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## Commentary

# Commentary on "Constraints on the Equations of State of stiff anisotropic minerals: rutile, and the implications for rutile elastic barometry" [*Miner. Mag.* 83 (2019) pp. 339–347]

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### Abstract

The conclusion of Zaffiro *et al.* (2019; Constraints on the Equations of State of stiff anisotropic minerals: rutile, and the implications for rutile elastic barometry. *Mineralogical Magazine*, **83**, 339–347) that the Mie–Grüneisen–Debye (MGD) Equation of State (EoS) cannot fit the available data for rutile is shown to be incorrect, even though rutile exhibits significant anisotropic thermal pressure which invalidates the quasi-harmonic approximation used as the basis for the MGD EoS. The refined parameters for the MGD EoS of rutile are: $K_{TR0}$ = 205.05(25) GPa, $K'_{TR0}$ = 7.2(5), $\theta_D$ = 399(20) K, $\gamma_0$ = 1.40(2) and $q$ = 1.5(7). This EoS predicts volumes, bulk moduli and volume thermal expansion coefficients for rutile at metamorphic conditions that are statistically indistinguishable from those predicted by the 'isothermal' type of EoS reported previously.

In a recent paper Zaffiro *et al.* (2019) compiled from the literature an internally consistent dataset to constrain the volume and cell parameter variation with *P* and *T* of the mineral rutile, $TiO_2$. The dataset consists of 111 data, made up of 17 direct measurements of elastic moduli, 12 direct measurements of dimensional changes with temperature by interferometry and 82 determinations of unit-cell parameters by diffraction. Some of these data were determined at elevated or low *T* at room pressure, and some at elevated *P* at room temperature. There are no available data at simultaneous non-ambient *T* and *P*. Assumptions must therefore be made about either the type of EoS and/or some of the values of its parameters in order to obtain a *P–V–T* EoS for rutile.

Zaffiro *et al.* (2019) explored whether a thermal-pressure EoS could be used to fit the data of rutile. A Birch–Murnaghan EoS was used to describe the compressional behaviour of rutile at room temperature in combination with a Mie–Grüneisen–Debye (MGD) EoS to describe the thermal pressure. The MGD EoS is based on the quasi-harmonic approximation (Anderson, 1995), in which the thermal pressure is derived from a simplified phonon density of states (the Debye model) characterised by the Debye temperature $\theta_D$:

$$\theta_D = \theta_{D0} \, exp\left(\frac{\gamma_0 - \gamma(V)}{q}\right) \qquad (1)$$

It is assumed that $q$ is a constant parameter. Therefore $\theta_D$ is only dependent on the volume $V$ through the thermal Grüneisen parameter $\gamma$:

$$\gamma(V) = \gamma_0 \left(\frac{V}{V_0}\right)^q \qquad (2)$$

The parameters $V_0$, $\theta_{D0}$ and $\gamma_0$ are the values at room conditions. The increase in thermal pressure due to an increase in temperature above room temperature $T_0$ is then:

$$\Delta P_{th}(T, V) = \frac{3nR\gamma}{V}\left[TD\left(\frac{\theta_D}{T}\right) - T_0 D\left(\frac{\theta_D}{T_0}\right)\right]$$
$$= \frac{\gamma(V)}{V}[\Delta E_{th}(T, \theta_D(V)) - \Delta E_{th}(T_0, \theta_{D0})] \qquad (3)$$

in which $D\left(\frac{\theta_D}{T}\right)$ represents the Debye function, $R$ is the gas constant and $n$ is the number of atoms in the formula unit corresponding to the molar volume $V$.

The analysis of rutile by Zaffiro *et al.* (2019) further assumed that the value of the parameter $q$ was 0, which corresponds to the value of $\gamma$ being independent of volume and thus the same for all *P* and *T*. This is consistent with the limited experimental data for rutile (see discussion on p. 343 of Zaffiro *et al.*, 2019). With $q = 0$
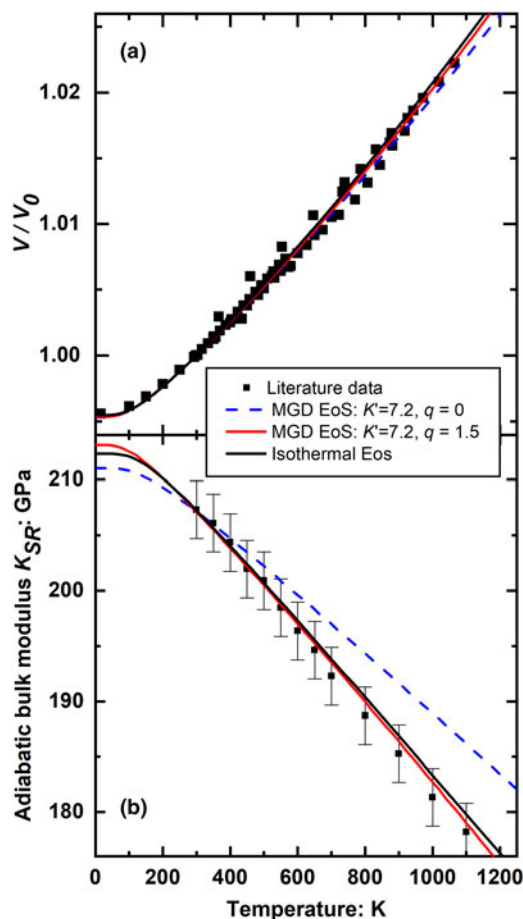
**Fig. 1.** (*a*) The volume variation of rutile with temperature is well-reproduced by all of the EoS. (*b*) The adiabatic Reuss bulk modulus data is well-fitted by both the previously published isothermal EoS (Zaffiro *et al.*, 2019), and an MGD thermal-pressure EoS with *q* = 1.5. It is not fitted by an MGD EoS with $K'_{TR0} \sim 7.2$ and *q* = 0. The data sources are listed in table 1 of Zaffiro *et al.* (2019).

the high-temperature measurements of the adiabatic bulk modulus (Isaak *et al.*, 1998) cannot be fit (Fig. 1) when the value of the pressure derivative of the bulk modulus $K'_0$ is ~7 a value derived from the available high-pressure data. Therefore Zaffiro *et al.* (2019) concluded that a MGD EoS cannot fit the data of rutile. However, the bulk modulus in the MGD EoS at high temperatures also depends on the value of *q* (e.g. Anderson, 1995; Jackson, 1998; Kroll *et al.*, 2012; Angel *et al.*, 2019a), in addition to $K'_0$ and $K_0$. This can be seen clearly if the total pressure is written out in full, using a 3<sup>rd</sup>-order Birch–Murnaghan EoS (Birch, 1947) for the isothermal compression:

$$P(T, V) = P(T_0, V) + \Delta P_{th}(T, V)$$

$$= \frac{3K_{T0}}{2}\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right]\left\{1 + \frac{3}{4}(K'_{T0} - 4)\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]\right\}$$

$$+ \frac{\gamma(V)}{V}[\Delta E_{th}(T, \theta_D(V)) - \Delta E_{th}(T_0, \theta_{D0})]$$

$$(4)$$

The bulk modulus at any *P* and *T* is $K_T = -V\left(\frac{\partial P}{\partial V}\right)_T$. Equation 4 shows that the derivative $(\partial P/\partial V)_T$ depends on not only the first

term, $P(T_0, V)$, but also on the values of $\gamma(V)$ and $\theta_D(V)$ in $\Delta P_{th}(T, V)$, which in turn depend on the value of *q* (Equations 1 and 2; Jackson, 1998; Kroll *et al.*, 2012). An increase in the value of *q* leads to a decrease in the bulk modulus at high temperatures and ambient pressure (Fig. 1).

We have therefore re-fitted the self-consistent dataset of rutile with a MGD EoS including refinement of the parameter *q* using *EosFit7c* (Angel *et al.*, 2014) and the same methods as Zaffiro *et al.* (2019). Because the parameters $\theta_{D0}$, $\gamma_0$ and *q* appear in the expression for the thermal pressure (Equations 3, 4) their values are correlated with one another and the value chosen for the molar volume, $V_0$, at ambient conditions (e.g. Jackson, 1998; Kroll *et al.*, 2012). This correlation makes no significant difference to the properties of rutile (e.g. bulk modulus and thermal expansion) predicted by the MGD EoS, but it means that the parameter values are only valid when used with the chosen value of $V_0$. We therefore rescaled the experimental data for volumes (Zaffiro *et al.*, 2019) to a common $V_0 = 18.82$ cm³/mol (Holland and Powell, 2011), and then refined its value to allow for the various small inconsistencies in 'room' conditions between experimental datasets. We also removed the over-weighting of the room-pressure determination of the bulk modulus (Isaak *et al.*, 1998) which is necessary to stabilise refinement of the parameters of the isothermal-type EoS (Zaffiro *et al.*, 2019).

The simultaneous refinement of all EoS parameters for the MGD EoS is stable and the refined parameter values are listed in Table 1. In particular, the refined value of $\gamma_0 = 1.40(2)$ agrees with the values estimated from experiments (Isaak *et al.*, 1998). With *q* = 1.5(7), $\gamma$ is predicted to increase slightly with increasing temperature at room pressure, for example $\gamma = 1.44$ at 1100 K. Figure 1*a* shows that the volume variation of rutile with temperature is equally-well described by the MGD EoS with *q* = 0 or *q* = 1.5, as well as the isothermal type of EoS (Zaffiro *et al.*, 2019). Figure 1*b* shows that the high-temperature bulk modulus data of rutile is reproduced with *q* = 1.5 and a value of $K'_0 = 7.2(5)$ that is consistent with the high-pressure data. Therefore, the conclusion drawn by Zaffiro *et al.* (2019) that the MGD EoS cannot fit the published data of rutile is incorrect, as it was based on the incorrect assumption that *q* = 0. Although rutile does exhibit anisotropic thermal pressure (fig. 3 in Zaffiro *et al.*, 2019), the conclusion that this prevents a MGD EoS from fitting the data is also incorrect. This is not unreasonable because the unit-cell strains along the isochors are small, ~0.5% per 1000 K of temperature increase (fig. 3*b* in Zaffiro *et al.*, 2019). Therefore the phonon mode wavenumbers will change along the isochor by an amount $\sim \sum_i 0.005\omega_{i0}\gamma_i$ per 1000 K where $\omega_{i0}$ is the frequency at room conditions and the $\gamma_i$ are the components of the Grüneisen tensor for each phonon mode (Angel *et al.*, 2019b). Using the values of the $\gamma_i$ for rutile (Musiyachenko, unpublished data) the wavenumber shifts would not exceed 11 cm⁻¹ per 1000 K along the isochor. For 10 of the 15 phonon modes of rutile, the calculated shifts are less than 1% of the phonon mode wavenumbers at room conditions, and therefore they might be expected to have a minimal effect on the thermodynamics.

As noted above, the values of the parameters $\theta_{D0}$ and $\gamma_0$ are correlated with the value of $V_0$ in the least-squares procedure and, as a consequence, they are also sensitive to the weighting schemes applied to the experimental data, especially those close to room conditions. Extensive analysis shows that the variation in individual parameter values is less than 1 estimated standard deviation of the values. Nonetheless it is possible to reduce this

**Table 1.** EoS parameters for rutile.

| | MGD EoS (This work) | q-compromise MGD EoS (This work) | Isothermal EoS (Zaffiro et al., 2019) |
|---|---|---|---|
| $V_0$ (cm³/mol) | 18.8236(10) | 18.8233(9) | 18.820 fixed |
| $K_{TR0}$ (GPa) | 205.05(25) | 204.91(16) | 205.14(15) |
| $K_{SR0}$ (GPa) | 207.17(25) | 207.06(16) | 207.30(14) |
| $K'_{TR0}$ | 7.2(5) | 7.4(3) | 6.9(4) |
| $K''_{TR0}$ (GPa⁻¹) | –0.077 implied value | –0.094 implied value | –0.075 implied value |
| $\alpha_{V0}$ (K⁻¹) | – | – | 2.526(16) × 10⁻⁵ |
| | $\theta_{D0}$ = 399(20) | $\theta_{D0}$ = 412(15) | $\theta_E$ = 328(12) |
| $\delta_T$ | – | – | 7.6(6) |
| $\delta'$ | – | – | 0.0 fixed |
| $\gamma_0$ | 1.40(2) | 1.41(2) | 1.4 fixed |
| $q$ | 1.5(7) | – | 0.0 fixed |
| $\chi^2_w$ | 2.74 | 2.73 | 3.05 |

All EoS use a Birch–Murnaghan 3rd-order EoS for the compressional part at ambient temperature. For a full definition of the thermal part of the EoSs, see Angel et al. (2018). These parameters are available in the supplementary materials (see below) and at www.rossangel.net as .eos files that can be used in the *EosFit* suite of programs.

correlation. Kroll *et al.* (2019) noted that the values of both $\theta_D$ and $\frac{\gamma(V)}{V}$ vary very weakly with $T$ and $P$ and proposed a modification of the MGD in which they are kept constant. Because the first condition corresponds to a value of $q = 0$ (Eqn. 1) and the second to a value of $q = 1$ (Eqn. 2) we name this the 'q-compromise' thermal-pressure model. The removal of the parameter $q$ greatly reduces the correlation between the remaining parameters whose values change very little compared to the full refinement of the MGD EoS (Table 1), and results in a marginally better quality of fit to the data ($\chi^2_w$) with one less parameter.

At metamorphic conditions the volumes, bulk moduli and thermal expansion coefficients predicted by both versions of the MGD EoS (Table 1) and isothermal EoS are indistinguishable within the uncertainties derived from the least-squares fits of the parameters. As a consequence there are only small differences in the isomekes (Rosenfeld and Chase, 1961) of rutile with garnets; those with the MGD EoS of rutile maintain positive slopes to higher temperatures than those of the isothermal EoS (fig. 5 in Zaffiro *et al.*, 2019) before developing $dP/dT < 0$ with further temperature increase. The conclusion that rutile inclusions trapped in garnets during metamorphism should, from the EoS, exhibit negative pressures is still valid and independent of the type of EoS chosen to model the $P$–$V$–$T$ behaviour of rutile.

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