The Canadian Mineralogist
Vol. 36, pp. 1577-1585 (1998)

CALCULATED H-ATOM POSITIONS IN MICAS AND CLAY MINERALS

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ABSTRACT

The Static Structure-Energy Minimization (SSEM) technique was used to calculate the H-atom positions in phlogopite, clinochlore, kaolinite, margarite, muscovite and dickite using four interaction terms: Coulombic interaction, repulsion, covalency and polarization. Interaction within the OH groups was calculated using a Morse potential. Two steps were taken to locate the H-atom position(s): (1) relaxing the H positions from those of the hydroxyl O-atoms with symmetry constraints, and (2) relaxing the H positions obtained in step (1) without symmetry constraints for the H atoms only. Phlogopite, clinochlore and kaolinite give results that agree well with the neutron-diffraction values. The split-site model of margarite was successfully reproduced. In muscovite, two H-atom positions are predicted, represented with a split H-atom model in space group *C2/c*. For dickite, six H-positions are predicted rather than the four that are observed by diffraction. This result helps explain the apparent disagreement between the diffraction experiment that located four unique H-atom positions, and the IR experiments that suggest six OH-stretching bands.

Keywords: Static Structure-Energy Minimization, H-atom positions, micas, clays, chlorite.

SOMMAIRE

Nous nous sommes servis de la technique de minimisation de l'énergie statique de la structure pour calculer la position des atomes d'hydrogène dans la phlogopite, le clinochlore, la kaolinite, la margarite, la muscovite et la dickite au moyen de quatre termes d'interaction: interaction coulombique, répulsion, covalence et polarisation. L'interaction au sein des groupes OH a été calculée en utilisant le potentiel de Morse. Nous avons adopté deux moyens pour localiser les atomes d'hydrogène: (1) relachement des atomes H des positions imposées par les contraintes de symétrie des groupes hydroxyle, et (2) relachement des positions H obtenues dans l'étape (1) sans contraintes de symétrie des seuls atomes H. Dans le cas de phlogopite, clinochlore et kaolinite, les résultats concordent bien avec les valeurs obtenues par diffraction neutronique. Le modèle d'un site partagé pour le cas de la margarite a été reproduit correctement. Dans la muscovite, deux atomes H sont localisés, et représentés par un modèle à sites partagés dans le groupe spatial *C2/c*. Pour la dickite, six atomes H sont prédits plutôt que les quatre qui sont connus par observations en diffraction. Ce résultat aide à comprendre la différence apparente entre les résultats de diffraction, qui localisent quatre sites uniques des atomes H, et les résultats obtenus par spectroscopie infra-rouge, qui indiquent six bandes d'étirement du couple OH.

(Traduit par la Rédaction)

Mot-clés: minimisation de l'énergie statique de la structure, position des atomes H, micas, argiles, chlorite.

INTRODUCTION

Experimental determination of H-atom positions in the crystal structures of clay minerals can be very difficult because the H-atom is not a strong scatterer of X-rays nor a coherent scatterer of neutrons. Hydrogen has one electron, making its X-ray scattering power very weak. Moreover, high-quality crystals (free of deformation and stacking disorder) are needed in order to reliably determine H-atom positions. However, this criterion is very rarely satisfied: stacking disorder is very common in clay minerals (Brindley 1980), making the detection of H-atoms even more difficult. Neutron diffraction may offer a solution to the problem (as shown by examples cited later). However, H has strong incoherent scattering from the two possible nuclear spin-states of ^{1}H (Von Dreele 1989). Consequently, high signal-to-noise ratio may be difficult to obtain because

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of the exceptionally high contribution from the incoherent background. Therefore, it is often necessary to use theoretical calculations to assist in locating H-atom positions in clay minerals.

Unlike clay minerals, micas often occur in large crystals, which make detailed single-crystal structure studies possible. Hydrogen-atom positions in several mica minerals have been determined experimentally using single-crystal neutron diffraction. Reproducing these H-atom positions using computer simulation [the Static Structure-Energy Minimization (SSEM) technique] will be a useful check on the accuracy of analogous calculations of H-atom positions in clay minerals.

PREVIOUS WORK

Calculation of H-atom positions or O–H orientations in phyllosilicates began in the early 1970s. The ionic model was used, and only the Coulombic (electrostatic) energy was calculated with respect to O–H orientation in the structure (Giese 1971). The approach was applied to numerous dioctahedral and trioctahedral phyllosilicates to determine their O–H orientations (Giese 1979, 1984). This early work was not concerned with O–H distance, and the calculation of total energy was limited to one unit-cell. The method was further developed by Abbott *et al.* (1989) and Abbott (1992, 1994), who also considered Born repulsion and used energy-minimization techniques.

Developed in parallel is the SSEM method (Catlow & Price 1990) for periodically repeating structures, which has been used to calculate H-atom positions in kaolinite (Collins & Catlow 1991) and, with minor modification, the complete structures of micas (Collins & Catlow 1992). The agreement of the calculated structures and physical properties to the observed values indicates that the interaction model used in the calculation (including "electrostatic", repulsion, polarization and bond-bending terms) is applicable in general to micas and clay minerals. Here, we use the SSEM method to calculate the H-atom positions in micas and clay minerals. All H-atom positions in a structure are considered simultaneously by fixing the rest of the structures (unit-cell dimensions, and atomic coordinates of non-H atoms) at the values determined by single-crystal X-ray-diffraction experiments.

THE CALCULATION

Most models used in SSEM calculations usually involve two types of atom interactions: a Coulombic attraction and a Born-type repulsion (Born & Huang 1954). The Coulombic attraction has the form

$$U_c = \frac{q_i q_j}{r_{ij}} \qquad (1)$$

in which q_i and q_j are the formal charges of the atoms, and r_{ij} is the interatomic distance. For repulsion, the Born-type potential (Born & Huang 1954) is usually used:

$$U_R = \lambda_{ij} \exp(-\frac{r_{ij}}{\rho_{ij}}) \qquad (2)$$

where λ_{ij} and ρ_{ij} are atom-pair parameters, which are usually determined empirically (Kunz & Armbruster 1992) or semi-empirically (Post & Burnham 1986). A slightly different form of the repulsive interaction, the Buckingham potential, is also in common use:

$$U_R = \lambda_{ij} \exp(-\frac{r_{ij}}{\rho_{ij}}) + C_{ij}\, r_{ij}^{-6} \qquad (3)$$

The extra coefficient, C_{ij}, is atom-pair specific and is determined as are λ_{ij} and ρ_{ij}.

For silicate minerals, extensive work has shown that it is necessary to include terms involving bond-bending and polarization in order to reproduce accurately both crystal structure and physical properties (Sanders *et al.* 1984). The bond-bending interaction is approximated by the harmonic potential function

$$U_B = k_B\, (\theta_i - \theta_0)^2 \qquad (4)$$

in which k_B is a constant for SiO_4 and AlO_4 tetrahedra, and $(\theta_i - \theta_0)$ is the difference between the O–(Si,Al)–O angle in the structure and the ideal O–(Si,Al)–O angle of 109.47°. Polarization can be modeled with the core–shell model of Dick & Overhauser (1958):

$$U_p = k_p\, d^2 \qquad (5)$$

where k_p is an atom-specific constant and d is the core–shell separation.

With this model potential, atomic positions can be calculated with an accuracy of 1–3% for simple ordered structures (Purton & Catlow 1990). In more complicated structures, the differences tend to be larger than 5%. Determining how reliable such a model is in predicting H-atom positions in micas and clay minerals is one of the objectives of the present study.

The SSEM program used in the present work is *WMIN* (Busing 1981). A subroutine, *THRBD*, was added to the original program to include three-body and polarization terms (see equations 4 and 5), tailored for silicate structures.

There are two stages in determining the H-atom positions: (1) location of the H-atom position(s) (presumed unknown) in the vicinity of the corresponding hydroxyl O-atom(s). Unit-cell dimensions and non-H atom positions are all fixed at the experimentally determined values. Space-group symmetry of the crystal (determined experimentally), based on the arrangement of the non-H atoms, is used, such that H-atom(s) conform to this symmetry; (2) relaxation of the space-group symmetry of the H-atom position(s) located in stage (1) to $P1$, with the unit-cell dimensions and the non-H atom positions still fixed at the experimental values. Possible deviation of the H-atom positions from the symmetry of the non-H atoms will be detected at this stage (see later discussions on individual species).

The potentials used in the SSEM calculations include Coulombic interactions, repulsion, covalency and polarization (of the forms in equations 1 to 5). For the interaction between O and H of the OH groups, a Morse potential was used (Saul *et al.* 1985), of the form

$$V_{OH} = D_e\{1 - \exp[-\beta(r - r_e)]\}^2 \tag{6}$$

in which D_e is the OH bond-energy, β is a parameter to be determined, and r and r_e are the observed and ideal O–H distances, respectively. Parameters used in these potentials are given in Table 1. In the SSEM calculation, six cycles of Rosenbrock search was used to reduce the probability of the minimization falling into a local minimum. The search was then switched to Newton's method to speed up convergence.

Al–Si disorder

All of the minerals considered here contain significant Al–Si disorder at the tetrahedrally coordinated sites in their structures. There is no way in which any energetic calculation can be done correctly on such a crystal. Either one approximates the crystal by a cluster or one assumes translational symmetry. In the first case, the calculation is done on an ordered arrangement, and there is no approximation with regard to site populations. However, the calculation can be affected by the size of the cluster and by the medium-range structure, which is usually not known. Moreover, the cluster does not experience the field of the crystal. In the second case, the calculation is done for the whole crystal (rather than a small cluster) *via* incorporation of translational symmetry, but some averaging of the real structure must occur, and the calculation must have some way of incorporating "composite atoms". It is also possible to combine these two approaches by embedding a large cluster in a "crystal", generally by using a unit cell that is a multiple of the true "average" unit cell.

Both of these approaches have been used for silicate minerals with reasonable success. Abbott (1991, 1994) has used the cluster method to examine the H environment in amphibole and muscovite. Abbott *et al.* (1989) and Winkler *et al.* (1991) have used translational-symmetry methods with averaged atom parameters for structure-energy calculations. Both approaches have produced useful results. Here, we use translational symmetry and appropriate values of fractional charge for Al–Si disorder.

TABLE 1. POTENTIAL PARAMETERS USED IN THE STRUCTURE-ENERGY CALCULATION

Short-range repulsion: Born/Buckingham-type and Morse potentials*				
	λ (kCal/mol)	ρ (Å)	C (kCal/mol·Å^{-6})	Ref.
Si^{4+}–O^{2-}	29607	0.3025	245.860	[1]
Al^{3+}–O^{2-}	33675	0.29912		[2]
K^{1+}–O^{2-}	1505142	0.2134		[3]
Mg^{2+}–O^{2-}	32942	0.2945		[5]
Ca^{2+}–O^{2-}	160461	0.2516		[3]
O^{2-}–O^{2-}	524946	0.149	642.9	[1]
	D_o (kCal/mol)	r_o (Å)	β (Å^{-1})	
$H^{0.426+}$–$O^{1.426-}$	162.63	0.9485	2.1986	[4]
	Bond-bending interaction**			
	k_B (kCal/rad^2)		θ_O (°)	
O^{2-}–Si^{4+}–O^{2-}	48.3631		109.47	[1]
	Shell-core interaction between O-shell and O-core***			
		k_P (kCal/Å^2)		
O(core)$^{+0.86902}$–O(shell)$^{-2.86902}$		1728		[1]

* *c.f.* equations 2, 3 and 6** *c.f.* equation 4; *** *c.f* equation 5

[1] Sanders *et al.* (1984), [2] James (1979), [3] Post & Burnham (1986), [4] Saul *et al.* (1985), [5] Price & Parker (1984).

RESULTS AND DISCUSSION

The micas and clay minerals selected for this study have near-end-member chemical compositions and have H-atom positions determined by neutron diffraction. These minerals can be divided into the following groups:

(1) Minerals with non-split H-atoms: phlogopite (Rayner 1974), clinochlore (Joswig *et al.* 1980) and kaolinite (Bish 1993);

(2) Minerals with split H-atom positions: margarite (Joswig *et al.* 1983);

(3) Minerals with uncertain H-atom positions: muscovite (Rothbauer 1971), dickite (Bish & Johnston 1993).

All minerals were assumed to be of end-member chemical composition in the calculations.

Phlogopite, clinochlore and kaolinite

H-atom positions were calculated with the symmetry constraints $C2/m$, $C\bar{1}$ and $C1$ for phlogopite, clinochlore and kaolinite, respectively, and are given in Table 2. H-atom positions calculated with symmetry relaxed to $P1$ are given in Table 3.

Phlogopite has only one unique H-atom position in the average $C2/m$ structure. The calculation reproduces the H-atom position determined by neutron diffraction (Table 3) within 2σ (σ: standard deviation). In clinochlore, the differences range from 0 to 34σ, with an average of 10σ. Such differences may be attributed to the fact that the calculation assumed ideal chemical composition, whereas the mineral used for the neutron-diffraction study has a chemical composition off ideal (Joswig *et al.* 1980). Nevertheless, even the largest difference (the *x* coordinate of H2 with Δ = –0.017) represents only a difference of 0.09 Å. Comparison of the calculated and the observed coordinates for kaolinite is more difficult, as the standard deviations of the observed coordinates, determined by powder neutron-diffraction, vary from 0.0001 to 0.006 (a factor of 60). It should be noted that (1) the calculated coordinates with the greatest differences correspond to the experimentally determined coordinates with the largest standard deviations; (2) the coordinates determined to higher precision (with standard deviations of 0.000*n*) all agree with the calculated values to the third decimal place, the accuracy of the SSEM method.

After SSEM calculation with the symmetry relaxed to *P*1, the H-atom positions obtained for each of the three minerals (Table 3) retain the corresponding symmetry of the non-H atom configuration. There is extensive evidence (Farmer & Russel 1964, Rayner 1974, Joswig *et al.* 1980, Johnston *et al.* 1990, Hess & Saunders 1992, Bish 1993) that H atoms in these minerals do obey the symmetry of the non-H atoms. Such a result suggests that the SSEM procedure is a good test of the presence of specific elements of symmetry in the arrangement of H atoms in micas and clay minerals.

Muscovite

There is reasonable agreement between the calculated and experimentally determined H-atom positions

TABLE 2. COMPARISON OF CALCULATED (FIRST ROW) AND EXPERIMENTAL (SECOND ROW) H-POSITIONS IN PHLOGOPITE, CLINOCHLORE AND KAOLINITE WITH SYMMETRY CONSTRAINTS

	x	*y*	*z*
	Phlogopite* $KMg_3(AlSi_3)O_{10}(OH)_2$		
H	0.0981	0.0000	0.3050
	0.0992(40)	0.0000	
Δ	–0.0011		–0.0031
	Clinochlore** $Mg_{12}(Si_8O_{20})(OH)_{16}$		
H1	0.7129	0.3418	0.1405
	0.7139(5)	0.3339(3)	0.1399(3)
Δ	–0.0010	0.0079	0.0006
H2	0.1023	0.0131	0.3632
	0.1193(5)	0.0054(3)	0.3632(2)
Δ	–0.0170	0.0076	0.0000
H3	0.1406	0.3326	0.3627
	0.1301(5)	0.3353(3)	0.3629(2)
Δ	0.0105	–0.0027	–0.0002
H4	0.6184	0.1585	0.3625
	0.6143(5)	0.1594(3)	0.3635(2)
Δ	0.0041	–0.009	–0.0010
	Kaolinite*** $Al_2Si_2O_5(OH)_4$		
H1	0.152	0.0624	0.337
	0.145(3)	0.0651(1)	0.326(6)
Δ	0.007	–0.0027	0.011
H2	0.063	0.1681	0.736
	0.063(3)	0.1638(1)	0.739(1)
Δ	0.000	0.0043	–0.003
H3	0.020	0.5111	0.731
	0.036(3)	0.5057(2)	0.732(1)
Δ	–0.016	0.0054	–0.001
H4	0.575	0.3201	0.736
	0.534(3)	0.3154(2)	0.728(1)
Δ	0.041	0.0047	0.008

* observed H-position taken from Rayner (1983);
** observed H-position taken from Joswig *et al.* (1980);
*** observed H-positions taken from Bish (1993).

TABLE 3. H-ATOM POSITIONS IN PHLOGOPITE, CLINOCHLORE AND KAOLINITE PROJECTED BACK INTO THE ASYMMETRIC UNITS AFTER SSEM WITHOUT SYMMETRY CONSTRAINTS

Symmetry operation	*x*	*y*	*z*
	Phlogopite		
H11 *x*, *y*, *z*	0.0976	0.0000	0.3035
H12 –*x*, *y*, –*z*	0.0976	0.0000	0.3035
H13 ½+*x*, ½+*y*, *z*	0.0976	0.0000	0.3035
H14 ½–*x*, ½+*y*, –*z*	0.0972	0.0000	0.3035
Mean	0.0975	0.0000	0.3035
Determined with symmetry	0.0981	0	0.3050
Experimental*	0.0992(40)	0	0.3081(15)
	Clinochlore		
H1 All†	0.7134	0.3418	0.1420
Determined with symmetry	0.7129	0.3418	0.1405
Experimental**	0.7139(5)	0.3339(3)	0.1399(3)
H2 All†	0.1004	0.0143	0.3616
Determined with symmetry	0.1023	0.0131	0.3632
Experimental**	0.1193(5)	0.0054(3)	0.3632(2)
H3 All†	0.1420	0.3326	0.3610
Determined with symmetry	0.1406	0.3326	0.3627
Experimental**	0.1303(5)	0.3353(3)	0.3629(2)
H4 All†	0.6171	0.1577	0.3607
Determined with symmetry	0.6184	0.1585	0.3625
Experimental**	0.6143(5)	0.1594(3)	0.3635(2)
	Kaolinite		
H1 All†	0.155	0.0648	0.344
Determined with symmetry	0.152	0.0624	0.337
Experimental***	0.145(3)	0.0651(1)	0.326(2)
H2 All†	0.062	0.1683	0.740
Determined with symmetry	0.063	0.1681	0.736
Experimental***	0.063(3)	0.1638(1)	0.739(1)
H3 All†	0.020	0.5096	0.735
Determined with symmetry	0.020	0.5111	0.731
Experimental***	0.036(3)	0.5057(2)	0.732(1)
H4 All†	0.577	0.3180	0.739
Determined with symmetry	0.575	0.3201	0.736
Experimental***	0.534(3)	0.3154(2)	0.728(1)

* Rayner (1974), ** Joswig *et al.* (1980), *** Bish (1993).
† all (pseudo-)symmetry-equivalent positions are identical.

in the structure of *C2/c* muscovite (Table 4). The eight H-atom positions determined with the symmetry of the H positions relaxed to *P*1 are listed in Table 5 (projected back into the asymmetric unit of the *C2/c* structure). There are eight independent H-atom positions in space group *P*1. If each of these positions is transformed back to the x y z position of the asymmetric unit of the *C2/c* muscovite structure (Table 5), the H-atom positions fall into two sets labeled H1j and H2j (j = 1,4) in Table 5. The average values of the x and y coordinates for each set bracket the experimental values. The slightly greater difference of the z coordinates is probably related to the inadequate description of H bonding in the calculation (Collins & Catlow 1991). Overall, the result is in accord with the anisotropic-displacement model of Rothbauer (1971), in which the H-atom shows clear evidence of anisotropic displacement. The *P*1 calculation indicates this anisotropic model to be an envelope of two positions of the split-H atom, separated by 0.44 Å, in accord with Abbott *et al.* (1989), who also proposed two kinds of OH orientation (two H-atom positions) in the muscovite structure. The H2 position has atomic coordinates similar to those of the single H-atom position calculated with *C2/c* symmetry constraints (Table 5), suggesting that H2 is energetically more favorable than H1. Careful examination of the relative positions of H1 and H2 indicates that H2 corresponds to the "type-2" minimum of Abbott *et al.* (1989), which is energetically more favorable than the "type-1" minimum (corresponding to H1 position in the present work). These remarkably similar results produced by the two different approaches prompted experimental verification, discussed elsewhere (Liang *et al.* 1998).

TABLE 4. H-ATOM COORDINATES* IN MUSCOVITE (*C2/c*), MARGARITE (*Cc*) AND DICKITE (*Cc*)

	x	y	z
	Muscovite		
H(calc)	0.3987	0.6322	0.0815
H(exp)*	0.3727(7)	0.6499(4)	0.0599(2)
Δ	0.0260	–0.0177	0.0216
	Margarite		
H1(calc)	0.449	0.581	0.107
H(11B)*(exp)**	0.439(3)	0.591(2)	0.098(1)
diff.	0.010	–0.010	0.009
H(11A)*(exp)**	0.3663(7)	0.6550(5)	0.0620(3)
H2(calc)	0.566	0.386	0.904
H(12B)*(exp)**	0.561(4)	0.399(3)	0.905(1)
diff.	0.005	–0.013	0.001
H(12A)*(exp)**	0.6325(9)	0.3452(5)	0.9396(4)
	Dickite		
H1(calc)	0.4911	0.2014	0.1147
H1(exp)***	0.4795(9)	0.1848(4)	0.1549(5)
Δ	0.0116	0.0166	–0.0402
H2(calc)	0.3077	0.2543	0.3615
H2(exp)***	0.2957(8)	0.2558(5)	0.3627(3)
Δ	0.0120	–0.0015	–0.0012
H3(calc)	0.297	0.9329	0.3596
H3(exp)***	0.326(1)	0.9456(5)	0.3515(4)
Δ	–0.029	–0.0127	0.0081
H4(calc)	0.2690	0.5739	0.3595
H4(exp)***	0.2891(9)	0.5813(6)	0.3605(3)
Δ	–0.0201	–0.0074	–0.0010

** Rothbauer (1971), **Joswig *et al.* (1983),
*** Bish & Johnston (1993).

Margarite

In margarite, the H-atom positions occur in pairs that are sufficiently close together that they can be represented by a split H-atom model (Joswig *et al.* 1983). Reproducing such a split-atom model will be a stringent test of the SSEM procedure. From the non-H configuration of Joswig *et al.* (1983), assuming non-split H-atoms that obey the *Cc* symmetry of the non-H atoms, SSEM calculation gave two H-atom positions (Table 4): H1 and H2.

The H-atom positions calculated without symmetry constraints (and then transformed back into the asymmetric unit for *Cc* symmetry) are given in Table 6. The space-group symmetry *Cc* is no longer maintained for the H atoms. The experimentally observed split H-atom model is reproduced, but the agreement between the calculated and experimentally determined coordinates is poor (Table 6). The coordinates of H11 differ from those of the experimentally determined equivalent, H(11A), by as much as 0.2 Å. One of the H-atom positions that comprise H11 (corresponding to the symmetry operation $x, -y, {}^{1}/_{2}+z$) matches very closely the observed H(11A) position. This raises the possibility of further splitting of H11 (to H111 and H112, Table 7). Such splitting is in accord with the split H-atom model of muscovite (see above). Margarite and muscovite have

TABLE 5. THE EIGHT H-ATOM POSITIONS PROJECTED BACK INTO THE ASYMMETRIC UNIT OF THE *C2/c* MUSCOVITE CELL

Symmetry operation	x	y	z
H11 x, y, z	0.3629	0.6509	0.0643
H12 $-x, -y, -z$	0.3642	0.6515	0.0642
H13 $\frac{1}{2}+x, \frac{1}{2}+y, z$	0.3629	0.6509	0.0643
H14 $\frac{1}{2}-x, \frac{1}{2}-y, -z$	0.3646	0.6516	0.0642
H1	0.3637	0.6512	0.0642
H21 $-x, y, \frac{1}{2}-z$	0.3932	0.6438	0.0766
kH22 $x, -y, \frac{1}{2}+z$	0.3642	0.6442	0.0766
H23 $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	0.3961	0.6436	0.0772
H24 $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	0.3944	0.6445	0.0765
H2	0.3945	0.6440	0.0767
H-position calculated in *C2/c*	0.3987	0.6322	0.0815
H-position observed*	0.3727(7)	0.6499(4)	0.0599(2)

* Rothbauer (1971).

a similar sheet-configuration except that tetrahedrally coordinated Al and Si are ordered into different sites in margarite, giving rise to *Cc* rather than *C*2/*c* symmetry.

TABLE 6. H-ATOM POSITIONS IN MARGARITE CALCULATED WITHOUT SYMMETRY CONSTRAINTS

	x	*y*	*z*
	H1		
x, –*y*, *z*+½	0.3672	0.6633	0.0718
x+½, –*y*+½, *z*+½	0.4186	0.6304	0.0991
H11	0.3929	0.6468	0.0854
H(11A)*	0.3663(7)	0.6550(5)	0.0620(3)
diff.	0.0266	–0.0082	0.0234
x, *y*, *z*	0.439	0.576	0.104
x+½, *y*+½, *z*	0.438	0.579	0.103
H12	0.439	0.578	0.104
H(11B)*	0.439(3)	0.591(2)	0.098(1)
diff.	0.000	–0.013	0.006
	H2		
x, –*y*, *z*+½	0.5898	0.3657	0.9023
x+½, –*y*+½, *z*+½	0.5903	0.3668	0.9022
H21	0.5900	0.3662	0.9022
H(12A)*	0.6325(9)	0.3452(5)	0.9396(4)
diff.	–0.0425	0.021	–0.0374
x, *y*, *z*	0.551	0.425	0.896
x+½, *y*+½, *z*	0.556	0.419	0.898
H22	0.553	0.422	0.897
H(12B)*	0.561(4)	0.399(3)	0.905(1)
diff.	–0.008	0.023	–0.008

* determined by neutron diffraction (Joswig *et al.* 1983).

There is close correspondence of H111 and H112 in margarite to H1 and H2 in muscovite (Table 7). The present calculations suggest further splitting, and this is supported experimentally by the elongate-displacement model of H(11A), with U_{33} twice as large as U_{11} and U_{22} (Joswig *et al.* 1983). The coordinates of the two H-atom positions that comprise the H21 position are very similar (Table 6), although the displacement model for H(12A) (Joswig *et al.* 1983), which is equivalent to H21 in the present study, shows elongation and hence further splitting, similar to H(11A). This splitting was not reproduced by the calculation, probably because the calculation was done assuming a dioctahedral configuration and complete order of tetrahedrally coordinated non-H atoms, while using a non-H atomic configuration of a sample that has minor trioctahedral character (minor *M*1-site occupancy) and partial compositional (Al, Si) disorder (Joswig *et al.* 1983).

Dickite

The calculated H-atom positions in space group *Cc* show poor agreement with the observed values (Table 4). The sixteen H-atom positions determined with the symmetry relaxed to *P*1 (Table 8) fall into six groups. The agreement between the calculated and the observed H1 and H2 coordinates is improved by a factor of ten. There is also similar improvement in the agreement between the calculated and observed coordinates of H3 and H4, given that the two observed H-atoms correspond to the calculated H31 and H42 sites, respectively. The results indicate that (1) instead of representing all four H-atoms as occupying single sites in

TABLE 7. SPLIT H-ATOM POSITIONS IN MARGARITE AS COMPARED TO MUSCOVITE

	Margarite				Muscovite		
	x	*y*	*z*		*x*	*y*	*z*
H111	**0.3672**	**0.6633**	**0.0718**	H1	0.3656(19)	0.6560(13)	0.0522(10)
H(11A)*	0.3663(7)	0.6550(5)	0.0620(3)				
diff.	0.0009	0.0083	0.0098				
H112	**0.4186**	**0.6304**	**0.0991**	H2	0.3883(25)	0.6380(17)	0.0720(15)
H12	**0.439**	**0.578**	**0.104**				
H(11B)*	0.439(3)	0.591(2)	0.098(1)				
diff.	0.0000	–0.013	0.006	Generated by the $\bar{1}$-operation from H1 and H2			
H211**	0.6328	0.3367	0.9282	H1′	0.6344	0.3440	0.9478
H(12A)*	0.6325(9)	0.3452(5)	0.9396(4)				
H212	**0.5900**	**0.3662**	**0.9022**	H2′	0.6117	0.3620	0.9280
H212**	0.5814	0.3696	0.9009				
H22	**0.553**	**0.422**	**0.897**				
H(12B)*	0.561(4)	0.399(3)	0.905(1)				
diff.	–0.008	0.023	–0.008				

* from Joswig *et al.* 1983; ** hypothetical, derived from the $\bar{1}$ equivalent of H111 or H112. The highlighted are the H-atom positions calculated in margarite.

TABLE 8. H-POSITIONS* IN DICKITE CALCULATED WITH *P*1 SYMMETRY

	x	*y*	*z*
H1			
x, *y*, *z*	0.4898	0.1744	0.1580
x, –*y*, *z*+½	0.4794	0.1803	0.1669
x+½, *y*+½, *z*	0.4900	0.1743	0.1580
x+½, –*y*+½, *z*+½	0.4786	0.1805	0.1667
H1	0.4844	0.1774	0.1624
H1**	0.4795(9)	0.1848(4)	0.1549(5)
diff.	0.0049	–0.0074	0.0075
H2			
x, *y*, *z*	0.2952	0.2605	0.3664
x, –*y*, *z*+½	0.3170	0.2535	0.3636
x+½, *y*+½, *z*	0.2951	0.2605	0.3664
x+½, –*y*+½, *z*+½	0.3170	0.2465	0.3636
H2	0.3061	0.2552	0.3650
H2**	0.2957(8)	0.2558(5)	0.3627(3)
diff.	0.0104	–0.0006	0.0023
H3			
x, *y*, *z*	0.328	0.9340	0.3589
x+½, *y*+½, *z*	0.328	0.9341	0.3588
H31	0.328	0.9340	0.3588
H3**	0.326(1)	0.9456(5)	0.3515(4)
diff.	0.002	–0.0166	0.0073
x, –*y*, *z*+½	0.253	0.9281	0.3643
x+½, –*y*+½, *z*+½	0.253	0.9285	0.3643
H32	0.253	0.9283	0.3643
H4			
x, *y*, *z*	0.2463	0.5656	0.3585
x+½, *y*+½, *z*	0.2462	0.5656	0.3585
H41	0.2462	0.5656	0.3585
x, –*y*, *z*+½	0.2971	0.5802	0.3658
x+½, –*y*+½, *z*+½	0.2972	0.5802	0.3658
H42	0.2972	0.5802	0.3658
H4**	0.2891(9)	0.5813(6)	0.3605(3)
diff.	0.0081	–0.0011	0.0053

* projected back into the asymmetric unit of the *Cc* dickite structure;
**determined from neutron diffraction (Bish & Johnston 1993).

space group *Cc*, two of the H atoms (H3 and H4) occupy split sites; (2) interactions between H-atoms can be important in determining equilibrium H-atom positions in the structure.

The result that there are probably six unique H-atom positions in the dickite structure helps explain the previous apparent disagreement between diffraction and spectroscopic results on the OH-groups in dickite. Infrared spectroscopy shows six OH-stretching bands (corresponding to at least six unique OH-groups) in dickite (Farmer & Russel 1964, Johnston *et al.* 1990, Joswig & Drits 1986, Prost *et al.* 1989, Sen Gupta *et al.* 1984), whereas diffraction experiments show only four unique H-atom positions. The strong bands at 3620, 3655 and 3731 cm^{-1} were assigned to the four OH-groups located by the diffraction experiments [the band at 3655 cm^{-1} is known to be due to overlapping of two (O–H2 and O–H4, Table 9) OH stretching bands], but the two weak bands at 3691 and 3717 cm^{-1} were left unassigned. The postulate that the H3 and H4 sites are actually split into (H31, H32) and (H41, H42) sites explains the existence of the two additional bands. The OH-stretching frequency is strongly influenced by details of H-bonding (Nakamoto *et al.* 1955). Longer H...O distances and smaller O–H...O angles give higher stretching-frequencies, and *vice versa*. This relation is maintained in the correspondence of the H...O distances and O–H...O angles of the four experimentally observed H-atoms (assuming that H3 ≡ H31 and H4 ≡ H42, Tables 8 and 9), and their assignment to the IR bands where the above criteria are applicable. For H32, the H...O distance (2.15 Å) is shorter and the O–H...O angle (176°) is larger than the corresponding values of H31 (2.28 Å and 144°, respectively). This means that the O–H32 stretching will give a frequency lower than that of O–H31 stretching (3731 cm^{-1}), probably corresponding to one of the weak bands at 3717 and 3691 cm^{-1}. This is in accord with the suggestion of Bish & Johnston (1993) based on the large displacement-factor and anisotropy at the H3 site in the structure, as refined from neutron-diffraction data. For H41, the H...O distance (1.96 Å) is greater, and the O–H...O angle (156°) is smaller, than the corresponding values of H42 (1.92 Å and 167°, respectively). As O–H42 gives a stretching frequency at 3655 cm^{-1}, O–H41 should give a stretching frequency higher than 3655 cm^{-1}, probably corresponding to the 3691 cm^{-1} band in the low-temperature IR spectrum.

The large intensity of the band at 3731 cm^{-1} is somewhat puzzling. For similar populations at OH sites, the band intensity is inversely proportional to the frequency (Hermansson *et al.* 1991, Burns & Hawthorne 1994). The population of the H3 site (H31) is similar or less than those of H1, H2, or H4. As the stretching frequency of O–H3 (O–H31) is the highest in the spectrum, its intensity should be smaller than the intensities of the two major bands associated with H1, H2 and H4(H42).

TABLE 9. CALCULATED AND EXPERIMENTAL HYDROGEN BONDS IN DICKITE

	d_{O-H} (Å)		$d_{H...O}$ (Å)	∠ O–H...O (°)	IR Frequency (cm^{-1})**
OH1	0.99 0.94*				3620
OH2	1.00 0.96*	...O1	1.93 1.97*	166 164*	3655
OH31	0.99 0.95*	...O3	2.28 2.36*	144 140*	3731
OH32	0.99		2.15	176	3717 ?
OH41	1.00	...O2	1.96	156	3691 ?
OH42	1.00 0.94*		1.92 1.99*	167 166*	3655

* determined by neutron diffraction (Bish & Johnston 1993);
** low-temperature FTIR data (Bish & Johnston 1993).

However, this is not the case. Further study of the vibrational attributes is needed using Raman spectroscopy.

CONCLUSIONS

Using the SSEM method, with the input of space-group symmetry, unit-cell dimensions, and non-H atomic coordinates, H-atom positions of the OH group(s) in micas and clay minerals can be located to an accuracy of ~0.10 Å. Split H-atom models can be reproduced, and relative energies of the split positions can also be resolved.

The H-atom position in muscovite is predicted to be split, with the position closer to the *c* axis energetically more favorable than the position closer to the basal plane. Similar splitting is predicted for margarite. In addition to the diffraction-determined four unique H-atom positions in dickite, two more H-atom positions were identified in the dickite structure: the experimentally determined H3 and H4 positions are split into (H31, H32) and (H41, H42) pairs, respectively. The total of six unique H-atom positions explains the presence of six OH-stretching bands in the vibrational spectrum of dickite.

ACKNOWLEDGEMENTS

We thank R.N. Abbott, Jr. and J.E. Post for their comments. This work was funded by the Natural Sciences and Engineering Research Council of Canada in the form of a Graduate Fellowship to J-JL and Operating, Major Equipment and Infrastructure Grants to FCH.

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Received June 16, 1996, revised manuscript accepted July 12, 1998.