

ATOMISTIC SIMULATION OF LAYERED SILICATES IN THE MUSCOVITE-CELADONITE SYSTEM

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INTRODUCTION

Order-disorder in aluminosilicates is an important phenomenon, which significantly affects thermodynamic stability of these minerals.

In 2:1 phyllosilicates order-disorder phenomena occur in the octahedral and in the tetrahedral sheets. These minerals are involved in a variety of petrologically important reactions (Mottana *et al.*, 2002).

Phengites $[KAl_{2-y}(Fe,Mg)_y(Si_{3+y}Al_{1-y})O_{10}(OH)_2]$; ideally $y = 0.5$] the dioctahedral micas of the muscovite-celadonite series (nomenclature after Rieder *et al.*, 1998), are important phases of high pressure rocks (Compagnoni, 1977). Phase equilibria of phengites are used for geothermobarometry of metamorphic assemblages (Coggon & Holland, 2002; Sassi *et al.*, 1994; Massonne & Schreyer, 1987). Knowledge of the thermodynamics of mixing and order-disorder effects in phengites is important for improving accuracy of a variety of geothermobarometers (Török, 1996).

The experimental results on the order-disorder in phengites are contradictory due to the difficulty in discriminating between quasi-isoelectronic atoms Mg, Al, Si.

Computer simulation methods provide an important tool for the understanding of the structure and the chemistry of phyllosilicates minerals at molecular level.

Atomistic calculations based on ionic concept, where short-range interactions between the ions are modeled with Born-Mayer potentials, have been proved to being able to provide sufficient accuracy in reproducing structural and thermodynamic properties of many minerals.

Modeling of 2:1 dioctahedral phyllosilicates with the empirical potentials is difficult because of the necessity to reproduce anisotropy of the structural properties within and between the layers.

Empirical interatomic potentials have been used in structural studies of phyllosilicates with various types of substitutions (muscovite, margarite, pyrophyllite, beidellite, montmorillonite, smectites and illites) (Skipper *et al.*, 1995; Teppen *et al.*, 1997; Bosenick *et al.*, 2001; Sainz Diaz *et al.*, 2004; Palin *et al.*, 2001). Unfortunately, fine structural features such as interlayer spacing, cannot always be reproduced with the empirical potentials to a sufficient level of accuracy. Thermodynamic properties of micas predicted based of such potentials are not very reliable.

In particular, based on the results of simulation studies, Palin *et al.* (2001) have found consistency between the calculated and experimental ^{29}Si NMR data on muscovite at about 3000 K. Based on these simulations the authors concluded that muscovite and micas in nature do not achieve thermodynamic intra-crystalline equilibrium. This conclusion seems to be in a contradiction with the common use of micas as ion exchangers. The layered structure of micas provides means for fast ion diffusion. A high level of consistency between ^{29}Si NMR data obtained on natural and synthetic micas (Herrero *et al.*, 1987; Herrero & Sanz, 1991; Circone *et al.*, 1991, Sanz *et al.*, 2006) also suggests that the Al/Si

distribution in micas in hydrothermal experiments is able to achieve equilibrium at least at 600°C. Here the conclusion of Palin *et al.* (2001) is revisited based on the results of first principles calculations.

Ab initio methods based on density functional theory (DFT) with periodic boundary conditions have previously been applied in studies of structure-property relations of various phyllosilicate (Tunega & Lischka, 2003; Sainz-Diaz *et al.*, 2005). The strength of *ab initio* calculations was demonstrated by McConnell *et al.* (1997), who showed that empirical potentials lead to an overestimates of the Coulombic energy term (by ~ 30%) compared to the *ab initio* model in determinations of the enthalpy of disorder for exchange between Al and Si in simple aluminosilicate structures.

In the light of these observations, we decided to check accuracy of empirical potentials for two end members celadonite and muscovite by comparing the excess energies predicted with the potentials and with DFT.

We have found a very good linear correlation between empirical and *ab initio* excess energies. However, the excess energies predicted with empirical potentials appear to be significantly larger than those predicted *ab initio*. This shows that empirical potentials can be used to assess relative energy values of different configuration provided that the results are appropriately corrected. Here we show that Monte Carlo simulations of temperature-dependent properties of micas constrained with the excess energies determined *ab initio* or with the results of empirical potentials calculations, which are scaled based on *ab initio* results, are able to predict sensible thermodynamic results.

THERMODYNAMICS OF THE MUSCOVITE-CELADONITE JOIN

Atomistic methods can be applied to calculate the variations of energy between ordered and disordered structures along solid solutions joints. For instance, Vinograd *et al.* (2004, 2007a, 2007b) have done such calculations in garnets, pyroxenes and carbonates.

Using large supercells allows the generation of disordered compounds and the study of ordering. Substituting atoms are randomly positioned in the supercell. In this way, Short Range Order (SRO) is easily avoided, and Long Range Order (LRO) can be neglected if the supercells are large enough. However, using very large supercells to compute lattice enthalpies is highly time-consuming. It is obvious that executing this process takes considerably longer for large cells containing numerous atoms. For this reason, using empirical potentials based software like GULP (General Utility Lattice Program) (Gale & Rohl, 2003) or a software package which uses density functional theory like CASTEP (Clark *et al.*, 2005) alone is not ideal.

Another method, known as Cluster Expansion (CE) (Connolly & Williams, 1983, Sanchez *et al.*, 1984) based on the *Js* formalism allows a reliable estimation of the lattice energy of very large supercells. The *Js* formalism is derived from the cationic ordering theory (Bosenick *et al.*, 2001, Warren *et al.*, 2001).

For solid solutions and end-member phases which show order/disorder effects (such as the Al/Si ordering in the tetrahedral sheet of micas), at least a few dozen of structures per composition are necessary to represent energetic variations between disordered and ordered structures (Dove, 2001). When the energies of these structures are calculated with force-field methods, the necessary statistics can be achieved by varying the cation distribution and by picking up the sufficient number of structures at random. A large number of such structures do not create a problem, as the energy minimization of each of the structures can be performed fast. On the contrary, when *ab initio* approaches are used, the number of the sampled structures should be minimized drastically. This implies that there is a need for algorithms,

which permit extracting maximum of thermodynamically important information from minimum number of the sampled structures.

The thermodynamic models of celadonite and muscovite were developed using 14 and 22 configurations respectively. These configurations were selected by random search, however, care was taken to check that each accepted configuration differs from the previously selected ones in terms of the pairwise distribution. This requirement ensures that there is always a unique solution in terms of the J s. The other concern was to include configurations which cover a wide spectrum of energies. The energies of the selected configurations were thus initially calculated with a force field model and the sets showing significant variations in lattice energies were selected for the further quantum mechanical calculations. Below we demonstrate that despite the small number of the calculations the models are in good agreement with available experimental data.

The cluster expansion algorithm adopted here is based on the following equation:

$$E_i \approx \frac{1}{2} \sum_n z_n P_{AB}^{(n)} J_n + E_0 \quad (1)$$

where z_n , $P_{AB}^{(n)}$ and J_n are the coordination number, fraction of AB-type pairs and effective interactions for a pair of sites at the distance n . J_n corresponds to the energy of the exchange reaction $AA + BB = 2AB$ between atoms A and B located at n -th distance. E_i is the energy of a given configuration and E_0 is a constant term for a given composition, which involves contributions to the excess energy not included in the J_n sum. J is known as the “exchange interactions vector”. Values of J are of crucial importance in the following Monte Carlo simulation. A value of J is associated with each characteristic distance separating neighbouring atoms.

The sign of the J value indicates type of a pair of cations which is energetically favorable. Negative J s indicate an ordering tendency (dissimilar pairs are favored) and positive values indicate a clustering tendency (similar pairs are favored).

The values of the J s are calculated in order to reproduce the lattice energies computed with *ab initio* or with a force-field model and to predict the energies of other possible configurations, which are not explicitly sampled. The procedure includes counting numbers of AB-type pairs for each structure and finding the values of the J s via a least squares fit to the computed energies of these structures. The pairs are sorted by distance and thus the obtained J s describe interactions between all possible pairs of neighbours. Here this procedure is applied to the end-members, muscovite and celadonite, and to another composition that lies in the middle of the join, i.e. the ideal phengite. In this study the interaction range is limited by 7 Å. The least squares solution implies that the vector \mathbf{J} is found by solving the matrix equation:

$$\mathbf{J} = \mathbf{P}^{-1} \mathbf{E} \quad (2)$$

where \mathbf{P} is the matrix of the frequencies of AB pairs and \mathbf{E} is the vector of the energies.

When the J s are known it is easy to calculate the lattice energy of any configuration by counting the numbers of AB-type pairs and by multiplying these numbers by the J s. Thus it appears possible to permute a large number of structures in a reasonable time. The algorithm used in this study allows the evaluation of the lattice energy of tens of millions of structures with thousands of substituting atoms.

The supercells adopted for the Monte Carlo simulations are typically much larger than those used for CASTEP or GULP calculations. The energy of the initial configuration is calculated by explicitly counting the numbers of AB pairs at all distances. Subsequent calculations of the energy changes during

the Monte Carlo simulation involve only the counting of the changes in the number of AB pairs around two randomly chosen atoms. This allows to greatly decrease the calculation time required at each Monte Carlo step and thus to perform millions of Monte Carlo steps in a few seconds.

In order to simulate the Boltzmann distribution of the configurational states, it is necessary to repeat this operation millions of times by randomly swapping the atoms. The procedure is known as the Metropolis algorithm. A configuration is set up with either an ordered or random distribution of cations. In essence, a cation pair is randomly selected, and the position of the two cations are switched. This yields the energy change:

$$E \rightarrow E + \Delta E \quad (3)$$

If the energy change is negative or zero, the pair is swapped. On the other hand, if the change in the energy is positive, the swap is accepted with the probability:

$$P(E \rightarrow E + \Delta E) = \exp(-\beta\Delta E) \quad (4)$$

where $\beta = 1 / (K_B \cdot T)$ (K_B is Boltzmann's constant in J/K/mol: $K_B = 1.6803 \cdot 10^{-23}$ J/K; T is the temperature in K), ΔE is the energy variation between the two subsequent configurations. This algorithm moves the system to a thermodynamic equilibrium, what means that the configurational states occur with correct thermodynamic weighting corresponding to the given temperature. The more energetically unfavorable is the state, the lower is the probability that this state is sampled. The average configurational enthalpy is thus a function of the temperature. Usually about 10-20 million Monte Carlo steps are required to attain the equilibrium state for a system containing 3-6 thousand of exchangeable sites (e.g. Vinograd *et al.*, 2007a).

Monte Carlo simulations can be also used for the calculation of thermodynamic functions such as the entropy and the free energy, using the method of thermodynamic integration (Warren *et al.* 2001).

Muscovite end-member

The calculated J_n (see Fig. 1 and Table 1) constants have been used to predict the temperature dependent disorder in the compound. For these calculations, we have created a $6 \times 6 \times 6$ unit cell containing 3456 exchangeable atoms with periodic boundary conditions. Each state different in temperature was sampled with 20 million Monte Carlo steps. The last 10 million steps were used for calculating the average enthalpy.

The temperature dependent properties have been calculated in the interval of 273-1400 K with a step of 25 K. Additional annealing runs have been performed to find the ground state. To do this we have fixed the initial temperature at 573 and then decreased the temperature in small steps to 173 K. The resulting structure of pure muscovite is represented in Fig. 2.

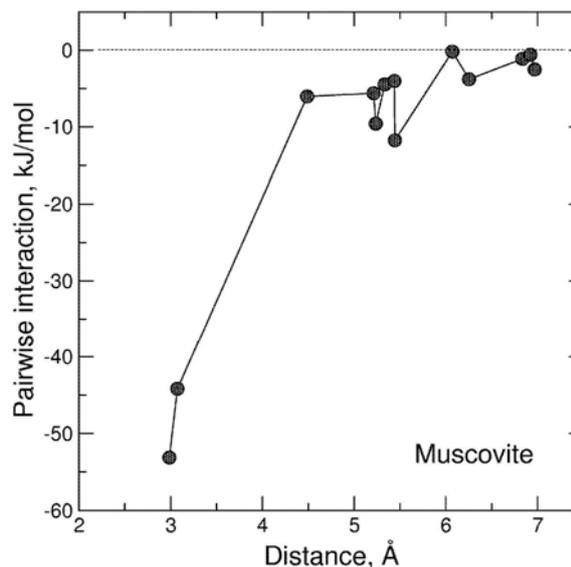


Fig. 1 - The cluster expansion of the pairwise effective interactions for the muscovite end-member as a function of the interatomic separation.

Table 1 - Assigned J parameters and E_0 value for muscovite. The J values are in kJ/mol of cations.

T-T		
$d(\text{\AA})$		J
2.985		-53.119400
3.073		-44.172200
4.488		-6.026460
5.213		-5.614780
5.236		-9.579990
5.334		-4.448600
5.439		-3.994210
5.445		-11.750800
6.071		-0.184058
6.253		-3.783050
6.835		-1.127040
6.921		-0.589442
6.967		-2.514490
E_0	=	21.709125

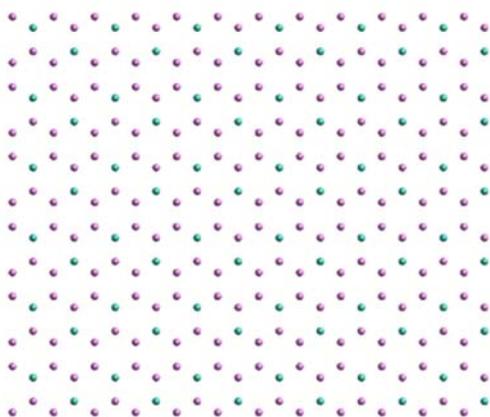


Fig. 2 - Structure of the tetrahedral sheet of muscovite at the end of the ground state search where atoms are represented by spheres. The atom sizes are arbitrary scaled. Pink spheres = Si^{4+} ions, light blue spheres = Al^{3+} ions.

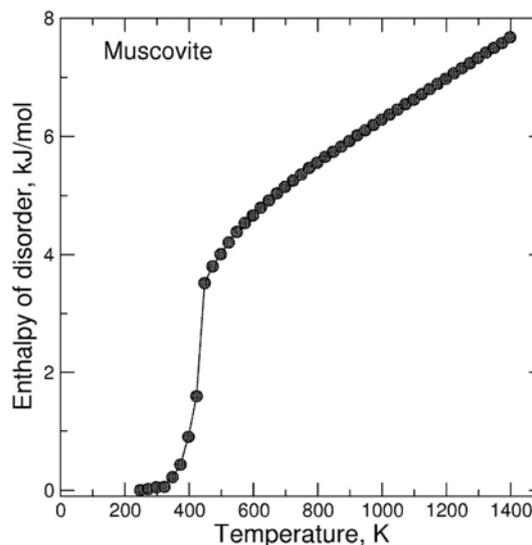


Fig. 3 - The enthalpy of disorder predicted with Monte Carlo simulations.

The enthalpy of disorder as function of the temperature is reported in Fig. 3.

The configurational entropy reflects the effects of short-range (SRO) and long-range order (LRO).

We observe that the ordered structure remains stable up to the temperature of about 400-450 K and then rapidly disorders (see Fig. 4). The development of LRO is manifested by the rapid decrease in

entropy below 450 K. Thus our results are consistent with the common observation that muscovites and other layer silicates with similar Al/Si ratio have SRO, but no LRO.

The Frankfurt MC code permits evaluation of the Long Range Order parameter (LRO)

$$Q_j = [P_{A\alpha} - P_{A\beta}] / [P_{A\alpha} + P_{A\beta}] \quad (5)$$

where $P_{A\alpha} = P_A(1+Q)$ and $P_{A\beta} = P_A(1-Q)$ are the probabilities of finding an A (*i.e.* Al or Si) atom in the nonequivalent sublattices α and β of the structure (Fig. 5).

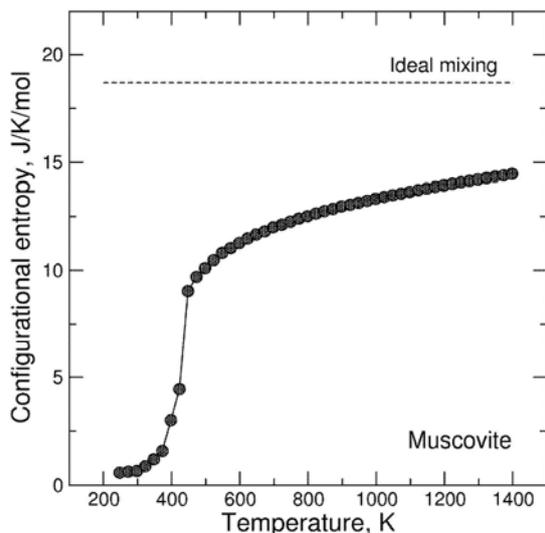


Fig. 4 - Configurational entropy calculated by thermodynamic integration.

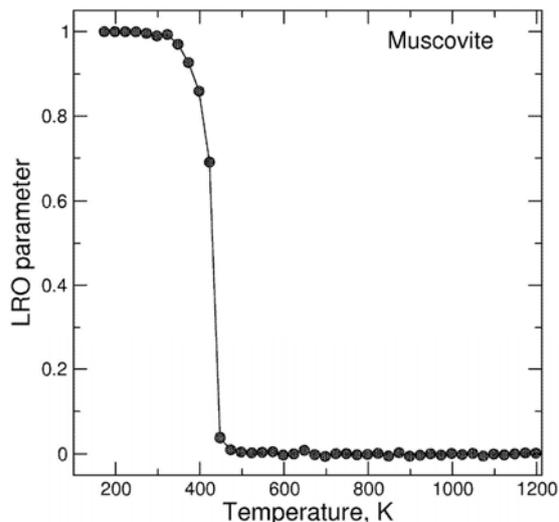


Fig. 5 - The temperature dependence of the LRO parameters Q_T as calculated for muscovite from Monte Carlo simulations.

Nuclear Magnetic Resonance methods are sensitive to short-range aspects of a structure, and are often used to provide quantitative information about short-range order. The experimental data consist of a series of peaks in the NMR spectra. Each peak corresponds to a specific short-range configuration, and the intensity of the peak gives the relative probability of the particular configuration occurring in the crystal.

There have been a number of ^{29}Si NMR studies of layer silicates aimed at determining the short-range order within the tetrahedral sheets (Herrero *et al.* 1987; Herrero & Sanz, 1991; Circone *et al.*, 1991; Sanz *et al.*, 2006). The NMR spectra give four peaks corresponding to the different combinations of Al/Si cations in the three neighbouring tetrahedral sites around each Si cation. The intensities of these peaks can be calculated from short-range order in the MC configurations. Specifically, in this work we calculated the probabilities of forming cluster of four cations with a central Si and three cations in the surrounding triangle in the sheets of the muscovite structure, $[\text{Si}(\text{SiSiSi})]$, $[\text{Si}(\text{AlSiSi})]$, $[\text{Si}(\text{AlAlSi})]$ and $[\text{Si}(\text{AlAlAl})]$. These clusters have been actually observed in ^{29}Si magic-angle spinning NMR experiments, so there is a bridge linking the MC simulations to the experimental data.

Our calculated peaks are in very good agreement with the spectral data by Sanz *et al.* (2006) (Fig. 6), although their sample, with about the same composition of the tetrahedral sheet of muscovite, is phlogopite. Since the data of Sanz *et al.* (2006) show that the ^{29}Si NMR intensities are mainly sensitive to

the Al/Si ration, but not to the types of octahedral or interlayer cations, the observed agreement validates our model.

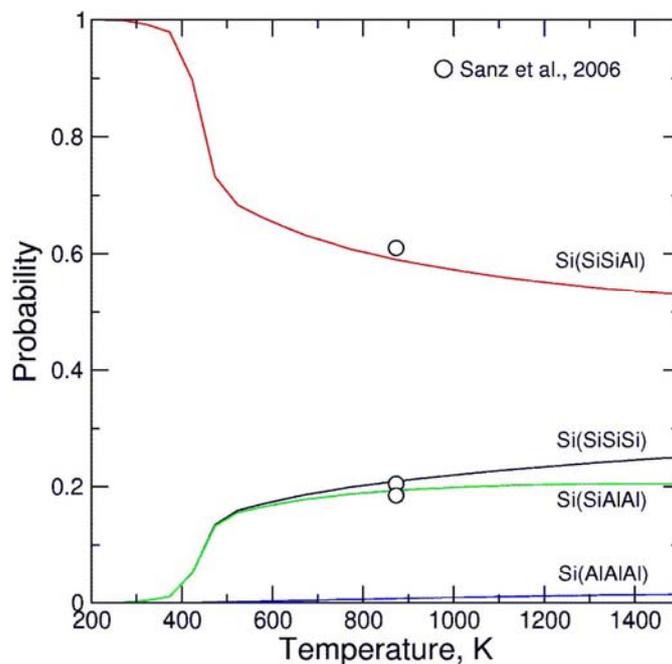


Fig. 6 - The calculated NMR spectra in function of the temperature for muscovite. It is possible to note the matching of our calculated data with experimental data of Sanz *et al.* (2006) with $x_{Al} = 0.25$. The sample in question is relative to phlogopite.

In the previous study by Palin *et al.* (2001), the match between experimental data and their Monte Carlo results was at about 2860 K. They explained this result by invoking kinetic reasons.

Our results do suggest that the Al/Si distribution in layer silicates achieves thermodynamic equilibrium even at temperatures typical for hydrothermal process. Moreover, our model of muscovite appears to be quantitative and, therefore, can be used as a one-mineral geothermometer.

Although this conclusion seems to be consistent with the results of Sanz & Robert (2006) and other NMR studies of layer silicates, it requires further experimental and theoretical validation.

Celadonite end-member

The model of order/disorder in celadonite was also developed using a $2 \times 1 \times 1$ of $1M$ supercell.

The supercell permits identification of 5 different pairwise interactions with distances ranging from about 3 to 6 Angstroms. The J s were derived with the cluster expansion technique similar to that described for muscovite.

The Monte Carlo simulation has been performed with a $8 \times 8 \times 8$ supercell multiple of the unit cell of muscovite. This supercell contains 4096 exchangeable atoms. The ground state structure of celadonite is an ordered structure.

The celadonite model has an order/disorder transformation and the LRO permits to locate the ordering temperature between 850 and 875 K.

Ideal phengite composition

As we have shown, the *ab initio* calculations can be directly used to calculate the J_s for the end-member structures. It would seem obvious that the same can be done for any intermediate composition including phengite. However, this task is more complicated, because in phengite the order/disorder occurs on two sublattices corresponding to the tetrahedral (Al^{3+} , Si^{4+}) and the octahedral (Mg^{2+} , Al^{3+}) sheets. Consequently, there are more types of interactions and, thus, many configurations need to be considered to calculate the J_s .

The simulations of phengite were performed with a different method, which combined force-field and *ab initio* calculations. 11 structures of phengite have been optimized with CASTEP and with GULP using the potential set of Palin *et al.* (2001).

These results have been used to derive an empirical correction factor, which was subsequently applied to the result of our force-field calculations on a much larger set of configurations.

The model undergoes an order/disorder transformation at the temperature of about 225-275 K. The T-configurational entropy trend analysis suggests that above the order/disorder transition phengite retains a significant amount of SRO.

CONCLUSION

The main conclusion is that *ab initio* calculations at present provide a possibility to significantly increase accuracy in the description of the order/disorder and mixing phenomena in minerals. This in turn means that soon it will be possible to significantly improve accuracy of geothermometers currently used in petrology.

We have shown that the results obtained based on *ab initio* calculated excess energies are in good agreement with the experiment. Specifically, we have shown that the thermodynamic properties of the both end-members of the muscovite-celadonite solid solution are significantly affected by order/disorder effects. Although LRO effects are predicted to occur at rather low temperatures, which are not relevant for typical parameters of crystallization of metamorphic rocks, SRO remains significant at higher temperatures. The configurational entropies of muscovite and celadonite differ significantly from the values predicted by the model of ideal mixing.

We have seen, however, that the increased accuracy of atomistic simulation studies opens a possibility for the development of a new approach to the thermometry of metamorphic rocks.

The intracrystalline distribution in layer silicates appears to be a good indicator of the temperature.

REFERENCES

- Bosenick, A., Dove, M.T., Myers, E.R., Palin, E.J., Sainz-Diaz, C.I., Guiton, B.S., Warren, M.C., Craig, M.S. (2001): Computational methods for the study of energies of cation distributions: applications to cation-ordering phase transitions and solid solutions. *Mineral. Mag.*, **65**, 193-219.
- Circone, S., Navrotsky, A., Kirkpatrick, R.J., Graham, C.M. (1991): Substitution of $^{[6,4]}\text{Al}$ in phlogopite: mica characterization, unit-cell variation, ^{27}Al and ^{29}Si MAS-NMR spectroscopy, and Al-Si distribution in the tetrahedral sheet. *Am. Mineral.*, **76**, 1485-1501.
- Clark, S.J., Segall, M.D., Pickard, C.J., Hasnip, P.J., Probert, M.J., Refson, K., Payne, M.C. (2005): First principles methods using CASTEP. *Z. Kristallogr.*, **220**, 567-570.
- Coggon, R. & Holland, T.J.B. (2002): Mixing properties of phengitic micas and revised garnet-phengite thermobarometers. *J. Metam. Geol.*, **20**, 683-696.

- Compagnoni, R. (1977): The Sesia-Lanzo zone: high pressure-low temperature metamorphism in the austroalpine continental margin. *Rend. Soc. It. Mineral. Petrol.*, **33**, 335-374.
- Connolly, J.W.D. & Williams, A.R. (1983): Density-functional theory applied to phase transformations in transition-metal alloys. *Phys. Rev.*, **B27**, 5169-5172.
- Dove, M.T. (2001): Computer simulations of solid solutions. *EMU Notes Mineral.*, **3**, 225-250.
- Gale, J.D. & Rohl, A.L. (2003): The General Utility Lattice Program (GULP). *Mol. Simul.*, **29**, 291-341.
- Herrero, C.P. & Sanz, J. (1991): Short-range order of the Si, Al distribution in layer silicates. *J. Phys. Chem. Solids*, **52**, 1129-1135.
- Herrero, C.P., Gregorkiewitz, M., Sanz, J., Serratosa, J.M. (1987): ²⁹Si MAS-NMR spectroscopy of mica-type silicates: observed and predicted distribution of tetrahedral Al-Si. *Phys. Chem. Minerals*, **15**, 84-90.
- Massonne, H.J. & Schreyer, W. (1987): Phengite geobarometry based on the limiting assemblage with K-feldspar, phlogopite, and quartz. *Contrib. Mineral. Petrol.*, **96**, 212-224.
- McConnell, J.D.C., De Vita, A., Kenny, S.D., Heine, V. (1997): Determination of the origin and magnitude of Al/Si ordering enthalpy in framework aluminosilicates from ab initio calculations. *Phys. Chem. Minerals*, **25**, 15-23.
- Mottana, A., Sassi, F.P., Thompson, J.B., Guggenheim, S. (2002): Micas: crystal chemistry and metamorphic petrology. *Rev. Mineral. Geochem.*, **46**, 499 p.
- Palin, E.J., Dove, M.T., Redfern, S.A.T., Bosenick, A., Sainz-Díaz, C.I., Warren, M.C. (2001): Computational study of tetrahedral Al-Si ordering in muscovite. *Phys. Chem. Minerals*, **28**, 534-544.
- Rieder, M., Cavazzini, G., D'Yakonov, Y.S., Frank-Kamenetskii, V.A., Gottardi, G., Guggenheim, S., Koval, P.V., Müller, G., Neiva, A.M.R., Radoslovich, E.W., Robert, J.L., Sassi, F.P., Takeda, H., Weiss, Z., Wones, D.R. (1998): Nomenclature of the micas. *Can. Mineral.*, **36**, 905-912.
- Sainz-Díaz, C.I., Palin, E.J., Hernández-Laguna, A., Dove, M.T. (2004): Effect of the tetrahedral charge on the order-disorder of the cation distribution in the octahedral sheet of smectites and illites by computational methods. *Clays Clay Miner.*, **52**, 357-374.
- Sainz-Díaz, C.I., Escamilla-Roa, E., Hernández-Laguna, A. (2005): Quantum mechanical calculations of trans-vacant and cis-vacant polymorphism in dioctahedral 2:1 phyllosilicates. *Am. Mineral.*, **90**, 1827-1834.
- Sanchez, J.M., Ducastelle, F., Gratiás, D. (1984): Generalized cluster description of multicomponent systems. *Physica*, **128A**, 334-350.
- Sanz, J., Robert, J.L., Diaz, M., Sobrados, I. (2006): Influence of charge location on ²⁹Si NMR chemical shift of 2:1 phyllosilicates. *Am. Mineral.*, **91**, 544-550.
- Sassi, F.P., Guidotti, C.V., Rieder, M., De Pieri, R. (1994): On the occurrence of metamorphic 2M₁ phengites: some thoughts on polytypism and crystallization condition of 3T phengites. *Eur. J. Mineral.*, **6**, 151-160.
- Skipper, N.T., Chang, F.R.C., Sposito, G. (1995): Monte-Carlo simulation of interlayer molecular-structure in swelling clay-minerals. 1. Methodology. *Clays Clay Miner.*, **43**, 285-293.
- Teppen, B.J., Rasmussen, K., Bertsch, P.M., Miller, D., Schäfer, L. (1997): Molecular dynamics modeling of clay minerals. 1. Gibbsite, kaolinite, pyrophyllite, and beidellite. *J. Phys. Chem. B*, **445**, 1579-1587.
- Török, K. (1996): High-pressure/low temperature metamorphism of the Ko-hegy gneiss, Sopron (W-Hungary); Phengite barometry and fluid inclusions. *Eur. J. Mineral.*, **8**, 917-925.
- Tunega, D. & Lischka, H. (2003): Effect of Si/Al ordering on structural parameters and the energetic stabilization of vermiculites: a theoretical study. *Phys. Chem. Minerals*, **30**, 517-522.
- Vinograd, V.L., Sluiter, M.H.F., Winkler, B., Putnis, A., Hälenius, U., Gale, J.D., Becker, U. (2004): Thermodynamics of mixing and ordering in the pyrope-grossular solid solution. *Mineral. Mag.*, **68**, 101-121.
- Vinograd, V.L., Winkler B., Gale J.D. (2007a): Thermodynamics of mixing in diopside-jadeite, CaMgSi₂O₆-NaAlSi₂O₆, solid solution from static lattice energy calculations. *Phys. Chem. Minerals*, **34**, 713-725.
- Vinograd, V.L., Burton, B.P., Gale, J.D., Allan, N.L., Winkler, B. (2007b): Activity-composition relations in the system CaCO₃-MgCO₃ predicted from static structure energy calculations and Monte Carlo simulations. *Geochim. Cosmochim. Acta*, **225**, 304-313.
- Warren, M.C., Dove, M.T., Myers, E.R., Bosenick, A., Palin, E.J., Sainz-Díaz, C.I., Guiton, B., Redfern, S.A.T. (2001): Monte Carlo methods for the study of cation ordering in minerals. *Mineral. Mag.*, **65**, 221-248.