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2 **Stability and adhesion of calcite/montmorillonite assembly.**

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10

11 **Abstract**

12 We analyze here the technical connection between the (104) calcite and (001)  
13 montmorillonite surfaces at the atomic level, as well as the conditions to obtain a stable  
14 assembly. To this end, the appropriate force field is used to describe the bonding character at  
15 the interface. Results show that, in the x direction, the elastic energy provided by calcite to  
16 ensure good adhesion at the interface is lower than the one of clay. While in the y direction, it  
17 is rather the clay's atoms which provide energy for the accommodation to calcite.  
18 Furthermore, we have evaluated, additionally, the adhesion energy, the interfacial distance  
19 and the work of separation. We also show that the presence of water molecules at the  
20 interface absorb the excess energy and thus contribute to the stabilization of the interface.

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## 36 **I. Introduction**

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38 The alkaline earth carbonates have been a subject of considerable interest in the Earth  
39 sciences because they are the most abundant C-bearing species in the crust, and they represent  
40 a major reservoir for C within the Earth's mantle carbonates (Berg 1986; Canil 1990 ; Katsura  
41 and Ito 1990; Kraft et al. 1991; Bakri and Zaoui 2011; Ayoub et al. 2011; Bouibes et al. 2013;  
42 Bouibes and Zaoui 2014; Zaoui and Shahrour 2010). We can find them in aquatic systems  
43 forming huge amounts of scale and ocean sediment (Morse et al. 1990), in the atmosphere  
44 (Usher and Mackenzie 2007) and as part of the sediment and rock record (Morse 2007). These  
45 minerals affect the chemistry of aquatic systems by regulating pH and alkalinity through  
46 dissolution/precipitation equilibrium. Moreover, they can govern the mobility and cycling of  
47 metal contaminants and radionuclides via ion exchange, adsorption, and co-precipitation  
48 reactions (Van Cappellen 1993). Calcite ( $\text{CaCO}_3$ ) is one of the most abundant mineral species  
49 on the surface of this planet and is stable at ambient conditions. It is one of the constituents of  
50 argillite, a mineral rock used for the wastes disposal.

51 On the other hand, swelling clays are one of the important components of engineered barriers  
52 around underground storage sites of high-activity radioactive waste due to their properties of  
53 low permeability and high retention capacity of cations. Many theoretical and experimental  
54 works have been paid for describing the behavior of diffusion of water and some cations in  
55 smectite clay (Nye 1979; Cebula et al. 1981; Sposito 1981; Chang et al. 1995; Chang et al.  
56 1997; Chang et al. 1998; Spoel 1998; Sutton and Sposito 2001; Marry and Turq 2003;  
57 Kosakowski et al. 2008; Yang and Zaoui 2013; Benazzouz et al. 2013; Zheng and Zaoui  
58 2013; Yang and Zaoui 2013; Benazzouz and Zaoui 2012; Zheng and Zaoui 2011; Zheng et al.  
59 2011; Zheng et al. 2010; Berghout et al. 2010; Tunega et al. 2012).

60 The study of calcite/montmorillonite interface is particularly of great importance since it helps  
61 to clarify many issues on the nuclear waste disposal. In fact, in the Underground Research  
62 Laboratory in France, an excavation damaged zone (EDZ) is observed around galleries in the  
63 Callovo- Oxfordian argillite (ANDRA 2005). It is characterized by the appearance of micro-  
64 fissures whose density decreases as the distance from the wall increases. Argillite is a mineral  
65 rock used for the isolation of the high-level radioactive wastes. It is mainly constituted of clay  
66 (20-60%) and calcite (10-75%). The analysis of this mineral especially the interaction  
67 between calcite and clays at the atomic level will give a clear picture about the strength of the  
68 bonds and the mechanical behaviour of such rock at the storage conditions.

69 In this paper, we focus on the structural and energetic properties of the interface between the  
70 calcite (104) and montmorillonite (001) surfaces using nanoscale tools. We will discuss the  
71 conditions to obtain a stable interface of the assembly. Our first goal is to describe the

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72 interatomic bonding between the atomic constituents of calcite and clay at the interface. Then,  
73 we will evaluate some thermodynamic properties of  $\text{CaCO}_3$  and montmorillonite, taken  
74 separately. Finally, we will study the lattice mismatch between the two compounds at the  
75 interface, the adhesion energy, the work of separation, as well as the elastic energy at the  
76 interface.

77

## 78 **II. Description of the potential model and construction of the supercell**

79 Several force fields have been developed to describe the interactions in  $\text{CaCO}_3$  to mainly  
80 reproduce the structural and thermodynamic properties of carbonates (Pavese et al. 1992. De  
81 Leeuw and Parker 1998; Archer et al. 2003; Pavese et al. 1996; Raiteri et al. 2010; Raiteri et  
82 al. 2010; Fisler et al. 2000). On the other hand, empirical potential models have been  
83 proposed to explore the bulk properties and surface of  $\text{CaCO}_3$  (Sekkal and Zaoui 2013;  
84 Sekkal et al. 2008; Pavese et al. 1996; Dove et al. 1992; Catti et al. 1993). Parker et al.  
85 (Parker et al. 1993). Recently, a special attention was devoted to develop new potential  
86 models to describe the interactions between  $\text{CaCO}_3$  and water. In 2011, Xiao et al. (Xiao et al.  
87 2011) derived a new set of parameters for calcium carbonate, which accurately reproduces the  
88 elastic and shear moduli of the aragonite phase. It is a new forcefield taking into account the  
89 aqueous environment using the TIP3P water model (Jorgensen et al. 1983). This is the  
90 potential model that we have used for (104) surface of  $\text{CaCO}_3$ . The clay mineral model  
91 considered here is a Wyoming-type Montmorillonite, with the unit cell formula  
92  $N_{a_{0.75}}[Si_{7.75}Al_{0.25}](Al_{3.5}Mg_{0.5})O_{20}(OH)_4 \cdot nH_2O$ . We have used the ClayFF potential model  
93 (Cygan, 2004), which was well tested for clays.

94 At the interface, we have described the interactions between the last layer of the calcite  
95 ( $\text{Ca}^{2+}\text{CO}_3^{2-}$ ) and the first layer of clay ( $\text{SiO}_2$ ) using the model of Guillot-Sator (Guillot and  
96 Sator 2007) according to the following formula:

97

$$98 \quad E(\text{interface}) = Z_i Z_j / r_{ij} + B_{ij} e^{-r_{ij}} / \rho_{ij} - C_{ij} / r_{ij}^6$$

99

100 Where  $R_{ij}$  is the interatomic distance and  $Z$  is the ionic charge.  $B$ ,  $C$ , and  $\rho$  are the empirical  
101 parameters given in Table 1.

102 To ensure a good accommodation at the interface, we built a "supercell" by duplicating the  
103 unit cell of calcite 11 times in the x direction and 4 times in the y direction (Figure 1). For  
104 clay system, we duplicate the unit cell 3 times in the x direction and 5 times in the y direction.  
105 Therefore, the obtained lattice mismatch is 1.58% for the x direction and 2.9% for the y  
106 direction. Thus, the dimension of the simulation box is (5.53 x 10.39 x 70.50) nm,  $\alpha = 90^\circ$  and

107 the number of atoms is 26 280 (Figure 2). Calculations are performed using Molecular  
108 Dynamics method in NPT ensemble allowing all individual ionic coordinates and lattice  
109 parameters to vary.

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### 112 **III. Discussion**

#### 113 ***III. 1. Thermodynamic properties of calcite and montmorillonite***

114 We have conducted, first, a comparative study of the thermodynamic properties of calcite and  
115 montmorillonite by evaluating the heat capacity at constant volume ( $C_v$ ) and entropy ( $S$ ) of  
116 the two systems:

$$C_v = \left( \frac{\partial E_{tot}}{\partial T} \right)_v$$
$$S = R \ln Z + RT \left( \frac{\partial \ln Z}{\partial T} \right)$$

117

118  $E_{tot}$  is the total energy of the system,  $T$  is the temperature,  $Z$  is the partition function.

119 For calcite, we have applied a set of temperatures from 300K to 1000K. Calculations are  
120 performed in NPT ensemble where temperature and pressure are kept constant during the  
121 simulation. Using the "Gear-Predictor-Corrector" algorithm, the equations of motion are  
122 solved using a timestep of 1 femtosecond. After equilibration, the optimum total energy is  
123 obtained, from which we have evaluated the heat capacity and the entropy as shown in  
124 Figures 3.

125 We noticed, first, that the quantities  $C_v$  and  $S$  vary positively with the change of temperature.  
126 Furthermore, we find that the variation of  $C_v$  is higher for montmorillonite: the slope of the  
127 curve is equal to  $2.78E^{-6}$  for  $CaCO_3$  and  $3.32E^{-5}$  for montmorillonite. The same holds for the  
128 entropy:  $6.285E^{-6}$  for  $CaCO_3$  and  $7.54E^{-5}$  for montmorillonite. These results show that under  
129 temperature effect, there is a presence of a thermal agitation and a disorder which is higher in  
130 the case of montmorillonite.

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#### 132 ***III.2. Evaluation of the lattice mismatch, the elastic energy, the adhesion energy and the*** 133 ***work of separation at the interface***

134 We evaluate, here, the lattice mismatch between the two surfaces. Each atom has an intrinsic  
135 energy called elastic energy that is released during relaxation. In this part, we will see how  
136 atoms relax at the interface (Figure 4) and then we will calculate the change in the elastic  
137 energy based on the lateral stress applied to the interface.

138 We have considered two procedures: First, we applied a lateral stress in the x direction once  
139 on calcite and once on montmorillonite, taken separately. In other words, we have expanded  
140 the lattice parameter "a" of calcite up to the value of the clay; while for clay, we have  
141 compressed the lattice parameter "a" up to the value of calcite. For each constraint, we have  
142 equilibrated the system until it reaches its optimal energy. The obtained results are plotted in  
143 Figure 4. We remark that in the case of calcite, the energy difference between the final state  
144 (calcite with the lattice parameter of the clay) and the initial state is equal to 73.25 eV,  
145 whereas for clay, this difference is too much higher (several orders of magnitude). Therefore,  
146 we conclude that in the x direction, it is easier for calcite to provide energy to relax and to  
147 accommodate with the atoms of montmorillonite at the interface.

148 The same procedure is performed in the y direction, by compressing calcite and expanding  
149 clay (Figure 5). The obtained energy difference for calcite is of  $7.35 \cdot 10^8$  eV; for  
150 montmorillonite it is equal to 149.74 eV. Therefore, in the y direction, it is easier for the clay  
151 to provide the necessary energy to relax and accommodate its atoms at the interface with  
152 those of calcite.

153 We discuss now the parameters which ensure the stability of the assembly. Indeed, the whole  
154 interface is associated to the appearance of excess free energy called interface energy. This is  
155 given by the energy of adhesion ( $E_{ad}$ ) and later by the work of adhesion ( $W_{ad}$ ), which are  
156 expressed through the Dupré equation:

157

$$158 \quad E_{ad} = \gamma_c + \gamma_a - \gamma_{ca}$$

$$159 \quad W_{ad} = \gamma_c + \gamma_a - \gamma_{ca}/a$$

160 where

161  $\gamma_c$  : surface free energy of calcite,

162  $\gamma_a$  : surface free energy of clay,

163  $\gamma_{ca}/a$  : Energy of the calcite / clay interface.

164

165 The variation of the adhesion energy (or separation) and the work of separation as a function  
166 of the distance of separation are shown in Figure 6. These calculations are performed by  
167 varying the distance of separation between clay and calcite surfaces from 1.5 Å to 4 Å in  
168 order to set the ideal distance between the two systems constituting the interface. The  
169 adhesion energy is found to be 0.26 eV and the work of separation being  $4.61 \cdot 10^{-5}$  eV / Å<sup>2</sup>.  
170 We have deduced from Figures 6 the separation distance between the clay and the calcite  
171 which is about 3 Å.

172 Finally, let us look to the stability of the interface when adding water molecules between the  
173 last layer of calcite ( $Ca^{2+}$ ,  $CO_3^{2-}$ ) and the first layer of clay ( $SiO_2$ ). By varying the distance of

174 separation at the interface, we have equilibrated the system at each time, and the  
175 corresponding total energies are plotted in Figure 7. We underline that for distances less than  
176 2.5 Å, the presence of water has the effect of absorbing the excess energy provided by the  
177 system and thereby stabilize the interface.

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### 179 **Implications**

180 The main purpose here is to clarify the structural and energetic stability of the calcite  
181 /montmorillonite interface, which directly linked to the nuclear waste disposal. In fact, an  
182 excavation damaged zone (EDZ) is observed around galleries in the Callovo- Oxfordian  
183 argillite, which is characterized by the appearance of micro-fissures. Before analysing the  
184 behaviour of the interface between the clay and calcite under the effect of anisotropic stress, it  
185 is important to evaluate the lattice mismatch between the two compounds at the interface, the  
186 adhesion energy, the work of separation, as well as the elastic energy at the interface. These  
187 quantities inform us about the conditions to obtain a stable interface of the assembly.

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## Table

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350 **Table 1:** Potential parameters for  $O_c$ - $O_m$ ,  $O_c$ -Si and  $O_m$ -Ca (Sator & Guillot, 2007).  $O_c$  is the  
351 oxygen of  $CO_3^{2-}$  molecule,  $O_m$  is the oxygen of  $SiO_2$ .  
352

Pair interaction	B (KJ/mol)	$\rho$ (Å)	C(A <sup>6</sup> KJ/mol)
$O_c$ - $O_m$	435285.0	0.265	4105.09
$O_c$ -Si	4853815.5	0.161	4467.07
$O_m$ -Ca	15019679.1	0.178	4077.45

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### Figures caption

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373 Figure 1: Construction of the calcite/clay supercell. Top view of calcite (104) (left), and  
374 montmorillonite (001) (right). Blue spheres represent Calcium atoms; red spheres are Oxygen  
375 atoms; green spheres are Carbon atoms; pink spheres are Silicon atoms.

376 Figure 2: Atomistic assembly of the calcite/clay supercell viewed from the (xz) plane (a),  
377 from (yz) plane (b).

378 Figure 3: (a) Variation of the heat capacity with temperature. (b) Variation of entropy with  
379 temperature.

380 Figure 4: : Variation of the total energy with strain along x direction for calcite (a),  
381 montmorillonite (b).

382 Figure 5: Variation of the total energy with strain along y direction for calcite (a),  
383 montmorillonite (b).

384 Figure 6: (a) Variation of the energy of separation with the interfacial distance. (b) Variation  
385 of the work of separation with the interfacial distance.

386 Figure 7: (a) Presence of water molecules at the interface. (b) Variation of the total energy  
387 with the interfacial distance in the presence of water molecules.

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