

Scientific report on EuroMinSci-sponsored Short Term Visit

Visit title	Order-disorder phenomena in phlogopite
Visit by	Dr Erika J. Palin, Department of Earth Sciences, University of Cambridge, Cambridge, UK (EJP)
Visit hosted by	Dr Alberto García, Institut de Ciències de Materials de Barcelona, Barcelona, Spain (AG)
Visit date	17/9/2007 – 21/9/2007

Purpose of the visit

To begin the study of order-disorder phenomena in the trioctahedral phyllosilicate phlogopite, $K^{[6]}(Mg,Al)_3^{[4]}(Si,Al)_4O_{10}(OH,F)_2$ using an existing approach, the “*J* formalism”, whereby atomistic simulations using parameterised interatomic potentials are used to generate a set of pair interaction parameters which are then used in Monte Carlo (MC) simulations of cation ordering as a function of temperature (Bosenick et al. 2001, Warren et al. 2001). EJP and co-workers have used this method extensively in previous investigations of cation ordering behaviour, for example on dioctahedral phyllosilicates such as muscovite (Palin et al. 2001), and also minerals with the spinel structure (Palin & Harrison 2007).

The methodology is also potentially of use in investigating the thermodynamics of other order-disorder processes, e.g. cation ordering in other mineral systems besides those mentioned above, Fe alloy behaviour (with possible relevance to the Earth’s core), NMR experiment/simulation comparison, etc.

Description of work carried out during the visit

During the first part of the visit, AG and EJP discussed the methodology for the study of order-disorder phenomena in phlogopite.

The “ideal” chemical formula of phlogopite is $K^{[6]}Mg_3^{[4]}(Si_3Al)O_{10}(OH)_2$, from which it can be seen that the only crystallographic site in which compositional variation occurs is the tetrahedral site. Therefore, the initial part of the study would focus on the order-disorder behaviour of the tetrahedral sheets, with Al:Si = 1:3. This initial investigation formed the bulk of the work which was carried out during the visit.

The construction of the initial interatomic potential model for phlogopite and the geometry optimisations using the General Utility Lattice Program (GULP, Gale 1997) were performed by EJP before the visit commenced. This meant that the work during the visit could focus on constructing the Al/Si ordering model for phlogopite.

The structure of phlogopite was compared with that of muscovite, a dioctahedral phyllosilicate with similar chemical formula to that of phlogopite, and identical tetrahedral composition (Al:Si = 1:3). The aim was to construct an analogous set of parameters to those used for muscovite and to use these in MC runs. The symmetry of

tetrahedral sheets in phlogopite is higher than that in muscovite, and hence certain distinct parameters in muscovite could be grouped in phlogopite. The tetrahedral ordering model for phlogopite therefore comprised eleven J s. Four of these describe ordering in one tetrahedral sheet, and the remaining seven describe the coupling between adjacent tetrahedral sheets.

Values for the eleven J s were obtained via the usual method of multilinear regression. MC simulations were then performed using these values.

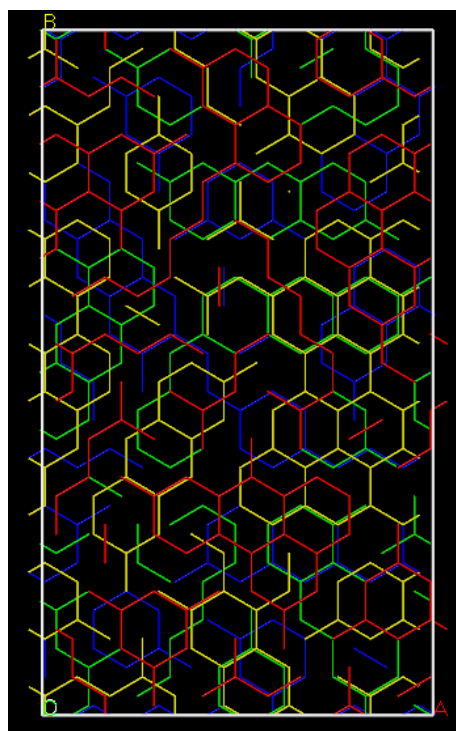
Results

The values of J_{1-4} , the parameters describing ordering in one tetrahedral sheet, are of similar magnitude to those in muscovite. The other J values are also comparable with those of muscovite.

Preliminary MC simulations were performed with a simulation box containing four adjacent tetrahedral sheets, each comprising 864 sites, so that there were 2304 cation sites in total. Simulations comprised an initial equilibration run of 25 million steps, followed by a production run of 25 million steps for the computation of statistical averages.

Two sets of simulations were performed. The first used all eleven J s, and the second just J_{1-4} , with J_{5-11} set to zero. The purpose of these simulations was to compare the behaviour of the system with and without coupling between sheets. (In muscovite it was found that the coupling between sheets could not compete with that within a sheet, such that even if there were a three-dimensional ordered structure, it was not possible for the system to access that structure because the ordering in each tetrahedral sheet set in first.)

This figure shows a sample output from a preliminary Monte Carlo simulation ($12 \times 12 \times 2$ supercell of the phlogopite unit cell), viewed down the c -axis. The four tetrahedral layers in the supercell have been coloured differently, and atoms interacting across J_3 distances have been linked together in each layer.



It is difficult to determine whether or not the interlayer J s have any effect from just these preliminary runs. Further calculations over larger temperature ranges will therefore be performed to investigate this point.

Future work

Naturally-occurring phlogopites usually undergo substitution for $^{[6]}Mg$ (via the Tschermak substitution, $^{[6]}Mg^{[4]}Si \leftrightarrow ^{[6]}Al^{[4]}Al$) and for OH, by F. In addition to the Al/Si ordering in the tetrahedral sheet, it is therefore pertinent to study (a) the octahedral Al/Mg order, and (b) the anion ordering of OH and F.

In case (a), since Al may occur in either the tetrahedral or octahedral sheets of phlogopite, there exists the possibility for coupling between the Al/Si and Al/Mg ordering processes, a phenomenon already observed by use of the J formalism to study the dioctahedral mica phengite (Palin et al. 2003). In case (b), experimental studies using sophisticated NMR techniques have shown a preference for the local octahedral environment of F to comprise three Mg nearest neighbours, with Al in the next coordination sphere (Fechtelkord et al. 2003a, b). Hence, in both cases, it should be possible to compare and contrast results with those from previous simulations and from experiments.

Projected publications/articles

We envisage that at least one publication should result from this visit.

Although EJP has worked on phyllosilicate minerals before, these have been dioctahedral phyllosilicates, and this is the first study where the subject has been a trioctahedral phyllosilicate. One possibility is to prepare a standalone publication about phlogopite; alternatively, the work could be incorporated into an existing manuscript, in preparation by EJP, which is intended to showcase the usefulness of the “ J formalism” to the clay minerals community. AG and EJP will discuss this once the work has been completed. ESF will of course be properly acknowledged in any publication.

Other comments

EJP gratefully acknowledges the ESF for making this visit possible, and AG and ICMAB for hosting it.

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Erika Palin
1st October 2007