Reply to the referee's comments:

The manuscript from Ulian et al. describes a Density Functional Theory (DFT) based computational study on the high-pressure structural evolution and the elastic properties of 1M and $2M_1$ polytypes of $KMg_3Si_3AlO_{10}(OH)_2$ phlogopite. More specifically, the calculations report the static equation of state parameters (K_0, K' and V_0) and the full elastic tensor for both polytypes, from which polycrystalline average properties (K_{voigt}, K_{reuss}, μ_{voigt}, μ_{reuss}, E, υ) and seismic anisotropy are derived. The novel aspect of this work relies on the adoption of a posteriori correction of the hybrid B3LYP functional to include the dispersion effects on the elastic properties of both polytypes.

The data obtained from the theoretical calculations are overall of good quality and valuable to the mineralogical community. Although the effort and success in predicting elastic properties (11 independent elastic constants) of monoclinic compounds are remarkable, the general presentation of the manuscript needs to be improved and parts of the text rephrased to carefully explain and discuss the methodology and new findings, to make it easier to understand to non-expert readers.

In addition, the manuscript in this current form lacks a comprehensive framework describing the relevance of phlogopite in geological sciences and in particular why it is important to have a firm knowledge of both polytypes elastic properties. This is now barely described in the introduction - where the authors only state "it is also important to know the elastic properties of this mineral to understand and explain geophysical observations in subduction zones". Proper citations necessary to provide context on how the results obtained could help understand geophysical observations (not detailed in the text) are also lacking. Some possible technological applications of phlogopite are mentioned in the introduction section, but besides a few citations, no more details are provided. This impacts directly the conclusions of the manuscript, which is only a short sum up of the main results obtained, without adding any sort of implications concerning Earth Sciences nor Material Sciences. Both the introduction and the conclusion of the manuscript therefore need to be considerably implemented by adding further context and implications.

While this manuscript represents the first attempt to calculate the elastic properties of $2M_1$ polytype, the full elastic tensor of phlogopite 1M was already provided by Chheda et al. (2014) (Chheda, T. D., Mookherjee, M., Mainprice, D., dos Santos, A. M., Molaison, J. J., Chantel, J., Manthilake, G., and Bassett, W. A.: Structure and elasticity of phlogopite under compression: Geophysical implications, Physics of the Earth and Planetary Interiors, 233, 1-12, 10.1016/j.pepi.2014.05.004, 2014). Importantly, despite adopting a more sophisticated computational method with respect to Chheda et al. (2014), from the current manuscript it is not clear what the improvement and the advancement with respect to the previous study are. In particular, the study by Chheda et al. (2014) reports the high-pressure evolution of the elastic constants and seismic anisotropy, describing the geophysical implications relevant to subducting zone settings, which are not presented in this manuscript, making it hard to judge the novelty of this work.

In conclusion, at the current stage, I believe the manuscript is unsuitable for publication in a broad-impact journal such as Solid Earth.

Answer: We thank the referee for the general positive opinion on our work. As reported in the following point-by-point answers, we amended the manuscript to better elucidate the scope of the present paper and to ameliorate the presentation and discussion of the results to meet the criteria of Solid Earth.

Specific comments:

1.Introduction

Line 44: when writing that the knowledge of phlogopite elastic properties could "explain geophysical observations in subduction zones" some context and citations should be provided. Which seismological/geophysical observations are attributed to phlogopite?

Answer: we thank the referee for pointing this issue out. We rewrote that section, including more information and citations related to both the geological/geophysical and technological implications of a more detailed knowledge of the elastic properties of phlogopite. The new paragraph now states:

"Micas, and then phlogopite, could be used as geothermobarometers to explain petrogenetic processes occurring in high-pressure and high-temperature (non-ambient) conditions (Guidotti and Sassi, 1976), being also a possible carriers of water and potassium in the Earth's mantle (Sudo and Tatsumi, 1990). Moreover, as suggested by Melzer and Wunder (Melzer and Wunder, 2001), since phlogopite may be formed in the mantle wedge that overlies a subducting slab, it could play a relevant role in the element ratios of large ions (K, Rb, Cs) in the subduction zone. From the technological perspective, phyllosilicates are considered low-cost insulating materials that could be used in two-dimensional optoelectronic applications, e.g., 2D transistors and heterostructures (Ulian and Valdrè, 2025), thanks to their easy exfoliation, which is related to the perfect cleavage on their (001) planes. Thus, a detailed knowledge of the elastic properties of phlogopite is of utmost importance for both geological studies, e.g., to explain geophysical observations involving phlogopite-bearing rocks (Geng et al., 2024;Van Reenen et al., 2023;Wang et al., 2023), and to devise new technological uses of this mineral for advanced applications (Cadore et al., 2022)."

Line 52: here you should provide more details on why it is important to include long-range interactions in the physical treatment of phlogopite. This would particularly benefit the non-expert readers.

Answer: according to the reviewer's suggestion, we included the following sentence to better elucidate this important point:

"Albeit the general consensus is that the TOT layers in micas are held together by the interlayer cations (K+), hence the interaction is mostly of Coulombic (electrostatic) nature, previous works on muscovite and phlogopite showed that the contribution from van der Waals interactions is non negligible in determining the crystal structure, elastic and thermodynamic properties of these minerals (Ulian and Valdrè, 2015c;Ulian and Valdrè, 2023a)."

Line 55: even if a complete knowledge of the elastic behaviour of both 1M and $2M_1$ polytypes is given, how can this improve the interpretation of geophysical observations in subduction zones? The stability of polytypes cannot be predicted by thermodynamics, since the presence of either 1M or $2M_1$ is not a matter of free energy differences, but rather kinetics. So even if some geophysical observations are attributed to phlogopite, it is extremely difficult to point out which polytype is the main responsible or, if both polytypes are present simultaneously, to try to understand the relative amounts.

Answer: we agree with the referee that, in general, the variations of the elasticity of phlogopite attributed to the two polytypes could be very small. As also reported in next comments, the two polytypes show almost identical bulk moduli (within the fitting uncertainty), however, the properties (Young's modulus, compressibility, shear modulus, …) derived from the elastic tensor showed small differences according to the direction of observation. This behaviour was indeed the one we expected, and the hypothesis behind

our study. We included the following sentence at the end of the paragraph pointed out by the referee to better explain the scope of our work:

"The differences in the elastic behaviour of the two phlogopite polytypes could be indeed subtle, especially in terms of the second-order elastic moduli tensor, where small variations in the directional properties between the 1*M* and 2M_1 are hypothesised."

2.Computational methods

Line 67-68: the paper of Grimme (2006), which is extremely important as it contains the theoretical details of the treatment of dispersion contributions, is not present in the References section.

Answer: The reference section now includes the fundamental work of Grimme (2006).

Line 68: the parameters that define the dispersion contribution to the total energy are not only functional-dependent, but also compound-dependent, so care should be taken when using the parameters adopted by other authors on different compounds with respect to the one investigated in this study. Since Civalleri et al. (2008) worked on "NH3, acetylene, CO2, urea, urotropine, propane, benzene, naphthalene, formamide, formic acid, 1,4-dichloro-benzene, 1,4-dicianobenzene, succinic anhydride and boric acid", can the parameters adopted for such compounds be directly employed for phlogopite as well? Civalleri et al. (2008) used the parameters reported in Table 1 of Grimme (2006), therefore one straightforward way to remove any doubt about the parameters employed for the calculations on phlogopite would be to add a table in the supplementary material with the C_6 parameter of K, Mg, Si, Al, O and H, the scaling factor s_6 adopted for the B3LYP functional, and the van der Waals radii of the various atoms. Moreover, the B3LYP-D* correction employed by Civalleri et al. (2008) consists of an empirical rescaling of the scaling factor of the B3LYP functional and of "the van der Waals radii of heavy atoms and hydrogen". As reported by Civalleri et al. (2008): "Proposed scaling factors were determined from a manual procedure by progressively increasing the atomic van der Waals radii and trying to find the best agreement between computed and experimental data". This means that the parametrization they performed is compound-specific and calibrated over experimental results on mostly organic compounds that do not contain K, Mg, Si or Al. Again, I suggest you provide more details on the parameters that were employed for your correction either in the supplementary material or directly in the computational methods section.

Answer: According to the referee's comment, we included the following sentence immediately after introducing the B3LYP-D* approach:

"According to the proposed methodology, the original B3LYP-D2 parameters were modified as s_6 = 1, the van der Waals radius of the hydrogen atom, R_{vdw}(H), was set to 1.30, and the R_{vdW} of the heavier atoms were scaled by a factor of 1.05, while the C_6 values were the same proposed in the DFT-D2 scheme (see Table S1 in the Supplementary Materials).",

and an additional table (Table S1) was included in the Supplementary Materials.

Line 72: For O basis set, I think it is better to cite this work: "L. Valenzano, F.J. Torres, K. Doll, F. Pascale, C.M. Zicovich-Wilson, R. Dovesi, "Ab Initio study of the vibrational spectrum and related properties of crystalline compounds; the case of CaCO3 calcite", Z. Phys. Chem. 220, 893-912 (2006). **DOI** 10.1524/zpch.2006.220.7.893", as it is the first study in which the different contraction exponents and coefficients for O were tested and that led to the 8-411d11G set.

Answer: According to the referee's suggestion, we replaced the reference of Valenzano et al. (2007) with the one from 2006.

3.Results and discussion

Lines 87-99: this section should go in the methods paragraph.

Answer: According to the referee's suggestion, we moved this paragraph in the Computational Materials section.

Lines 120-121: it is necessary to specify how many, and what volume states were considered, as this not only can affect the E-V fitting but also prevents the reproducibility of the calculations.

Answer: in the revised manuscript, we modified the sentence to include the number of unit-cell volumes and the relative variation concerning the equilibrium cell. The text now states:

"The compressional behaviour of phlogopite was modelled considering 10 different unit-cell volumes, both smaller (compressed, 7 volumes) and larger (expanded, 3 volumes), within 88% and 108% of the equilibrium geometry volume (V_{eq})."

Line 130 equation 1: the term (η^2-1)^3 should be a factor, not an exponent. Also, it would be better to specify the natural variable of energy: E(V).

Answer: we amended the term in Eq.(1) and we included the natural variable of energy, as per the suggestion. Now Eq.(1) is:

$$E(V) = E_0 + \frac{9}{16} K_0 V_0 \{K'(\eta^2 - 1)^3 + [(\eta^2 - 1)^2 (6 - 4\eta^2)]\}$$

Line 132: the term "dilaton" can be avoided as it's rarely used and can be confusing.

Answer: According to the suggestion, we removed the term from the text, stating that it is only a dimensionless parameter.

Lines 133-134: "The pressure values at each unit cell volume (reported in Table 2)…" Table 2 does not report any pressure value, nor unit cell volumes other than the equilibrium one. Are you referring to Table S2?

Answer: We thank you for pointing this out. Indeed, we referred to Table S1 for the 1*M* polytype and Table S2 for the 2M_1 one. We amended the sentence as:

"The pressure values at each unit cell volume (reported in Tables S1 and S2 for the 1*M* and 2*M*1 polytypes, respectively) were calculated ..."

Line 136 equation 3: As already commented for equation 1, the natural variable of pressure should be specified: P(V).

Answer: we amended equation (3) including the natural variable of pressure, as also done for Eq.(1). Now the formula is written as follows:

$$P(V) = P_0 + \frac{3}{2}K_0(\eta^7 - \eta^5)\left\{1 - \frac{3}{4}(4 - K')(\eta^2 - 1)\right\}$$

Line 137: "Table 3" could be a typo, probably you were referring to Table 2 instead?

Answer: Indeed, it was a typo. We amended the reference to the table, now correctly pointing to Table 2.

Lines 139-140, with reference to Figure 2: "In general, there is a fine agreement between the relative variation of the cited structural properties obtained from the present theoretical simulations and the experimental ones from X-ray diffraction". Please be more specific and define the differences between experiments and calculations, and between these calculations and the previous calculations from Chheda et al. (2014). You need to explain the deviation of computed volumes with respect to experiments at high pressures in Figure 2 (panels A, B and D)? Also, add Chheda et al. (2014) results to Figure 2 and provide the fit of P-V data.

Answer: According to the referee's suggestion, we added the results of Chheda and collaborators (2014) in Figure 2, alongside the experimental ones of Comodi et al. (2004) and Pavese et al. (2003). In addition, we included a supplementary figure (Figure S1) that reports the absolute values of the unit cell volume and lattice parameters as a function of pressure for the phlogopite-1M. This new figure better highlights the differences between our theoretical approach and that proposed by Chheda and co-workers. Finally, the section related to the experimental/theoretical comparison was expanded, according to the referee's comment.

Line 141: (comment on Table 2) I think that a valuable comparison that should have been provided to support the importance of dispersion correction in evaluating EoS parameters would have been a calculation of static EoS at B3LYP level with no dispersion correction, to see how different the K_0 (DFT) and K_0 (DFT/D*) actually are and how impactful dispersion effects are on compressibility. This comparison has been done in a previous paper by the authors (Ulian et al., 2021).

Answer: According to the referee's suggestion, we included in Table 2 and Table 3 the EoS fit results obtained for both polytypes, using the DFT/B3LYP approach without the modified DFT-D2 correction. It can be noted the significant drop in the bulk and axial moduli due to the absence of long-range interactions in the theoretical framework, which is in line with our previous results related to other phases (Ulian et al., 2021).

Line 141: (comment on Table 2) The theoretical bulk moduli of 1M and $2M_1$ polytypes provided by this work are almost identical, so how different is their compressional behaviour?

Answer: we agree with the referee, the two moduli are almost the same between the 1M and $2M_1$ polytypes. Hence, on a general basis, the two polytypes behave mostly the same under hydrostatic compression. However, the interesting result resides on the axial moduli, related to the *a* ,*b* and *c* behaviours upon compression. Indeed, while the $M_0(a)$ and $M_0(b)$ values are the same between the 1M and $2M_1$ phlogopite models, the $M_0(c)$ modulus is significantly higher in the latter polytype, with an increase

stiffness of about 10%. We included the following sentences to better explain the different elastic behaviour:

"In general, it can be noted that the K_0 values are almost the same between the two polytypes. However, the 1*M* and 2M_1 phlogopite models showed a slightly different behaviour in terms of axial compression. In fact, while the M_0(*a*) and M_0(*b*) values are the same between the two phlogopite models, the M_0(*c*) modulus is significantly higher in the 2M_1 polytype, with a stiffness increase of about 10% with respect to the 1*M* one."

Line 151: Please rephrase "Similar figures were calculated.."

Answer: according to the referee's suggestion, we rephrased the sentence as:

"Similar results were obtained by Chheda et al. (2014) from DFT simulations and by Pavese et al. (2003) from XRD experiments. Also, the recalculated values of Comodi et al. (2004) with the linearized formulation lead to a bulk modulus within 0.57% the value obtained from the PV EoS fitting."

Line 193: I believe it is not necessary to specify here which keyword allows to perform calculation of the elastic tensor in CRYSTAL.

Answer: according to the suggestion, we removed from the text the reference to the ELASTCON keyword used in CRYSTAL to perform the calculation of the elastic tensor.

Line 198: "whose values were reported". Maybe "are reported" is better?

Answer: we changed the verb to "are reported" as suggested by the reviewer.

Line 200: "the present simulations were in good agreement with the experimental results" by looking at Table 4, the presented results are rather different from the references provided… Again, please discuss the differences. Also, it would be useful to have a figure displaying the C_{ij} evolution with pressure. See for example Chheda et al. (2014)

Answer: We agree with the referee that the theoretical $C_{\alpha\beta}$ values are slightly different from the experimental ones, and we extended the discussion to better show the observed variations. However, the evolution of the elastic tensor components with pressure was not considered in the present work, which was more focused on the crystal-structure properties of phlogopite under pressure. This would be the topic of a subsequent work.

Lines 210-211: in the text the authors mention that there is a systematic overestimation due to 1) absence of thermal effects in the calculations and 2) presence of Pulay forces…. I have some concerns about this: thermal effects may explain the overestimation with respect to experimental values, however the C_{ij} reported in this study differ also from those of Chheda et al. (2014). Even if the overestimation with respect to plane waves calculations is to be attributed to the use of GTOs, PAW results are still in slightly better agreement with experiments. A routine is currently implemented in CRYSTAL that allows to remove eventual BSSE via a geometrical counterpoise method. Could that improve your results and mitigate the effect of the basis set? As reported in a previous comment in the equation of state section, it would have

been nice to see a comparison between a B3LYP-D* corrected and B3LYP non-corrected simulation. Also, if an overestimation is "systematic" an estimate of such overestimation should be reported to quantify the expected mismatch.

Answer: We thank the referee for pointing this out, as this is one of the key concepts that must be clear to readers. Let's focus on the theoretical aspects. It is possible to see from the results reported in Table 4 that the calculation of stresses/forces is rather sensitive to the employed approach. LDA is known to be an overbinding functional, thus, the elastic tensor components tend to be overestimated. Conversely, GGA functionals are underbinding and generally result in the opposite behaviour as shown by Chheda and collaborators (2014). Then, LDA and GGA represent the extremes of a range in which the elastic moduli should be found in athermal conditions. Hybrid functionals like B3LYP, being two rungs above GGAs in the Jacob's ladder conceived by Perdew, should provide elastic moduli that, ideally, fall between the LDA and GGA results. Hence, the results obtained from hybrid functionals should agree better with the experiments.

The above considerations will hold if we exactly use the same computational parameters in the simulations with different functionals: basis set quality, *k*-point sampling, convergence criteria, and so on. Thus, a different basis set type, such as localised Gaussian-type orbitals (our work) and plane waves (Chheda et al., 2014), is expected to lead to small or large variations. Compared to PW, GTOs are affected by BSSE, which in turn provide some bias in the calculation of forces/stresses due to Pulay stress, as explained with more details in the cited references (Ulian and Valdrè, 2018; Ulian et al., 2021). Generally, the more complete the basis set is, the lower the BSSE. However, considering the size of the phlogopite models, especially the $2M_1$ polytype, very large basis sets like the triple-ζ one proposed by Peintinger, Oliveira and Bredow (POB-TZVP) are computationally very expensive. This is why we chose a double-ζ basis set that was already tested in previous works on phyllosilicates, which provided results with adequate accuracy compared to experimental findings. Unfortunately, we could not employ the geometrical counterpoise (gCP) approach proposed by the research group of Prof. Grimme because of it is limited to a selection of general basis sets, such as the cited POB-TZVP. Moreover, gCP has been tested only for molecular crystals such as urea, and only recently we begun analysing its suitability for inorganic solid systems, such as realgar (see https://doi.org/10.1107/S1600576724000025). We are currently continuing these tests with other systems, however, a thorough analysis of the accuracy of the gCP method for minerals as complex as phlogopite was not within the purpose of the present work.

As suggested by the referee, we included the elastic tensor of both phlogopite polytypes calculated with the uncorrected B3LYP functional. It is possible to note that they are more in line with the experimental findings, even without the gCP correction. However, we must remember that our results are referred to athermal conditions, i.e., no zero-point energy and thermal contributions were included in the simulations. If we consider both BSSE and thermal effects, we expect that the elastic moduli will significantly drop below the experimental ones. From this perspective, albeit being larger, we suggest that the B3LYP-D* results are more in line with the elastic wave propagation measurements.

Regarding the term "systematic" we used when discussing the discrepancy between the previous theoretical results of Chheda et al. (2014) and the experimental measurements, the quantification of the overestimation is not trivial, as it depends on both BSSE and thermal effects. A crude estimation could be given from the absolute differences between the theoretical/experimental results, which are now reported in the text.

All this discussion was reported in the revised manuscript.

Line 245: where are equations (14) from?

Answer: The equations are from the work of Ranganathan and Ostoja-Starzewski (2008). This reference was included in the amended text before the mentioned equations.

Lines 277 – 280: A table with a comparison between the numerical values of V_P and V_S predicted in this work and those obtained by Chheda et al. (2014) (and maybe also Alexandrov et al., 1974) would make it easier and more straightforward to compare the presented results and the literature data.

Answer: following the referee's suggestion, we included a table (Table 6) in the revised manuscript to ease the comparison between the present results and those reported by Chheda et al. (2014) and Alexandrov et al. (1974).

Figures/Tables captions

Table 1: report error bars in the experimental data

Answer: according to the reviewer's suggestion, we included the errors associated with the different values, when available from the cited references.

Figure 2: "Evolution of (a) unit cell volume V/V_0…" should be "Evolution of normalized (a) volume (V/V_0), and lattice cell parameters (b) (a/a_0)…"

Answer: as suggested by the referee, we included the term "normalized" in the caption of Figure 2.

Table 4: there is an inconsistency between how the components of the elastic tensor are labelled: $C_{\alpha\beta}$ in equations 4 and 5 whereas C_{ij} in Table 4. Be consistent with the terminology.

Answer: we thank the referee for pointing this out. We amended this inconsistency by labelling the elastic tensor components using the "$C_{\alpha\beta}$" notation throughout the manuscript.

Supplementary materials

Table S1: if these are the volume states used for the E – V fitting, why is the equilibrium volume not included in the table? Usually when you perform EoS calculations with CRYSTAL the equilibrium volume is always included by default regardless of how many and which E – V points you consider. Same thing for Table S2 on the $2M_1$ polytype. In this second case, I guess that the data at P = 0 GPa are those reported in Table 1 of the manuscript, but for the sake of clarity and completeness I would leave them also in the tables provided in the supplementary section, and report in the computational methods section of the manuscript at least the P – V conditions you considered for your static EoS.

Answer: According to the referee's suggestion, we included the crystallographic properties of both 1M (Table S2 in the revised manuscript) and $2M_1$ polytypes (Table S3) obtained in equilibrium conditions (0 GPa).

Reply to the referee's comments:

The manuscript presents a Density Functional Theory (DFT) study on the elastic and compressional properties of the 1M and 2M1 polytypes of phlogopite. Using the B3LYP-D hybrid functional with explicit long-range dispersion corrections and Gaussian-type orbitals, the authors determine equations of state, second-order elastic constants, and directional anisotropies. The work provides the first reported elastic tensor for phlogopite-2M1 and expands the understanding of elastic behaviour in layered silicates. The study is well-organized, technically robust, and clearly written. The methodology is sound, the computational parameters are adequately described, and the results are discussed comprehensively with relevant experimental and theoretical comparisons. The work provides meaningful new data on phlogopite polytypes, particularly regarding elastic anisotropy and the influence of polytypism on mechanical behaviour.*

I find the manuscript suitable for publication in EGUsphere after minor revisions.

Answer: We thank the referee for the positive comments on our work. Please, find in the following the point-by-point answers to each concern.

1) The mismatch between the calculated volumes and experimental results becomes increasingly large with the increasing pressure. Both structures are stronger in calculations than in experiments. What could be the reason?

Answer: we thank the referee for pointing this out. The main reason of this behaviour is due to the computational framework. We performed DFT simulations in the so-called "static" conditions, meaning that zero-point and thermal effects are neglected. Thus, the minerals exhibited this generally stiffer behaviour that increases with pressure.

2) The authors use the B3LYP-D hybrid functional with Grimme D2 corrections, which is justified and in line with previous studies. However, it would be beneficial to include a short discussion on the expected accuracy of the B3LYP-D* method for high-pressure phases, referencing recent benchmarks on similar layered silicates.*

Answer: according to the referee's suggestion we included in Section 2, after the description of the B3LYP-D* approach, some references related to the previous works on talc, pyrophyllite, and muscovite. In the cited references, the accuracy was very high, with results comparable to the experimental data.

3) The analysis of the seismic anisotropy (Fig. 4) is clear and well executed. The authors might consider a more explicit discussion of the potential implications for seismic interpretations in phlogopite-bearing mantle regions or subduction zones, where polytype coexistence could affect anisotropic wave propagation.

Answer: following the referee's suggestion, we included a small paragraph discussing the possible implications associated with the co-presence of different polytypes, with slightly different off-diagonal elastic moduli, in mantle regions and subduction zones.