Computational study of the elastic behaviour of the 2M$_1$
Muscovite-Paragonite series

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Abstract Elastic properties are an important issue in explaining the behaviour of seisms and to ascertain the mineralogical composition of the Earth’s shells through which seismic waves pass. Computational methods can yield an additional, detailed, free-of-heterogeneity model knowledge of the mineral series of interest. Therefore, a computational study on the influence of the interlayer cation in the muscovite-paragonite (Ms-Pg) series on the crystal cell, internal geometry, and the elastic properties was made to shed light on the mineralogical, geophysical, and geochemical properties of the series. These properties have been calculated by means of Density Functional Theory (SIESTA2.0.2 code). The crystal structure and internal geometry agreed with the range of experimental values in the literature. In general, elastic stiffness constants (EC) agreed with the known experimental values. ECs of different interlayer cation configurations for the middle concentration sample showed very similar values, except for C$_{33}$. The majority of ECs, with the exception of C$_{33}$ and C$_{66}$, decreased as a function of Na* [Na/(Na+K)], many of which showed ideal crystalline solution behaviour, and some showed mixing terms. The polycrystalline bulk modulus registered similar values for the end members of the series and a minimum at Na*=0.5, although an estimate of the value at room temperature made the Pg stiffer than Ms; while the shear modulus showed a decreasing trend as a function of

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the Na\textsuperscript{+}. Velocities of the sound waves lowered as a function of Na\textsuperscript{+}. Local deformabilities were also studied, where the highest deformability was found for the interlayer space. The results are discussed in the framework of the mineralogical, geochemical, and geophysical knowledge of the series.

**Keywords** Muscovite-paragonite series, crystal structure, local geometries, elastic-stiffness constants, bulk and shear moduli, local deformabilities, DFT calculations.
INTRODUCTION

In seisms, the velocities of the acoustic waves are functions of the elastic properties of the materials they pass through, and from these two parameters it is possible to account for the structure, compositions and dynamics of the Earth’s shells. Thus, although the elastic properties of minerals are key geophysical data, it is frequently difficult to measure the exact elastic-stiffness constants (ECs), especially in natural minerals where cation order/disorder, morphological, crystal-chemical, and crystal-physical heterogeneities exist (Mondol et al., 2008). However, computational methods can yield reliable crystal structures and ECs free of these natural heterogeneities (Karki et al. 2001; Stixrude 2002; Stixrude and Peacor 2002; Weirich (2004), Ortega-Castro et al. 2010; and Millizer et al. 2011). This would help explain the crystal-chemical, crystal-physical, mineralogical, and petrological behaviour of minerals and aid interpretations of the seismologic data.

Phyllosilicates, found in the Earth’s crust and even in the upper mantle, are also found in subduction slabs in a wide compositional range, depending on the pressure (P), temperature (T), and composition of the bulk rock. Micas are 2:1 phyllosilicates (21P) (Moore and Reynold, 1989), and because of many different cation substitutions form a major group of minerals. Micas are also one of the sources of water in the deep subduction zones.

Because of their high chemical stability, micas have major industrial applications and include properties of films measuring several microns. Elastic, tough, and thermally resistant, micas have high dielectric strength, so that they are valuable in industries related to optics and electricity. Micas show a wide compositional formula, which allows the gradation of some of their properties depending on the composition.

Muscovite (Ms) [KAl$_2$(Si$_3$Al)O$_{10}$(OH)$_2$] is a dioctahedral mica, one of the most common and abundant minerals in metamorphic rocks (metapelites, shales, micaschists, gneiss, metabasites, etc.) and considered an useful petrogenetic indicator (Comodi and Zanazzi, 1997). Ms is an end member of the Ms-paragonite solvus. Paragonite (Pg) is the ideal end member of the series with Na$^+$ instead of K$^+$ as an interlayer cation. This series has substitutions on the octahedral (Oc or VI) sheet, particularly Ms, which can undergo the substitution of Fe$^{3+}$, Fe$^{2+}$ and Mg$^{2+}$, yielding celadonite and phengite series; in addition, different Al$^{3+}$ substitutions also take place on the tetrahedral (T or IV) sheet. Phengitic Ms
are stable at very high pressures in mature subduction zones, and they may be an important factor in the mass transfer of K (Peacock et al. 1994; Domanik and Holloway 1996). The Ms-Pg solvus changes the interlayer cations in contact with hydrothermal solutions of (Na,K)Cl, the Pg being less stable than Ms (Iiyama, 1964, Pascal and Roux, 1985). The Ms-Pg series was studied to be used as a geothermometer and a geobarometer (Guidotti et al, 1994; Blencoe et al. 1994). The effect of the Oc and interlayer cation substitutions on the crystal structure of this series was studied by Guidotti et al. (1992) (GEA92), highlighting an important lack of miscibility at the middle range of the solvus.

Ms was the first 21P to have its ECs measured. Aleksandrov and Ryzhova (1961), by means of ultrasonic measurements, provided 9 of the 13 ECs. Employing Brillouin scattering spectrometry, Vaughan and Guggenheim (1986) and McNeil and Grimsditch (1993) measured the 13 independent ECs of Ms. These authors found that Ms shows relatively little anisotropy along the \(ab\) basal plane and is much more anisotropic in planes where the \(c\) axis is included. By means of empirical interatomic potentials, Collins et al. (1992) calculated the ECs of Ms, and their pure normal and shear ECs being higher than the previous experimental values. Militzer et al. (2011) calculated the ECs and sound velocities of Ms, illite-smectite, kaolinite, dickite, and nacrite by using plane-wave methods in order to interpret the anisotropy of shales.

In the Ms-Pg series, a study of the crystal structure, elastic properties, and internal geometry changes as a function of the interlayer cations can help to interpret the mineralogical, geochemical, and geophysical behaviour of this series without natural heterogeneity. The suitability of this study was highlighted by Militzer et al. (2011): “…Other potentially important effects to be investigated included the role of intra-layer cation radius (e.g. Na substitution for K)…The elastic properties of naturally occurring clays depend on the degree and type of isomorphic substitution and interlayer cations, since it controls the strength of interlayer bonding…..”. In addition, the detailed knowledge of the internal geometry, crystal structure, and elastic properties of series can shed light on many aspects of such behaviour as geothermometer, geobarometer, and geochemical reactions.

The present work has the following aims: i) to determine the crystal structure and internal geometry as a function of the interlayer cations; ii) to ascertain the ECs as a function of the interlayer cations; iii) to elucidate how order/disorder of interlayer cations
can influence the ECs; and iv) to explain how the internal groups are deformed as a function of the normal strains and the interlayer cations.

METHODS

Computational methods

SIESTA2.0.2 code (Sánchez-Portal et al. 1997; and Artacho et al. 1999; Soler et al., 2005) has been used to calculate the electron density of the structure of the series by means of Density Functional Theory (Hohenberg and Kohn 1964; Kohn and Sham 1965). Both the internal geometry and the cell parameters have been optimized in the same run, by using an algorithm based on the Broyden method. Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (1996) (PBE) correlation-exchange functional was used, and one local density approximation (LDA) calculation on Ms has been also performed with the Ceperley-Alder exchange-correlation functional (Ceperley and Alder 1980). A mesh cut-off of 500 Ry and 15 and 9 \( k \)-points in the Monkhorst Pack grid were found to be adequate to offer a high level of convergence in the 84 and 168 atoms cells, respectively. Troullier-Martins norm-conserving pseudopotentials (Troullier and Martins 1991) were used. The convergence threshold of forces and stresses were 0.005 eV/Å and 0.002 GPa, respectively. All calculations were performed at a pressure of 0 GPa.

Our calculations were performed with numerical atomic orbitals, and double-\( \zeta \) plus polarization basis sets. The pseudopotentials and basis sets used in this work were previously optimised for a set of dioctahedral 2:1 phyllosilicates (Ortega-Castro et al. 2008, 2009). In a previous paper (Ortega-Castro et al. 2010), the high-pressure behaviour of Ms was calculated in both the local density approximation (LDA) with the Ceperley-Alder exchange-correlation functional (Ceperley and Alder 1980) and GGA-PBE approach, finding that the GGA yielded cell parameters closer to the experimental data than did LDA. In addition, White et al. (2009) demonstrated that GGA functional showed lower energies and more accurate geometries.

Elastic equations
ECs were calculated via the generalized Hooke’s law, expressed by the following tensor equation:
\[ \sigma_{ij} = C_{ijkl} \epsilon_{kl} \quad \forall i, j, k, l = 1, 2, 3 = x, y, z \quad (1) \]

Where \( \sigma_{ij} \) and \( \epsilon_{kl} \) stand for the \( ij \) and \( kl \) terms of the stress and strain tensors, respectively, and \( C_{ijkl} \) stands for the \( ijk\ell \) term of the EC tensor. This equation can be simplified in Voigt notation \( \sigma_p = C_{pq} \epsilon_q \) (Nye, 1957). Our calculated ECs will be given in this last notation.

We employed the finite-strain method (Gale et al. 2001, Milman and Warren 2001; Karki et al. 1997a, b; Adams and Oganov 2006; Oganov et al. 2001). ECs were calculated using strains of ±0.03 and ±0.02, with the exception of \( C_{33} \), which was calculated with strains of ±0.005. This last reduction in the strain came from the reduction of the linearity between the stress and strain for the normal EC associated with the \( c \) axis. ECs showed an error < 2.2 GPa, with the exception of \( C_{33} \) of the samples of Na* = Na+/(Na++K+) = 0.25 and 0.50, with an error < 3.7 GPa. No thermal or pressure effects were included in the calculations.

The bulk and shear moduli were calculated from the EC tensors with the Hashin and Shtrikman bounds (Hashin et al. 1962a, b), with the Watt and Peselnick (1980), and Watt (1979, 1980, 1987) methods. The average of both bounds could be considered a reliable value of the polycrystalline aggregate (Hill 1952).

The bond distances and other internal geometric deformations were calculated as:
\[ \delta^i_{jj} = \frac{l^i x^i - l^i_0}{l^i_0} \quad (2) \]

where \( l^i_{\text{eff}} \) is the \( i \) bond length, or average of internal distances or angles of one atomic group, when the crystal undergoes a particular normal strain (\( \epsilon_{jj} \)) and \( l^i_0 \) is the non-strained bond length. These were studied as a function of the normal strains as
\[ \delta^i_{jj} = f(\epsilon_{jj}) \quad (3) \]

We define the deformability of the \( i \) geometrical parameter as
\[ D^i_{jj} = \frac{\partial \delta^i_{jj}}{\partial \epsilon_{jj}} \quad (4) \]
where $\delta_{ij}$ was fitted to a linear function of the different $\varepsilon_{ij}$’s by the least-squares method. The deformabilities could be considered a suitable way to analyse the internal deformations and the bonding of the crystal.

**Crystalline Solutions**

An important issue when seeking to rationalize the physical quantities with the chemical composition in crystalline solutions arises by the ideal additive mixing law, that for the crystal cell volume can be written as $V = \sum_j X_j V_j$, where $V$ is the volume of any member of a crystalline solution, with a composition described by the molar fraction, $X_j$, with respect to the $j$-end-members of the crystalline solutions, with volume $V_j$. In the case of two components, a variable reduction to determine a single variable can be used to formulate a linear equation ($V = A_0 + A_1 X_2$). The separation of the ideal addition law, for a binary crystalline solution with the variable reduction, may also be written in the form of a polynomial equation (Waldbaum and Thompson 1968, $V = \sum_{i=0}^{3} A_i X_2^i$). This equation can be rearranged in an ideal addition law plus a mixing term, which, for the case of symmetrical crystalline solution form ($A_3 = 0$), can be written:

$$V = \left( \sum_{i=0}^{2} A_i \right) X_2 + A_0 (1 - X_2) - A_2 X_2 (1 - X_2)$$  \hspace{1cm} (5)

where the coefficient of the first term of the second member corresponds to the volume of the crystalline solution of the independent variable end-member; the second coefficient corresponds to the volume at the other end-member in the crystalline solution; and the last term is considered a mixing term, $\Delta V_{mix}$, which explains the excess of volume out of the ideal solution. If $A_3 \neq 0$ the equation is written as:

$$V = \left( \sum_{i=0}^{2} A_i \right) X_2 + A_0 (1 - X_2) - (A_2 + A_1) X_2 (1 - X_2)^2 - (A_2 + 2A_1) X_2^2 (1 - X_2)$$ \hspace{1cm} (6)

The two first terms have the same meaning as before, and the last terms are the asymmetrical mixing terms, where the coefficient of the first may be interpreted as the volume excess of the independent variable end-member, and the second one as the volume excess of the dependent variable end-member.
excess of the other end-member in the binary crystalline solution. Both of them are equal to
the Margules parameters (Waldbaum and Thompson 1968). All terms depend on pressure
and temperature.

For the case of cell parameters a similar ideal crystalline solution law is given by the
Vegard’s law ($a = \sum_j X_j a_j$), where $a$ is the cell axis of the any member of a solid solution,
with a composition described by the molar fraction, $X_j$, with respect to the $j$-end-members
of the crystalline solutions with $a_j$ axes. Separation of the Vegard’s law for the crystal
parameters could be described by mixing terms similar to Eqs. (5) and (6).

The ECs of a solid solution should follow similar ideal crystalline solution laws
(Isaak and Graham 1976, and Babuska et al. 1978) such as:

$\sum_k (C_{pq})_k = \sum_j X_j (C_{pq})^j$ \hspace{1cm} (7)

where $(C_{pq})$ is the $pq$ EC of the any member of the solid solution and $(C_{pq})^k$’s are the $pq k$-
end-member ECs of the series. Deviation from this approach could be also approached with
a mixing terms similar to Eqs. (5) and (6). If the additive law for volume is differentiated
with respect to pressure, and considering, in an initial approach, that the mixing terms are
not dependent on pressure, a similar additive law also results (Takahashi et al. 1970):

$V = \sum_j X_j V_j$ \hspace{1cm} (8)

where $B$ and $V$ are the bulk modulus and the volume of crystal cell of any member of a
solid solution, while the $X_j$’s represent the end-member molar fractions variables, with $V_j$
and $B_j$ end-member values. Deviation of this law might also be approached by mixing
terms. Similar expressions for the ECs can be used to analyse these properties (Babuska et
al. 1978). As Babuska et al. (1978) recommended, the simplest law must be used (Eq. 7) to
describe the systems, but when Eq. 7 is not sufficient to systematize the system, an
equation similar to Eq. 8 can be also used:

$V = \sum_j X_j \frac{V_j}{C_{pq}}$ \hspace{1cm} (9)

Crystal models
The 2M\textsubscript{1} Ms-Pg series model consists of a layered structure with different sheets (Fig. 1a):

i) The T-sheet is composed of SiO\textsubscript{4} tetrahedral units, which are joined by three oxygens in a tetrahedron base (the so-called basal oxygens), forming quasi-hexagonal rings. The remaining oxygens of the SiO\textsubscript{4} units, which are perpendicular to the basal plane, are the so-called apical oxygens. Some Si\textsuperscript{4+} cations may be replaced by Al\textsuperscript{3+}.

ii) The Oc-sheet is composed of aluminium oxy-hydroxide octahedra. All the apical oxygens of the T-sheet are shared with the Oc-sheet, and two oxygens of the octahedron are saturated with hydrogens. In the Oc-sheet, only two-thirds of the octahedra have their centres occupied with Al\textsuperscript{3+} (dioctahedral phyllosilicate series).

iii) In Ms-Pg series, two T-sheets and one Oc-sheet form T-Oc-T layers, belonging to the 21P series. The tetrahedra must rotate in order to fit both sheets properly. This fitting changes the hexagonal symmetry of the T sheet to a ditrigonal symmetry. This rotation is defined by the $\alpha$ angle. Crystal chemistry, pressure, and temperature affect the $\alpha$ angle (Comodi and Zanazzi 1997, Mercier et al. 2006, Ortega-Castro et al. 2010).

iv) Interlayer spaces occur between the T-Oc-T layers. The charge imbalance caused by isomorphic cation substitution in the tetrahedral sheet is compensated for by cations located in the interlayer space, such as K\textsuperscript{+} and Na\textsuperscript{+}. Different proportions of these cations occur in the Ms-Pg series. Interlayer cations are bonded to the layers by electrostatic forces, the distances of bonds are the largest in the structure, and the density of bonds is the smallest in the structure, so that the forces between the layers are the weakest in the structure (Fig. 1a) and responsible for the main chemical and physical properties of phyllosilicates.

v) The different stacks of the T-Oc-T sheets produce polytypism, the 2M\textsubscript{1} being the most frequent polytype in this series (Fig. 1a), although the 3T stacking is also found, and other more scarce polytypes are also described. The crystal structure in our series was of 2M\textsubscript{1} polytype (Fig. 1a).

vi) The structural formula of the Ms-Pg series is [K\textsubscript{1-x} Na\textsubscript{x} Al\textsubscript{2}(Si\textsubscript{3}Al)O\textsubscript{10}(OH)\textsubscript{2}]. We have calculated the elastic properties of five members of the series: Ms ($x = 0$), three intermediates with different concentrations of K\textsuperscript{+} and Na\textsuperscript{+} ($x = 0.25, 0.50,$ and $0.75$) and Pg ($x = 1$). Calculations for $x = 0, 0.5,$ and $1$ were performed with $1\times1\times2$ supercells (84...
atoms/supercell, Fig. 1a); while for \( x = 0.25 \) and 0.75 larger cells were needed, so 1\( \times \)2\( \times \)2
supercells (168 atoms per supercell) were built. All systems are given in the input file as a
single unit cell.
vii) In our 2\( \text{M}_1 \) model, two interlayer spaces are included (Fig. 1a). For the \( x = 0.50 \)
compound different interlayer cation configurations are studied. The interlayer cation
configuration in Figure 1a is called \( \text{c0} \).

RESULTS AND DISCUSSIONS

Structure

1. Crystal structure. Table 1 provides structural information on the calculated unit cells,
comparing them with the known experimental data of Ms and Pg. By plotting the \( a \) cell
parameter as a function of Na\( ^+ \) [Na/(Na+K)] (Fig. 2a), a general quadratic behaviour was
found, showing a symmetric mixing term, smaller than the symmetric mixing term of
GET92 (0.1 Å). However, from the data of Flux and Chatterjee (1986) and Roux and Hovis
(1996), we calculated the asymmetric mixing terms by fitting to a cubic equation (0.009
due to the parameter excess of Ms and -0.021 due to Pg, and 0.002 due to Ms and +0.066 Å
due to Pg, respectively) slightly different from those resulting from our data (0.08 and -0.01
due to Ms and Pg excess, respectively). Values in the work by Flux and Chatterjee (1986),
GEA92 (up to Na\( ^+=0.3 \) ), Roux and Hovis (1996), and other authors are included in Figure
2a. Our values closely parallel those of the Flux and Chatterjee (1986), GEA92, and Roux
and Hovis (1996) values and are between the values of the other experimental values
included in Figure 2a. GEA92 found \( a = 5.186 \) Å (average value of 5.187 Å) for Ms, which
agrees with our calculated value of 5.187 Å. Although the GEA92 samples in Figure 2a had
no octahedral substitutions, most of the different authors’ samples showed octahedral
substitutions, which can influence the cell parameters. The \( b \) axis as a function of Na\( ^+ \) (Fig.
2b) showed a similar behaviour to that of \( a \), with a higher quadratic coefficient. Therefore,
the mixing of both cations exerted stronger effects on the \( b \) than on the \( a \) axis. Our
symmetric mixing term (0.08 Å) was similar to the GEA92 term (0.0515 Å) and to the
Flux and Chatterjee (1986) term (0.044 Å). However, Roux and Hovis (1996) found
asymmetric mixing terms when a cubic polynomial was fitted to their data (-0.142 for the parameter excess of Ms and 0.20 Å for Pg), slightly different from ours parameter excess (+0.06 for Ms and 0.12 Å for Pg). The $b = 9.006$ Å of Ms was consistent with the values found by GEA92 (8.991 Å, and 8.992 Å for the average). These authors did not provide any values or functions for $a$ and $b$ for Pg’s. Eugster et al. (1972), in 1M polytypes, gave the $ab$ in Å² as a function of Na*, finding a symmetric term very close to our term (0.83 and 0.73 Å², respectively). The parameter $\frac{1}{2}csin\beta$ showed a clearly linear behaviour (Fig. 2c), where our slope was of the same order as the linear coefficient of the Ms’ of GEA92. However, GEA92, Flux and Chatterjee (1986) and Roux and Hovis (1996) found symmetric mixing terms. The experimental $\frac{1}{2}csin\beta$ values for the Ms and Pg end-members of the series were, respectively, 10.027 Å and 9.610 Å, and our calculated values were 10.028 Å and 9.533 Å (deviation of 0.8%), respectively. Although Ms computational values were identical to GEA92’s values, the increased Na* values were higher than ours (Fig. 2b). Computational values were between different authors’ values in the region of Ms’. In this cell parameter, the weak interactions of the interlayer space were included, and these interactions were determinant for the values of $\frac{1}{2}csin\beta$, so that the approach used overestimated the electron density in the interlayer space when Na* increased. The volume of the cell as a function of Na* (Fig 2c) showed a net quadratic behaviour with a downward concavity, which led to a symmetric mixing term of $\Delta V_{mix} = 14.7$ Å³ close to the Flux and Chatterjee (1986), and Roux and Hovis (1996) symmetric mixing term (15.8; and 30.0 Å³, respectively). Eugster et al (1972), for 1M polytypes, gave two fittings for the volume: i) with a symmetric mixing volume [26.15 Å³ (extrapolated to the equivalent volume of the 2M1 polytype)]; and ii) with asymmetric mixing terms [34.99 due to the Ms and 22.84 Å³ for the Pg excess of volume (extrapolated to the equivalent volume of the 2M1 polytype)]. In general, the mixing behaviour is similar to that calculated from the literature. Clearly, the mixing term on the volume came from the effects of the substitution on the $ab$ plane. Because of the positive sign of the $\Delta V_{mix}$, in an increasing pressure system, any member of the solid solution would migrate to K-richer compositions (GEA92, and Guidotti et al. 1998). The average values of GEA92 for the Ms and Pg samples were 935.0 and 876.8 Å³, respectively, and our values were 937.0 and 868.8 Å³
(deviation of 0.2% and 0.9%, respectively). LDA parameters showed larger deviations, especially those concerning to $\frac{1}{2}\sin\beta$ and volume (4% and 7%, respectively).

The linear function slope of $\frac{1}{2}\sin\beta$ as a function of Na* was 17-fold larger than $a$ and $b$ slopes, indicating the great anisotropy of these minerals, the importance of the layer stacking, and the effect of the cations in the interlayer space. In addition, the effective cationic Na⁺ radius (for a coordination number of 12, $r = 1.39$ Å, Shannon, 1976) is smaller than that of K⁺ ($r = 1.64$ Å, Shannon, 1976), hence the increase of the $r$(Na⁺)/$r$(K⁺) ratio affects the $c$ axis, in a stronger way than the $a$ and $b$ axis. Therefore, the crystal-chemistry behaviour of the series was similar to the experimental behaviour (GEA92). The computational situation could be considered to be a model behaviour for the series, free of cationic heterogeneity, order/disorder, miscibility gap, and morphology of the sample.

2. Local geometry. The local crystal-chemical and structural properties evolve as a function of the concentration of an element in a solid-solution rock-forming mineral series and they are related to the thermodynamic properties and stability of the minerals. However, most of the experimental studies associated with these properties use macroscopic and thus heterogeneous samples, giving average values of these properties. The knowledge of these properties in a real local environment free of the order/disorder and average compositional effects is key to determine the micro- and even the nano-behaviour. Computational studies, at a high theoretic level, can yield precise information on this matter, offering a detailed explanation for the local crystal-chemical behaviour of the crystalline solutions (Geiger, 2008), which in many cases is not provided by the experimental techniques. Therefore, we continued the study of our series by examining the local geometry as a function of Na*.

The <O-H> distance values were 2% higher than the experimental values and they were constant throughout the series. This could be because of: i) the dangling nature of these bonds in the structure; and ii) the hydrogen bonds that the H atoms form with the nearest oxygens (Mookherjee, 2001, Botella et al. 2004), which remain in average constants along the series. The average bond length between tetrahedral cations and their oxygens, <T-O>, were less 1% higher than the experimental values. In general, most of these distances are overestimated with respect to the experimental known data, which could come from the general known trend of the GGA method to overestimate the covalent bonds in molecules (Tran et al. 2007). The average distance increased as a function of Na*, in
agreement with the experimental behaviour of the end members of the series. \( \langle \text{Al}^{3+} - \text{O} \rangle \) distances calculated in the Oc-sheet were also close to the experimental value (deviation <1%), following the same trend as \( \langle \text{T-O} \rangle \) as a function of Na*.

Owing to the ditrigonal symmetry of the cavities, two types of distances could be defined from the interlayer cations (X) to the basal oxygens: i) the distance to the farthest oxygens (X···O_{outer}); and ii) the distance to the nearest oxygens (X···O_{inner}). Our calculated \( \langle \text{K}···\text{O}_{outer} \rangle \) and \( \langle \text{K}···\text{O}_{inner} \rangle \) were overestimated (2%) and underestimated (3%), respectively, with regard to the highest experimental values (Table 1); however, the corresponding \( \langle \text{Na}···\text{O} \rangle \) distances were both lower by 5% and 6%, respectively, compared to the experimental data. The behaviour of these distances with respect to Na* was approximately linear, decreasing with increasing Na*. The differences between the two distances, \( \Delta \langle \text{X}···\text{O} \rangle = \langle \text{X}···\text{O}_{outer} \rangle - \langle \text{X}···\text{O}_{inner} \rangle \), as a function of Na* are shown in Figure 3a. At increasing substitution, \( \Delta \langle \text{X}···\text{O} \rangle \) and their slopes are larger in Na+ than in K+ cavities. These variations could be due to the fitting of the cavities to the Na+ size, and, consequently, induce a lack of fitting in the K+ neighbour cavities, introducing some stability/instability with respect to the different cavity type in the mineral. This effect could be related to the gap of miscibility at the middle concentration range of the series. In general, our values showed larger values than the experimental values (Fig. 3a).

Another way to study the interactions of the interlayer cations and the basal oxygens was the average tetrahedral rotations (\( \langle \alpha \rangle \)), which were overestimated for the Ms and Pg values, a small deviation appearing for the last samples (Fig. 3b, Table 1). The \( \alpha \) angle of both Na+ and K+ ditrigonal cavities increased as a linear function of Na* (Fig. 3b, Table 1), the values and slope of \( \langle \alpha \rangle_{\text{Na}} \) being higher than \( \langle \alpha \rangle_{\text{K}} \), indicating that the higher charge/radius ratio of Na+ with respect to K+ increased the tetrahedral rotation (Muñoz-Santiburcio et al. 2011), and the \( \alpha \) angle would work as a hinge to open or close the tetrahedral cavities, depending on the cation inside. All this indicates that the variation of tetrahedral rotation in the K+ cavities as a function of Na* could be induced by rotations of the neighbouring Na+ cavities. Therefore, a better fitting between both T- and Oc-sheets occurred as the Na+ substitution increased (GEA92). In addition, substitutions in the Oc-sheet resulted in a decreasing of \( \alpha \) and therefore these Oc-substitutions would not be
favoured in higher Na-substituted members, which could explain the scarcity of Oc-
substituted Pg’s.

The difference of radii of the substitution cations, the rotation of the polyhedra of
the host place in the crystal structure, and the subsequent possible induction of
stability/instability in the crystal structure, producing a the gap of miscibility, was also
found in the KNa-hollandite, in which the medium- and high-concentrate Na hollandites
were not found to be stable (Mookherjee et al. 2009b and Deng et al. 2010) or were found
under very special conditions, as in meteorites.

Volumes of the Si and Al\(^{3+}\) tetrahedrons were also close to the experimental values
(Table 1) and increased as a function of the Na\(^*\). However, the Al\(^{3+}\) octahedrons showed an
opposite behaviour.

The Oc-, T-sheet, interlayer thickness, and layer volumes were also close to the
known experimental values, but the interlayer thickness was lower than the experimental
values, just noted in the \(\frac{1}{2}\alpha\sin\beta\) parameter analysis. However, the deviations were larger
than the \(\frac{1}{2}\alpha\sin\beta\) deviations, which were compensated for by the octahedral thickness
device which went in the opposite direction. The basal oxygen corrugation (\(\Delta z\)) showed
the largest deviations from the known experimental data. Most of them showed a general
declining trend with respect to increasing Na\(^*\).

**Elastic-stiffness constants**

Table 2 shows several sets of previous experimental and computational ECs. The
geometrical setting of the crystal in Cartesian coordinates is \(c \parallel z\), and \(b\) in the \(yz\) plane.
Although all calculations were performed in the P1 group, the ECs showed monoclinic
symmetry (Nye, 1957).

The 13 non-zero independent ECs of the Ms-Pg series are sorted into five groups: i)
\(C_{ii(i\leq3)}\) pure normal ECs; ii) \(C_{ii(3<i\leq6)}\) pure shear ECs; iii) \(C_{ij(i \neq j, \leq3)}\) mixed normal ECs; iv)
\(C_{ij(i\leq3)}\) mixed normal-shear ECs; and v) mixed shear ECs, where \(C_{46}\) is the only non-zero
member by symmetry considerations (Nye, 1957).

1. **ECs of Ms.** In the first group of ECs two sets were distinguished:
i) The high values of $C_{11}$ and $C_{22}$ were due to the strong covalent and coordination bonding character of the layer throughout the $x$-$y$ plane. These values were very similar (Table 2), indicating that the $xy$ plane was almost isotropic, in agreement with the equal values determined by Aleksandrov and Ryzhova (1961). These ECs were slightly higher (1%) than those of Vaughan and Guggenheim (1986), and McNeil and Grimsditch (1993) (Fig. 4a). The low deviation of these ECs could come from the low deviation of the $a$ and $b$ axes with respect to the experimental values of GEA92. However, the deviations of our cell parameters with respect to those of Vaughan and Guggenheim (1986) were greater, despite that their sample showed more octahedral and interlayer substitutions than in our sample. This was not taken into account in our calculations, and could induce other crystal-physical and crystal-chemical effects. Besides, the temperature effect was not taken into account in our calculations. Our computational values showed a maximum deviation of 7% with respect to the model 1 (GGA, $P = 0$ GPa, $E-E_i=0$ eV) values of Militzer et al. (2011). These deviations could come from the different geometry, the plane-wave basis set and electronic approaches used in those calculations. Nonetheless, they used as reliable values those coming from the LDA approach and the experimental cell parameters.

ii) The $C_{33}$ value was approximately 2.5-fold lower than those of $C_{11}$ and $C_{22}$ (Table 2). This low value of $C_{33}$ could be due to the following factors: 1) the stacking of layers and the interlayer space introduced between them along the $c$ axis; 2) the possibility of penetration of the cations in the ditrigonal cavity; 3) the attractive Coulomb forces between interlayer cations and layers; and 4) the repulsive forces between the basal oxygens on both sides of the interlayer space. The value of $C_{33}$ of Ms deviated from the maximum experimental value by approximately 11%, but elastic properties of the calculated mineral were approximately the same as the natural mineral (Fig. 4b). Nonetheless, other higher values have been reported for the elastic modulus of Ms: 79.3 GPa (determined by the nanoindentation technique in the direction normal to the basal plane, Zhang et al. 2009,) and the highest value of 100.8 Gpa (Mavko et
al. 1998). However, if we match our $\frac{1}{2}\sin\beta$ value with that of Vaughan and Guggenheim (1986), their parameter is shorter than ours, which could yield a higher value of $C_{33}$, although the variety of octahedral and interlayer cation substitutions of the sample used by Vaughan and Guggenheim (1986) and the temperature effect could have caused the lower value of $C_{33}$. In this sense, though, the intrinsic approaches at the DFT method used in this computational study should not be disregarded. On the other hand, White et al. (2009) showed reliable internal geometries by using the experimental crystal structure and optimizing the internal atomic geometry, as a consequence a pressure of ~ 1 GPa appeared in the cell. Millitzer et al. (2011) followed the same technique to compute their ECs. In our study, however, we established very accurate cell parameter values for Ms, when they were matched with the GEA92 values, and a pressure < 0.002 GPa was found in our cell. Therefore, the resulting differences in our EC values with respect to the experimental values might be explained in the inherent approaches of the DFT method used in this paper and the lack of substitution out of the interlayer cation substitutions.

In the pure shear ECs, $C_{66}$ was the stiffest, with values very close to the experimental ones. $C_{44}$ and $C_{55}$ were lower than $C_{66}$ and overestimated with respect to the Vaughan and Guggenheim’s (1986) and Millitzer et al.’s (2011) values (Fig. 4c and d). The involvement of the $c$ axis in the shears of $C_{44}$ and $C_{55}$ was possibly responsible for their higher values compared to experimental.

In the mixed-normal EC group, $C_{12}$, $C_{13}$, and $C_{23}$, our values were higher than the experimental values (Vaughan and Guggenheim 1986, and McNeil and Grimsditch 1993) (Fig. 4e). Nevertheless, the relationships between them (those of $C_{13}$ were approximately 1.7-fold lower than those of $C_{12}$) showed a trend quite similar to that of the experimental data. However, Collins et al. (1992) from calculation based on empirical potentials provided a value of $C_{12}$ approximately 4-fold greater than the other two constants. The involvement of the $c$ axis in our $C_{13}$, and $C_{23}$ values should be the origin of the high values found.
The mixed normal-shear constants, $C_{i5}$ ($i \leq 3$), were roughly comparable to the experimental values of Vaughan and Guggenheim (1986) (Fig. 4f). Meanwhile, $C_{46}$ showed a negative value as the experimental value of Vaughan and Guggenheim (1986) (Fig. 4c).

In general, our crystal structure and ECs agreed with the range of experimental values in Ms, in symmetry, individual values, and relative values between them. However, some misfits are shown, although the elastic behaviour of our computational mineral was approximately the same as that of the experimental mineral.

2 Influence of the interlayer cation ordering on the ECs. Different configurations for the Al$^{3+}$ substitutions in the tetrahedral sheet are possible. Millitzer et al. (2011) have demonstrated that ECs are not affected in a meaningful quantity for the different Al$^{3+}$/Si configurations of the tetrahedral sheets. However, the order/disorder effect of the ECs related to the interlayer cations have not yet been studied. We investigated this phenomenon in a simplified way by calculating the ECs in different cation configurations within the interlayer space.

The interlayer cation configuration used in our periodic cell models at Na$^*$=0.25/0.75 included one Na$^+$ or K$^+$ in the sequence of K$^+$s/Na$^+$s. Therefore, the Na$^*$=0.5 is the only member of our models which admits meaningful different interlayer cation configurations. In this sample, the Na$^+$ and K$^+$ were taken initially in an alternating configuration along the $b$ axis ($c_0$, Fig. 1a). From this model, three additional systems were designed: i) by duplicating the $b$ axis of configuration $c_0$ (Fig. 1a), and modifying the order of the cations in the lowest interlayer space of the supercell by joining two cations of the same atomic number, leaving the upper interlayer space of the model unchanged, the $2bc1$ configuration was established (Fig. 1b); ii) by duplicating the $a$ axis and alternating the cations in the highest interlayer space, and leaving the lowest interlayer space of the model as before, the $2ac1$ configuration was established (Fig. 1c); and iii) one interlayer space containing only Na$^+$ atoms and the other only K$^+$ atoms (Fig. 1d). This last configuration could be considered an interstratified mineral model, in which Ms and Pg are segregated into different layers.

Table 3 shows ECs of the $c_0$, $2ac1$, $2bc1$ and interstratified configuration. The crystal structure and internal geometry are completely optimized. The $c_0$ arrangement
showed the lowest Total Energy (TE) of the three configurations (c0, 2ac1, 2bc1). The cell parameters of the three configurations showed very close data. For \( \frac{1}{2}csin\beta \), these small differences might give the quadratic functional trend, as found by GEA92. These configurations had very similar ECs (the maximum difference being approximately 1 GPa) with the exception of \( C_{33} \), in which c0 and 2bc1 show the lowest and the highest values, respectively, with a difference of 4 GPa (5%). Nonetheless, the difference of TE between the two configurations was small, and both of them could be present in the mineral, so that \( C_{33} \) would increase its value in consequence. The bulk and shear moduli of the polycrystalline aggregate did not show such an increase (Table 3). In any case, our configurations changed only in one interlayer, so that if both interlayers had the same configuration we could expect a still greater increase in \( C_{33} \). Therefore, we could expect that a configuration with alternated cations along the \( b \) axis and aggregated cations along the \( a \) axis would present a lower \( C_{33} \). The other ECs and the moduli should change in small quantities. However, the interstratified configuration showed the lowest TE and larger changes in the ECs. The lowest TE of this compound with respect to the other configurations could be partially responsible for the lack of natural Ms’ and Pg’s with 0.38 <Na*< 0.85 (GEA92). The uniformity of tetrahedral rotation angle, \( \alpha \), on each surface could also stabilize the structure, explaining the trend of both minerals to segregate in the middle concentration range.

3. ECs of the Ms-Pg series. \( C_{11} \) follows an increasing trend with increasing Na* up to reach Na*= 0.5, afterwards decreasing, where the Pg reaches a value lower than the Ms (Table 2, Fig. 4a). \( C_{22} \) fluctuates in a 2 GPa range, the value for Pg being approximately equal to Ms. Both ECs can be approximately described by Eq. 9, with symmetric mixing terms. Because of the negative and positive signs for \( V/C_{11} \) and \( V/C_{22} \), the mixing terms might be considered as a defect and an excess of V/EC, respectively (Fig. 4a). Both ECs should not vary greatly along the series because of the stiff covalent bonds. However, the geometry of the layer changed along the series because of the shifts in the tetrahedral rotation induced by the interlayer cation substitution. The importance of the change in
geometry along the series was highlighted in the volume used in Eq. 9 to systematize the behaviour throughout the series.

$C_{33}$ increased as a function of Na$^+$ (Fig. 4b), which is consistent with the higher ionic potential of the increasing concentration of the smaller cations. In this representation the value of Na$^+*=0.5$ is outside of a possible regular quadratic function fitting; possibly the different values of $\alpha$ in the different Na$^+$ and K$^+$ cavities could yield the especially low value. This EC also can be described by Eq. 9 (Fig. 4b), with values of the mixing term due to a symmetric excess of $V/C_{33}$. The higher $C_{33}$ value of Pg could be explained as follows: i) Na cations possess a higher charge/radius than K$^+$, the Na$^+$ layer interactions being the strongest; and ii) the two basal surfaces of Pg at both sides of the interlayer space are the closest, so that in Pg the repulsive forces of both oxygen basal surfaces will be the highest when the crystal undergoes a compressive strain along the $c$ axis.

The elastic behaviour of $C_{44}$ and $C_{55}$ as a function of the Na$^+$ followed approximately a decreasing linear trend with Na$^+$ (Fig. 4c), associated with an ideal addition mixing behaviour (Eq. 7). Similar behaviour was also observed with $C_{46}$ (Fig. 4c). $C_{66}$ showed values within a narrow range (1.3 GPa), and its behaviour as a function of Na$^+$ was increasing and approximately linear, taking into account the three first terms and the last one. However, the point at Na$^+*=0.75$ showed a minimum (Fig. 5d). Nonetheless, $C_{66}$ was described by Eq. 9 without any mixing term.

The elastic behaviour of mixed normal ECs $C_{12}$, $C_{13}$, and $C_{22}$ showed a regular decrease from Ms to Pg (Fig. 4e). $C_{13}$ fitted to an ideal addition crystalline solution law (Eq. 7), and $C_{12}$ and $C_{23}$ showed the same behaviour with similar excess mixing terms (Fig. 4e).

$C_{15}$ and $C_{25}$ showed a decreasing trend with excess mixing terms (Eq. 7, Fig. 4f). $C_{35}$ showed a maximum at Na$^+*=0.5$, and it was not able to be fitted by any simple function.

Therefore, most of the ECs decreased as Na$^+$ increased, with the exception of $C_{33}$ and $C_{66}$, which showed the opposite trend, and $C_{11}$, $C_{22}$ and $C_{35}$, which acted irregularly. Both Eq. 7 and 9 were fitted in different ECs. Most of the mixing terms were in excess, except for $C_{11}$.

The bulk modulus of the polycrystalline aggregate of Ms showed larger values (68.4 GPa) than those of Vaughan et al. (1986) (Table 2). The last value came from the
application of the Voigt-Reuss-Hill approach to their ECs, but the composition of the
sample in that experiment showed many more cations in different concentrations than our
ideal sample. This and the heterogeneity of the sample could contribute to the elastic
properties and consequently to the calculated bulk modulus. Besides, in literature there are
many values for the bulk modulus for Ms and phengite micas (Table 4), from the lower
value of 52 GPa (Sekine et al., 1991), from shock wave experiments, to the higher value of
61.4 GPa (Faust and Knittle, 1994), from diamond anvil experiments with X Ray
diffraction. This dispersion of data (Table 4) could be attributed to the different samples,
heterogeneities, techniques, compositions and powdered or single-crystal samples. By
means of DFT calculations with pressure applied to a crystal with periodic conditions up
to 6 GPa, a value of 60.1 GPa was obtained (Ortega-Castro et al. 2010), close to the
value of Faust and Knittle. The present value for Ms coming from the application of the
Hashin-Schtrikman-Hill approaches to the DFT-ECs is out of the range of the known
values of bulk modulus of Ms, which could come from the ideal composition,
computational model, and physical approaches used in this work. Nonetheless, DFT
calculations were performed at 0 K, and the bulk modulus generally decreases at
increasing temperature. From Comodi et al. (2002) in Ms there was a \( \left( \frac{\partial B_T}{\partial T} \right)_p \) = -0.0146
GPa/K between 298 and 873 K, which could be considered linear from 0 K, and it could
yield an estimate of \( B_0 \) at 298 K, of 64.0 GPa, closer to the experimental values than the
value at 0 K (Table 4). In Pg, \( \left( \frac{\partial B_T}{\partial T} \right)_p \) = -0.0109 GPa/K (Comodi et al. 2002) could also
yield an estimate of 65.5 GPa, at room temperature, closer to the experimental values
(65.0 GPa ,Comodi et al. 1997, and 59.9 GPa Comodi et al. 2002) than the value of 0 K.
The effect of temperature softened the computational bulk modulus values and can aid
to explain the differences with the experimental values. Figures 4g showed the bulk
modulus of the polycrystalline compounds as a function of the Na\(^+\), which behaved
irregularly, with a minimum at 0.5. This lower resistance to the pressure of the middle
concentration sample could bring these minerals to migrate towards richer K\(^+\) or Na\(^+\).
minerals. This again could be a hint to understand the gap of miscibility in this series. Nonetheless, the order/disorder effects would increase the modulus value, but not to a large extent. The shear modulus of Ms was much closer (37.9 GPa) to the values of Vaughan and Guggenheim (35.3 GPa). Figures 4h showed the shear modulus as a function of the Na*, which decreased regularly with increasing Na*. By DFT methods, a similar softening as a function of Na* was noted in phase-X [(K,Na)2Mg2Si2O7, Mookherjee et al. 2009a]. Therefore, polycrystalline samples of Ms-Pg and phase-X series richer in K+ appeared to undergo the shear stress better than did the samples richer in Na+.

From these data the sound velocities can be determined, where the compressional and shear velocities (m/s) (Karki et al. 2001) decreased as a function of Na* (Fig. 5).

4. Discussion. In mafic, ultramafic and sedimentary rocks of subducted slabs, Na-K white micas are widespread. If the rocks are formed by a polycrystalline phase of the Ms-Pg series minerals, the members at the middle concentrations showed less resistance to the pressure and, depending on the mineral assemblage, the pressure and the temperature, these middle members could migrate to lower or higher Na* or segregate into interstratified minerals. All of these could contribute to cause the miscibility gap in the series. In addition, it is well known that Pg’s show a very restricted stability P-T range in high-pressure and high-temperature experiments (Domanik et al. 1996). Particularly during the prograde metamorphism of metapelites and metarhyolites of subsuction zones, Pg breaks down at 2.0-2.5 GPa and 550-700°C, forming kyanite and omphacite. Meanwhile, Ms and phengite show broad stability in the P-T compositional space. The nature of the mineral, the chemistry of the mineral assemblage, and the physical and chemical properties of the Pg minerals play an important role in the P-T existence range, but resistance to pressure should also be important in this solvus. Since the bulk modulus of the series was found to be higher at the Pg's, with temperature effect estimation, which should be more stable with respect to pressure in the rocks. However, event though the shear stress is not important at hydrostatic pressure, the layered structure and the weak forces between layers of these minerals could make that the lower shear and mixed ECs for Pg's be meaningful, thereby Pg's would be weaken at increasing pressure. Therefore, the differences in the shear and mixed ECs, the limited value of the Na+ in the Ms’ minerals, the tendency of the series to move to K-richer minerals, and the incorporation of the Mg2+ to the Oc sheet of phengites...
bolster the stability of the members richer in K⁺, and they became much more widespread in different lithologies. Both the Ms and Pg members of the series could admit Mg²⁺, Fe²⁺, and Fe³⁺ substitutions in the Oc sheet, but the high distortion of the α angle in the Pg samples should transform these “Oc-substituted-Pg’s” into unstable minerals. Na-substituted Ms’ underwent the unstabilization better than in the case of K-substituted Pg’s. This unstabilization could also contribute Pg’s to have their field of stability bounded in the P-T compositional spaces.

On the other hand, if (001)-oriented aggregates could be found in shales and in schists, the higher value of C₃₃ in Pg’s could make them more resistant to the direct pressure. In this case, Pg’s would increase the stability range in the P-T composition space, and the system would possibly evolve to Na-richer-substituted members at high pressure. Nonetheless, event though the shear stress is not important at hydrostatic pressure, the layered structure and the weak forces between layers of these minerals could make that the lower shear and mixed ECs weaken Pg’s with respect to the Ms’, setting a balance with the C₃₃ effect. All of this increases the anisotropy in shales and schists.

As with other phyllosilicates (e.g., talc, chlorite, and phase A) in subduction settings (Mainprice and Ildefonse, 2009), this series is highly anisotropic for seismic P- and S-waves. Despite its highly anisotropic character, compared to other phyllosilicates in subduction settings, it is very unlikely that Pg would exert a strong influence on the seismological properties of subduction, because of its low volume fraction and its limited stability along the common P-T-path of subducted crust.

Because of the higher resistance of Ms’/phengites, and in certain mineral assemblages, they are important to transport high amounts of volatiles to high P and T regions (Poli et al. 2002). At high pressures and over broad temperature intervals, Ms’/phengites can react to K-hollandite, a key mineral in the subducted sediment. In this way, Ms’/phengites could be one of the links in the K transport to K-hollandite, and the latter may move K from the deepest part in the subduction slabs to the upper mantle wedge in transporting K as a signature element (Mookjerhee et al. 2009b). All of this appears to agree with the depletion of K⁺ from the silicates on Earth to the core (Bukowinski, 1976; Lee and Jeanloz, 2003; Murphy et al., 2003; Lee et al., 2004).
Normal Strains

Strains affect the bonds and the atomic groups according to their bonding. Therefore, if the change in bond lengths and atomic group geometry are studied as a function of the strains, a bonding picture inside the crystal would result. Cousins (1978a, 1978b, and 1981) and Catti (1989) studied the inner elasticity, calculating the inner elastic-stiffness constants associated with the atoms or atomic groups. In the present work, our aim was to establish a landscape of the bonding by studying only the deformation of bonds or atomic groups from the strained cells, according to Eqs. 2-4 after the optimisation of the internal atomic coordinates.

Because of the layered structure, $C_{33}$ showed the most important variation as a function of Na*, and the normal stiffness along the $z$ axis was the softest. Therefore, only the most notable deformations and normal strains along the $z$ axis were shown, with the exception of the $\alpha$ angle variations.

Deformabilities as a function of Na* are shown in Table 5. Tetrahedra rotated according to the $xx$ or $yy$ strains in an effort to fit the T- and Oc-sheet when the cell was strained, and $\alpha$'s showed negative deformabilities (the value of $\alpha$ decreases from the negative to positive $\varepsilon_{xx}$ or $\varepsilon_{yy}$ strain). The intercepts of the previous equations applied to K$^+$ cavities was the $\alpha$ deformability of Ms, and the deformability of the Na$^+$ cavities could be considered as the deformability at the limit when Na* $\rightarrow$ 0. The tetrahedral rotations of the Na$^+$ cavities were, in absolute value, more deformable than those of K$^+$'s and decrease along the series (Table 5), which agrees with the greater slopes $\Delta$(Na···O) and $\alpha_{Na}$ as a function of Na* (Fig. 3). For $\varepsilon_{zz}$ the $\alpha$ deformability behaviour was the opposite and smaller than that of $\varepsilon_{xx}$- and $\varepsilon_{yy}$-strains (Table 5). When the strains were applied along the $z$ axis, where the weakest bond occurs, the $\alpha$ showed the lowest deformability.

The $\varepsilon_{zz}$ strain induced linear deformations on $<$T – O$>$ and $<$VIAl$^{3+}$ - O$>$ and their deformabilities ranged from 0.02 to 0.1 (Table 5). The $<$IVAl-O$_{basal/apical}$ were more deformable than the $<$Si-O$_{basal/apical}$, and the $<$T-O apical$>$ was less deformable than the basal one. The deformability variation as a function of the Na* showed different behaviour (Table 5): while the $<$T-O$_{basal}$ decreases with the increasing Na*, the $<$T-O$_{apical}$ increased. The $<$VIAl$^{3+}$ - O$>$ showed the lowest deformability of these bonds.
The $\epsilon_{zz}$ strains induced larger deformabilities at $<X^{+}\cdots O_{\text{outer}}>$ and $<X^{+}\cdots O_{\text{inner}}>$ than the previous distance deformabilities, between 3- and 10-fold larger than the previous deformabilities (Table 5). The Coulomb forces between the interlayer cations and the oxygens in the tetrahedral cavities were revealed with these large deformabilities. In general, the $<X^{+}\cdots O_{\text{inner}}>$ were greater than the $<X^{+}\cdots O_{\text{outer}}>$ deformabilities, which agreed with their thermal expansion coefficients (Mookherjee et al. 2002, Catti et al. 1989). The deformabilities decreased with increasing Na*, and in the Na cavities did so with higher slope than the K cavities.

T- and Oc-sheet thickness deformabilities registered values according to the $<T-O>$ deformability, increasing their values with Na* (Table 5). However, the interlayer space showed remarkable deformations, with slopes of around 2.6, indicating that the interlayer space was a heavily deformable region, which showed strong thermal expansion [Mookherjee et al. 2002 (phengite-2M1), Catti et al. 1989 (muscovite)]. This means once again that this was the weakest bonded region in the mineral. This easy deformation could be related to the possibility of swelling in the phyllosilicates, in such a way that other foreign molecules (such as water, polar molecules, etc.) could enter the interlayer space. However, this mineral series does not swell in a detectable way, and if the Ms-Pg series could deform its interlayer space to such a degree, we might expect larger deformabilities in typical swelling phyllosilicates, such as smectites. Furthermore, the small deformability of $<\alpha>$ as a function of $\epsilon_{zz}$ could be accounted for by the high deformability of the interlayer space, where any deformation along $c$ axis affected mainly the interlayer space, and the layers did not undergo any meaningful deformation.

**CONCLUSIONS**

The calculated crystal structure, bond lengths, angles, and other geometrical parameters were very close to the experimental range of values. The computational crystal chemistry showed a similar behaviour to that of natural minerals, even though in nature a miscibility gap appears, and therefore our series could be considered to be a general ideal series. The importance of the crystal-chemistry behaviour on the anisotropy of the crystal is shown. The differences of the geometrical features in the Na* and K* tetrahedral cavities could
induce an inertial behaviour to the octahedral substitution in the most Na-substituted members of the series, which agrees with the lack of octahedral substituted Pg samples.

Theoretical ECs agreed approximately with Ms values in the literature. The change of the ECs with the different interlayer cation configurations assayed in this work is small, with a maximum deviation of 5% from the lowest to the highest values. Some of them could be present in the mineral, where cation-aggregation regions could appear. However, the interstratified sample shows the higher EC values and the most stable total energy, and therefore a possible Ms and Pg segregation could be induced at the middle concentration member of the series. In general, the behaviour of ECs along the series appeared to have a decreasing stiffness with the increasing Na*, some of them showing linear behaviour. $C_{33}$ and $C_{66}$ increases with Na*. Most of them showed a deviation of the ideal crystalline-solution addition law, with mixing terms depending on the concentration, and in some of them the volume was an important variable to systematize the system. The bulk moduli of the polycrystalline aggregates showed small differences in the lowest and highest members of the series, with a minimum in the middle concentration member, but with an estimate of the bulk moduli at room temperature, the Pg turned out to be stiffer than Ms. So the geometrical features, the stiffness and the stabilities of the interstratified sample at the middle concentration range seem to justify the gap of miscibility in the series. The shear modulus showed a moderate decrease along the series. The lowest shear and mixed ECs of the Pg’s could justify the low range of existence of these minerals in the P-T space. The P and S velocities decrease as a function of Na*.

Normal strains, $\varepsilon_{ii}$, affected the bonds or other geometrical features of the structure according to their bonding. The strongest bonds showed the smallest deformabilities, these being less than one tenth of the $\varepsilon_{ii}$. Average distances between the basal oxygens and interlayer cations showed a high deformability in agreement with the weak interactions. The deformability of the interlayer space is the largest, according to its weakest bonding in the crystal structure. In general, deformabilities show linear functional behaviour with Na*.

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Table 1. Calculated and experimental structural parameters of Ms-Pg series (lengths in Å, angles in degrees, and volumes in Å³). Na*=Na⁺/(Na⁺+K⁺).

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<th>0.75</th>
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<td>1.651</td>
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<tr>
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<tr>
<td>M-OH</td>
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<td></td>
<td>0.668</td>
<td>0.681</td>
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<tr>
<td>K-O inner</td>
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<td></td>
<td>2.759</td>
<td>2.721</td>
<td>2.680</td>
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<tr>
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<td></td>
<td>0.758</td>
<td>0.789</td>
<td>0.838</td>
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<tr>
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<tr>
<td>Na-O inner</td>
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<td>2.680</td>
<td>2.618</td>
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<tr>
<td>Δ_ka</td>
<td>-</td>
<td></td>
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<td>0.746</td>
<td>0.746</td>
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<td>Tetrahedral rotation α (º)</td>
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<td>15.5</td>
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<tr>
<td>V. (Td) Si,Al (Å³)</td>
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<td>2.274</td>
<td>2.282</td>
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<td>2.078-2.085</td>
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<tr>
<td>Interlayer thickness (Å)</td>
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<tr>
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<td>307.1</td>
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<tr>
<td>Volume Interlayer (Å³)</td>
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<td>157.0</td>
<td>152.3</td>
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<td>139.0</td>
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</tr>
<tr>
<td>Basal oxygen corrugation Δ (Å)</td>
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<td>0.23-0.226</td>
<td>0.282</td>
<td>0.305</td>
<td>0.279</td>
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* Burnham and Radoslovish (1964) K_{0.66}Na_{0.34}Al_{2}(AlSi3)O_{10}(OH)2; Rothbauer (1971) K_{0.85}Na_{0.1}Al_{1.81}Fe_{0.14}Mg_{0.12}(Al_{0.9}Si_{3.1})O_{9.8}(OH)2; Guggenheim et al. (1987) K_{0.93}Na_{0.08}Al_{1.63}Fe_{0.01}Mg_{0.01}(Al_{0.9}Si_{3.1})O_{9.8}(OH)2; Catti et al. (1989) K_{0.86}Na_{0.11}Al_{1.93}Fe_{0.07}Mg_{0.02}(Al_{0.92}Si_{3.08})O_{10}(OH)2; GET92; Brigatti et al. (1998) Different compositions; Mookherjee and Redfern (2002) K_{0.95}Na_{0.05}Al_{0.76}Fe_0.14Mg_{0.10}2(Al_{0.75}Si_{3.25})O_{10}(OH)1.96F_{0.04}.
† Comodi and Zanazzi (1995) K_{0.9}Na_{0.07}Ba_{0.01}□_{0.02}Al_{1.84}Ti_{0.04}Fe_{0.07}Mg_{0.04}(Al_{1.99}Si_{2.99})O_{10}(OH)2; Lin & Baley, (1984) K_{0.5}Na_{0.2}Ca_{0.01}□_{0.024}(Al_{1.99}Fe_{0.028}Mg_{0.013}Ti_{0.003})(Al_{1.06}Si_{2.93})O_{10}(OH)2.
‡ Comodi and Zanazzi (1997) Na_{0.88}K_{0.10}Ca_{0.01}Ba_{0.01}(Al_{1.97}Ti_{0.007}Fe_{0.01}Mn_{0.006})Si_{3.01}Al_{0.99}O_{10}(OH)2: GEA92; Lin & Baley, (1984) K_{0.042}Na_{0.916}Ca_{0.018}□_{0.024}(Al_{1.99}Fe_{0.028}Mg_{0.013}Ti_{0.003})(Al_{1.06}Si_{2.93})O_{10}(OH)2.
# values are divided by 2.
τ = Obasal-T-Oapical bond angles; α (º) = ½ Σ_i=1,6 [120º - (Ob-Ob-Ob)_i]/6; Tetrahedral sheet thickness (Å) = [(mean z coordinate of basal O) – (mean z coordinate of apical O)]csin β; octahedral sheet thickness (Å) = [(mean z coordinate of “upper” O and OH in the...
octahedral sheet) – (mean z coordinate of “lower” O and OH in the octahedral sheet) \( c \sin \beta \), \( \Delta z \) (Å) = measure of distortion off coplanarity in z coordinate of the basal O atoms.
Table 2. Calculated and experimental elastic constants, Cij, (GPa) of the Ms-Pg series. Na*=Na’/(Na’+K’)

<table>
<thead>
<tr>
<th>Cij</th>
<th>Msâ</th>
<th>Msâ</th>
<th>Msâ</th>
<th>Msâ</th>
<th>Na* = 0.0</th>
<th>0.25</th>
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<td>11</td>
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<td>181.0</td>
<td>176.5</td>
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<td>178.7</td>
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<td>54.8</td>
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</tbody>
</table>

(a) Aleksandrov and Ryzhova (1961).
(b) Vaughan and Guggenheim (1986).
(c) McNeil and Grimsditch (1993).
(d) Calculations from plane waves, GGA P=0, Model 1. Militzer et al. (2011).
(e) Calculations based on empirical potential (Collins et al. 1992).
(g) Values from Voigt-Reuss-Hill equations.
Table 3.- Elastic-stiffness constants (GPa) at different interlayer cation configurations at Na/(Na+K) = 0.5.

<table>
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<tr>
<th>Ci</th>
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<th>2bc1</th>
<th>Interstr</th>
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<td>178.0</td>
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<td>74.8</td>
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<td>79.2</td>
<td>87.1</td>
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<tr>
<td>44</td>
<td>14.1</td>
<td>14.6</td>
<td>14.6</td>
<td>11.6</td>
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<td>23.3</td>
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<td>67.9</td>
<td>65.9</td>
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<td>32.8</td>
<td>32.1</td>
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<tr>
<td>Giso</td>
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<td>66.9</td>
<td>67.6</td>
<td>68.5</td>
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<tr>
<td>Gross</td>
<td>34.6</td>
<td>34.8</td>
<td>35.1</td>
<td>33.0</td>
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Total Energy (eV) -53840.32390 -53840.21336 -53840.30269 -53840.66671

| a (Å) | 10.321 | 10.327 | 5.162 | 10.311 |
| b (Å) | 8.975 | 8.970 | 17.934 | 8.951 |
| c (Å) | 19.653 | 19.651 | 19.619 | 19.662 |
| β(°) | 95.55 | 95.26 | 95.28 | 94.55 |

Vol (Å³) 1812.015 1812.696 1808.566 1808.960
Table 4.- Bulk modulus values for Muscovite from different experimental and computational studies.

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<th>Ref.</th>
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<td>Vaughgan et al. 1986</td>
<td>58.2^a</td>
</tr>
<tr>
<td>Sekine et al.,1991</td>
<td>52^b</td>
</tr>
<tr>
<td>Faust &amp; Knittle, 1994</td>
<td>61.4^c</td>
</tr>
<tr>
<td>Catti et al.,1994</td>
<td>56^c</td>
</tr>
<tr>
<td>Comodi &amp; Zanazzi, 1997</td>
<td>56^c</td>
</tr>
<tr>
<td>Smyth et al. 2000, Phengite</td>
<td>57^c</td>
</tr>
<tr>
<td>Comodi et al. 2002</td>
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<td>Curetti et al. 2006, Phengite</td>
<td>57.3^c</td>
</tr>
<tr>
<td>Ortega-Castro et al. 2010</td>
<td>60.1^c</td>
</tr>
<tr>
<td>This work</td>
<td>68.4^e</td>
</tr>
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</table>

(a) Brillouin Scattering  
(b) Shock wave  
(c) X-Ray Diffraction  
(d) Neutron Diffraction  
(e) DFT  
(+) An estimate of the bulk modulus at 298 K from Comodi et al. 2002.
Table 5.- Deformabilities as a linear function of the Na⁺.

<table>
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<tr>
<th>Molecular group</th>
<th>ε_i</th>
<th>D'_ij</th>
<th>slope</th>
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</thead>
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<td>2.06</td>
<td></td>
</tr>
<tr>
<td>&lt;α&gt;_&lt;Na&gt;xx</td>
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<tr>
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<tr>
<td>&lt;Si-O&gt;&lt;zz</td>
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<tr>
<td>&lt;Al-O&gt;&lt;zz</td>
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<tr>
<td>&lt;Si-O&gt;&lt;zz</td>
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<tr>
<td>&lt;Na-O&gt;&lt;zz</td>
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</table>

(a) Deformability of Ms, no clear linear behaviour was shown as a function of Na⁺.
(b) Deformability of Pg (regression was performed as a function of K⁺).
(c)
Figure 1. (a) Middle-concentration Na$^+$ compound of the 2M$_1$ Ms-Pg series, c0 interlayer cation configuration; (b) 2bc1 interlayer cation configuration; (c) 2ac1 interlayer cation configuration; (d) interstratified derivative. Sky- and navy-blue polyhedra account for the Al$^{3+}$ and Si$^{4+}$ cation polyhedra, respectively; the O, H, Na, and K cation are represented by red, white, yellow, and purple spheres, respectively.
\[ a = 5.186 - 0.03x - 0.03x^2 \]
\[ R^2 = 0.98; \ SD = 0.005 \]
\[ \Delta a_{\text{mix}} = 0.03x(1-x) \]

\[ b = 9.007 - 0.03x - 0.08x^2 \]
\[ R^2 = 0.995; \ SD = 0.005 \]
\[ \Delta b_{\text{mix}} = 0.08x(1-x) \]
Figure 2. Computational and experimental values of (a) a axis; (b) b axis; (c) ½csinβ; and (d) volume as a function of Na⁺/(Na⁺+K⁺) in the Ms-Pg series. Inserts: linear least-square fitting, correlation coefficient (R) or square correlation coefficient, standard deviation (SD) and mixing terms; and experimental values extracted from different references. (a) and (b) GEA92 for a and b axes in the Ms region, values from Eqs. 2 and 8, respectively, of Table 1 from GEA92; (c) GEA92 in the Ms region values from Eq. 14 of Table 1, and in the Pg region values from Eq. 26 of Table 2 from GEA92; and (d) GEA92 in the Ms region values.
from Eq. 20 of Table 1, and in the Pg region values from Eq. 30 of Table 2 from GEA92. Sid77 = values from Sidorenko et al. (1977); Flux86 = values from Flux and Chatterjee (1986); Gug87 = values from Guggenheim et al. (1987); Cat89/94 = values from Catti et al. (1989) and Catti et al. (1994); Roux96 = values from Roux and Hovis (1996); Bri98 = values from AG1 and/or RA1 and/or C3-29b samples from Brigatti et al. (1998); and Moo02 = values from Mookherjee and Redfern (2002).
Figure 3.- (a) Differences between the $<X^+\cdot\cdot\cdot\cdot\cdot O>_{outer}$ and $<X^+\cdot\cdot\cdot\cdot\cdot O>_{inner}$ (Å) as a function of the Na$^+/$(Na$^++$K$^+$); (b) average tetrahedral rotation ($<\alpha>$) for the K$^+$ and Na$^+$ ditrigonal cavities as a function of the Na$^+/$(Na$^++$K$^+$) in the unit cell. Inserts: linear least-square fitting and experimental values extracted from different references. Rot71 = values from Rottbauer (1971); Sid77 = values from Sidorenko et al. 1977; Sob77 = values from Soboleva et al. (1977) (Pg 1M); Lin84 = values from Lin and Bailey (1984); Knu86 = values from Knurr and Bailey (1986); Gug87 = values from Guggenheim et al. (1987);
Cat89/94 = values from Catti et al. (1989) and (1994), respectively; Cat94 = values from Catti et al. (1994); Com95 = values from Comodi et Zanazzi (1995); Bri89 = values from Brigatti et al. (1989); and Moo02 = values from Mookherjee and Redfern (2002).
\begin{align*}
V/C_{11} &= 5.237 - 0.458x + 0.131x^2 \\
R^2 &= 0.996; \quad SD = 0.011; \quad \Delta(V/C_{11})_{\text{mix}} = -0.131x(1-x)
\end{align*}

\begin{align*}
V/C_{22} &= 5.258 - 0.17x - 0.20x^2 \\
R^2 &= 0.98; \quad SD = 0.032; \quad \Delta(V/C_{22})_{\text{mix}} = 0.20x(1-x)
\end{align*}

\begin{align*}
V/C_{33} &= 13.14 - 3.1x - 2.3x^2 \\
R^2 &= 0.99; \quad SD = 0.24; \quad \Delta(V/C_{33})_{\text{mix}} = 2.3x(1-x)
\end{align*}
$$C_{44} = 22.4 - 14.3x; \ R = 0.995; \ SD = 0.6$$

$$C_{46} = -0.8 - 8.3x; \ R = 0.98; \ SD = 0.7$$

$$V/C_{66} = 13.901 - 1.99x; \ R = 0.991; \ SD = 0.073$$
\[ C_{12} = 65.2 - 6.1x - 5.1x^2; \quad R^2 = 0.97; \quad SD = 1.0 \]
\[ \Delta(C_{12})_{mix} = 5.1x(1-x) \]

\[ C_{13} = 39.2 - 13.0x; \quad R = 0.995; \quad SD = 0.6 \]

\[ C_{23} = 34.2 - 9.9x - 5.3x^2; \quad R^2 = 0.9997; \quad SD = 0.1 \]
\[ \Delta(C_{23})_{mix} = 5.3x(1-x) \]

\[ C_{15} = 14.1 + 5.0x - 9.6x^2; \quad R^2 = 0.97; \quad SD = 0.5 \]
\[ \Delta(C_{15})_{mix} = 9.6x(1-x) \]

\[ C_{25} = 0.8 - 0.8x - 13.4x^2; \quad R^2 = 0.995; \quad SD = 0.6 \]
\[ \Delta(C_{25})_{mix} = 13.4x(1-x) \]

\[ C_{35} = 14.1 + 5.0x - 9.6x^2; \quad R^2 = 0.97; \quad SD = 0.5 \]
\[ \Delta(C_{35})_{mix} = 9.6x(1-x) \]
**Figure 4.** - $C_{ij} (a) – (f)$, bulk (B) (g) and shear (G) (h) moduli as a function of $Na^+/(Na^++K^+)$, V/EC in Å$^3$/GPa. Inserts: linear least-square fitting and experimental values extracted from different references. In (a) – (h) AR61 = experimental values from Aleksandrov and Ryzhova (1961); VG86 = values from Vaughan and Guggenheim (1986); McG93 = values from McNeil and Grimsditch (1993); Mil11 = values from Militzer et al. (2011); Coll92 = values from Collins et al. (1992). In (g) and (h) B- and G- (B+ and G+) means Hashin-Shtrikman lower bound (upper bound) of the bulk and shear moduli; Hill
means Hashin-Shtrikman-Hill average; VG86 means bulk and shear Voigt-Reuss-Hill average, respectively, from Vaughan and Guggenheim (1986).
Figure 5.- P and S wave velocities (Karki et al., 2001) from the Hashin-Shtrikman-Hill modulis.