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Rational *ab initio* modeling for low energy hydrogen-bonded phyllosilicate polytypes

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Topics for the talk

Part 1

Concepts:

- Geometrically distinguishable stackings of 2 kaolin layers (Newnham 1962)
- Energy independence of non-adjacent layers
- Energy distinguishable low-energy structures (Mercier & Le Page 2008)
- No layer rotation upon solid state transformation (Dera et al. 2003)

Part 2

Model generation and ab initio quantum optimization

Part 3

Zero-pressure results

- Low energy / low enthalpy
- H vs P graph for kaolin polytypes
- Diagenetic interpretation

Part 4

Kaolin under high pressure (HP)

- New translations and HP phases predicted (Mercier & Le Page 2009)
- New HP polytypes observed (Welch & Crichton 2010)
- More HP polytypes predicted (Mercier, Le Page & Desgreniers 2010)

Part 5

Concln: When experiment is stalled, inexpensive theory can

- sift through “*known facts*”
- produce experimentally verifiable/falsifiable predictions

Progress
acceleration

Problem

Kaolin minerals are extremely abundant
and technologically important

but still

our knowledge of this system is an accumulation
of facts with many unanswered questions.

Why only four
minerals?

No explanation for observed
diagenetic sequence

Why those four?

Why is nacrite
rare?

Try *ab initio* quantum methods

Which polytype is stable under given
pressure and temperature conditions?

The ideal kaolin layer $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

The architecture of the kaolin layer derives from that of lizardite, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, by replacing the three Mg^{2+} ions within the mesh by two Al^{3+} ions and a vacancy $\square$.

This substitution destroys the threefold symmetry of lizardite and has been performed by replacing the Mg^{2+} atom at $2/3, 2/3, z$ along $[110]$ in the lizardite mesh by a vacancy.

As a result, the point-group symmetry is reduced from $31m$ to m .

Fig. 4

Energy independence for non-adjacent layers

Adjacent layers

Total energy U_{tot} is sum of energy for isolated kaolin layers plus corrections ΔA , ΔB , etc. for hydrogen bonding at single interfaces.

$$U_{\text{tot}} = U_A + U_B + U_C + \dots = n U_{\text{layer}} + \Delta A + \Delta B + \Delta C + \dots$$

As one of ΔA , ΔB , ΔC etc. is lower than all other ones, independence of non-adjacent layers implies that only transformations with that lowest energy ΔK are involved in the lowest-energy crystal stacking.

$[(R, T)]$ repeated

$[(R, T): (-R, T^*)]$ repeated

From stackings of two kaolin layers to low-energy phases

Hydrogen bonding between layers allows:

Mercier & Le Page (2008)
Acta Cryst. B 64: 131-143

Dera et al. (2003) Am. Min. 88: 1426-1435

dickite $\Leftrightarrow$ HP-dickite at $\sim 2\text{GPa}$

“Layer-shift phase transition does not provide a method of interconversion between the polytypes that differ by rotation of 1:1 layers”

Polytype transformations involving rotation of layers, like

kaolinite $\Rightarrow$ dickite or dickite $\Rightarrow$ nacrite

must occur through dissolution/recrystallization or reconstructive solid-solid mechanisms

Polytype Builder Tool operates on an ideal kaolin layer to create ideal polytype models with *Materials Toolkit*

Polytype builder

This polytype builder takes as input a P1 description of a (001) layer to be assembled into a polytype. All atom coordinates must be between 0 and 1. The top of the layer must be just below $z=1$. It then builds the polytype by implementing the operations below:

Same operation

(a) once and then the inverse operation

(b) repeated until a translation is generated.

Each new layer is automatically translated from the previous one by the thickness of the input cell, and then operated upon, KEEPING TRACK OF ITS ROTATED REFERENCE SYSTEM AND TRANSFORMED ORIGIN.

The new center of rotation is the transformed centre of rotation while the new translation is rotated from that applied to the previous layer.

Trigonometric rotation of each layer with respect to the previous one

$\pi /$ <== must be integers and preserve the (a,b) net.

Translation of the first new layer after its rotation

a + b does not have to be fractional

User-defined sequence of rotations and translations

the sequence of operations defined below.

Type in lines, each with 2 integers and 2 reals standing for the contents of the 4 dialog boxes above. The line below means: rotate by $2\pi / 3$ and then translate by $a/2 + b/3$. The rotation and translation are in the standard reference system of the previous layer.

You can type in as many lines as you want, but the sum of rotations should be an integer number of turns in order to imply periodicity.

Sequence:
(R,T)
(-R,T*)

Repeated application
of a same (R,T)

Any sequence of
(R,T) operations
with $\sum (R) = 2k\pi$

Ab initio optimization of ideal models

Straightforward implementation of *ab initio* modeling with *Materials Toolkit* quantum interface

Quantum
execution
on Athlon
Windows PCs:
~ 2 d each
(2-layer models)
up to
~ 2 weeks
(6-layer models)

Table 2

Low-energy stackings of two kaolin layers

Note: 1 meV per kaolin f.u. $\approx$ 0.0955 kJ mol⁻¹.

	Rotation					
	0	$\pi/3$	$2\pi/3$	π	$4\pi/3$	$5\pi/3$
(a) Repeated operations [K _i]						
Translation: 0						
Model No.	[K1]	[K2a]	[K3a]	[K4]	[K3a]*	[K2a]*
Space group	Cm	P6 ₃	P3 ₁	Cmc2 ₁	P3 ₂	P6 ₃
Free energy difference (meV per f.u.)	69	18	119	45	—	—
Volume difference (Å ³)	0.614	0.925	-1.081	0.459	—	—
Translation: $(2a + b)/3$						
Model No.	[K5a]	[K6a]	[K7a]	[K8a]	[K10a]*	[K9a]*
Space group	P1	P6 ₃	P3 ₁	P2 ₁	P3 ₂	P6 ₃
Free energy difference (meV per f.u.)	137	76	117	50	—	—
Volume difference (Å ³)	-2.863	0.433	-2.879	0.236	—	—
Translation: $(a + 2b)/3$						
Model No.	[K5a]*	[K9a]	[K10a]	[K8a]*	[K7a]*	[K6a]*
Space group	—	P6 ₃	P3 ₁	—	P3 ₂	P6 ₃
Free energy difference (meV per f.u.)	—	35	105	—	—	—
Volume difference (Å ³)	—	0.439	0.297	—	—	—
Translation: $a/3$						
Model No.	[K11a]	[K12a]	[K13a]	[K14a]	[K16a]*	[K15a]*
Space group	P1	P6 ₃	P3 ₁	P2 ₁	P3 ₂	P6 ₃
Free energy difference (meV per f.u.)	0	41	12	46	—	—
Volume difference (Å ³)	0.000	0.658	-0.085	-0.619	—	—
Translation: $b/3$						
Model No.	[K11a]*	[K15a]	[K16a]	[K14a]*	[K13a]*	[K12a]*
Space group	P1	P6 ₃	P3 ₁	P2 ₁	P3 ₂	P6 ₃
Free energy difference (meV per f.u.)	—	53	9	—	—	—
Volume difference (Å ³)	—	0.606	0.087	—	—	—
Translation: $2(a + b)/3$						
Model No.	[K17]	[K18a]	[K19a]	[K20]	[K19a]*	[K18a]*
Space group	Cm	P6 ₃	P3 ₁	Cmc2 ₁	P3 ₂	P6 ₃
Free energy difference (meV per f.u.)	72	183	107	131	—	—
Volume difference (Å ³)	-1.430	-1.387	-1.468	-0.972	—	—
(b) Succession of operations [K _i] and then [K _j]*, the enantiomorph of [K _i]						
Translation: 0						
Model No.	—	[K2b]	[K3b]	—	[K3b]* = [K3b]	[K2b]* = [K2b]
Space group	—	Cc	Cc	—	Cc	Cc
Free energy difference (meV per f.u.)	—	29	106	—	—	—
Volume difference (Å ³)	—	0.438	-0.860	—	—	—
Translation: $(2a + b)/3$						
Model No.	[K5b]	[K6b]	[K7b]	[K8b]* = [K8b]	[K10b]* = [K10b]	[K9b]* = [K9b]
Space group	Cc	Cc	Cc	Cc	Cc	Cc
Free energy difference (meV per f.u.)	135	78	112	51	—	—
Volume difference (Å ³)	-0.796	-0.061	-2.843	0.250	—	—
Translation: $(a + 2b)/3$						
Model No.	[K5b]*	[K9b]	[K10b]	[K8b]* = [K8b]	[K7b]* = [K7b]	[K6b]* = [K6b]
Space group	Cc	Cc	Cc	Cc	Cc	Cc
Free energy difference (meV per f.u.)	—	39	132	—	—	—
Volume difference (Å ³)	—	-2.179	-0.826	—	—	—
Translation: $a/3$						
Model No.	[K11b]	[K12b]	[K13b]	[K14b]* = [K14b]	[K16b]* = [K16b]	[K15b]* = [K15b]
Space group	Cc	Cc	Cc	Cc	Cc	Cc
Free energy difference (meV per f.u.)	14	32	8	24	—	—
Volume difference (Å ³)	0.189	0.367	0.046	1.016	—	—
Translation: $b/3$						
Model No.	[K11b]*	[K15b]	[K16b]	[K14b]* = [K14b]	[K13b]* = [K13b]	[K12b]* = [K12b]
Space group	Cc	Cc	Cc	Cc	Cc	Cc
Free energy difference (meV per f.u.)	—	32	2	—	—	—
Volume difference (Å ³)	—	0.321	0.208	—	—	—
Translation: $2(a + b)/3$						
Model No.	—	[K18b]	[K19b]	—	[K19b]* = [K19b]	[K18b]* = [K18b]
Space group	—	Cc	Cc	—	Cc	Cc
Free energy difference (meV per f.u.)	—	182	112	—	—	—
Volume difference (Å ³)	—	-1.350	-1.706	—	—	—

kaolinite-II

Welch &
Crichton (2010)
Am. Min.
95: 651-654

kaolinite

nacrite

Blind optimization
of 36 ideal models
gives all four
polytypes then
known, including
their distortions.HP-dickite
(dickite-II)Dera et al. (2003)
Am. Min.
88: 1428-1435

dickite

Other main observations

- Lowest energy is for kaolinite
- Next lowest energy is for dickite
- Half-a-dozen solutions with competitive energy
- Nacrite and HP-dickite are NOT among the very low energy solutions
- Highest energy is 183 meV ($\sim 18\text{kJ/f.u.}$) higher than kaolinite

r.m.s. value
of calculated energy difference
between the
16 analogous EDT and EDT:EDT* stackings

$\sim 13 \text{ meV} = \sim 1.2 \text{ kJ/mol}$
per formula unit
($\sim \frac{1}{2} k_B T$)

wide occurrence of
stacking disorder
in kaolin samples

energy contribution
due to
non-adjacent layers
interactions

ab initio energy
calculation error

both capped to $\approx 13 \text{ meV}$

Mercier & Le Page (2008)
Acta Cryst. B 64: 131-143

Free Energy *versus* Enthalpy

stable phase of
a material
at given pressure P

lowest enthalpy H

$$H = U + PV$$

U : total energy
 V : volume at P

$P = 0$

lowest energy:
kaolinite

next lowest energy:
dickite

calculable from
from 0P results

P small

$$\Delta H = \Delta U + P\Delta V$$

enthalpy difference between
a given (polytype) phase and kaolinite

Stability of kaolin polytypes at 0K

Experimental measurements of free energy

	experimental enthalpy diff.	<i>ab initio</i> total energy diff.
kaolinite --dickite	-14.3(4.3) Ligny & Navrotsky 1999	-0.2(1.2) this work
	-18.5(3.3) Fialips et al. 2003	
	discrepancy	
dickite --nacrite	-3.6(4.8) Ligny & Navrotsky 1999	-5.5(1.2) this work
	full agreement

Experimental enthalpy of kaolinite too negative by ~15kJ/mol

$$\Delta H(P, T = 300\text{K})$$

dickite $\leftrightarrow$ HP-dickite
exp. phase transition

This diagram derives from the $T=0\text{K}$ diagram by two assumptions:

- (1) a correction for a 2GPa bias in all calculated P
- (2) a shift to the left by 5 MPa K^{-1} for the line about HP-dickite

narrow stability range for nacrite
wedged between
kaolinite at low P and HP-dickite at high P

$$\Delta H(P, T = 600\text{K})$$

no more
stability
range for
nacrite at
 $T > \sim 450\text{K}$

Mercier & Le Page (2008) *Acta Cryst. B* 64: 131-143

Diagenesis of kaolin minerals

No direct solid-state transformation of kaolinite into dickite or nacrite occurs at any point in the process.

⇒ The kaolinite ↔ dickite and kaolinite ↔ nacrite transformations involve layer-layer rotations and would require reconstruction of kaolin layers.

Kaolinite, nacrite and HP-dickite crystallize in the pores of sandstones according to their respective thermodynamic domain of stability.

HP-dickite transforms reversibly into dickite via a solid-state reaction around 2 GPa. The phase observed in the laboratory is therefore dickite, which is metastable at ambient conditions, whereas the phase that formed *in situ* is HP-dickite.

Nacrite forms at pressure and temperature combinations not found with normal geothermal gradient.

We have explained

- Existence of the four known kaolin polytypes
- Diagenetic sequence and coexistence of kaolin minerals
- Role of HP-dickite in diagenetic sequence
- Stacking defects observed in kaolinite (Bookin et al. 1989)

Not Explained

- Non-observation of additional kaolin polytypes
(They might synthesize, but at zero pressure only.)

Question marks raised (more experimental work needed)

- High P - T transformations of kaolinite $\leftrightarrow$ nacrite $\leftrightarrow$ dickite
- Experimental free energy value of kaolinite

Ab initio compression of kaolinite at 0K

Mercier & Le Page (2009)
Mat. Sc. & Tech. 25: 437-442

zero pressure
Mercier & Le Page (2008)

energy independence between
second-neighbour layer

moderate pressure
Mercier & Le Page (2009)

energy independence between
third-neighbour layer

what
happens
here

barely depends on
what happens

here

$$U_{\text{tot}} = U_{\text{layer}} + \Delta A + \Delta B + \Delta C + \dots$$

stacking of single layers

$$U_{\text{tot}} = U([A:B], [C:D], \dots) = \langle U \rangle + \Delta[B:C] + \Delta[D:E] + \dots$$

stacking of pre-assembled *pairs of layers*

ab initio results
implied that
kaolinite
would transform
upon compression

*But the two lowest
enthalpy models
that resulted
accidentally
are in fact
**not any of the
19 stackings
originally built***

five-fold
silicon
coordination

new family of
kaolin polytypes
based on
translations
not possible
at low pressure

Novel $-\mathbf{a}/3$, $-\mathbf{b}/3$ and $(\mathbf{a}+\mathbf{b})/3$ translations

(not possible at low pressure)

Experimental compression of Keokuk kaolinite to 7.8 GPa

Welch & Crichton (2010) Am. Min. 95: 651-654

kaolinite-I 3.4 GPa
(ambient phase)

kaolinite-II 4.5 GPa

kaolinite-III 7.8 GPa

Model [K5a] (Mercier & Le Page 2008)
Model [KT1]a (Mercier & Le Page 2009)

**Novel $-a/3$ translation
predicted by
Mercier & Le Page 2009**

**Model [KP01]a in
Mercier et al. (2010) Am. Min. 95: 1117-1120
...and also more predicted phases...**

More HP polytypes predicted

Mercier et al. (2010)
Am. Min. 95: 1117-1120

kaolinite-IV

nacrite-II

dickite-III

TABLE 1a. Repeated application of (R,T)

Translation T	Rotation R					
	0	$\pi/3$	$2\pi/3$	π	$4\pi/3$	$5\pi/3$
–a/3	[KP01]a	[KP11]a	[KP21]a	[KP31]a	[KP22]a*	[KP12]a*
Space group	<i>P1</i>	<i>P6₁</i>	<i>P3₁</i>	<i>P2₁</i>		
H (eV/fu)	–105.645	–105.550	–105.609	–105.659		
V/fu (Å ³)	131.84	132.15	132.21	132.27		
–b/3	[KP01]a*	[KP12]a	[KP22]a	[KP31]a*	[KP21]a*	[KP11]a*
Space group		<i>P6₁</i>	<i>P3₁</i>			
H (eV/fu)		–105.642	–105.539			
V/fu (Å ³)		132.59	132.21			
(a+b)/3	[KP03]a	[KP13]a	[KP23]a	[KP33]a	[KP23]a*	[KP13]a*
Space group	<i>Cm</i>	<i>P6₁</i>	<i>P3₁</i>	<i>Cmc2₁</i>		
H (eV/fu)	–105.576	–105.632	–105.620	–105.579		
V/fu (Å ³)	131.51	132.25	132.14	131.61		

TABLE 1b. Repeated application of the sequence [(R,T):(R*,T*)]

Translation T	Rotation R					
	0	$\pi/3$	$2\pi/3$	π	$4\pi/3$	$5\pi/3$
–a/3	[KP01]b	[KP11]b	[KP21]b	[KP31]b	=[KP22]b	= [KP12]b
Space group	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>		
H (eV/fu)	–105.608	–105.557	–105.622	–105.636		
V/fu (Å ³)	131.88	132.10	131.62	132.38		
–b/3	=[KP01]b	[KP12]b	[KP22]b	=[KP31]b	= [KP21]b	= [KP11]b
Space group		<i>Cc</i>	<i>Cc</i>			
H (eV/fu)		–105.633	–105.535			
V/fu (Å ³)		131.93	131.84			
(a+b)/3	=[KP03]a	[KP13]b	[KP23]b	=[KP33]a	= [KP23]b	= [KP13]b
Space group	<i>Cm</i>	<i>Cc</i>	<i>Cc</i>	<i>Cmc2₁</i>		
H (eV/fu)	–105.576	–105.648	–105.624	–105.579		
V/fu (Å ³)	131.51	132.24	131.76	131.62

SUMMARY

From assumed energy independence of non-adjacent kaolin layers we have:

- shown that only 36 crystalline stackings could have lowest energy
- built idealized models for them and optimized them ab initio

MLP08

From this optimization, we have:

- rationalized the existence of the four known kaolin polymorphs
- proposed H/P/T graphs explaining known facts about kaolin system
- exposed as inconsistent an experimental measurement of free energy
- predicted a new family of phases for compression of kaolinite
- that family has subsequently been observed independently
- predicted a further phase transformation in kaolinite
- predicted structures that dickite-III and nacrite-II might adopt upon compression

MLP08

MLP09

WC10

MLPD10

Concluding remarks

Complementarity of experiment and *ab initio* modeling

Disparate experimental facts
about a crystal-chemical system of materials
allow no further scientific deduction

Ab initio modeling:

- helps to rationalize the crystal chemistry of the materials system
- proposes explanations for the phase changes observed in the system
- predicts verifiable facts and exposes dubious concepts

MLP08

MLP09

MLPD10

we are back
here,
after one full turn
around the loop

kaolin
system

until
everything
makes sense

WC10

- New experimental facts, explained or not

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