <sub>5</sub>	–	0.23–0.41
H <sub>2</sub> O+	11.11–15.77	1.40–19.89
H <sub>2</sub> O–	0.10–15.77	0.18–19.89
Cr <sub>2</sub> O <sub>3</sub>	0.00–0.42	0.33–0.52
NiO	0.00–0.30	0.00–1.71
C	–	0.46–4.83

Table 1: Comparison of composition of Canadian Serpentinite and Carbonaceous Chondrites

velocity are measured. Using the Rankine-Hugoniot equations the pressure and density can be calculated. If the shock velocity is  $U_s$  and the particle velocity is  $u_p$  then from the Rankine-Hugoniot equations we find

$$\rho = \frac{\rho_0 U_s}{U_s - u_p} \quad (1)$$

$$P = P_0 + \rho_0 U_s u_p \quad (2)$$

Figure 1 shows the hugoniot data. From the data it is seen that there is a low pressure phase upto about 40 GPa, a possible mixed phase region between about 40 to 50 GPa, a high pressure phase upto about 130 GPa and a possible very high pressure phase is suggested by the 2 points above 130 GPa.

The shock data gives a series of points on the equation of state of the material. Programs like ANEOS use these series of points to extrapolate the entire equation of state.

We will try to model, using ANEOS, the low pressure phase and the high pressure phase. The version of ANEOS used cannot model solid-solid phase transitions and the liquid-solid transition simultaneously.

Figure 1: Hugoniot shock data calculated using equations 1, 2. The lines are calculate using the linear fit to the shock velocity – particle velocity data.

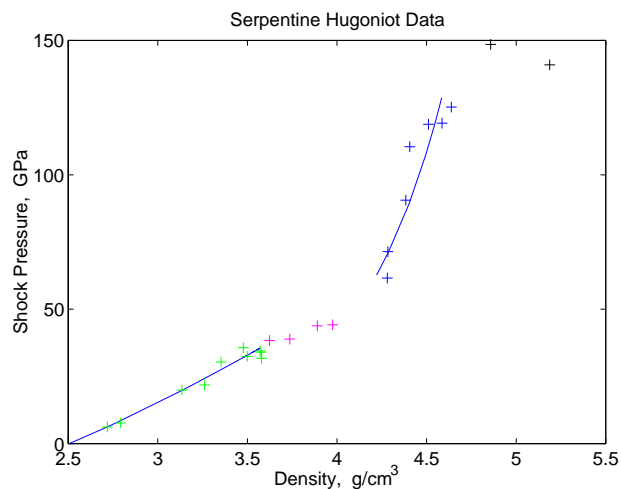


Figure 2: Shock velocity – particle velocity plot. The lines are are a linear fit to the low pressure phase and the high pressure phase.

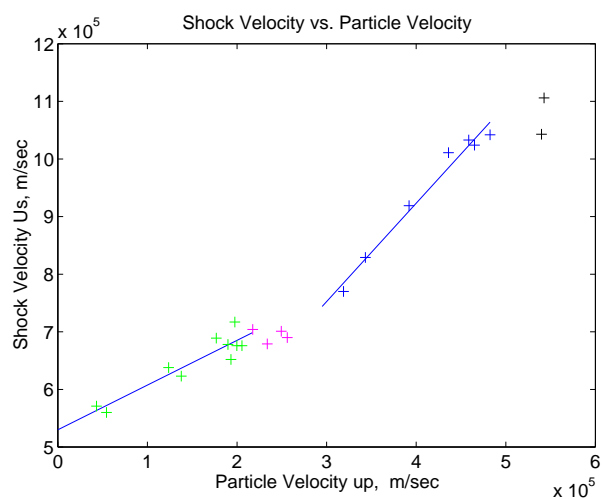


Table 2: ANEOS equation of state parameters for Serpentine.

Variable	Value	Section	Description
ZB(1)	5		Number of Elements in this material.
ZB(2)	4		Switch for type of Equation of State. Compute as a solid-gas with electronic terms and treat the liquid-vapour region in detail.
ZB(3)	2.50	3.1	$\rho_0$ , reference density, g/cm <sup>3</sup> .
ZB(4)	0	3.1	$T_0$ , reference temperature, eV. Default to 298 K.
ZB(5)	0	3.1	$P_0$ , reference pressure, dyne/cm <sup>3</sup> .
ZB(6) <sup>†</sup>	$-5.352 \times 10^{-5}$	3.2	$-S_0$ , intercept of the Hugoniot linear Shock velocity – particle velocity relation
ZB(7)	0.51	3.2	$\Gamma_0$ , reference Grüneisen coefficient.
ZB(8)	$3.892 \times 10^{-2}$	3.2	$\theta_0$ , the Debye temperature, eV.
ZB(9) <sup>†</sup>	0.73015	3.2	$S_1$ , slope of the Hugoniot linear Shock velocity – particle velocity relation
ZB(10)	2		Three times the limiting value of the Gruneisen coefficient for large compressions. Usually 2, which means the limiting value is the expected 2/3.
ZB(11)	$2.5 \times 10^{11}$	3.4	$E_s$ , zero temperature evaporation energy, erg/g.
ZB(12) <sup>†</sup>	0.1871	3.5	$T_m$ , melting temperature, eV.
ZB(13)	0		Parameter for low-density cold-curve modification to move critical point. Normally zero
ZB(14)	0		Parameter for low-density cold-curve modification to move critical point. Normally zero
ZB(15)	0		$H_0$ , thermal conductivity coefficient. If zero thermal conduction is not included.
ZB(16)	0		Temperature dependance of thermal conduction.
ZB(17)	0		$\rho_{\min}$ , lowest allowed solid density. Defaults to $0.8\rho_0$ .
ZB(18)	3.7778	3.6	$\rho_1$ , density at the beginning of the solid-solid phase transition.
ZB(19)	4.1516	3.6	$\rho_2$ , density at the end of the solid-solid phase transition.
ZB(20)	$4.25 \times 10^{11}$	3.6	$P_{\text{ctr}}$ , pressure at the center of the solid-solid phase transition at zero temperature.
ZB(21)	$4.3627 \times 10^{12}$	3.6	$dP/d\eta$ , at the beginning of the high pressure phase transition
ZB(22)	$2.0 \times 10^{12}$	3.6	$d^2P/d\eta^2$ , at the beginning of the high pressure phase transition
ZB(23)	0		$H_f$ , heat of fusion for melt transformation
ZB(24) <sup>†</sup>	0		$\rho_l/\rho_s$ , ratio of liquid density to solid density at the melt point.

<sup>†</sup> These variables have multiple meanings depending on the value supplied.

### 3 ANEOS Parameters

ANEOS in the form we have it is a FORTRAN code of approximately 3000 lines that can given two independent thermodynamic variables can calculate the rest for any material.

To generate the thermodynamically complete and *consistent* EOS, ANEOS formulates everything in terms of the Helmholtz free energy with the density and temperature as the independent variables. The notable advantage of ANEOS over the SESAME data base is that the tabulated EOS does not have to be thermodynamically consistent and in most cases is probably not.

The fundamental assumption in the ANEOS formulation is that the EOS may be written as a superposition of terms appropriate to various physical phenomena. In particular

$$F(\rho, T) = E_c(\rho) + F_n(\rho, T) + F_e(\rho, T),$$

where the subscript  $c$  refers to the zero-temperature isotherm or *cold curve*,  $n$  refers to the nuclear or atomic component, and  $e$  refers to the electronic component. Though these effects are not independent ANEOS minimizes their coupling.

According to the third law of thermodynamics, the entropy must vanish at zero temperature, so the energy and free energy are identical. Both  $F_n$  and  $F_e$  are defined to vanish at zero temperature.

With the density and the temperature as independent variables all other thermodynamic functions can be calculated from derivatives of the free energy. For example the pressure becomes

$$P = \rho^2 \frac{\partial F}{\partial \rho} \quad (3)$$

$$= \rho^2 \frac{dE_c}{d\rho} + \rho^2 \frac{\partial F_n}{\partial \rho} + \rho^2 \frac{\partial F_e}{\partial \rho} \quad (4)$$

$$= P_c(\rho) + P_n(\rho, T) + P_e(\rho, T). \quad (5)$$

To model any material ANEOS requires 24 parameters. These parameters are found from various experimental data. Unfortunately the different experiments use different samples of serpentine. In most cases the samples are more correctly called serpentinite, a mixture of all three polymorphs with added impurities.

#### 3.1 Reference Density, Pressure and Temperature

The reference density, temperature and pressure apply to the low pressure phase. The reference pressure is normally set to zero, the reference temperature is normally 20 C. For the reference density we use the mean density of the samples used in [2].

### 3.2 Cold Curve

ANEOS uses an interpolation function  $P_c(\eta)$ , where  $\eta = \rho/\rho_{00}$  and  $\rho_{00}$  is the density at zero temperature.

The input parameters required for the cold curve calculation are the density, bulk modulus and the Grüneisen coefficient at zero temperature. Unfortunately exact values for these parameters are unknown, so ANEOS uses the values at room temperature, and a power series to predict the zero temperature values.

ANEOS variables  $ZB(6)$  and  $ZB(8)$  have dual meanings depending on the values supplied.

If the reference bulk modulus is supplied in  $ZB(6)$ , then  $ZB(8)$  will be the choice of model to use when calculating the Grüneisen coefficient  $\Gamma$ . The three models to choose from are the Slater-Landau model, the Dugdale-McDonald model and the free-volume theory [1, 5].

On the other hand variables  $ZB(6)$  and  $ZB(8)$  can contain the linear shock velocity – particle velocity intercept and slope respectively. From the Hugoniot data the reference bulk modulus is calculated as well as the equation for the Grüneisen coefficient  $\Gamma$ . When this form of the variables is used the results should be checked for validity.

From [2] we have a reference bulk modulus and a reference Grüneisen coefficient for serpentine. The bulk modulus is 63.5 GPa and the reference Grüneisen coefficient is 0.51.

Using the intercept value of 5.352 km/s (table 2) from the linear hugoniot relation and the following equation from [1],

$$B_0 = \rho_0(s_0^2 - 3\Gamma^2 N_0 k T_0)$$

the calculated bulk modulus from ANEOS is 73 GPa.

### 3.3 Debye Temperature

Aneos models the nuclear contribution to the equation of state by using the Debye-Grüneisen equation of state.

The Debye model for solids assumes that the solid can be described as a lattice of coupled atoms vibrating collectively. Since the solid contains  $N$  atoms there are only  $3N$  oscillating modes possible, and the maximum frequency  $\nu_D$  can be determined. The maximum frequency  $\nu_D$  is normally expressed as a temperature, the Debye characteristic temperature, using

$$h\nu_D = kT_D$$

, where  $h$  is Plank's constant and  $k$  is Boltzman's constant.

The Debye temperature can be found for any material using the shear wave velocity  $v_s$ , and the pressure wave velocity  $v_p$ , of the material. From

Table 3: Seismic data for Serpentine

Density	Pressure	Shear	Mean	Debye	Bulk	Reference
	Wave	Wave	Speed	Temperature	Modulus	
g/cc	km/sec	km/sec	km/sec	K	GPa	
2.81	7.03	3.61	4.043	530	90	[9, 10]
2.636	5.240	2.780	3.107	399	45	[6]
2.714	5.800	3.120	3.483	452	56	[11]

the Debye model it can be shown (see [5])

$$T_D = \frac{h}{k} \left( \frac{9N}{4\pi} \frac{\rho}{\overline{M}} \right)^{1/3} \left( \frac{2}{v_s^3} + \frac{1}{v_p^3} \right)^{-1/3}, \quad (6)$$

where  $N$  is Avagadro's number,  $\overline{M}$  is the mean molecular weight,

The mean sound speed for an isotropic material is defined as

$$\frac{3}{v_m^3} = \left( \frac{2}{v_s^3} + \frac{1}{v_p^3} \right),$$

and in CGI units, 6 becomes

$$T_D = 251.45 \left( \frac{\rho}{\overline{M}} \right)^{1/3} v_m$$

Table 3 lists the various sources for seismic data and the debye temperatures they produce. The mean molecular weight for serpentine is 19.80.

The Debye temperature used was taken from the data that produced the most consistent bulk modulus. A bulk modulus of 56GPa for serpentine is a resonable estimate for the shock data we are using [2]. Tyberczy *et al.* quote a bulk modulus of 64Gpa. So the Debye temperature we will use is 452K.

### 3.4 Sublimation Energy

Benz *et al.*, [3], modified the sublimation energy until the correct evaporation temperature (3350 K) at atmospheric pressure for Forsterite was obtained.

Using the same procedure, and the same evaporation temperature we find the sublimation energy for serpentine.

### 3.5 Melt Temperature

The melt temperature for serpentine is problematic as before serpentine melts it will go through several dehydration reactions. Also as it is made up

of three polymorphs how this occurs will depend on the constituents in the sample tested.

The formation of serpentine is thought to occur in nature via the action of water on Olivine at low temperatures. One of the constituents of Olivine is Forsterite which has the chemical formula of  $\text{Mg}_2\text{SiO}_4$ .

The melt temperature of Forsterite is  $2171^\circ\text{C}$  for the crystal–liquid transition. The melt temperature for the glass–liquid transition is  $1400^\circ\text{C}$  [15].

Lacking the melt temperature for Serpentine the best we can do is the melt temperature for Forsterite. The crystal–liquid melt temperature for Forsterite is used by Benz *et al.* [3] for the melt temperature of Dunite.

### 3.6 Solid–Solid Phase Transition

The solid–solid phase transition is dealt in an approximate manner. The transition cases are restricted to temperature independent transitions. This means that all changes can be made to the cold curve. No changes are made to the thermal components. Though this procedure is not the full story it does allow a partial treatment of phase changes.

The code can model either first order or second order phase transitions. A first order phase transition occurs when there is an obvious mixed phase region. In a mixed phase region the pressure remains constant even though the compression is increasing. A second order transition is a special case of a first order transition, there is no mixed phase region. The cold curve is piecewise continuous at the border between the two phases.

From Figure 1 it can be seen that the phase transition for Serpentine is second order, with a mixing region between 45 to 50 Gpa.

To model the transition ANEOS smoothly interpolates between the cold curve for the low pressure phase and the high pressure phase. To do this it needs the density at the start and end of the mixing phase. The cold curve pressure, and first and second derivative at the start of the high pressure phase. this means that from the hugoniot data we must calculate the properties of the high pressure phase cold curve.

#### 3.6.1 Metastable Hugoniot

The first step in finding the cold curve for the high pressure phase is to transform the hugoniot data for the high pressure phase into the metastable hugoniot [12, 13, 8].

The Rankine-Hugoniot equations relate the pressure, energy, and density behind a steady-state disturbance or shock to the quantities in front of the disturbance or shock. The state of the undisturbed material ahead of the shock (ie Pressure, energy and density) is often referred to as the centering point of the corresponding Hugoniot curve.

Table 4: Constants used to calculate the metastable Hugoniot

Initial Density (Low Pressure Phase)	2.5 g/cc
Initial Density (High Pressure Phase)	3.6 g/cc
Grüneisen Ratio (High Pressure Phase)	1.0
Transition Pressure	42.5 Gpa

The centering point of the Hugoniot data plotted in Figure 1 is serpentine. The metastable hugoniot for the high pressure phase has the centering point shifted to its zero-pressure metastable state.

It is possible to shift the initial conditions of a known Hugoniot using the initial conditions and the Grüneisen equation of state

$$\gamma = V \left( \frac{\partial P}{\partial E} \right)_V = V \frac{P_m - P_h}{E_m - E_h}, \quad (7)$$

where  $\gamma$  is the Grüneisen ratio,  $m$  refers to the metastable Hugoniot and  $h$  refers to the original Hugoniot at the same specific volume  $V$ . This equation can be used to solve for  $P_m$ , the pressure of the metastable Hugoniot.

Using the Rankine-Hugoniot equation for energy, Equation 7 can be rewritten as the pressure difference between the raw Hugoniot data with the low pressure phase as the starting material and the metastable Hugoniot, with the high pressure phase as the starting material.

$$\Delta P = \frac{\rho\gamma(xP - 2\rho_h\Delta E_0)}{\rho_h(2 + \gamma) - \rho\gamma}, \quad (8)$$

where  $x = (\rho_m - \rho_h)/\rho_m$ , and  $\Delta E_0$  is the difference in formation energy of the low pressure phase and the high pressure phase.

To find the energy difference we can use the fact that the Gibbs free energy

$$G = E + PV - TS \quad (9)$$

is constant across a phase change. We equate the Gibbs free energy across the phase transition and assume that the entropy change is negligible and solve for the difference in formation energy at the transition pressure.

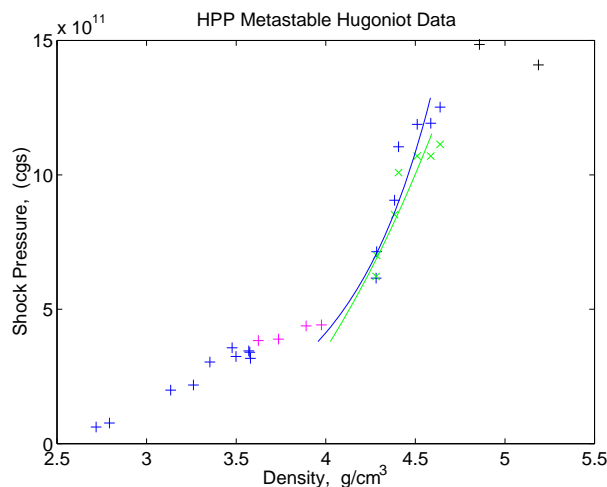
Figure 3 shows the metastable Hugoniot for the high pressure phase calculated using the Rankine-Hugoniot equations, and equations 8 and 9. The constants used to calculate the metastable hugoniot are listed in table 4

### 3.6.2 High Pressure Phase Cold Curve

To calculate the 0°K isothermal equation of state we start with the Mie-Grüneisen equation of state, 7,

$$P_H - P_K = \gamma(E_H - E_K)/V, \quad (10)$$

Figure 3: Metastable Hugoniot (lower curve) for the high pressure phase, calculated from the raw hugoniot (upper curve) data.



where in this case,  $P_H$  is the pressure on the metastable Hugoniot,  $P_K$  is the pressure necessary to compress the material at  $0^\circ\text{K}$  to the same specific volume  $V$  as the metastable Hugoniot. The internal energy  $E_K$  for the isothermal compression is given by

$$P_K = - \left( \frac{\partial E_K}{\partial V} \right)_T \quad (11)$$

The two most popular forms of the volume dependence of the Grüneisen ratio,  $\gamma$ , was given by Slater and later by Dugdale and McDonald (see [5]). Both forms of the volume dependence can be written as

$$-2(\gamma + \beta)/V = \frac{\frac{d^2(P_K V^\alpha)}{dV^2}}{\frac{d(P_K V^\alpha)}{dV}}, \quad (12)$$

where  $\alpha$  and  $\beta$  are constants. In Slater's formula  $\alpha = 0$  and  $\beta = 2/3$ , and in Dugdale and McDonald's formula  $\alpha = 2/3$  and  $\beta = 1/3$ .

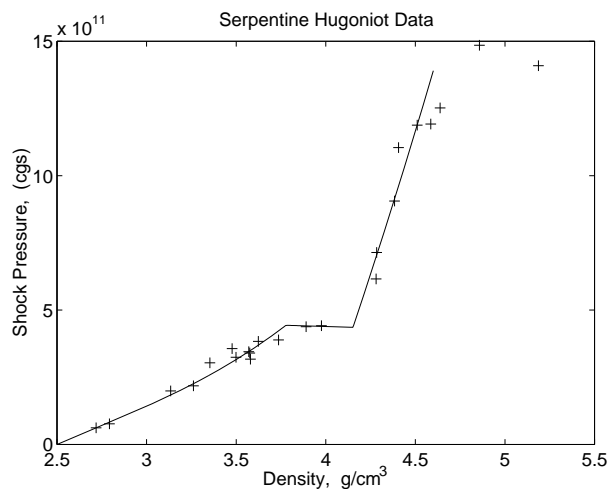
Equations 10, 11 and 12 are the basic equations that determine the  $0^\circ\text{K}$  isothermal  $P$ - $V$  relation or the *Cold-Curve*.

The initial conditions required to solve 10, 11 and 12 are given in [14].

## 4 Results and Conclusion

Figure 4 shows the hugoniot points calculated by ANEOS using the input data from table 2. The ANEOS fit is remarkably good.

Figure 4: ANEOS fit to the Serpentine Hugoniot data. The transition pressure used is 4.25 GPa.



The best fit to the hugoniot data was achieved when the transition pressure was placed at 4.25 GPa, a figure slightly higher than suggested by Tyburczy *et al.* [2]. The higher transition pressure also means that the linear fit to the shock velocities in the low pressure regime are slightly different than found in [2].

Due to the nature of the serpentine some of the material constants required by ANEOS are ill defined. In those cases we have employed known constants from the Forsterite. A possible parent material of serpentine.

Even with these caveates the ANEOS fit to the shock hugoniot data is remarkably good.

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