

# **Supplementary Materials: Supplementary Information for "Classical Polarizable Force Field to Study Hydrated Hectorite: optimization on DFT calculations and validation against XRD data"**

## **References**

1. Tesson, S.; Salanne, M.; Rotenberg, B.; Tazi, S.; Marry, V. A classical polarizable force field for clays: Pyrophyllite and talc. *J. Phys. Chem. C* **2016**, *120*, 3749-3758, DOI:10.1021/acs.jpcc.5b10181
2. Jahn, S.; Madden, P. A. Modeling earth materials from crustal to lower mantle conditions: a transferable set of interaction potentials for the CMAS system. *Phys. Earth Planet. Inter.* **2007**, *162*, 129-139, DOI:10.1016/j.pepi.2007.04.002
3. Tesson, S.; Louisfremea, W.; Salanne, M.; Boutin, A.; Rotenberg, B.; Marry, V. Classical polarizable force field to study dry charged clays and zeolites *J. Phys. Chem. C* **2017**, *121*, 9833-9846, DOI:10.1021/acs.jpcc.7b00270
4. Tesson, S.; Louisfremea, W.; Ferrage, E.; Rotenberg, B.; Salanne, M.; Boutin, A.; Marry, V. Classical polarizable force field to study hydrated charged clays and zeolites *in prep.*

| Ion pair (ij)                    | $A_{ij}$ (Ha) | $B_{ij}$ ( $\text{\AA}^{-1}$ ) | $C_6^{ij}$ (Ha. $\text{\AA}^6$ ) | $C_8^{ij}$ (Ha. $\text{\AA}^8$ ) | $b_n^{ij}$ ( $\text{\AA}^{-1}$ ) | damping interaction<br>between $q_i$ and $\mu_j$ |                                  | damping interaction<br>between $q_j$ and $\mu_i$ |                                  |
|----------------------------------|---------------|--------------------------------|----------------------------------|----------------------------------|----------------------------------|--------------------------------------------------|----------------------------------|--------------------------------------------------|----------------------------------|
|                                  |               |                                |                                  |                                  |                                  | $c_{ij}(-)$                                      | $b_D^{ij}$ ( $\text{\AA}^{-1}$ ) | $c_{ji}(-)$                                      | $b_D^{ji}$ ( $\text{\AA}^{-1}$ ) |
| O-O                              | 28.4          | 5.49                           | 1.33                             | 7.35                             | 2.72                             | 5.00                                             | 5.38                             | 5.00                                             | 5.38                             |
| O-Al                             | 60.0          | 3.33                           | 0.0477                           | 0.156                            | 4.17                             | -                                                | -                                | 4.73                                             | 4.75                             |
| O-Mg                             | 86.3          | 3.66                           | 0.0477                           | 0.156                            | 4.17                             | -                                                | -                                | 5.00                                             | 4.47                             |
| O-Si                             | 29.4          | 2.84                           | 0.0477                           | 0.156                            | 4.17                             | -                                                | -                                | 3.17                                             | 5.06                             |
| O-H <sub>OH</sub>                | -             | -                              | -                                | -                                | -                                | -                                                | -                                | 1.86                                             | 2.00                             |
| O-O <sub>OH</sub>                | 99.0          | 3.60                           | 0.974                            | 5.25                             | 2.72                             | 2.44                                             | 3.37                             | -                                                | -                                |
| O <sub>OH</sub> -Si              | 980           | 4.82                           | 0.0477                           | 0.156                            | 4.17                             | -                                                | -                                | 4.27                                             | 3.85                             |
| O <sub>OH</sub> -Al              | 20.3          | 3.15                           | 0.0477                           | 0.156                            | 4.17                             | -                                                | -                                | 1.62                                             | 3.37                             |
| O <sub>OH</sub> -Mg              | 35.6          | 3.49                           | 0.0477                           | 0.156                            | 4.17                             | -                                                | -                                | 1.45                                             | 3.06                             |
| O <sub>OH</sub> -O <sub>OH</sub> | 79.5          | 3.30                           | 0.974                            | 5.25                             | 2.72                             | 4.98                                             | 3.23                             | 4.98                                             | 3.23                             |
| O <sub>OH</sub> -H <sub>OH</sub> | -             | -                              | -                                | -                                | -                                | -                                                | -                                | 0.124                                            | 2.10                             |

**Table S1:** Parameters of the PIM force field for the interactions between clay atoms[1]. The parameters  $C_6^{ij}$ ,  $C_8^{ij}$  and  $b_n^{ij}$  between cations and O are equal to the interactions O<sub>OH</sub>-X in Jahn and Madden[2]. The repulsion and dispersion interactions between cations are negligible because the electrostatic repulsion predominates.

| Ion pair (ij)      | $A_{ij}$ (Ha) | $B_{ij}$ ( $\text{\AA}^{-1}$ ) | $C_6^{ij}$ (Ha. $\text{\AA}^6$ ) | $C_8^{ij}$ (Ha. $\text{\AA}^8$ ) | $b_n^{ij}$ ( $\text{\AA}^{-1}$ ) | damping interaction |                           | damping interaction              |                           |
|--------------------|---------------|--------------------------------|----------------------------------|----------------------------------|----------------------------------|---------------------|---------------------------|----------------------------------|---------------------------|
|                    |               |                                |                                  |                                  |                                  | $c_{ij}$ (—)        | between $q_i$ and $\mu_j$ | $b_D^{ij}$ ( $\text{\AA}^{-1}$ ) | between $q_j$ and $\mu_i$ |
| Na-O               | 30.0          | 3.30                           | 0.0477                           | 0.156                            | 4.17                             | 2.13                | 4.33                      | 1.76                             | 3.65                      |
| Na-O <sub>OH</sub> | 4020          | 6.00                           | 0.0477                           | 0.156                            | 4.17                             | 3.47                | 5.68                      | 4.87                             | 3.01                      |
| Na-H <sub>OH</sub> | -             | -                              | -                                | -                                | -                                | -                   | -                         | 3.92                             | 2.72                      |
| Na-Al              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 3.34                             | 3.70                      |
| Na-Si              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 3.77                             | 3.66                      |
| Na-Mg              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 0.0128                           | 2.15                      |
| Cs-O               | 20.0          | 2.75                           | 0.0477                           | 0.156                            | 4.17                             | 0.219               | 5.94                      | 0.600                            | 2.87                      |
| Cs-O <sub>OH</sub> | 4000          | 5.10                           | 0.0477                           | 0.156                            | 4.17                             | 0.00558             | 5.69                      | 4.95                             | 2.45                      |
| Cs-H <sub>OH</sub> | -             | -                              | -                                | -                                | -                                | -                   | -                         | 2.40                             | 5.87                      |
| Cs-Al              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 0.932                            | 2.00                      |
| Cs-Si              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 3.61                             | 3.38                      |
| Cs-Mg              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 3.90                             | 2.01                      |
| Ca-O               | 20.0          | 2.54                           | 0.0478                           | 0.156                            | 4.17                             | 0.0280              | 6.00                      | 4.77                             | 5.48                      |
| Ca-O <sub>OH</sub> | 5000          | 5.65                           | 0.0478                           | 0.156                            | 4.17                             | 0.00088             | 6.00                      | 4.98                             | 4.15                      |
| Ca-H <sub>OH</sub> | -             | -                              | -                                | -                                | -                                | -                   | -                         | 5.00                             | 3.63                      |
| Ca-Al              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 4.92                             | 2.96                      |
| Ca-Si              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 2.59                             | 5.400                     |
| Ca-Mg              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 3.65                             | 5.77                      |
| Sr-O               | 20.1          | 2.52                           | 0.0478                           | 0.156                            | 4.17                             | 2.18                | 5.77                      | 2.11                             | 4.46                      |
| Sr-O <sub>OH</sub> | 5000.0        | 5.42                           | 0.0478                           | 0.156                            | 4.17                             | 0.00147             | 5.99                      | 1.83                             | 2.96                      |
| Sr-H <sub>OH</sub> | -             | -                              | -                                | -                                | -                                | -                   | -                         | 4.99                             | 2.06                      |
| Sr-Al              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 5.00                             | 2.77                      |
| Sr-Si              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 4.79                             | 4.50                      |
| Sr-Mg              | -             | -                              | -                                | -                                | -                                | -                   | -                         | 4.52                             | 5.67                      |

**Table S2:** Parameters of the PIM force field for the interactions between counterions and clay atoms[3]. The parameters  $C_6^{ij}$ ,  $C_8^{ij}$  and  $b_n^{ij}$  between cations and O are equal to the interactions  $O_{OH}-X$  in Jahn and Madden[2]. The repulsion and dispersion interactions between cations are negligible because the electrostatic repulsion predominates.

| Ion pair (ij)                   | $A_{ij}$ (Ha) | $B_{ij}$ ( $\text{\AA}^{-1}$ ) | $C_6^{ij}$ (Ha. $\text{\AA}^6$ ) | $C_8^{ij}$ (Ha. $\text{\AA}^8$ ) | $b_n^{ij}$ ( $\text{\AA}^{-1}$ ) | damping interaction       |                           | damping interaction              |                                  |
|---------------------------------|---------------|--------------------------------|----------------------------------|----------------------------------|----------------------------------|---------------------------|---------------------------|----------------------------------|----------------------------------|
|                                 |               |                                |                                  |                                  |                                  | between $q_i$ and $\mu_j$ | between $q_j$ and $\mu_i$ | between $q_i$ and $\mu_j$        | between $q_j$ and $\mu_i$        |
|                                 |               |                                |                                  |                                  |                                  | $c_{ij}(-)$               | $c_{ji}(-)$               | $b_D^{ij}$ ( $\text{\AA}^{-1}$ ) | $b_D^{ji}$ ( $\text{\AA}^{-1}$ ) |
| O-MW                            | -             | -                              | -                                | -                                | -                                | 5.00                      | 1.84                      | 5.02                             | 5.16                             |
| O-OW                            | 360           | 3.76                           | 0.974                            | 5.25                             | 2.72                             | -                         | -                         | -                                | -                                |
| O-HW                            | -             | -                              | -                                | -                                | -                                | -                         | -                         | -                                | 1.50                             |
| O <sub>OH</sub> <sup>-</sup> MW | -             | -                              | -                                | -                                | -                                | 2.86                      | 0.486                     | 5.04                             | 5.01                             |
| O <sub>OH</sub> <sup>-</sup> OW | 101           | 4.34                           | 0.974                            | 5.25                             | 2.72                             | -                         | -                         | -                                | -                                |
| O <sub>OH</sub> <sup>-</sup> HW | -             | -                              | -                                | -                                | -                                | -                         | 0.736                     | -                                | 1.60                             |
| MW-Al                           | -             | -                              | -                                | -                                | -                                | -                         | 1.50                      | -                                | 3.34                             |
| MW-Mg                           | -             | -                              | -                                | -                                | -                                | -                         | 2.88                      | -                                | 4.00                             |
| MW-Si                           | -             | -                              | -                                | -                                | -                                | -                         | 5.00                      | -                                | 5.00                             |
| MW-H <sub>OH</sub>              | -             | -                              | -                                | -                                | -                                | -                         | 0.738                     | -                                | 1.60                             |
| OW-Al                           | 112           | 4.23                           | 0.0477                           | 0.156                            | 4.17                             | -                         | -                         | -                                | -                                |
| OW-Mg                           | 150           | 3.17                           | 0.0477                           | 0.156                            | 4.17                             | -                         | -                         | -                                | -                                |
| OW-Si                           | 72.1          | 5.62                           | 0.0477                           | 0.156                            | 4.17                             | -                         | -                         | -                                | -                                |
| Na-MW                           | -             | -                              | -                                | -                                | -                                | 0.684                     | 5.00                      | 1.56                             | 5.01                             |
| Na-OW                           | 711           | 5.06                           | 0.134                            | 0.157                            | 3.00                             | -                         | -                         | -                                | -                                |
| Na-HW                           | -             | -                              | -                                | -                                | -                                | -                         | 0.0600                    | -                                | 1.60                             |
| Cs-MW                           | -             | -                              | -                                | -                                | -                                | 2.95                      | $3.00 \times 10^{-4}$     | 2.52                             | 5.03                             |
| Cs-OW                           | 269           | 3.63                           | 2.04                             | 4.64                             | 1.80                             | -                         | -                         | -                                | -                                |
| Cs-HW                           | -             | -                              | -                                | -                                | -                                | -                         | 0.0700                    | -                                | 1.51                             |
| Ca-MW                           | -             | -                              | -                                | -                                | -                                | 3.00                      | $3.00 \times 10^{-4}$     | 3.33                             | 5.04                             |
| Ca-OW                           | 57.9          | 3.33                           | 0.506                            | 0.751                            | -                                | -                         | -                         | -                                | -                                |
| Ca-HW                           | -             | -                              | -                                | -                                | -                                | -                         | 0.0700                    | -                                | 1.60                             |
| Sr-MW                           | -             | -                              | -                                | -                                | -                                | 2.04                      | 1.47                      | 2.99                             | 5.03                             |
| Sr-OW                           | 41.6          | 2.99                           | 0.916                            | 1.58                             | -                                | -                         | -                         | -                                | -                                |
| Sr-HW                           | -             | -                              | -                                | -                                | -                                | -                         | 0.0700                    | -                                | 1.53                             |

**Table S3:** Parameters of the PIM force field for the interactions between water and the other atoms[4]. The parameters  $C_6^{ij}$ ,  $C_8^{ij}$  and  $b_n^{ij}$  between OW and clay cations are equal to the interactions O<sub>OH</sub>-X in Jahn and Madden[2]. Dispersion interactions between divalent cations and OW have no damping[? ]. The dipole-charge interactions are carried by the fourth site MW.

**Table S4:** Atomic polarizabilities

| species                           | O     | OH   | Na    | Cs   | Ca    | Sr    | MW   |
|-----------------------------------|-------|------|-------|------|-------|-------|------|
| polarizability ( $\text{\AA}^3$ ) | 0.907 | 2.39 | 0.180 | 2.02 | 0.440 | 0.810 | 1.44 |