

- results of Shen *et al.* (8), who independently calibrated their spikes. Consequently, we recommend a refined value for $\lambda(^{187}\text{Re})$ of $(1.666 \pm 0.017) \times 10^{-11} \text{ year}^{-1}$.
17. K. L. Rasmussen, F. Ulf-Möller, H. Haack, *Geochim. Cosmochim. Acta* **59**, 2049 (1995).
 18. E. R. D. Scott, H. Haack, T. McCoy, *ibid.*, in press.
 19. R. J. Walker, J. W. Morgan, M. F. Horan, G. N. Grossman, *Lunar Planet. Sci.* **24**, 1477 (1993).
 20. The partitioning of refractory elements between metallic solid and metallic melt in Fe-Ni systems is strongly dependent on the S (and P) content of the parental melts. Because of the limited experimental data for the correlation of k_{Re} and k_{Os} with S concentration (24), we calculated the Re and Os distribution coefficients as follows. We assumed k_{Ir} in IIA, IIIA, IVA, and IVB groups as 20, 3.5, 1.7, and 1.3, respectively, on the basis of the correlation of k_{Ir} with S concentration from (25). Using Ir abundances from (26) and our Os data, we calculated k_{Os} from the slopes of Os-Ir lines [slope = $(k_{\text{Ir}} -$

- $1)/(k_{\text{Os}} - 1)]$. Similarly, k_{Re} 's were calculated from slopes of Re-Os lines. This procedure gave the following distribution coefficients: for Os, 28, 4.5, 2.0, 1.4; and for Re, 22, 3.8, 1.8, 1.3 in the IIA, IIIA, IVA, and IVB groups, respectively. To calculate the parental melt compositions, we assumed that the Re and Os abundances in the first crystals to form from each melt were equal to their abundances in those meteorites with the highest Os (or Ir) concentrations [Negrillos (IIA), Costilla Peak (IIIA), Jamestown (IVA), Cape of Good Hope (IVB)]. From these concentrations and the above calculated k_{Re} and k_{Os} , the following parental melt concentrations (in parts per billion) are obtained for Re and Os, correspondingly: 220, 2380 (IIA); 380, 4140 (IIIA); 210, 2200 (IVA); 2440, 34300 (IVB).
21. E. R. Rambaldi, *Earth Planet. Sci. Lett.* **36**, 347 (1977).
22. W. R. Kelly and J. W. Larimer, *Geochim. Cosmochim. Acta* **41**, 93 (1977).
23. S. B. Shirey and R. J. Walker, *Anal. Chem.* **34**, 2136 (1995).

24. J. H. Jones and D. J. Malvin, *Metall. Trans. B* **21B**, 697 (1990); J. H. Jones and A. J. G. Jurewicz, *Eos* **75**, 694 (1994).
25. J. H. Jones and M. J. Drake, *Geochim. Cosmochim. Acta* **47**, 1199 (1983).
26. J. T. Wasson, X. Ouyang, J. Wang, E. Jerde, *Geochim. Cosmochim. Acta* **53**, 735 (1989), and references therein.
27. K. Ludwig, U.S. Geol. Surv. Open File Rep. OF 88-0557 (1988).
28. J.-F. Minster, L.-P. Ricard, C. J. Allegre, *Earth Planet. Sci. Lett.* **44**, 420 (1979).
29. We thank R. S. Clarke, M. Ivanova, and J. T. Wasson for meteorite samples. Comments by R. W. Carlson and two anonymous reviewers helped to improve this manuscript. Supported by National Aeronautics and Space Administration grant NAGW 3625 and by Geological Society of America Student Research grant 5710-95.

4 August 1995; accepted 27 November 1995

The Swelling of Clays: Molecular Simulations of the Hydration of Montmorillonite

S. Karaborni,* B. Smit, W. Heidug, J. Urai, E. van Oort

The swelling of clay minerals on contact with an aqueous solution can produce strong adverse effects in the exploration and production of gas and oil. Molecular dynamics and Monte Carlo simulations were used to study the mechanism of swelling of sodium-montmorillonite. The simulations showed that the abundant clay mineral has four stable states at basal spacings of 9.7, 12.0, 15.5, and 18.3 angstroms, respectively. The amount of swelling and the locations of the stable states of sodium-montmorillonite are in good quantitative agreement with the experimental data.

Clays are important in many applications, such as drug and agrochemical delivery, purification and recycling of water streams, geological disposal of radioactive wastes, catalysis and catalysis support, and cosmetics. In the context of oil and gas production, swelling in clays is an important factor when drilling wells through mudrocks. The drilling engineer must ensure, through the use of drilling fluids, that the stresses induced in the region near the boreholes do not exceed the strength of the mudrock. Excessive stress could lead to severe drilling problems and even to the collapse of a well (1). Growing environmental concerns currently require the replacement of oil-based drilling fluids by more benign water-based solutions. The development of such high-performance fluids requires a molecular insight into the factors that control the swelling of clays.

Clays have a characteristic layered structure. Between these layers, water can adsorb, which results in strong repulsive forces that cause the clays to expand to as much as

several times their original thickness (2). Clay hydration studies have been conducted since 1933 (3), yet there is no clear understanding of the swelling mechanism. We report here on our simulation results for a montmorillonite clay that is of interest to the drilling industry because of its strong tendency to swell (1). Molecular simulations were performed in the grand-canonical ensemble (4, 5), that is, at constant chemical potential, volume, and temperature (μ , V , and T , respectively). The simulations modeled a typical experiment with a surface force apparatus in which the force is measured as a function of a fixed separation, for example, between two mica sheets immersed in water (2). In our simulations, the distance between the clay layers was fixed after each incremental increase in the interlayer distance, and the system was allowed to take or reject water molecules until equilibrium was reached. Initial tests of our simulation code, which is a combination of molecular dynamics and Monte Carlo techniques, showed that the interlayer water could reach very high densities. The random insertion of a water molecule into a dense system is difficult, and therefore the equilibration step is extremely lengthy. To facilitate the insertion of water molecules, we used the orientational-bias

Monte Carlo technique (6, 7).

Sodium-montmorillonite (Na-Mt) clays from different regions of the world have slightly different chemical structures and charge distributions. Our model for Na-Mt, water, and ions is similar to that developed from ab initio calculations by Skipper and

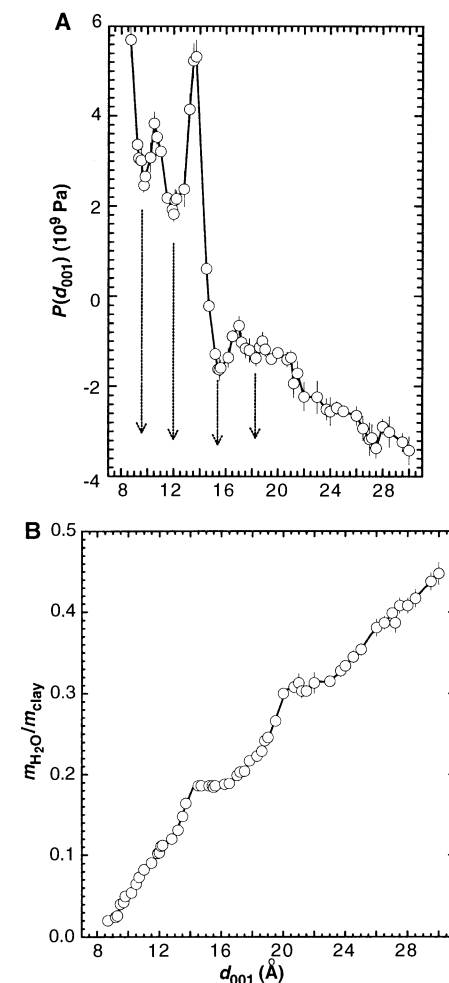


Fig. 1. Average simulated properties of Na-Mt as a function of basal spacing d_{001} . (A) Disjoining pressure $P(d_{001})$. (B) Ratio of water weight to clay weight, $m_{\text{H}_2\text{O}}/m_{\text{clay}}$, in units of grams per gram.

S. Karaborni and B. Smit, Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research BV), P.O. Box 38000, 1030 BN Amsterdam, Netherlands.
W. Heidug, J. Urai, E. van Oort, Koninklijke/Shell Exploration and Production Laboratory, Volmerlaan 6, 2280 AB Rijswijk, Netherlands.

*To whom correspondence should be addressed.

co-workers (8–10). In this model, the hydroxyl bond in the clay lattice was calculated to be normal to the clay surface. However, Hawkins and Egelstaff found that this bond is roughly parallel to the surface in dry montmorillonite (11). If water or other solvents are present, the direction of the hydroxyl bond is less apparent (11, 12). In the absence of direct evidence of this bond orientation, we simulated clays with the hydroxyl bond normal as well as parallel to the surface. We found that a model clay with a normal orientation of the hydroxyl bond gives a better agreement of simulation results with experimental data and yields a lower overall disjoining pressure, which means that a perpendicular orientation of the O–H bond is more likely than a parallel orientation of this bond.

Several simulations were performed in the grand-canonical ensemble (13). In this ensemble, the disjoining pressure, $P(d_{001})$, can be calculated directly from the simulations (14). To focus on the effects caused by the water-clay interactions, we subtracted the contributions of the direct interactions between the clay layers from $P(d_{001})$. Oscillations in the disjoining pressure were observed (Fig. 1A), as expected from measurements of the distance between smooth mica surfaces in aqueous solutions (2). The states in which the disjoining pressure was a local minimum were located at 9.7, 12.0, 15.5, and 18.3 Å (Fig. 1A). These local minima

Table 1. Basal spacings (d_{001}) of the stable phases of Na-Mt (in angstroms) compared with experimental data from measurement of several Na-Mt clays. The ratio of water weight to clay weight, $m_{\text{H}_2\text{O}}/m_{\text{clay}}$, is given in parentheses in units of milligrams per gram. ND, not determined.

States, spacings, and $m_{\text{H}_2\text{O}}/m_{\text{clay}}$ values				Reference
0	1	2	3	
9.7 (43)	12.0 (103)	15.5 (186)	18.3 (223)	Simulation (this work)
9.6	12	15	18	(15)
ND	ND	15.5	18.5	(16)
9.55 (18)	12.49 (111)	15.55 (183)	18.1	(17)
9.8 (68)	12.3 (109)	15.4 (217)	ND	(18)
9.5	12.4	15.4	19.0	(19)
9.8 (58)	12.6 (114)	ND	ND	(20)
9.6 (12)	12.3 (80)	15.2 (170)	ND	(21)
9.8 (47)	12.2 to 12.7 (100)	15.6 (204)	18.3 to 19.0	(11)
ND	ND	15.5	18.5	(22)
9.6	12.5 (100)	15.5	ND	(23)

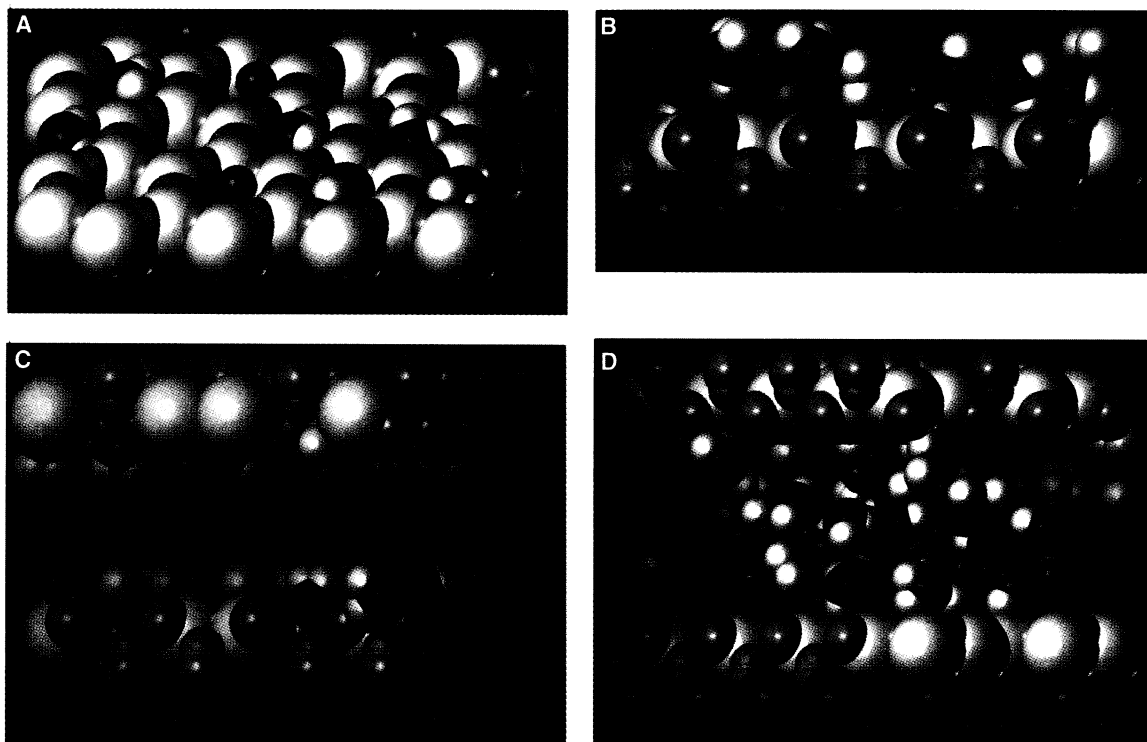
are in excellent agreement with the stable states measured experimentally for different Na-Mt clays (Table 1).

The swelling of the Na-Mt was mostly nonuniform in our simulations (Fig. 1B). There were regions where an increase in basal spacing did not induce an increase in the amount of water. These plateau regions occurred at ~ 15.5 and ~ 21 Å. Considering the significant differences among the various experimental measurements, the amount of Na-Mt hydration calculated in the simulations is in good agreement with that measured experimentally in various Na-Mt clays [see Table 1 (15–23)].

The snapshots of the stable states of

Na-Mt in Fig. 2 show that at 9.7 and 15.5 Å (Fig. 2, A and C, respectively), some water molecules were in the hexagonal microcavities of the clay; the water oxygens formed strong bonds with the hydroxyl protons of Na-Mt. At 12.0 and 18.3 Å (Fig. 2, B and D, respectively), there were no embedded water molecules; instead, the water protons formed hydrogen bonds with oxygens at the surface of the clay. The location of the sodium ions also differed in the different states. At 9.7 and 15.5 Å, all ions were directly next to the clay surface, whereas at 18.3 Å, and to a lesser extent at 12.0 Å, sodium ions were separated by one water molecule from the clay surface. Our results

Fig. 2. Snapshots of the hydrated Na-Mt in its stable states. (A) Perspective view of the clay surface at $d_{001} = 9.7$ Å. Only the bottom surface with embedded water molecules and neighboring sodium counterions is shown. (B) Side view at $d_{001} = 12.0$ Å. Only the bottom surface with all water molecules and sodium counterions is shown. (C) Side view at $d_{001} = 15.5$ Å. Top and bottom clay surfaces with embedded water molecules and all sodium counterions are shown. One layer of water molecules in the interlamellar space has been removed. (D) Side view at $d_{001} = 18.3$ Å. All clay atoms, water molecules, and sodium counterions are shown. Color code: Water molecules are in red (O) and white (H); sodium counterions are in green (Na^+); montmorillonite atoms are in yellow (Si), orange (O in tetrahedral sheets and O in OH groups), blue (H in OH groups), and pink (all atoms in the octahedral sheet).



are in agreement with previous investigations that have suggested that sodium ions should be very close to the clay surface (20).

Clearly, water at basal spacings smaller than ~ 25 Å cannot be considered similar to bulk water. In the direction normal to the interface, the density distribution regularly changed when the basal spacing was increased (Fig. 3). At very small spacing, ≤ 9.8 Å, all molecules were entirely inside the hexagonal cavities. At basal spacings of >10.2 Å, water molecules originally in the microcavities progressively desorbed, and at 12.0 Å, the oxygen peak at ~ 4 Å disappeared. At 12.0 Å, water molecules in the interlayer space formed a single layer. In this layer, molecules were locally organized in three distinct and nonsuperimposed levels that were separated by less than 1 Å. The formation of three levels is optimal because the levels closest to the clay surfaces include molecules with both hydrogen atoms pointing to the clay surface, and the middle level includes water molecules with one hydrogen atom pointing to each level.

At 15.5 Å, water molecules in the interlayer space readsorbed inside the hexagonal cavities, and there was only one layer of molecules in the interlayer space. At 18.3 Å, water molecules in the microcavities desorbed and simultaneously formed a second and third layer. At 20.7 Å, water molecules readsorbed inside the hexagonal cavities and three layers remained in the interlayer space. At ~ 23.5 Å, a fourth and fifth layer formed simultaneously. Effectively, the interlayer space at no time contained only two or four layers of water molecules.

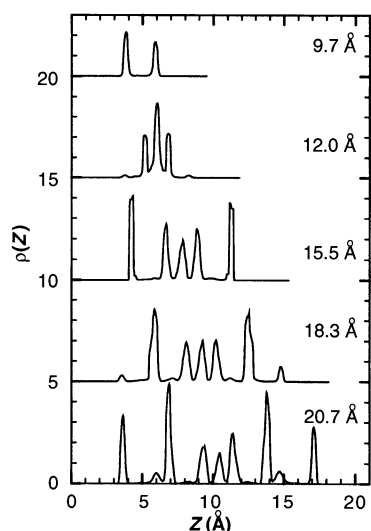


Fig. 3. Density distributions $\rho(z)$ of water oxygens as a function of the distance z from the octahedral sheet. Results are shown for basal spacings of 9.7, 12.0, 15.5, 18.3, and 20.7 Å. Note that the peak at ~ 4 Å appears in one state and disappears in the next state.

The swelling proceeded from the dry state through the formation of one, three, and then five water layers. This behavior is completely different from what is widely believed to be the hydration sequence of Na-Mt—that is, successive transitions from one, to two, to three, to four layers and so on (22).

This complex swelling behavior could explain not only the intricate adsorption and desorption branches that have been measured in this clay (17, 21), but also the many variations in the specific surface area of Na-Mt calculated by means of Brunauer-Emmett-Teller (BET) theory applied to water sorption isotherms (24, 25). There is some experimental indication for the predicted mechanism. For example, Trillo and co-workers (25) have argued that the measured amount of water in the interlamellar space at ~ 15.2 Å (not counting water in the hexagonal cavities or on the external surfaces) is not the amount that would be expected in two full monolayers but is approximately the same amount of water as in one full monolayer.

The uptake of water by Na-Mt appears to be controlled by the competition between the formation of hydrogen bonds between the water protons and the oxygens in the tetrahedral sheets of the clay and the adsorption of water in the clay hexagonal cavities. The stable states of Na-Mt are those in which the balance is totally shifted toward only one type of interaction between the water molecules and the clay. Unstable states are those in which the two types of interactions occur simultaneously in the same clay. The inability (balanced competition) of water molecules to form simultaneously favorable interactions with the oxygens in the tetrahedral sheets of the clay and the hydroxyl groups in the hexagonal cavities creates a frustration effect. This could be the reason for the excessive swelling of Na-Mt. Expanding this clay would require a transition from one optimal orientation of water molecules near the clay surfaces to a second similarly optimal orientation. Understandably, this transition requires less free volume and is therefore easier to make than a transition that requires the simultaneous addition of a full layer of water molecules, which would be necessary if water molecules have only one optimal orientation near the clay surfaces. We hope that the mechanism proposed here will stimulate experimental work that can be used to validate our predictions.

REFERENCES AND NOTES

- G. M. Bol and S.-W. Wong, *Soc. Petrol. Eng. SPE* 24975 (1992).
- R. G. Horn, *J. Am. Chem. Soc.* **73**, 1117 (1990); J. N. Israelachvili, *Surf. Sci. Rep.* **14**, 109 (1992).
- U. Hoffman, K. Endell, D. Wilm, *Z. Krist.* **86**, 340 (1933).
- D. J. Adams, *Mol. Phys.* **29**, 307 (1975).
- A. Delville, *J. Phys. Chem.* **97**, 9703 (1993).
- D. Frenkel, G. C. A. M. Mooij, B. Smit, *J. Phys. Cond. Matter* **4**, 3053 (1992).
- On average, 100,000 time steps were used for equilibration at every interlayer distance. During equilibration and at equilibrium, we attempted moves every third time step, using orientational-bias Monte Carlo methods to delete or insert water molecules in the interlayer space. The success rate depended very much on the lattice spacings. For example, at 9.8 Å, $\sim 0.7\%$ of the insertion or deletion moves were accepted, whereas at 26 Å, $\sim 14\%$ of the moves were successful.
- N. T. Skipper, K. Refson, J. D. C. McConnell, *J. Chem. Phys.* **94**, 7434 (1991).
- The model used for water-water interactions is the ab initio-derived Matsuoaka-Clementi-Yoshimine (MCY) model [J. C. Owicki and H. A. Scheraga, *J. Am. Chem. Soc.* **99**, 7403 (1977)], which we supplemented by including internal angle flexibility of the water molecules. The model we used for sodium-water interactions was the Bounds model [D. G. Bounds, *Mol. Phys.* **54**, 1335 (1985)]. This model gives the correct number of water molecules in the first coordination shell of sodium (8).
- Montmorillonite, a dioctahedral smectite, is usually present in the form of ≤ 2 - μm microplatelets [A. C. D. Newman, in *Chemistry of Clays and Clay Surfaces*, A. C. D. Newman, Ed. (Wiley, New York, 1987), pp. 255–260]. The layers of montmorillonite carry a net negative charge, primarily because of octahedral substitution of some Al cations by Mg cations. The montmorillonite used in the simulation had a net charge of $-0.5e$ per unit cell [per $\text{O}_{10}(\text{OH})_2$]; that is, one of four Al cations in the octahedral sheet was replaced by a Mg cation. Sixteen unit lattices were used in the simulations, and periodic boundary conditions in all directions were applied. The net negative charge of the clay was balanced by eight sodium cations placed randomly in the interlayer. This ensured that the entire system, including clay, water, and counterions, was electroneutral.
- R. K. Hawkins and P. A. Egelstaff, *Clays Clay Miner.* **28**, 19 (1980).
- R. Alvero, M. D. Alba, M. A. Castro, J. M. Trillo, *J. Phys. Chem.* **98**, 7848 (1994); R. Pusch, *Appl. Clay Sci.* **2**, 343 (1987); R. F. Giese, *Clays Clay Miner.* **27**, 213 (1979); W. F. Bleam, *Rev. Geophys.* **31**, 51 (1993).
- Fifty-eight interlayer distances (d_{001}) ranging from 8.7 to 30 Å were simulated. The simulations were performed at $T = 300$ K, with a chemical potential for water, μ , of -42.8 kJ, corresponding to a reservoir pressure of roughly 1×10^5 Pa and a water density of ~ 996 kg/m³.
- M. Schoen, D. J. Diestler, J. H. Cushman, *J. Chem. Phys.* **87**, 5464 (1987).
- D. J. Cebula, R. K. Thomas, S. Middleton, R. H. Ottewill, J. W. White, *Clays Clay Miner.* **27**, 39 (1979).
- A. M. Posner and J. P. Quirk, *J. Colloid Sci.* **19**, 798 (1964).
- J. M. Cases *et al.*, *Langmuir* **8**, 2730 (1992).
- R. W. Mooney, A. G. Keenan, L. A. Wood, *J. Am. Chem. Soc.* **74**, 1371 (1952).
- K. Norrish, *Discuss. Faraday Soc.* **18**, 120 (1954).
- R. Keren and I. Shainberg, *Clays Clay Miner.* **27**, 145 (1979).
- F. Kraehenbuehl, H. F. Stoeckli, F. Brunner, G. Kahr, M. Muller-Vonmoos, *Clay Miner.* **22**, 1 (1987).
- P. G. Slade, J. P. Quirk, K. Norrish, *Clays Clay Miner.* **39**, 234 (1991).
- J. J. Fripiat, A. Jelli, G. Poncelet, J. Andre, *J. Phys. Chem.* **69**, 2185 (1965).
- R. W. Mooney, A. G. Keenan, L. A. Wood, *J. Am. Chem. Soc.* **74**, 1367 (1952).
- J. M. Trillo, J. Poyato, M. M. Tobias, M. A. Castro, *Clay Miner.* **25**, 485 (1990).
- We thank A. van Helden and D. Frenkel for helpful comments on the manuscript, and the Shell group for permission to publish these results.

5 October 1995; accepted 7 December 1995