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Ab initio exploration of layer slipping transformations in kaolinite up to 60 GPa

P. H. J. Mercier* and Y. Le Page

Kaolinite transformation into other kaolin layer polytypes under pressure is of interest in many materials or industrial applications as well as in seismology. Assuming that this transformation would involve a layer slipping mechanism similar to that of the reversible dickite to HP dickite transformation observed at 2 GPa, the authors undertake here an exploratory study of corresponding transformations. Neglecting contributions from third neighbour layers and beyond to differences in total energy, it is concluded that 19 stacking models of kaolin layers are prime candidates for the lowest enthalpy under moderate pressure. *Ab initio* compression of those models up to 60 GPa shows that, although several of the above models come close to kaolinite in enthalpy, kaolinite probably survives compression up to ~ 12 GPa. Beyond this pressure, a new family of kaolin polytypes with lower enthalpy than kaolinite, resulting from a different layer slipping mechanism, is spontaneously produced by *ab initio* compression. The silicon coordination transforms gradually from tetrahedra to triangular dipyramids with no drastic change to layer architecture. Corresponding distinguishable transformations between adjacent layers resulting from this new coordination are translations $-a/3$ and $(a+b)/3$, which are not possible translations at zero pressure. Numerous low enthalpy new polytypes based on those translations are possible. Compression to 20 GPa of two kaolin polytypes among the 19 models created above have spontaneously resulted, one into the repeated $(a+b)/3$ polytype with symmetry Cm , and the other one into the repeated $-a/3$ polytype with symmetry $P1$. As both models derive from kaolinite by a layer slipping mechanism and have very similar enthalpies, both considerably lower than that of kaolinite, those phases and the polytypes from the same family are prime candidates for post-kaolinite phases beyond ~ 12 GPa.

Keywords: *Ab initio* modelling, Pressure, Layer slipping transformations, Kaolinite

Introduction

Among the known kaolin polytype minerals, namely kaolinite, dickite, nacrite and HP dickite, all with formula $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$, kaolinite (Fig. 1) is by far the most abundant one at the surface of the Earth. In spite of the wide use of kaolinite as raw materials in many industrial applications and the possible relevance of clay minerals in subduction zones¹ for the occurrence of earthquakes, limited research seems to have been devoted to the evolution of the various kaolin minerals under pressure, presumably in view of great experimental difficulties. In spite of those difficulties, the crystal structure of high pressure dickite (HP dickite) is derived by Dera *et al.*² from a high pressure diffraction experiment. This exposes the layer slipping mechanism

of the reversible dickite $\leftrightarrow$ HP dickite transformation at ~ 2 GPa. Essentially, through an atomic scale translation, the network of hydrogen bonds linking the hydroxyls at the top of kaolin layers switches reversibly to different silicate oxygen atoms at the bottom of the next layer. This switch results in a lower enthalpy at the given pressure. The authors of that enlightening study postulate the generality of the corresponding mechanism among hydrogen bonded phyllosilicates. The authors endorse here this plausible viewpoint, and attempt to explore the implications of that same mechanism in the case of kaolinite, in order to derive its possible phase transformations under pressure in the hope of promoting future experimental work. A density functional theory study of the bulk modulus and other elastic constants of kaolinite up to 23 GPa has been reported by Sato *et al.*³

Background

In a prior *ab initio* study⁴ of kaolin minerals at zero pressure, it is assumed that the contribution of

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1 Perspective view of kaolinite

interactions between non-adjacent kaolin layers to total energy is negligible, as illustrated in the left part of Fig. 2. Under this assumption, the total energy U of a given stacking made of the sequence of k interlayer

transformations A, B, C... can be expressed as

$$U(A,B,C \dots) = k \langle U \rangle + \Delta A + \Delta B + \Delta C + \dots \quad (1)$$

where $\langle U \rangle$ is an average energy per layer, while ΔA , ΔB , ΔC ... are small energy corrections attached to each of the n possible different interlayer transformations. As one, say ΔM , among the n possible Δ values is smaller than the $(n-1)$ other ones, it follows that the stacking made of just M type interlayer transformations has lower total energy than any other stacking according to equation (1). Polytypes with the lowest total energy must then belong to one of two categories. Category (a) corresponds to the repeated application of a same energy distinguishable transformation (EDT) between adjacent kaolin layers. Twenty such EDTs exist, four of which are pure translations. Category (b) corresponds to the successive application of an EDT and its enantiomorphic transformation EDT*. As sixteen distinguishable EDT* operations exist, a total of 36 models had to be considered by Mercier and Le Page⁴ and were optimised *ab initio*. All four known kaolin minerals were found among the 36 polytype models created in this way. Kaolinite and dickite had the lowest energy, with half a dozen other polytypes having extremely competitive total energies. Kaolinite is the stable phase at moderate pressures, while dickite remains metastable. Back of an envelope enthalpy calculations based on zero pressure total energy and cell volume showed that nacrite had the lowest enthalpy at pressures greater than ~ 4 GPa. The same calculations showed that the enthalpy of HP dickite became lower than that of dickite ~ 5.6 GPa, allowing the transformation of metastable dickite into metastable HP dickite. In other words, a rough, new and rational picture of the known kaolin minerals emerged from this modelling study based on the assumption of negligible interaction between non-neighbouring layers. Among

2 Hypothesis of independence between kaolin layers: on left, at zero pressure, interactions limited to those between adjacent layers were sufficient to explain all known kaolin polytypes at zero or low pressures; on right, and in view of stronger interactions between adjacent kaolin layers, same concept is extended here to independence between third neighbour layers

other things, the study showed that the root mean square value of this interaction can be capped to 13 MeV per formula unit, or 1.25 kJ per mole, thus essentially justifying the basic assumption for that study.

Under pressure, the assumption of negligible interaction between non-neighbouring layers will not necessarily hold as stronger bonding of atoms is formed between adjacent layers with increasing pressure. The authors accordingly abandon the prior assumption of energy independence from non-adjacent layers, and adopt instead a revised assumption of independence from third neighbour layers and beyond, and adapt accordingly the modelling part of this study. This is illustrated in the right part of Fig. 2. As kaolin layers are approximately 7 Å thick, the authors are extending in this way the range of interactions taken into account from about 8 Å in Mercier and Le Page⁴ to about 15 Å here, thus nearly doubling that range.

Instead of considering independent kaolin layers stacked according to transformations 1 to *n* as in the authors' prior study, they now consider units made of *k* preassembled pairs of layers with stacking symbols [*A:B*], [*C:D*], etc.... The first letter in the bracket describes how the second layer in the pair is obtained from the first layer. The second letter in the bracket describes how the first layer from the next block is derived from the second layer from the given block. In other words, *B* and *D* are now interfaces between preassembled two layer blocks *A* and *C*. As interfaces *B* and *D* are now two layers apart, the authors can assume independence of what happens at the two interfaces and write

$$U([A : B].[C : D], \dots) = UA + \Delta B + UC + \Delta D + \dots \quad (2)$$

where *UA* is the energy of a pair of layers corresponding through operation *A*, while ΔB is a correction term having to do with the given interface *B*. Again, as one of the *U* values, say *UP* is smaller than the other (*n*−1) *U* values, while one of the Δ values, say ΔQ , is smaller than the other (*n*−1) Δ values, it follows that the repeated stacking [*P:Q*] has lower energy than all other possible stackings. In the case where *P* and *Q* would be identical, the authors would be back to cases studied in their previous paper.

In other words, the authors are back to a situation quite similar to that in Mercier and Le Page,⁴ except that, instead of building blocks made of single kaolin layers, they are made of double layers. The same concept of EDT and EDT* with the same energies, as well as that of the two routes (a) and (b) apply with no change. The concepts are in place. The authors can now start modelling.

Modelling

The stacking in kaolinite involves no rotation between kaolin layers. According to the general scheme for layer slipping transformations proposed by Dera *et al.*,² the stackings that kaolinite can transform to can involve no rotations either. In the reference system of Mercier and Le Page,⁴ kaolinite transformations can then only involve interlayer translations 0, (2*a*+*b*)/3, (*a*+2*b*)/3, *a*/3, *b*/3 or 2(*a*+*b*)/3. Separating the EDTs and the corresponding EDT*, and using the prefix KT (K as in

kaolin and T as in translation) to avoid confusion with prefix K used in the authors' previous study, those operations can be designated as KT0, KT1, KT1*, KT2, KT2* and KT3 respectively. Combinations of single EDTs and routes (a) and (b) would then produce the candidates for the lowest energy models: [KT0]a, [KT1]a, [KT1]b, [KT2]a, [KT2]b and [KT3]a, corresponding to only six models, already studied at zero pressure in previous work. The stacking symbols used here are made of a repeated object in between square brackets and a method for repeating it, which is either (a) or (b). The (a) stands for simple translational repeat of the object, while (b) stands for translational repeat of a pattern made of the succession of the object and its enantiomorph.

For the reasons stated in the background section, the authors also have to consider the two layer groupings [KT1:KT0], [KT2:KT0], [KT2:KT1], [KT2:KT1*], [KT3:KT0], [KT3:KT1] and [KT3:KT2] as EDTs of their own. The corresponding EDT* enantiomorphic pairs of layers are [KT1*:KT0], [KT2*:KT0], [KT2*:KT1*], [KT2*:KT1], [KT3:KT1*] and [KT3:KT2*] because [KT3:KT0] is its own enantiomorph. To this list of EDT and EDT* correspond seven (a) type double layer models plus six (b)-type models. Adding the six one layer models above, the authors are then talking of 19 energy distinguishable models to be considered as low enthalpy candidates for layer slipping transformations in kaolinite, at least under moderate pressures, listed in Table 1. In this table, kaolinite is model no. 4, namely [KT2]a. No other model in Table 1 corresponds to a known kaolin polytype. Translations spelled out in Table 1 relate one layer referred to its standard origin to the next layer.

Table 1 The 19 possible low enthalpy models for reversible displacive transformations of kaolinite under pressure derived here. These models were derived under the assumption that contributions from third-neighbour layers and beyond to differences in total energy can be neglected

Model #	Symbol	1→2	2→3	3→4	4→1	Space group	Z
1	[KT0]a	0				Cm	2
2	[KT1]a	$\frac{(2a+b)}{3}$				P1	1
3	[KT1]b	$\frac{(2a+b)}{3}$	$\frac{(a+2b)}{3}$			Cc	4
4	[KT2]a	$\frac{a}{3}$				P1	1
5	[KT2]b	$\frac{a}{3}$	$\frac{b}{3}$			Cc	4
6	[KT3]a	$\frac{2(a+b)}{3}$				Cm	2
7	[KT1:KT0]a	$\frac{(2a+b)}{3}$	0			P1	2
8	[KT1:KT0]b	$\frac{(2a+b)}{3}$	0	$\frac{(a+2b)}{3}$	0	Cc	8
9	[KT2:KT0]a	$\frac{a}{3}$	0			P1	2
10	[KT2:KT0]b	$\frac{a}{3}$	0	$\frac{b}{3}$	0	Cc	8
11	[KT2:KT1]a	$\frac{a}{3}$	$\frac{(2a+b)}{3}$			P1	2
12	[KT2:KT1]b	$\frac{a}{3}$	$\frac{(2a+b)}{3}$	$\frac{b}{3}$	$\frac{(a+2b)}{3}$	Cc	8
13	[KT2:KT1*]a	$\frac{a}{3}$	$\frac{(a+2b)}{3}$			P1	2
14	[KT2:KT1*]b	$\frac{a}{3}$	$\frac{(a+2b)}{3}$	$\frac{b}{3}$	$\frac{(2a+b)}{3}$	Cc	8
15	[KT3:KT0]a	$\frac{2(a+b)}{3}$	0			Cm	4
16	[KT3:KT1]a	$\frac{2(a+b)}{3}$	$\frac{(2a+b)}{3}$			P1	2
17	[KT3:KT1]b	$\frac{2(a+b)}{3}$	$\frac{(2a+b)}{3}$	$\frac{2(a+b)}{3}$	$\frac{(a+2b)}{3}$	Cc	8
18	[KT3:KT2]a	$\frac{2(a+b)}{3}$	$\frac{a}{3}$			P1	2
19	[KT3:KT2]b	$\frac{2(a+b)}{3}$	$\frac{a}{3}$	$\frac{2(a+b)}{3}$	$\frac{b}{3}$	Cc	8

3 Enthalpy difference of 19 models studied here with respect to kaolinite (model 4) as function of pressure up to 60 GPa

Computations

All polytype structure model generation, preparation of data files for quantum optimisation and interpretation of optimisation results was performed with Materials Toolkit.⁵ All *ab initio* computations were performed with VASP.^{6,7} The optimisation procedure followed closely the procedure detailed in the section 2 of Mercier and Le Page.⁴ Final calculation of total energy, enthalpy and residual stress was similarly performed with $6 \times 6 \times 6$ k-mesh for all models at all pressures.

Results

Quantitative results of computations up to 60 GPa are fully reported in Supplementary Tables S1–19, one table for each of the 19 models implemented, plus one for the ideal starting models. Most subtables in Table S1 contain nine entries, one for each pressure used in the *ab initio* simulations performed to construct compression curves up to 60 GPa for each model. Enthalpy values for the various models and various pressures are reported numerically in Table S1. Enthalpies for kaolinite and for phases that are competitive at given pressures are also reported in graphical form in Fig. 3.

Analysis and discussion

Generation of models

The purpose of the rationale presented in the background section above is to extend the simple but effective approach used by Mercier and Le Page⁴ to the case of stronger interlayer interactions caused by pressure. In the authors' prior study, this simple

rationale led them to explore only 36 one, two, three and six layer models. This constitutes a considerable saving of computation effort, considering that there are more than half a million distinct six layer stackings, just counting those involving no EDT* and no repetition of a same EDT transformation. The authors nevertheless came up with all four known kaolin polytypes, as well as a handful of zero pressure competitive models among the 36 models derived from the concept of infinitesimal influence between non-adjacent layers. Here, the authors are led to investigate only 19 one, two and four layer models for the lowest enthalpy, where blind generation of distinguishable polytypes would again create an intractable number of models with one, two, three or four layers. The authors would also lack a rationale for stopping the search at four or at any other number of layers. Future work will decide whether this plausible extension is also supported by experiment. If conclusions presented here turned out to be supported by experiment, the present study would then pave the way for similar work about other phyllosilicates. Even if disproved later by experiment, the present work would still have the merit of having promoted and guided corresponding experimental work through simplification of the interpretation part of the experiment.

It might be argued that a distance of 15 Å between interfaces is insufficient to ensure independence of what happens at the interfaces between the two layer blocks considered here. Extension to three layer blocks of the reasoning presented in the background section above is immediate. Three layer blocks have a distance of 21 Å between interfaces, ensuring even lower dependence between what happens at one interface and what happens at the other one. Considering those models as well would increase both (i) the number of models to be considered from 19 to about 100 and (ii) the maximum number of atoms per primitive cell from 68 to 102. Corresponding computations would be barely feasible today while error free book keeping would constitute a challenge.

Similar to what the authors did in their previous study, they calculated powder patterns for ideal models 7–19 from Supplementary Table S1 (URL www.maney.co.uk/mstables) as a precaution against modelling errors that would lead to duplicate or enantiomorphic models. Calculated powder patterns for models nos. 12 and 14 (respectively stackings [KT2:KT1]b and [KT2:KT1*]b) turned out to be numerically identical, raising the question for their identity, enantiomorphism or homometricity. The repeat pattern of model no. 12 develops as [KT2:KT1:KT2*:KT1*]. It is superposable to its enantiomorph [KT2*:KT1*:KT2:KT1] with a two layer origin shift. However, it is distinguishable from model no. 14, which develops as [KT2:KT1*:KT2*:KT1] or its superposable enantiomorph [KT2*:KT1:KT2:KT1*]. All tetrahedra in the silica sheet of kaolin layers point along +z. Their stacking is accordingly polar along that direction. The symbols that represent stackings of kaolin layers can then only be read from left to right and cannot be reversed. Ideal stackings 12 and 14 are therefore not superposable and not enantiomorphic: they are then homometric. As neither model is involved in the main conclusions of this manuscript, the item will presumably remain a geometrical curiosity, but the authors felt that it was nevertheless worth reporting.

4 Silicate–aluminate layer architecture for models 3 and 18 at 23 GPa

Layer slipping transformations under pressure of the other kaolin phases can be established in the same way, with a similar degree of modelling and computational complexity. The authors felt that, in view of the greater abundance of kaolinite in nature, the kaolinite case constituted a more urgent problem than that of other polytypes of kaolin minerals like dickite or nacrite.

Compression of models

Figure 3 was obtained by first fitting a polynomial expression to the enthalpy of compressed kaolinite (model 4) versus pressure, and then subtracting the value for the expression from that of the enthalpy of the 19 polytypes at their computed pressure. The computed pressure does not necessarily come out precisely as the pressure that was aimed for because the enthalpy calculation is performed with a finer k-mesh than the structure optimisation.

On this graph (Fig. 3), data points for most of the 19 models essentially fall on the horizontal corresponding to kaolinite compression (model 4). Six models deviate considerably from this compact group. Model 1 has significantly higher enthalpy than that for kaolinite, and is therefore of no interest here. Enthalpies for models 9, 11 and 13 are very similar and somewhat lower than that for kaolinite. As they are not close to the lowest enthalpy, their relevance here is minimal. Model 3 and model 18 have very similar enthalpies, both much lower than that of kaolinite in the range 15 to 60 GPa. At 60 GPa, this enthalpy difference is nearly 1.4 eV per formula unit. The authors concentrate below on those two models 3 and 18.

Plots for the two corresponding structures at 23 GPa show that, although the two structures differ in symmetry (*Cm* for model 3 and *P1* for model 18, both printed in Table 2), they display the same basic silicate–aluminate layer architecture as kaolinite (Fig. 4a), and very similar crystal chemistries. In both cases, the basal Si atoms of the resulting layers are now in apical position directly above OH ions from the aluminate layer below. Analysed in terms of the reference system in

5 Kaolin layer *d* spacings for kaolinite (model 4) and model 3 as function of pressure up to 60 GPa

Table 2 Crystal structures of low-enthalpy models at 23 GPa

(a) Model 3									
SPGNAME=Cm; CELEDG=4-6504 8-4156 6-3576; CELANG=90 105-463 90 degrees									
ATOM=	1	Si	4b	1	0-19067	0-16697			
ATOM=	2	Al	4b	1	0-16566	0-33797	0-34987		
ATOM=	3	O	4b	1	0-27490	0-17355	0-17986		
ATOM=	4	O	4b	1	-0-00344	0-32562	0-84427		
ATOM=	5	O	2a	.m.	0-01878	0-00000	0-84567		
ATOM=	6	O	4b	1	0-05567	0-17825	0-51305		
ATOM=	7	O	2a	.m.	0-53923		0	0-50882	
ATOM=	8	O	2a	.m.	0-75391		0	0-19016	
ATOM=	9	H	4b	1	0-20626	0-09691	0-50977		
ATOM=	10	H	2a	.m.	0-64471		0	0-66451	
ATOM=	11	H	2a	.m.	-0-04646		0	0-16939	
Cell volume=239-8007 Angstrom**3. Mass of cell formula=516-3232 g. Specific gravity=3575-364 kg/m**3.									
(b) Model 18									
SPGNAME=P1; CELEDG=4-7110 4-8610 6-0948 Angstroms; CELANG=98-343 97-293 118-409 degrees.									
ATOM=	1	Si	1a	1	0-60745	0-30688	-0-08694		
ATOM=	2	Si	1a	1	0-27923	0-64581	-0-09153		
ATOM=	3	Al	1a	1	0-12998	0-83001	0-46033		
ATOM=	4	Al	1a	1	0-45552	0-47549	0-46197		
ATOM=	5	O	1a	1	0-48874	0-20603	0-63139		
ATOM=	6	O	1a	1	0-20730	0-57638	0-62973		
ATOM=	7	O	1a	1	0-31322	-0-00377	-0-02767		
ATOM=	8	O	1a	1	0-62511	0-64921	-0-03467		
ATOM=	9	O	1a	1	-0-03697	0-32318	-0-05858		
ATOM=	10	O	1a	1	0-38093	0-73614	0-27858		
ATOM=	11	O	1a	1	0-06684	0-10550	0-29864		
ATOM=	12	O	1a	1	0-74804	0-44101	0-28191		
ATOM=	13	O	1a	1	0-83349	0-83634	0-61216		
ATOM=	14	H	1a	1	0-61544	-0-09434	0-31189		
ATOM=	15	H	1a	1	0-06103	0-05239	0-13647		
ATOM=	16	H	1a	1	0-82848	0-29196	0-31165		
ATOM=	17	H	1a	1	0-87116	0-01639	0-72913		
Cell volume=118-3443 Angstrom**3. Mass of cell formula=258-1616 g. Specific gravity=3622-375 kg/m**3.									

Mercier and Le Page,⁴ the corresponding interlayer translations are respectively $(a+b)/3$ and $-a/3$ for models 3 and 18. Such transformations are not energetically possible at room pressure, but they are shown here to be energetically quite favourable above 15 GPa.

The phenomenon that is observed in both cases is that linear O–Si–O bridges perpendicular to aluminate layers links the silicate–aluminate layers. Analysis of possible such interlayer translations for parallel, unrotated layers, similar to the analysis in the authors' prior study,⁴ shows that $(a+b)/3$ and $-a/3$ are the only two possible such EDTs.

Hydrogen bond networks

The switch from tetrahedral to triangular dipyramidal coordination for silicon is accompanied by a drastic rearrangement of the hydrogen bond network between silicate–aluminate layers. Before the switch, the aluminol–hydrogen atoms of the top three OH groups in the aluminate slab are each pointing to a basal oxygen of the silicate groups of the next silicate–aluminate layer (e.g. see Figs. 2 and 3 in Mercier and Le Page⁴). After the switch, one of those three aluminol–hydrogen atoms points apically along the axis of the hexagons of silicate groups, establishing no hydrogen bond with a single oxygen atom. In contrast, the other two aluminol–hydrogen atoms now point toward the vacancy within the gibbsite-like aluminate layer.

Kaolin layer d spacings

Figure 5 reports the kaolin layer d spacings (in other words, $1/c^*$) under pressure for model 4 (kaolinite) and model 3 (model [KT1]b from Table 1 that spontaneously transforms around 12 GPa to the novel Cm model with interlayer translation $(a+b)/3$) as calculated from simulation results in Table S1. Figure 5 exposes clearly the much greater compressibility of model 3 than kaolinite (model 4). Although compression of kaolinite proceeds smoothly in the computer to pressures exceeding 60 GPa, a layer slipping transformation would lead to the Cm phase with much lower enthalpy. The authors expect this transformation to occur spontaneously in nature. Due to the several possibilities for the displacement vector, the authors expect the resulting material to be translationally disordered parallel to the silicate–aluminate layers, making full structure analysis quite

difficult. The diffraction signature of the transformation would then be a jump of $1/c^*$ from the top curve in Fig. 5 to the bottom curve. That jump may be abrupt if all layers switch to the new coordination at the same time, or gradual if some layers switch while others do not.

Conclusion

In a study aiming at disclosing low enthalpy kaolin polytypes deriving from kaolinite through a layer slipping transformation similar to that observed in dickite at 2 GPa, the authors serendipitously exposed a new family of polytypes. Those polytypes, based on unexpected translations by $-a/3$ and $(a+b)/3$ between adjacent silicate–aluminate layers, have lower enthalpy than kaolinite at pressures greater than 12–15 GPa. At 60 GPa, the enthalpy of the new polytypes is 1.4 eV per formula unit lower than that of kaolinite. As they derive from kaolinite by additional atomic scale translations $a/3$ or $b/3$ with no layer to layer rotation, those polytypes are prime candidates for a possible transformation of kaolinite at moderate pressures.

Table S1 contains a wealth of untapped structural information, like the evolution of silicate and aluminate coordination under pressure for the various models. The authors have no plans to exploit this information further and leave it to interested readers.

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