Thermodynamics of chlorite: atomistic modelling of Tschermak and di-trioctahedral substitution

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Résumé

Chlorite is a common 2:1 phyllosilicate found in volcanic, sedimentary and metamorphic rocks. The diverse crystal chemistry of chlorite makes it a great candidate for deciphering the Pressure-Temperature (PT) conditions of crystallisation of a paragenesis, even though measuring the formula unit remains a complex task (varying iron speciation, water content and vacancies). Inferring PT conditions for metamorphic chlorite requires good thermodynamic modelling of major substitutions (homovalent Fe-Mg, Tschermak and di-trioctahedral). Currently, thermodynamic models are radically opposed regarding the di-trioctahedral substitution as it is either ignored or a solvus is predicted but with opposite temperature evolution. The uncertainties of measurement coupled with textural interpretation of equilibrium explains the current discrepancies of chlorite thermodynamic models, hindering petrologic interpretation.

Following recent developments in atomistic modelling for thermodynamic integration, this study aims at estimating new thermodynamic properties of Tschermak and di-trioctahedral substitution for chlorite, independent from petrologic and experimental constraint as simulations only represent equilibrium. Monte Carlo (MC) simulations of chlorite supercells (12x9x2 unit cell, 1536 formula unit) were performed in the MASH (MgO-Al2O3-SiO2-H2O) system between the clinochlore, sudoite and amesite endmembers; following the Dove (2001) method. This approach enables the calculation of a unit cell energy based on its configuration, provided cation-exchange energies (*Js*) are properly calibrated. About two thousand chlorite supercells (4x4x1) were simulated using semi-empirical potentials (*General Lattice Utility Program*, GULP) to calibrate the exchange energies for the Tschermak and di-trioctahedral substitution. Gibbs free energy of mixing was calculated from the cation-ordering MC simulations of the ternary system. Strong short-range ordering was observed in the simulations, over the entire temperature range of chlorite stability. Cation ordering is particularly pronounced in the tetrahedral sheet and shows a marked variation with changes in composition, along the Tschermak binary. The simulations also constrain the solvus between sudoite (di-trioctahedral chlorite) and clinochlore (tri-trioctahedral chlorite), and its temperature evolution. In time, this model will be compared to literature compiled data and to new detailed analysis – including iron oxidation state and light elements – of metamorphic chlorite from blueschist- and eclogites-facies metapelites from the *Schistes Lustrés* complex (Western Alps).

Mots-Clés: chlorite, atomistic modelling, thermodynamics, Tschermak, ditri, octahedral

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