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RESEARCH ARTICLE

Comparative Analysis of Grüneisen Parameters for Selected Geophysical Minerals Using Advanced Equations of State

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ABSTRACT: The Grüneisen parameter (γ) is a critical dimensionless quantity that provides insights into the thermal and elastic properties of geophysical minerals under high-pressure conditions. In this study, we investigate the Grüneisen parameter for three key geophysical minerals—MgO, Al_2O_3, and Mg_2SiO_4—using three advanced equations of state (EOS): Vinet-Rydberg, modified Lennard-Jones (mL-Jones), and Brennan-Stacey. The study employs Stacey's formulation to calculate γ, offering a comprehensive evaluation of the parameter across varying compression ratios (V/V_0). The results reveal a consistent decrease in the Grüneisen parameter as the compression ratio declines from 1 to 0.9 for all three minerals. Among the EOS models, the modified Lennard-Jones equation consistently shows the least sensitivity to compression, followed by the Vinet-Rydberg equation, while the Brennan-Stacey equation exhibits the highest sensitivity. For MgO, the Grüneisen parameter decreases from 1.125 to 1.01245, 1.11012, and 0.98935 for Vinet-Rydberg, mL-Jones, and Brennan-Stacey EOS, respectively. Similar trends are observed for Al_2O_3 and Mg_2SiO_4, with notable differences in sensitivity between the EOS models. These findings underscore the importance of selecting the appropriate EOS model when studying thermodynamic properties, as the sensitivity of γ to compression can significantly influence theoretical predictions. The results also highlight the utility of the Grüneisen parameter in modeling geophysical phenomena, including mantle convection, seismic wave propagation, and phase transitions within Earth's interior. This study contributes to a deeper understanding of the thermoelastic behavior of geophysical minerals under extreme conditions.

Keywords: Grüneisen parameter, Geophysical minerals, Equations of state (EOS), High-pressure thermodynamics.

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1. INTRODUCTION

The Equation of State (EOS) plays a pivotal role in the theoretical investigation of physical and thermodynamical properties of geophysical minerals, especially when studying the Grüneisen parameter (γ) at very high pressure [1-3]. Geophysical minerals, which encompass a wide range of substances present in the Earth's crust and mantle, exhibit diverse behaviors under extreme conditions of high pressure and temperature. Understanding these behaviors is essential for elucidating the physical and chemical processes that govern Earth's internal dynamics. The EOS is a mathematical framework that establishes relationships among thermodynamical variables such as pressure (P), temperature (T), and volume (V). It describes how the volume of a mineral changes in response to variations in pressure and temperature, making it a cornerstone for interpreting mineral properties under geophysical conditions [4-6].

The Grüneisen parameter (γ), derived from the EOS, is a dimensionless quantity that characterizes the thermal and elastic properties of geophysical minerals. It provides a measure of the coupling between thermal and mechanical effects within a mineral's structure. More specifically, it

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quantifies the extent to which the volume of a geophysical mineral changes with temperature at constant pressure, thereby reflecting its thermal expansivity and elasticity [7-9]. The parameter serves as a crucial link in understanding the interplay between a mineral's thermal, elastic, and vibrational properties. This is particularly important for modeling the behavior of Earth's interior, where extreme pressures and temperatures exist, such as those found in the mantle and core [10].

The study of the Grüneisen parameter (γ) has profound implications for geophysics, as it aids in predicting the behavior of minerals under conditions vastly different from those on Earth's surface [11]. The parameter is instrumental in theoretical models that simulate conditions deep within the Earth, enabling predictions of how minerals respond to compression and heating. These predictions are critical for a variety of geophysical phenomena, including mantle convection, phase transitions, and seismic wave propagation [12]. For instance, the propagation of seismic waves through Earth's interior is influenced by the elastic properties of minerals, which in turn are governed by their Grüneisen parameters. Hence, the parameter serves as a key variable in interpreting seismic data and understanding the composition and structure of Earth's interior layers.

Recent advancements in high-pressure experimental techniques and theoretical modeling have significantly improved the accuracy of EOS calculations and the determination of Grüneisen parameters. Researchers from various disciplines now use EOS to calculate γ by fitting experimental data or theoretical models to observed thermodynamical properties of minerals. This process often involves measuring the relative volume changes (V/V0) of a mineral as a function of pressure and temperature and comparing these measurements with predictions derived from the EOS. The analysis of γ provides insights into critical mineral properties such as elasticity, heat capacity, and thermal expansion coefficient, which are essential for modeling Earth's geodynamic processes [11-13].

The EOS and its derived parameters are not only confined to geophysics but also find applications in materials science, planetary science, and other interdisciplinary fields. For example, the study of minerals under extreme conditions has implications for understanding the composition of other planetary bodies, as well as for the development of materials with specific thermal and mechanical properties. Additionally, the Grüneisen parameter has been used in interpreting high-pressure experimental data obtained from diamond anvil cells and other advanced techniques. These experiments simulate conditions similar to Earth's deep interior, providing invaluable data for validating theoretical models and enhancing our understanding of Earth's composition and behavior [14-17].

The EOS and its application in determining the Grüneisen parameter (γ) represent indispensable tools for advancing our understanding of geophysical minerals. These tools enable scientists to uncover the physical and chemical processes that govern Earth's internal dynamics, from the mantle to the core [18-21]. By bridging the gap between theoretical models and experimental observations, the EOS enhances our ability to predict and interpret the behavior of minerals under extreme conditions. This understanding is fundamental for addressing broader questions about Earth's evolution, dynamics, and its role in supporting life. As research in this field continues to evolve, the integration of advanced experimental techniques and theoretical models will further expand our knowledge of geophysical minerals and their significance in Earth's system.

2. METHOD OF ANALYSIS

To describe the Grüneisen parameter (γ) of geophysical minerals, three different Equations of State (EOSs) have been employed. Each EOS provides a unique mathematical framework to model the behavior of minerals under varying pressure and temperature conditions, facilitating the evaluation of γ, which is critical for understanding their thermal and elastic properties. The EOSs considered in this study are the modified Lenard-Jones EOS (mL-Jones EOS), the Vinet-Rydberg EOS, and the Brennan-Stacey EOS.

2.1. Modified Lenard-Jones EOS

The modified Lenard-Jones EOS (mL-Jones EOS) has been widely used in geophysics due to its ability to describe the volume-pressure relationship of minerals under extreme conditions [16, 17]. The mL-Jones EOS is expressed as:

$$P = \left(\frac{K_0}{p}\right)(g)^{-p}\left[g^{-p} - 1\right] \tag{1}$$

Where $p = \frac{K_0^{'}}{3}$ and $g = \left(\frac{V}{V_0}\right)$, P is the pressure, V is the volume [16, 17]. These parameters capture the specific interactions within the mineral structure, allowing for a precise description of its compressibility and volume changes. This EOS is particularly effective in modeling materials with strong interatomic forces, making it suitable for many geophysical applications.

2.2. Vinet-Rydberg EOS

The Vinet-Rydberg EOS is another widely used model for predicting the behavior of geophysical minerals under high pressure [18]. It is given by:

$$P = 3K_0(1-u)u^{-2}\exp[\Omega(1-u)] \tag{2}$$

Where $u = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}$ and $\Omega = \frac{3(K'_0 - 1)}{2}$, K_0 is the bulk modulus at zero pressure, $u = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}$ is the relative volume parameter, and V_0 is the initial volume [18]. This EOS is particularly advantageous for describing the compression of minerals at very high pressures, as it incorporates an exponential term that accounts for the anharmonic behavior of atomic vibrations. The Vinet-Rydberg EOS is widely regarded for its accuracy and simplicity in predicting the pressure-volume relationship for minerals subjected to extreme geophysical conditions.

2.3. Brennan-Stacey EOS

The Brennan-Stacey EOS is an alternative approach that is also used to model the Grüneisen parameter [19]. It is expressed as:

$$P = \frac{3K_0}{(3K_0^{'} - 5)} u^{-4} \left[\exp\left\{ \frac{(3K_0^{'} - 5)}{3} (1 - u^3) \right\} - 1 \right] \quad (3)$$

Where $u = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}$, K_0 is the bulk modulus, and V/V_0 is the relative volume [19]. This EOS is particularly effective for describing the pressure dependence of minerals with complex atomic arrangements, providing a robust framework for calculating their thermodynamic properties. The Brennan-Stacey EOS is known for its ability to accommodate non-linear pressure-volume relationships, making it highly versatile in geophysical applications.

2.4. Prediction of Grüneisen Parameter

The Grüneisen parameter (γ) can be derived using the formula proposed by Borton and Stacey [20]:

$$\gamma = \frac{\left(\frac{1}{2}\right)K_T^{'} - \frac{1}{6} + \frac{2.35}{3}\left(1 - \frac{P}{3K_T}\right)}{1 - \left(\frac{4}{3}\right)\left(\frac{P}{K_T}\right)} \quad (4)$$

This formula links the thermodynamic properties of the mineral, providing a practical method for predicting γ under varying geophysical conditions. By combining the EOSs with this formula, it is possible to calculate γ accurately, enabling the analysis of thermal and elastic behavior in geophysical minerals. The use of these three EOSs, in conjunction with the Borton and Stacey formula, allows for a comprehensive investigation of the Grüneisen parameter. These methods provide critical insights into the thermal, mechanical, and elastic properties of geophysical minerals, enhancing our understanding of their behavior under extreme conditions.

3. RESULTS AND DISCUSSION

The study evaluates the Grüneisen parameter (γ) for three geophysical minerals—MgO, Al_2O_3, and Mg_2SiO_4 using three different Equations of State (EOSs): the Vinet-Rydberg EOS, modified Lenard-Jones (mL-Jones) EOS, and Brennan-Stacey EOS. These analyses provide a comprehensive understanding of how the Grüneisen parameter varies with compression ratio (V/V_0) for each mineral. Table 1 summarizes the bulk modulus (K_0) and Grüneisen parameter (γ) of the studied minerals under uncompressed conditions ($V/V_0 = 1$). The results obtained from theoretical calculations are discussed below, with visual representations in Figures 1, 2, and 3.

For MgO, the initial Grüneisen parameter at when there was no compression (V/V0 = 1) is consistently 1.125 across all three EOS models. As the compression ratio decreases from 1 to 0.9, a noticeable decline in the Gruneisen parameter is observed across all models. The Vinet-Rydberg EOS shows a gradual decrease from 1.125 to 1.01245, while the mL-Jones and Brennan-Stacey EOS exhibit similar trends, ending at 1.11012 and 0.98935 respectively. This suggests that under increased compression, the modified Lenard-Jones EOS predicts a slower reduction in the Grüneisen parameter in comparison to the other two Equations of State (EOS). Figure 1 illustrates these trends, showing that the modified Lenard-Jones EOS predicts the least sensitivity, followed by the Vinet-Rydberg EOS, with the Brennan-Stacey EOS showing the most significant decrease. This highlights the importance of the EOS model selection for accurate predictions of γ under varying pressure.

Table 1. Bulk modulus (K_0) and initial Grüneisen parameter (γ) for geophysical minerals.

Geophysical minerals	**K_0 (GPa)**	$K_0^{'}$	Initial γ ($V/V_0 = 1$)
MgO	162	4.15	1.125
Al_2O_3	252	3.99	1.045
Mg_2SiO_4	127	5.40	1.75

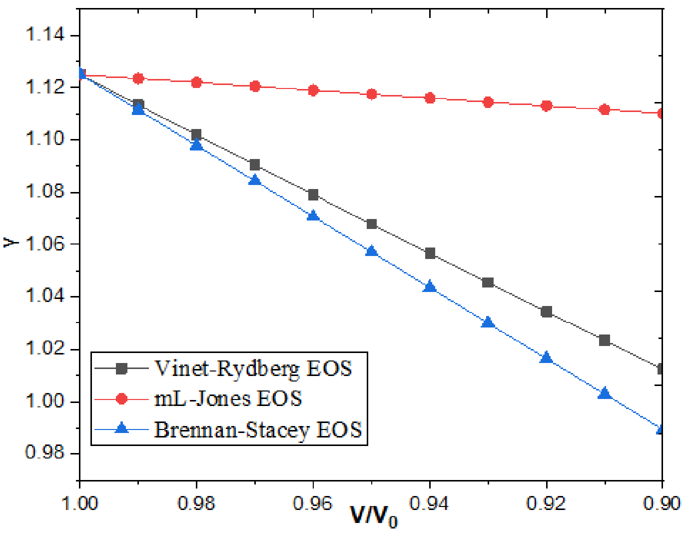

Fig. 1. Displays the variation of γ with V/V_0 for MgO using the three EOS models. The graph illustrates that the modified Lenard-Jones EOS predicts the slowest decline, followed by the Vinet-Rydberg EOS, with the Brennan-Stacey EOS showing the steepest reduction.

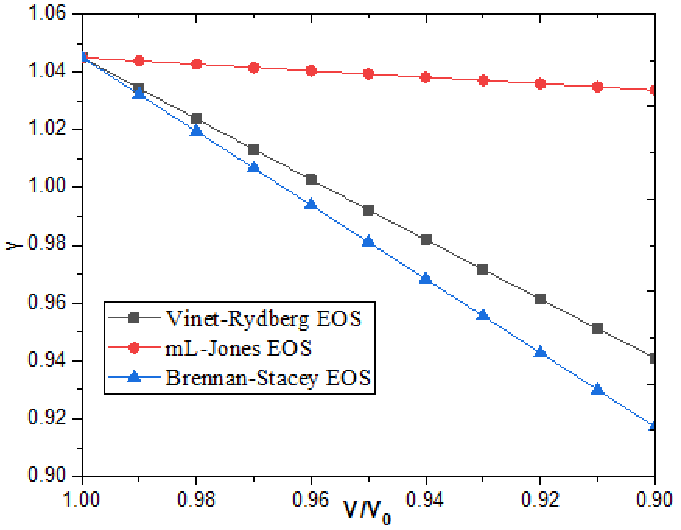

Fig. 2. Represents the variation of γ for Al_2O_3. The trends are consistent with those observed for MgO, with the mL-Jones EOS demonstrating the least sensitivity and the Brennan-Stacey EOS the most.

For Al_2O_3, the initial Grüneisen parameter that is Grüneisen parameter at when there was no compression is 1.045 at V/V0 = 1 for all EOSs. As the material is compressed through hydrostatic pressure, the Vinet-Rydberg EOS indicates a reduction from 1.045 to 0.941 at V/V0 = 0.9. The mL-Jones EOS also shows a similar decrement from 1.045 to 1.03374, and the Brennan-Stacey EOS predicts a more significant decrease to 0.91727. This trend indicates that the Brennan-Stacey EOS is giving very sensitive response to compression in Al_2O_3 compared to the other EOS models. Figure 2 depicts these variations, with the mL-Jones EOS showing the most gradual decline and the Brennan-Stacey EOS exhibiting the steepest reduction. These results emphasize that Al_2O_3 exhibits varying compressibility depending on the EOS model used, which could impact its theoretical predictions under geophysical conditions.

In the case of Mg_2SiO_4, the Grüneisen parameter at when there was no compression is 1.75 across all three EOS models. As compression increases, the Vinet-Rydberg EOS shows a decline from 1.75 to 1.55446 at V/V0 = 0.9. The mL-Jones EOS predicts a decrease from 1.75 to 1.6907, while the Brennan-Stacey EOS shows a reduction to 1.55252. Similar to MgO and Al2O3, the modified Lenard Jones EOS exhibits a more gradual decline in the Gruneisen parameter under compression compared to the Brennan-Stacey EOS and Vinet-Rydberg EOS. Overall, the results indicate that the Grüneisen parameter for all three materials decreases with increasing compression. The modified Lenard Jones EOS consistently shows the least sensitivity to compression, followed by the Vinet-Rydberg EOS, while the Brennan-Stacey EOS generally exhibits the greatest sensitivity. These variations highlight the importance of selecting an appropriate EOS model when studying the thermodynamic properties of materials under varying pressure conditions. Figure 3 presents these results, with the mL-Jones EOS demonstrating the least sensitivity to compression, while the Brennan-Stacey EOS exhibits the most pronounced reduction. This suggests that Mg_2SiO_4 undergoes significant structural and elastic changes under compression, as predicted by the Brennan-Stacey EOS.

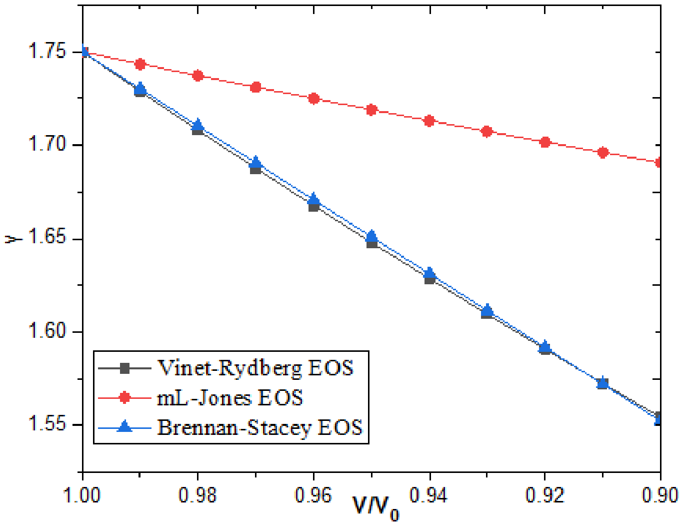

Fig. 3. Shows the variation of γ for Mg_2SiO_4. Similar trends are observed, emphasizing the consistency of each EOS model's behavior across different minerals.

The study reveals common trends across all three minerals. The Grüneisen parameter (γ) decreases with increasing compression (V/V_0). The modified Lenard-Jones EOS consistently predicts the least sensitivity to compression for all minerals, suggesting that it models their thermodynamic stability effectively under high-pressure conditions. The Vinet-Rydberg EOS shows moderate sensitivity, making it a balanced choice for predicting the thermodynamic properties of geophysical minerals. The Brennan-Stacey EOS consistently exhibits the greatest sensitivity to compression, highlighting its utility in capturing the extreme behaviors of minerals under high-pressure conditions. These variations underscore the importance of selecting an appropriate EOS model based on the specific material and conditions being studied. For instance, the modified Lenard-Jones EOS may be more suitable for modeling minerals in moderately compressed states, while the Brennan-Stacey EOS could be preferred for conditions involving extreme compression. The results demonstrate that the choice of EOS significantly impacts the predicted behavior of the Grüneisen parameter under compression. While the modified Lenard-Jones EOS provides a more stable prediction, the Brennan-Stacey EOS captures more pronounced changes under extreme compression. These insights are essential for theoretical studies and practical applications involving geophysical minerals in high-pressure environments, such as mantle convection modeling and seismic wave analysis. Further studies could extend these methods to other geophysical minerals and explore the effects of temperature on γ.

4. CONCLUSION

In this theoretical investigation, we have analyzed the Grüneisen parameter (γ) for three geophysical minerals—MgO, Al_2O_3, and Mg_2SiO_4—using three advanced equations of state (EOS): Vinet-Rydberg, modified Lennard-Jones (mL-Jones), and Brennan-Stacey. The study demonstrates that the Grüneisen parameter decreases as the compression ratio (V/V_0) declines from 1 to 0.9, reflecting the coupling between thermal and mechanical effects in the mineral structure. For MgO, all three EOS models predict a similar initial Grüneisen parameter ($\gamma = 1.125$) at $V/V_0 = 1$, but their sensitivities to compression vary significantly. The modified Lennard-Jones EOS exhibits the most gradual decrease, suggesting that it is less responsive to changes in pressure compared to the other models. A similar trend is observed for Al_2O_3 and Mg_2SiO_4, with the Brennan-Stacey EOS showing the highest sensitivity to compression. The findings highlight the critical role of EOS models in accurately predicting thermodynamic properties, as the choice of EOS significantly affects the calculated Grüneisen parameter. This variability underscores the need for careful selection of EOS models based on the specific mineral and research objectives. The Grüneisen parameter is an essential tool for understanding the thermoelastic behavior of geophysical minerals under extreme conditions, such as those found in the Earth's mantle and core. It provides valuable insights into processes like seismic wave propagation, mantle convection, and phase transitions. By advancing our understanding of γ through comparative analysis of EOS models, this study contributes to the broader field of geophysics and offers a foundation for future research into the thermal and elastic properties of minerals under high-pressure conditions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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