粘土鉱物学の基礎 (2)：粘土鉱物の構造

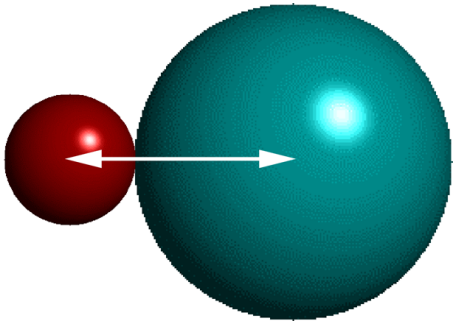
1）粘土鉱物の構造と分類
- ◆ ポーリングの原理と配位数
- ◆ 構造単位と基本構造
- ◆ 層電荷と分類基準
- ◆ 混合層鉱物
- ◆ 非晶質鉱物

2）粘土鉱物のX線回折
- ◆ X線回折の原理と回折プロフィル
- ◆ 混合層構造の判定
- ◆ 2八面体型と3八面体型
- ◆ ポリタイプ

ポーリングの原理 (Pauling's Rules)

1st Rule

The cation-anion distance = Σ radii



Can use R_C/R_A to determine the coordination number of the cation

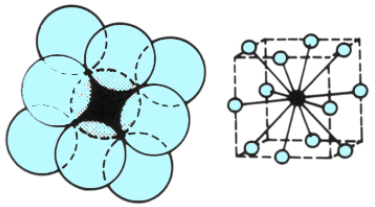
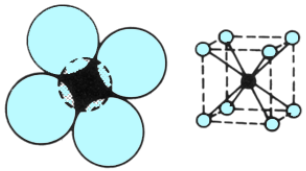
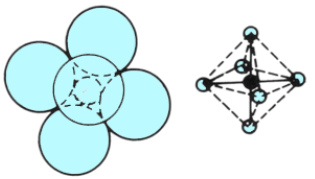
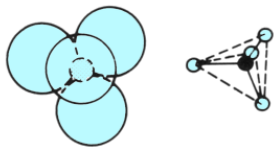
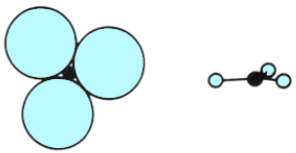
This is an important rule to constract crystal structure of clay minerals

配位数と原子配置

イオン半径と配位数

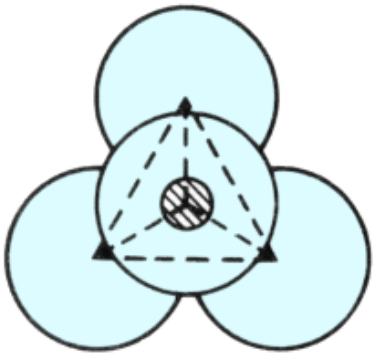
Cations	Radii	Coordination with O^{2-}	Anions
K^+	1.38 Å	8, 12	S^{2-} 1.84 Å
Na^+	1.02 Å	6, 8	
Ca^{2+}	1.00 Å	6, 8	Cl^- 1.81 Å
Mn^{2+}	0.83 Å	6	
Fe^{2+}	0.78 Å	6	O^{2-} 1.40 Å
Mg^{2+}	0.72 Å	6	
Fe^{3+}	0.64 Å	6	OH^- 1.40 Å
Ti^{4+}	0.61 Å	6	
Al^{3+}	0.535 Å	4, 6	F^- 1.33 Å
Si^{4+}	0.26 Å	4	
C^{4+}	0.15 Å	3	

イオン半径と原子配置

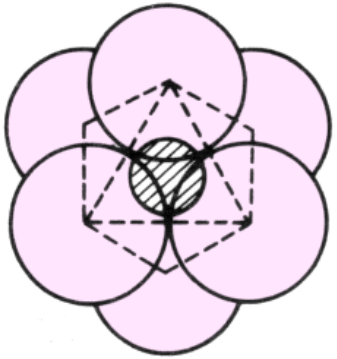
Radius ratio	Coordination number	Atomic structure
1	12	
0.73–1	8	
0.41–0.73	6	
0.22–0.41	4	
0.15–0.22	3	

粘土鉱物の構造単位

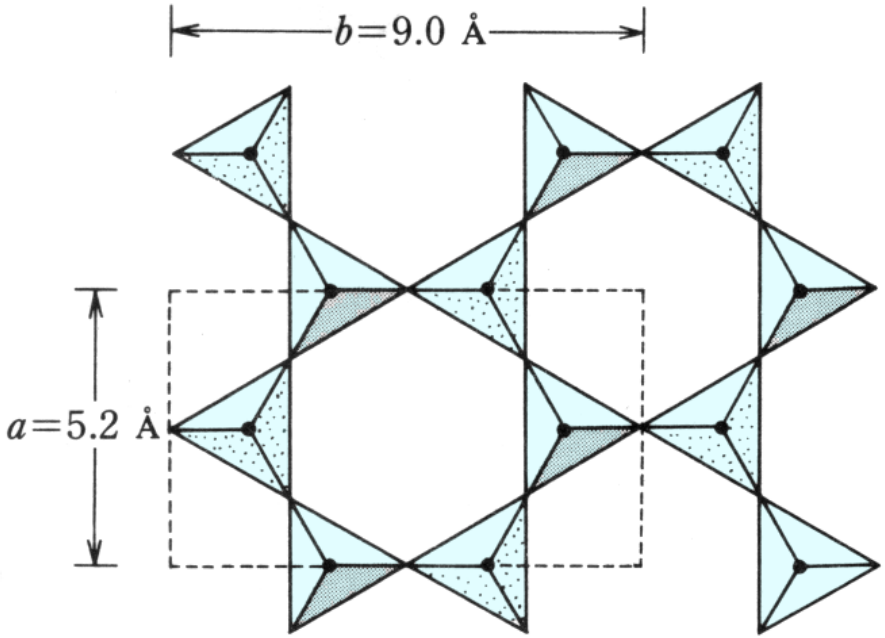
Si-O四面体 (SiO_4)



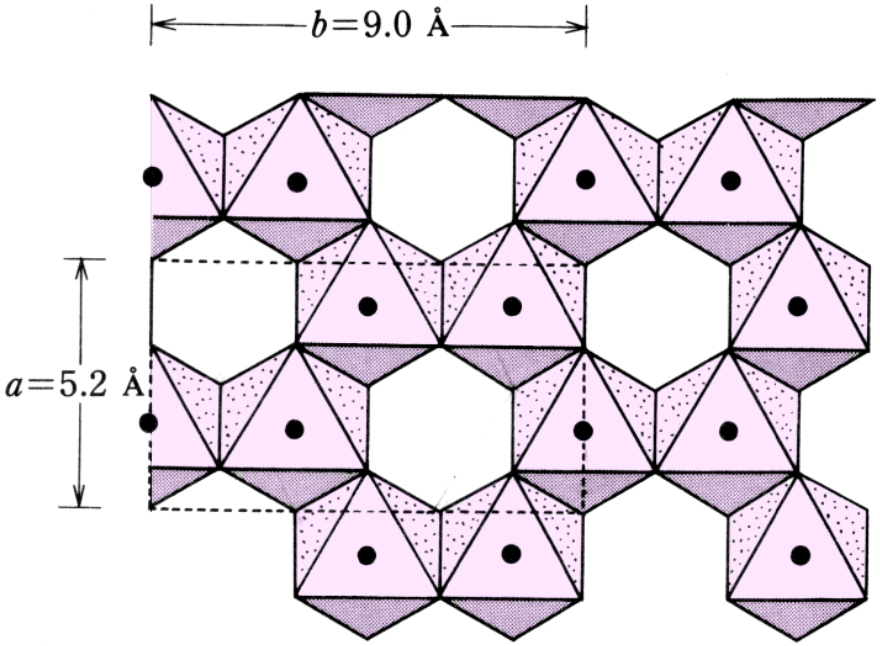
Al-O八面体 (AlO_6) or Mg-O八面体 (MgO_6)



四面体シート (Si_4O_{10} / 単位格子)

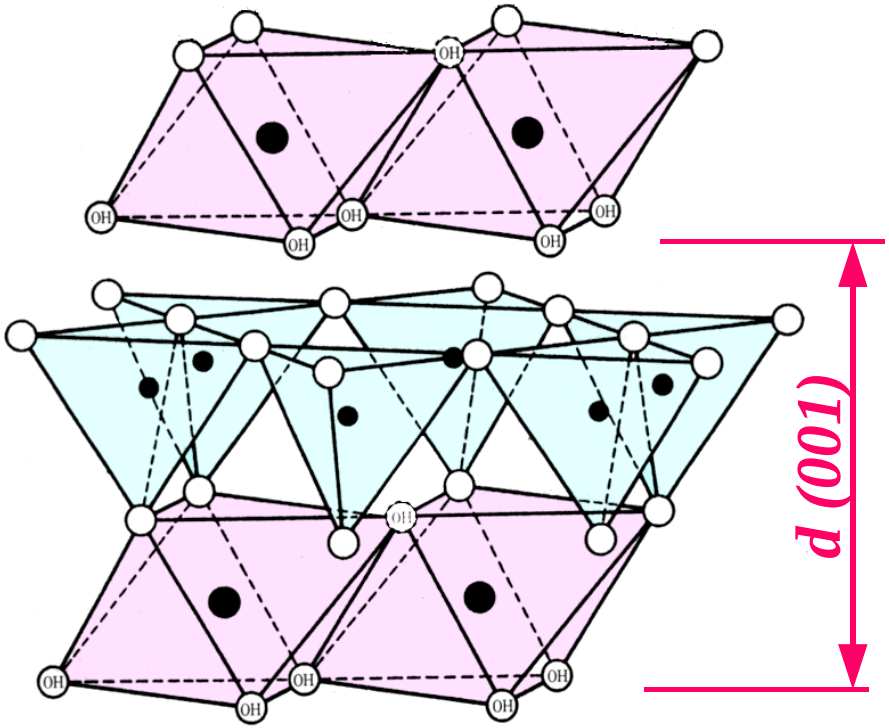


八面体シート (Al_4O_{12} or Mg_6O_{12}/ 単位格子)



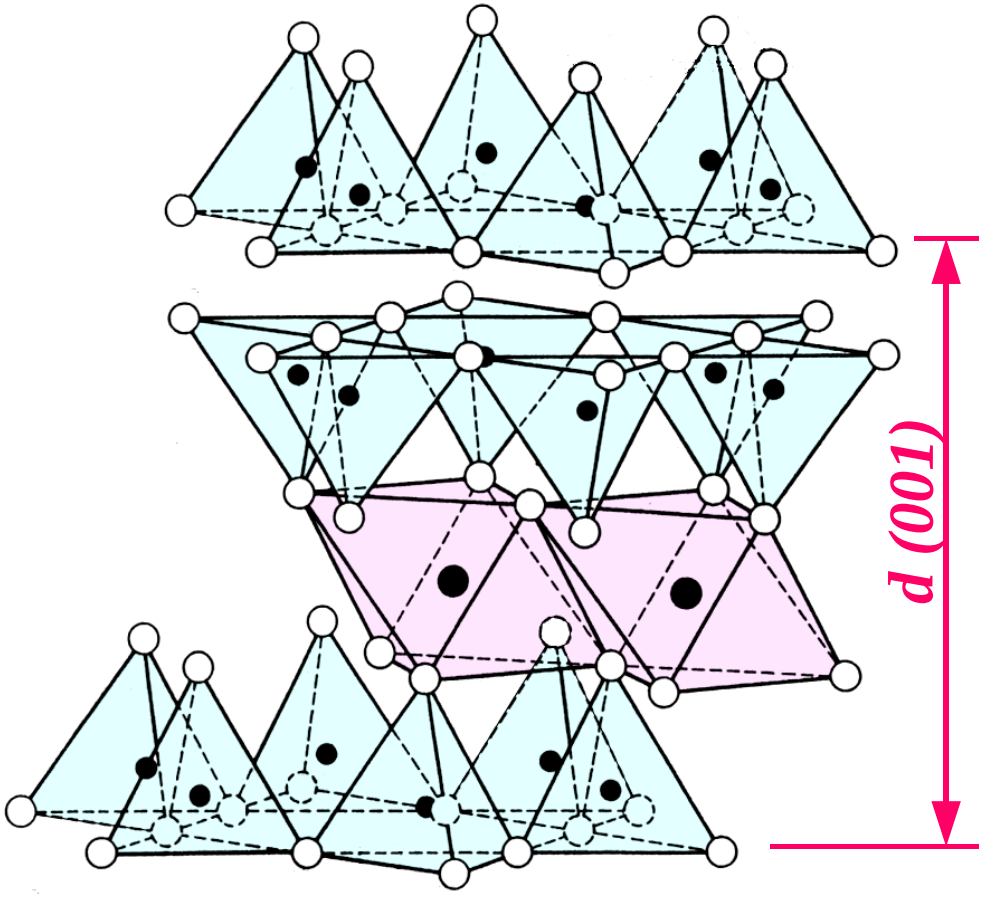
粘土鉱物の基本構造

A) カオリナイト構造



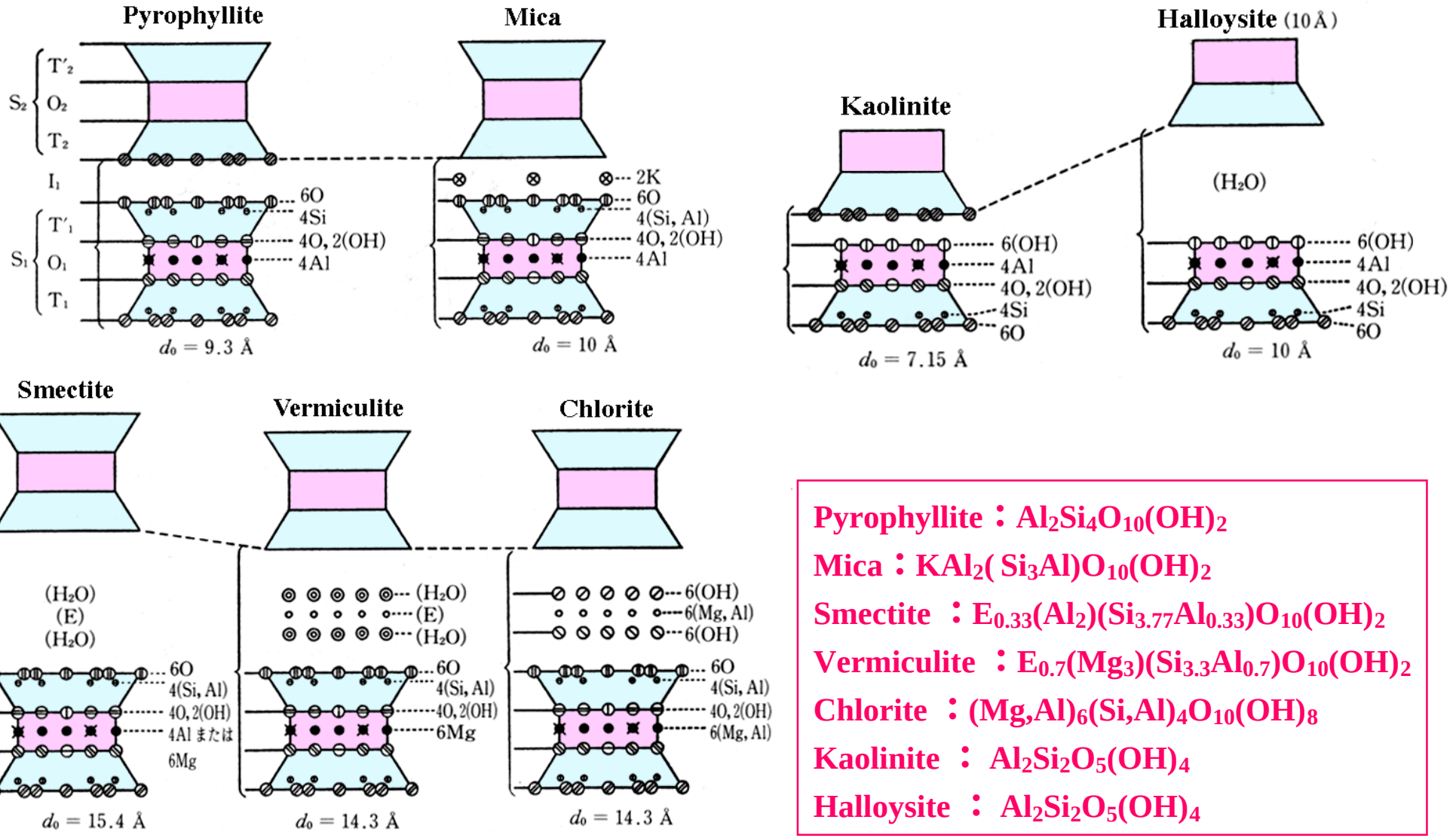
d (001) = 7.15 Å

B) パイロフィライト構造



d (001) = 9.3 Å

主な粘土鉱物の構造



Pyrophyllite：$Al_2Si_4O_{10}(OH)_2$

Mica：$KAl_2(Si_3Al)O_{10}(OH)_2$

Smectite ：$E_{0.33}(Al_2)(Si_{3.77}Al_{0.33})O_{10}(OH)_2$

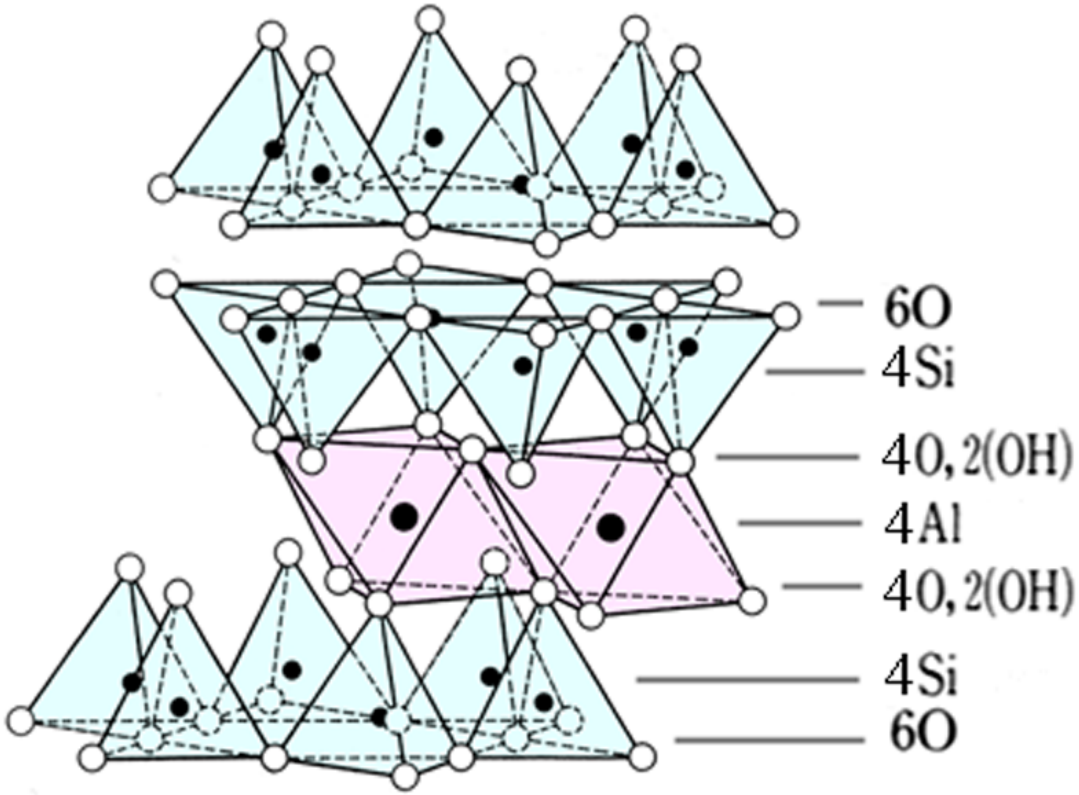
Vermiculite ：$E_{0.7}(Mg_3)(Si_{3.3}Al_{0.7})O_{10}(OH)_2$

Chlorite ：$(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$

Kaolinite ： $Al_2Si_2O_5(OH)_4$

Halloysite ： $Al_2Si_2O_5(OH)_4$

粘土鉱物の層電荷



Pyrophyllite：$Al_4Si_8O_{20}(OH)_4$

Total charge = (3×4)+(4×8) + (-2×20) +(-1×4)

= 12 + 32 + (-40) + (-4)

= 44 + (-44) = 0

Smectite group minerals

Montmorillonite

$$E_{0.33}\underbrace{(Al_{1.73}Mg_{0.33})}_{-0.33}Si_4O_{10}(OH)_2$$

Beidelite

$$E_{0.33}(Al_{2.00})\underbrace{(Si_{3.77}Al_{0.33})}_{-0.33}O_{10}(OH)_2$$

Nontronite

$$E_{0.33}(Fe^{3+}{}_{2.00})\underbrace{(Si_{3.77}Al_{0.33})}_{-0.33}O_{10}(OH)_2$$

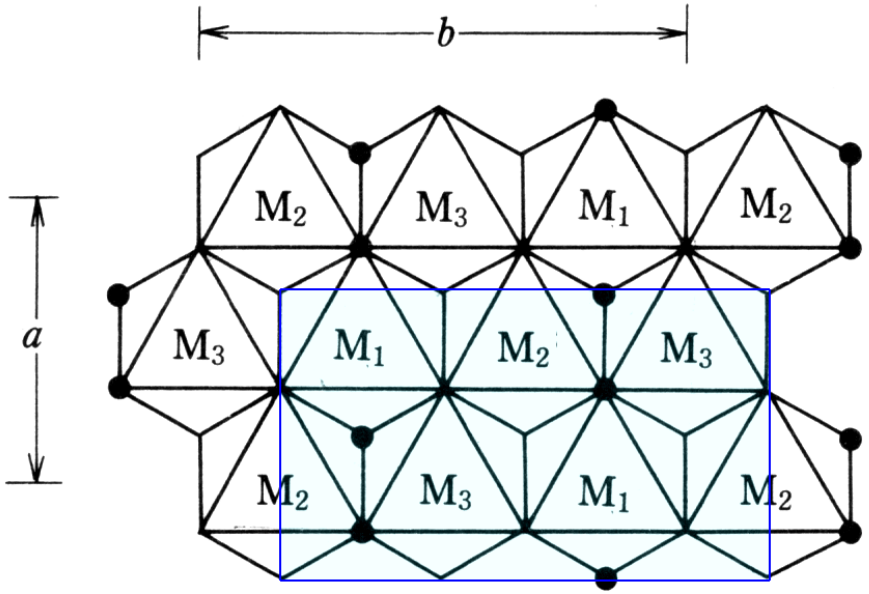
Saponite

$$E_{0.33}(Mg_{3.00})\underbrace{(Si_{3.77}Al_{0.33})}_{-0.33}O_{10}(OH)_2$$

Hectorite

$$E_{0.33}\underbrace{(Mg_{2.67}Li_{0.33})}_{-0.33}Si_4O_{10}(OH)_2$$

2八面体構造と3八面体構造



M_1 ……..... Trance position

M_2, M_3 ….. Cis position

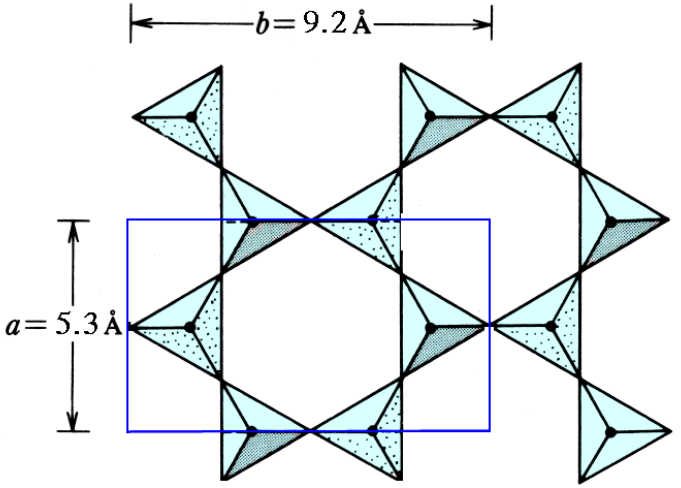
Brucite ($Mg(OH)_2$) → $Mg_6(OH)_{12}$

a = 5.40 Å, b = 9.36 Å

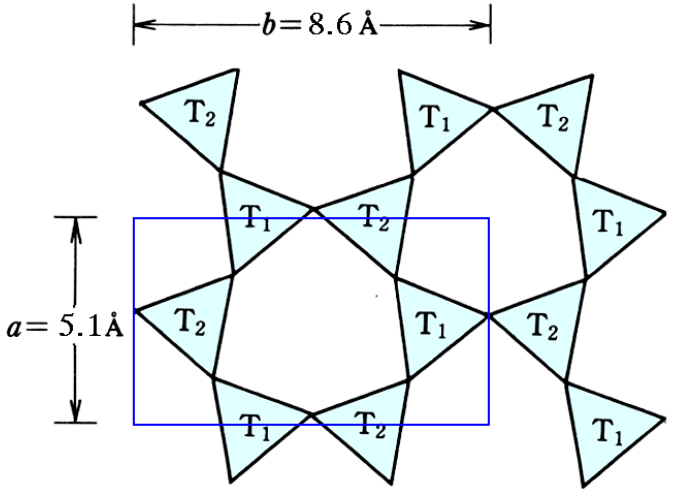
Gibbsite ($Al(OH)_3$) → $Al_4(OH)_{12}$

a = 5.08 Å, b = 8.64 Å

A) Trioctahedral type



B) Dioctahedral type



粘土鉱物の分類

TABLE 1.1. Classification of phyllosilicates related to clay minerals

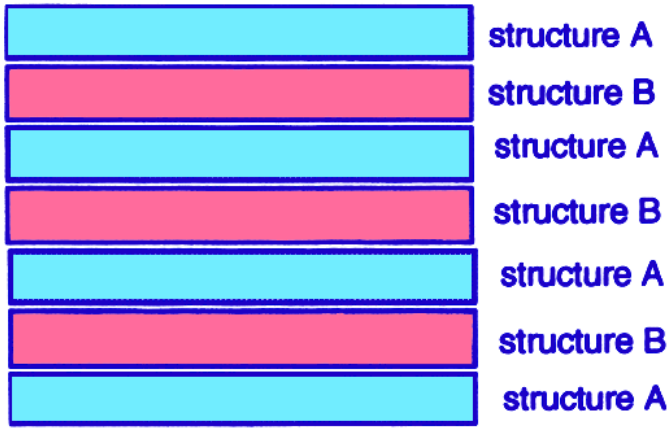
Layer type	Group (x = charge per formula unit)†	Sub-group	Species*
1:1	Serpentine–kaolin ($x \sim 0$)	Serpentines	Chrysotile, antigorite, lizardite, amesite
		Kaolins	Kaolinite, dickite, nacrite
2:1	Talc–pyrophyllite ($x \sim 0$)	Talcs	Talc, willemseite
		Pyrophyllites	Pyrophyllite
	Smectite ($x \sim 0{\cdot}2$–$0{\cdot}6$)	Saponites	Saponite, hectorite, sauconite
		Montmorillonites	Montmorillonite, beidellite, nontronite
	Vermiculite ($x \sim 0{\cdot}6$–$0{\cdot}9$)	Trioctahedral vermiculites	Trioctahedral vermiculite
		Dioctahedral vermiculites	Dioctahedral vermiculite
	Mica ($x \sim 1{\cdot}0$)	Trioctahedral micas	Phlogopite, biotite, lepidolite
		Dioctahedral micas	Muscovite, paragonite
	Brittle mica ($x \sim 2{\cdot}0$)	Trioctahedral brittle micas	Clintonite, anandite
		Dioctahedral brittle micas	Margarite
	Chlorite (x variable)	Trioctahedral chlorites	Clinochlore, chamosite, nimite
		Dioctahedral chlorites	Donbassite
		Di,trioctahedral chlorites	Cookeite, sudoite
2:1 inverted ribbons	Sepiolite-palygorskite (x variable)	Sepiolites	Sepiolite, loughlinite
		Palygorskites	Palygorskite

* Only a few examples are given.

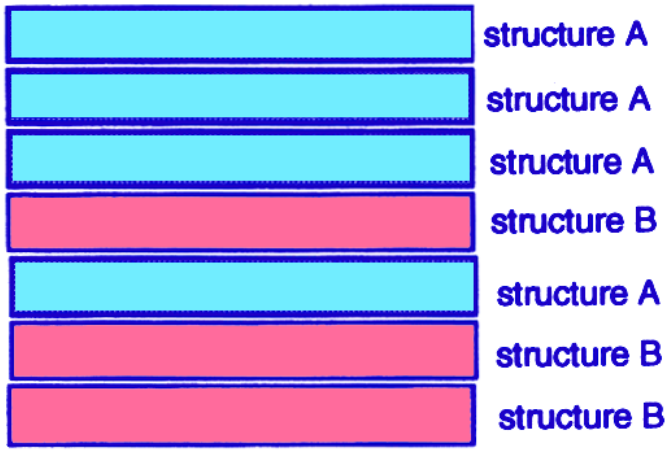
† x refers to an $O_{10}(OH)_2$ formula unit for smectite, vermiculite, mica and brittle mica.

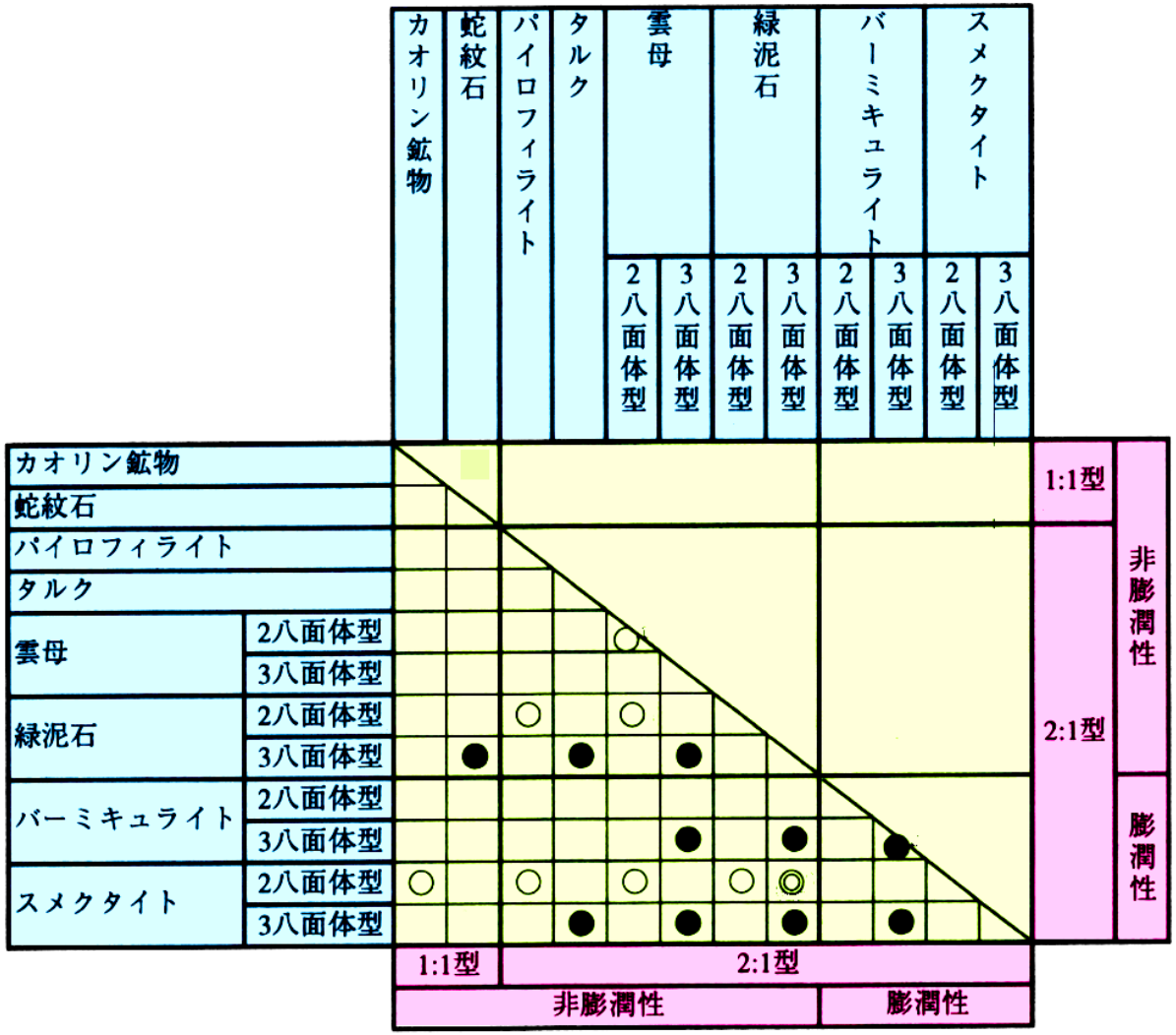
混合層粘土鉱物

Regular Mixed Layering

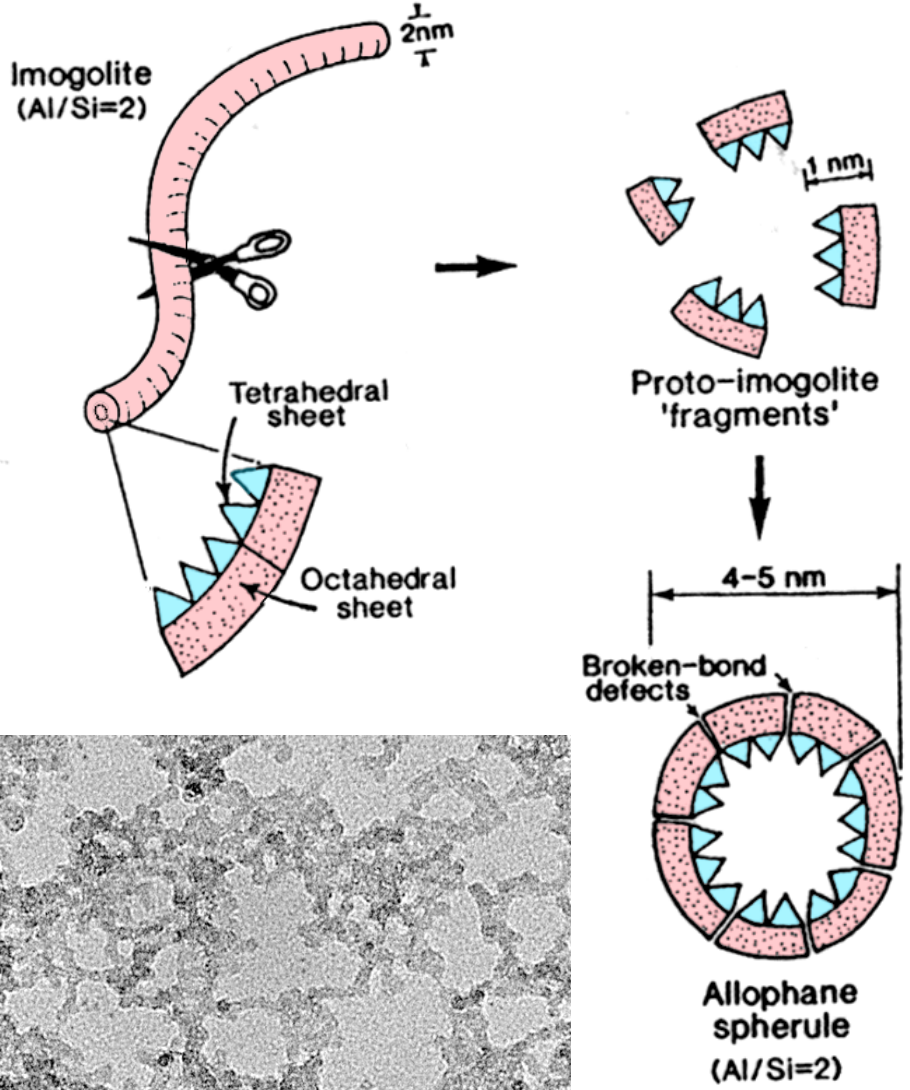


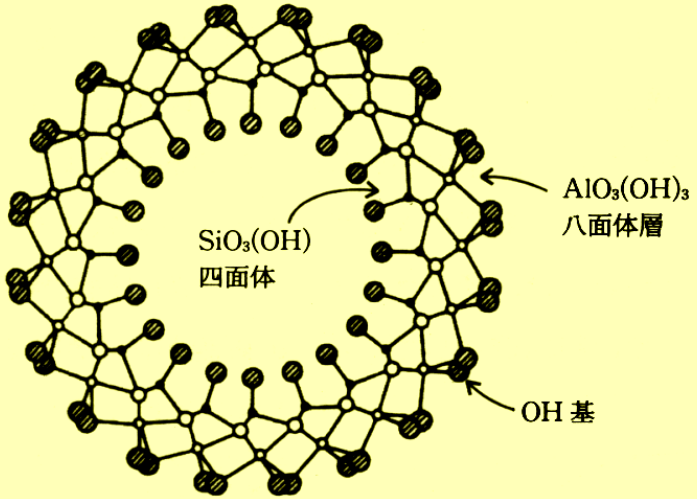
Random Mixed Layering





非晶質粘土鉱物と関連物質

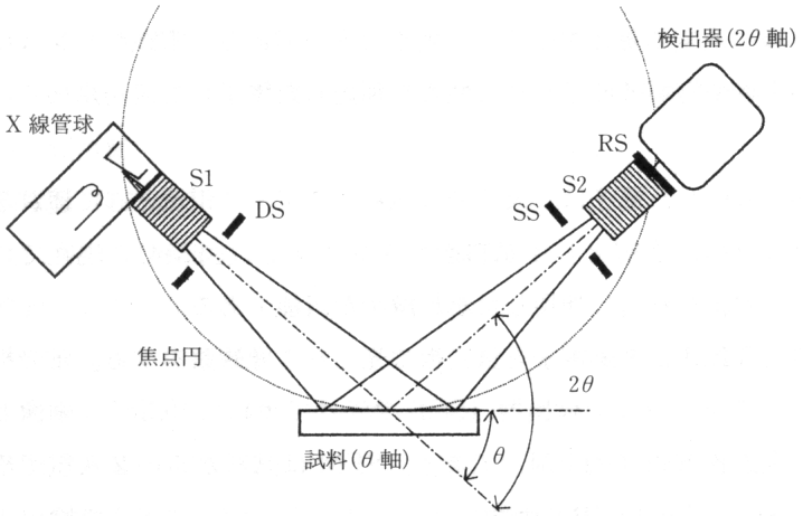




Stractural model of allophane

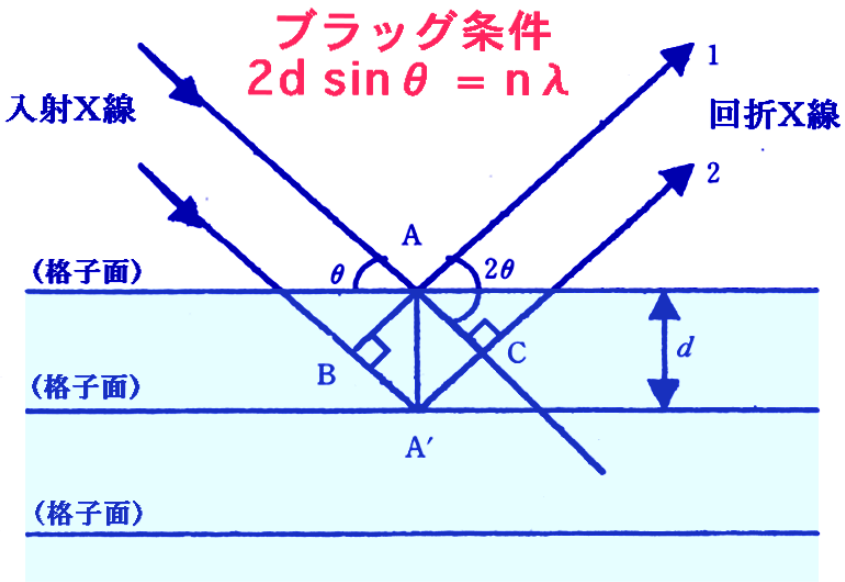
- **Allophane**
  - **Proto-imogolite allophane (Si/Al = 0.5)**
  - **Proto-halloysite allophane (Si/Al = 1.0)**
- **Hydrous feldspathoid**
- **Amorphous silica**
- **Amorphous $Al(OH)_3$**
- **Amorphous $Fe(OH)_3$**
- **Ferrihydrite**

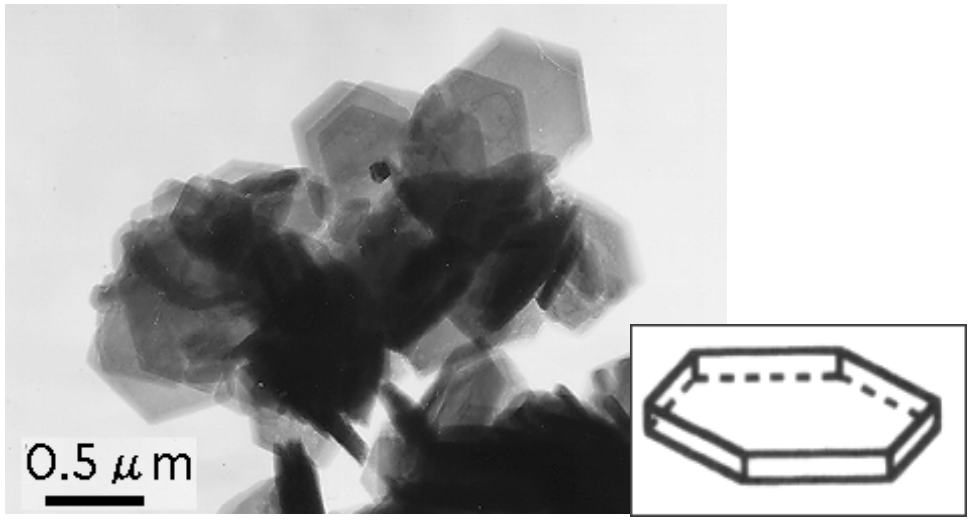
粘土鉱物のX線回折

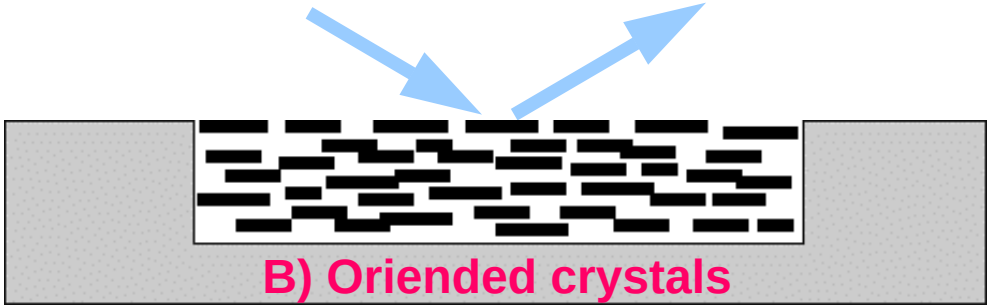


DS：発散スリット，SS：散乱スリット，RS：受光スリット，S1,S2：ソーラスリット

粉末 X 線回折装置のゴニオメータ光学系の例

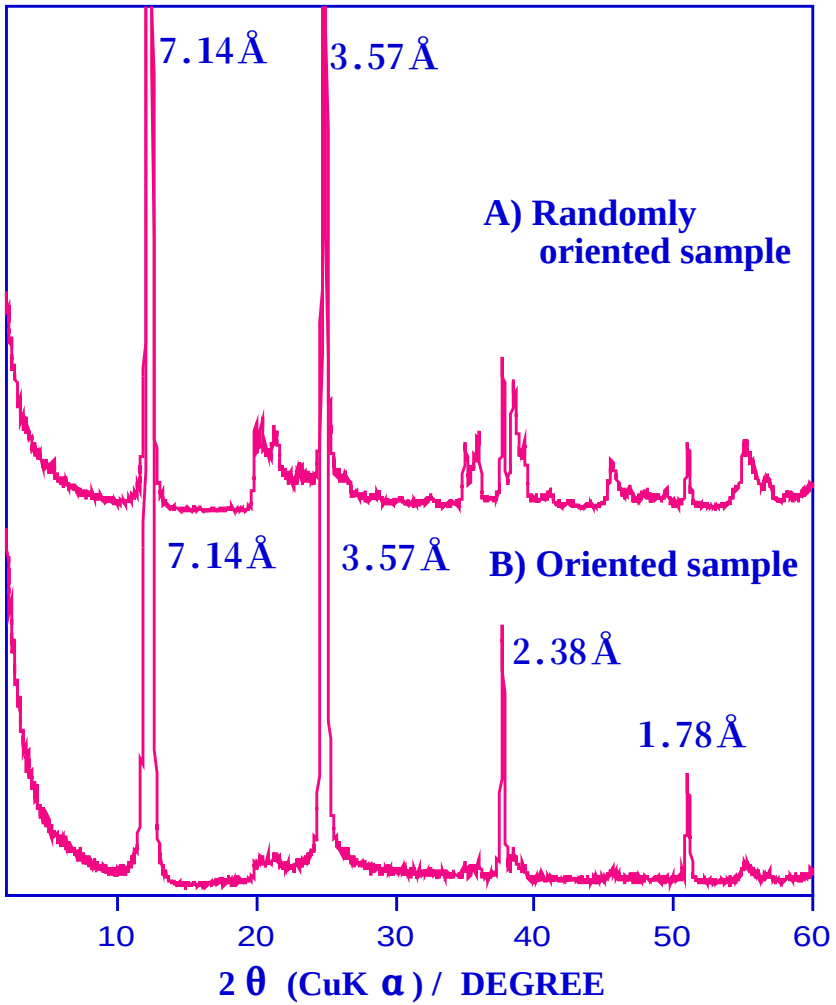




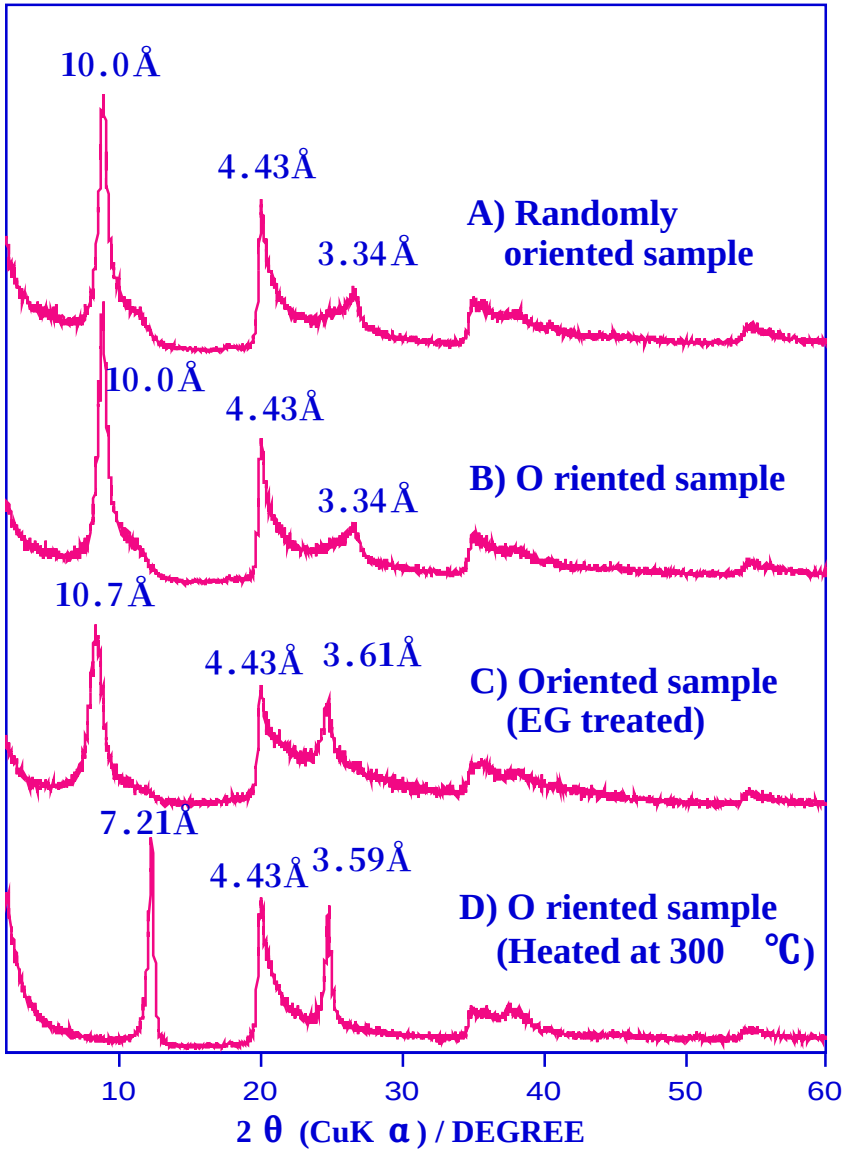


カオリナイトとハロイサイトのX線回折

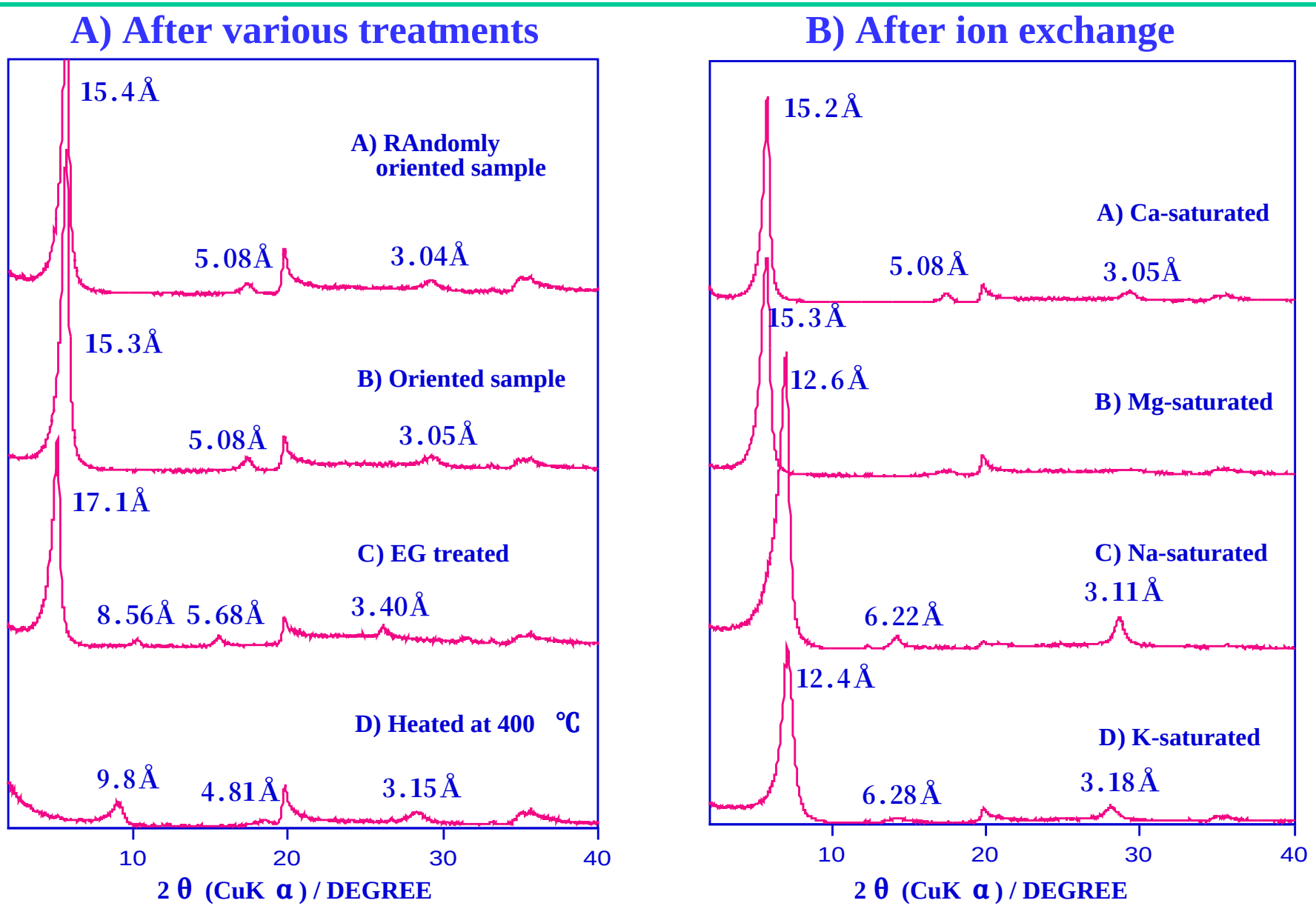
XRD profiles of kaolinite



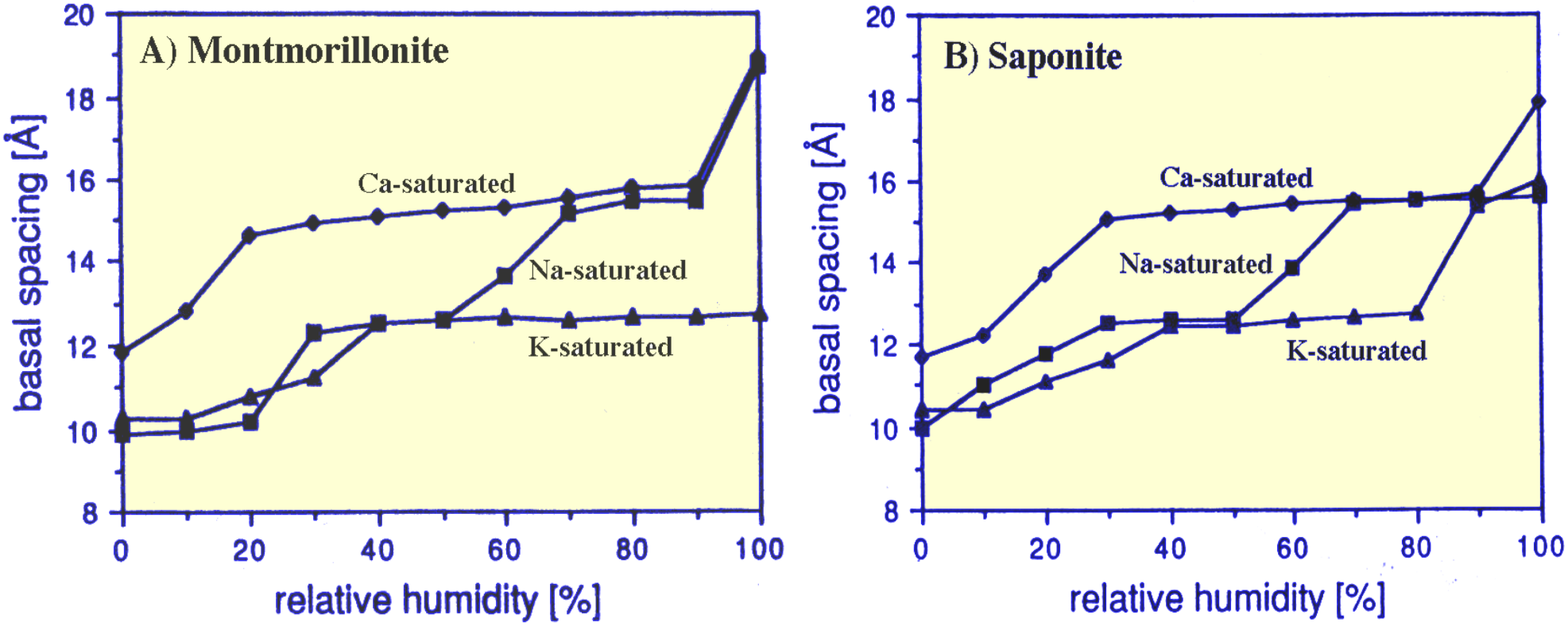
XRD profiles of halloysite



スメクタイトのX線回折



底面間隔の湿度変化



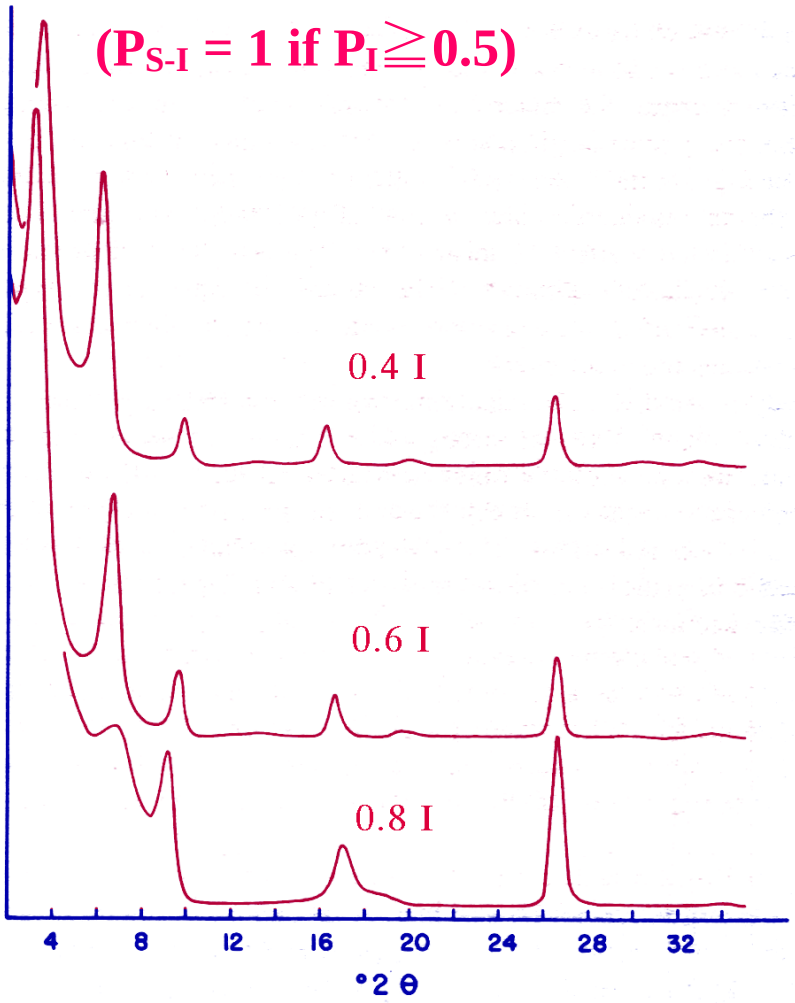
膨潤能力の比較

層間イオン：$Ca^{2+} > Na^{+} > K^{+}$

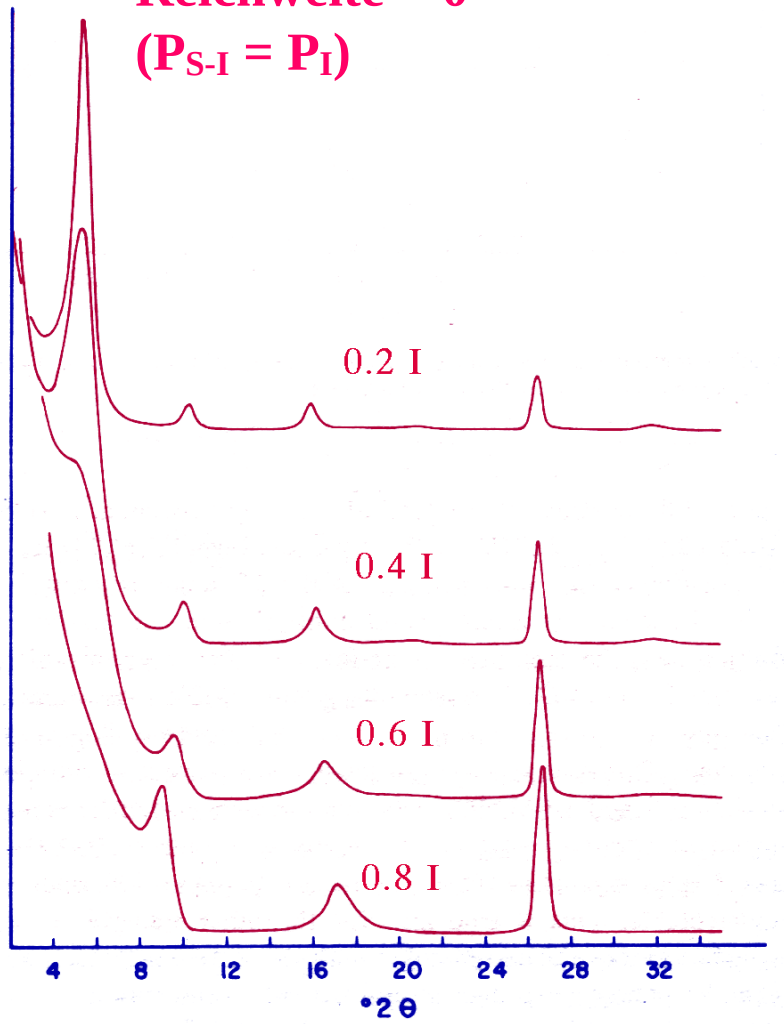
八面体構造：3八面体型 > 2八面体型

混合層粘土鉱物のX線回折プロフィル

Regularly Interstratified
illite/smectite
Reichweite = 1
(P_{S-I} = 1 if $P_I \geqq 0.5$)

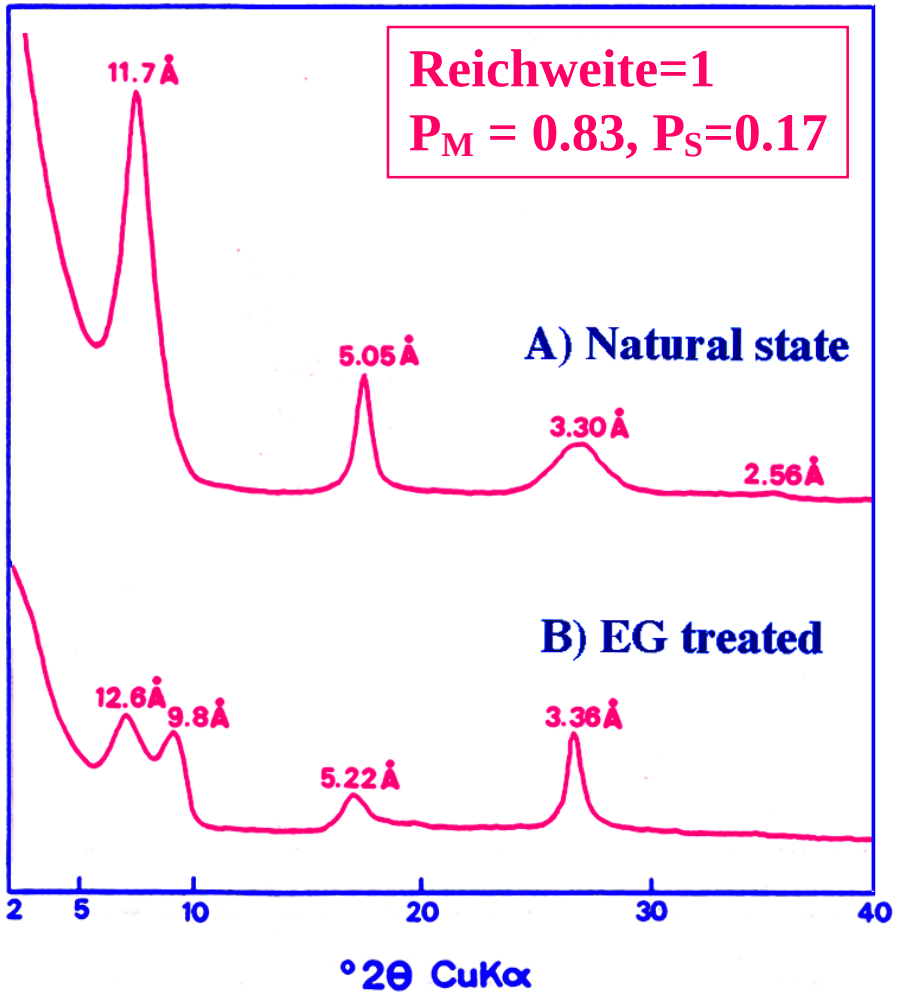


Randomly Interstratified
illite/smectite
Reichweite = 0
($P_{S-I} = P_I$)

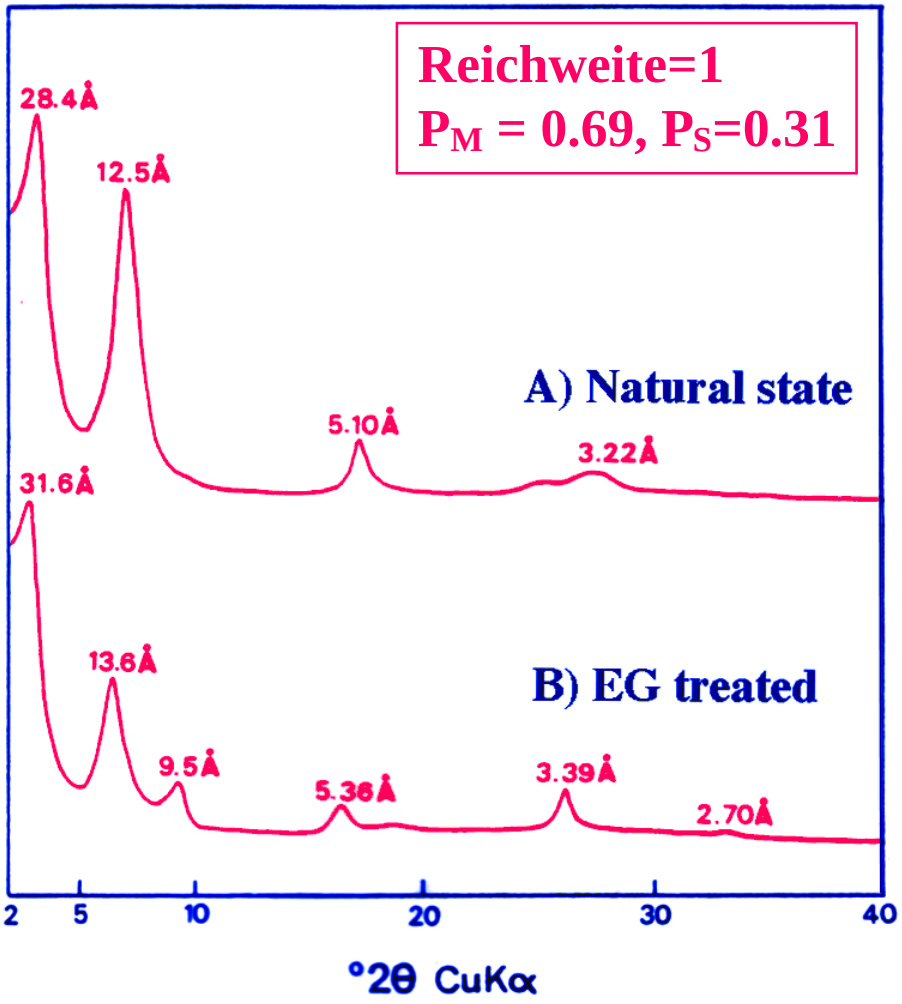


混合層粘土鉱物（イライト／スメクタイト）

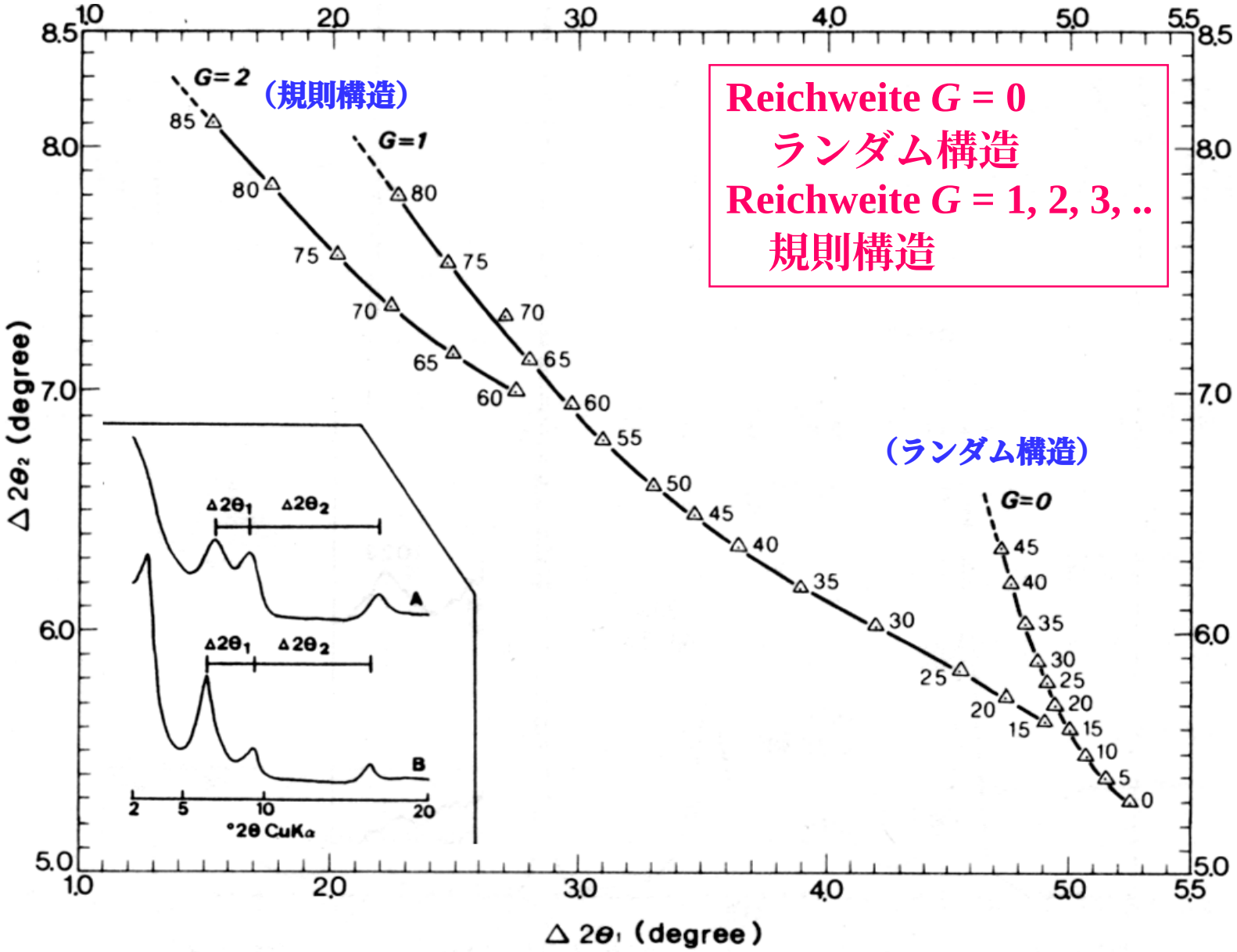
Sample A



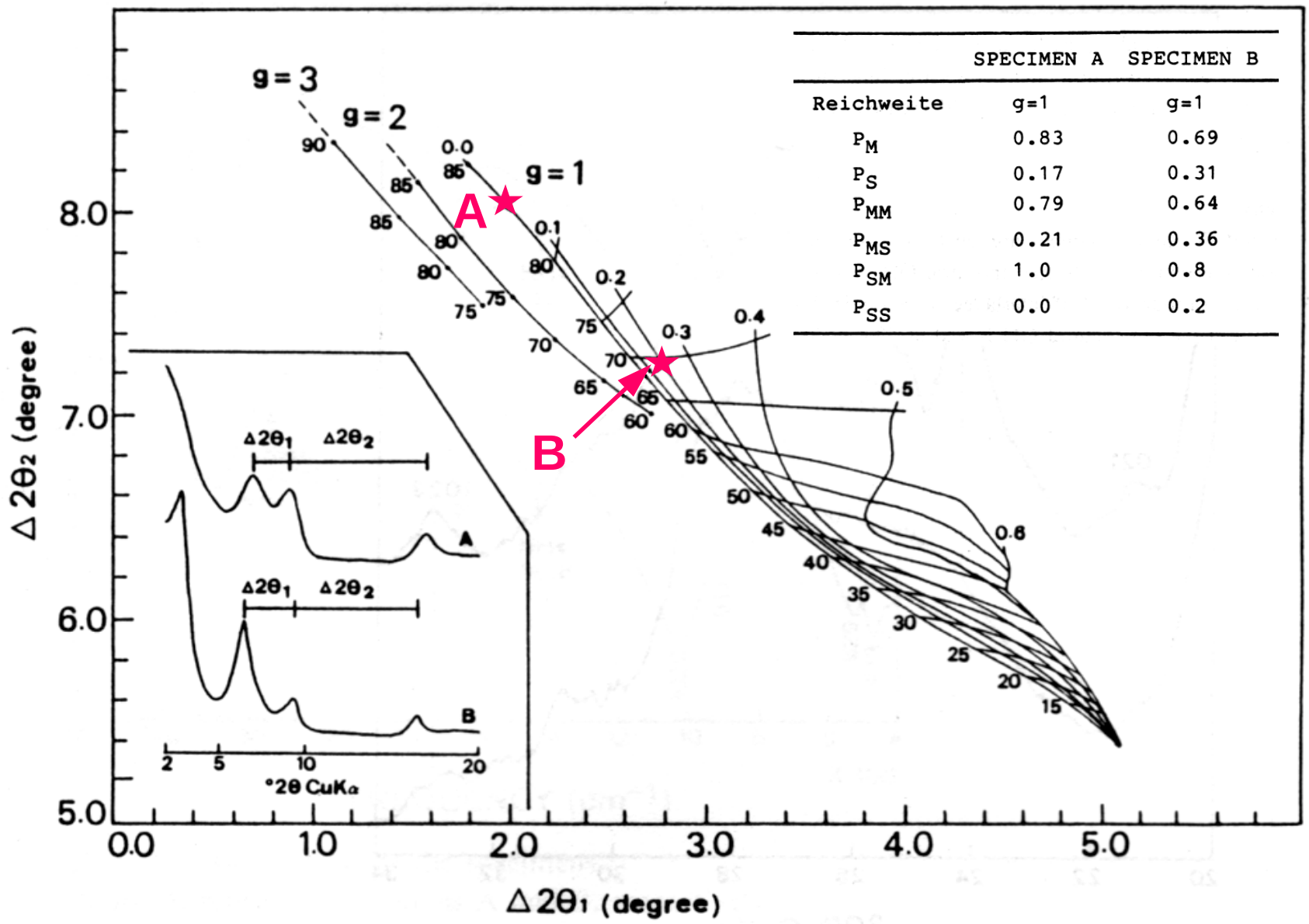
Sample B



混合層構造の判定図（渡辺の図）



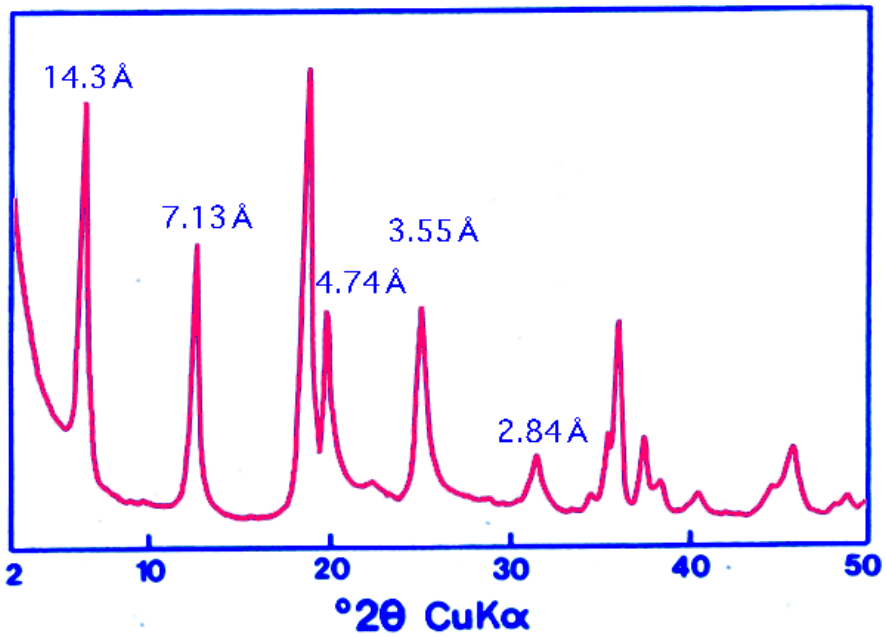
混合層構造の判定図（富田の図）



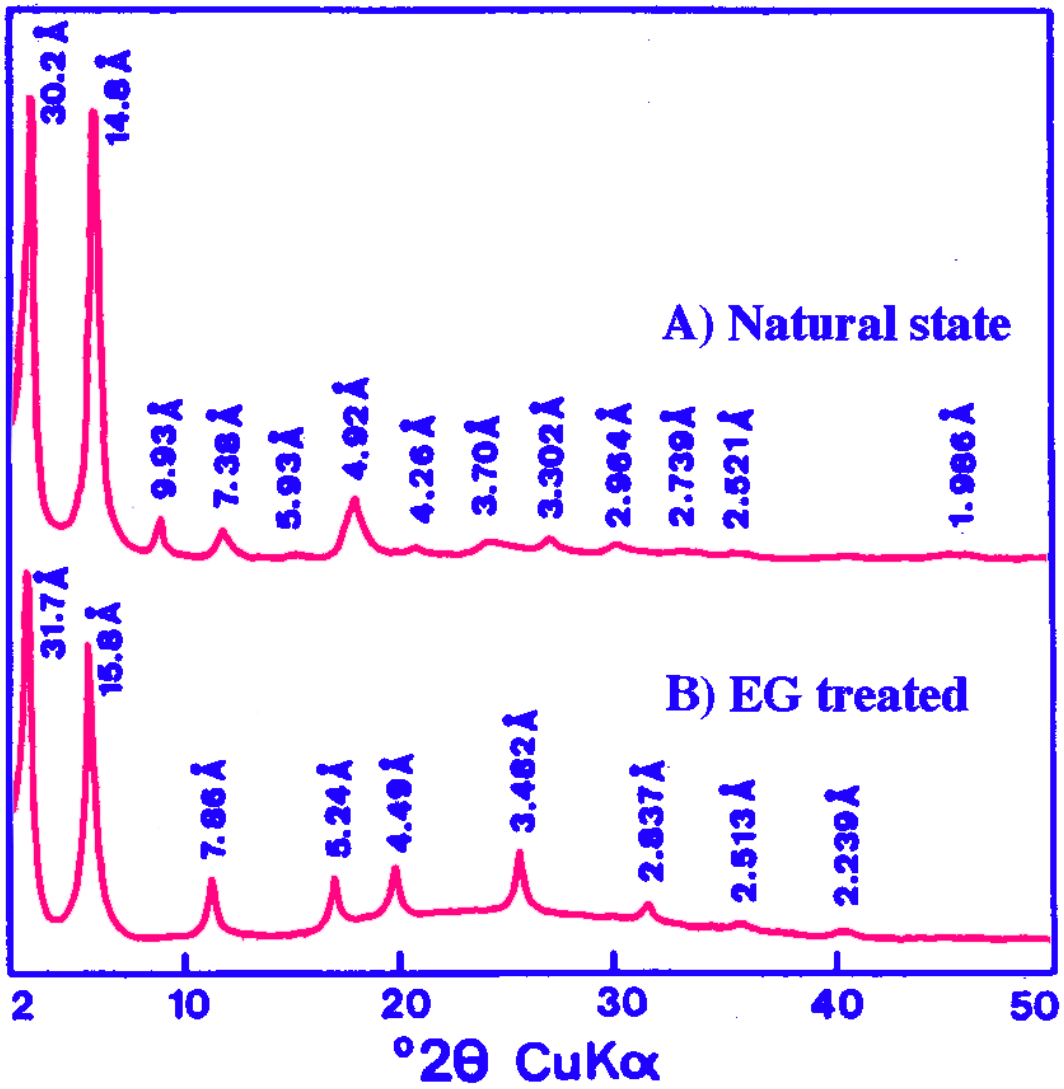
	SPECIMEN A	SPECIMEN B
Reichweite	g=1	g=1
P_M	0.83	0.69
P_S	0.17	0.31
P_{MM}	0.79	0.64
P_{MS}	0.21	0.36
P_{SM}	1.0	0.8
P_{SS}	0.0	0.2

混合層粘土鉱物（緑泥石／スメクタイト）

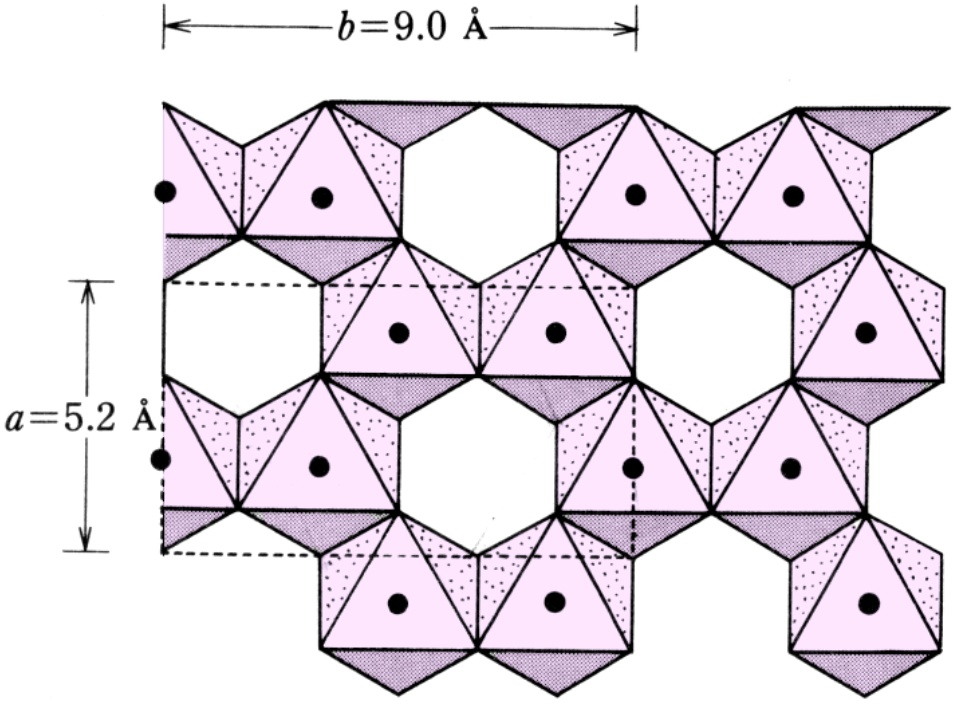
XRD profile of chlorite



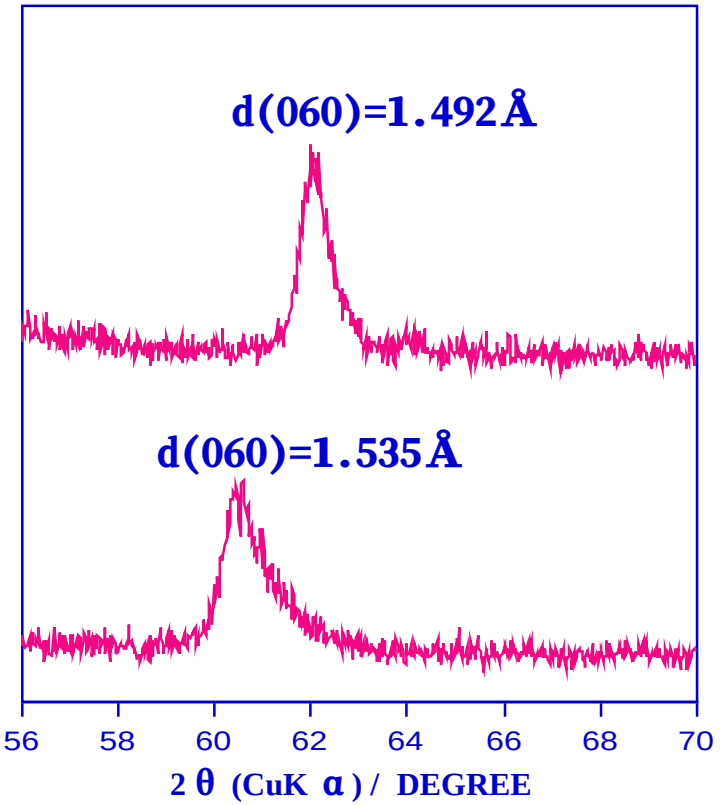
XRD profiles of tosudite



2八面体型と3八面体型の判別方法

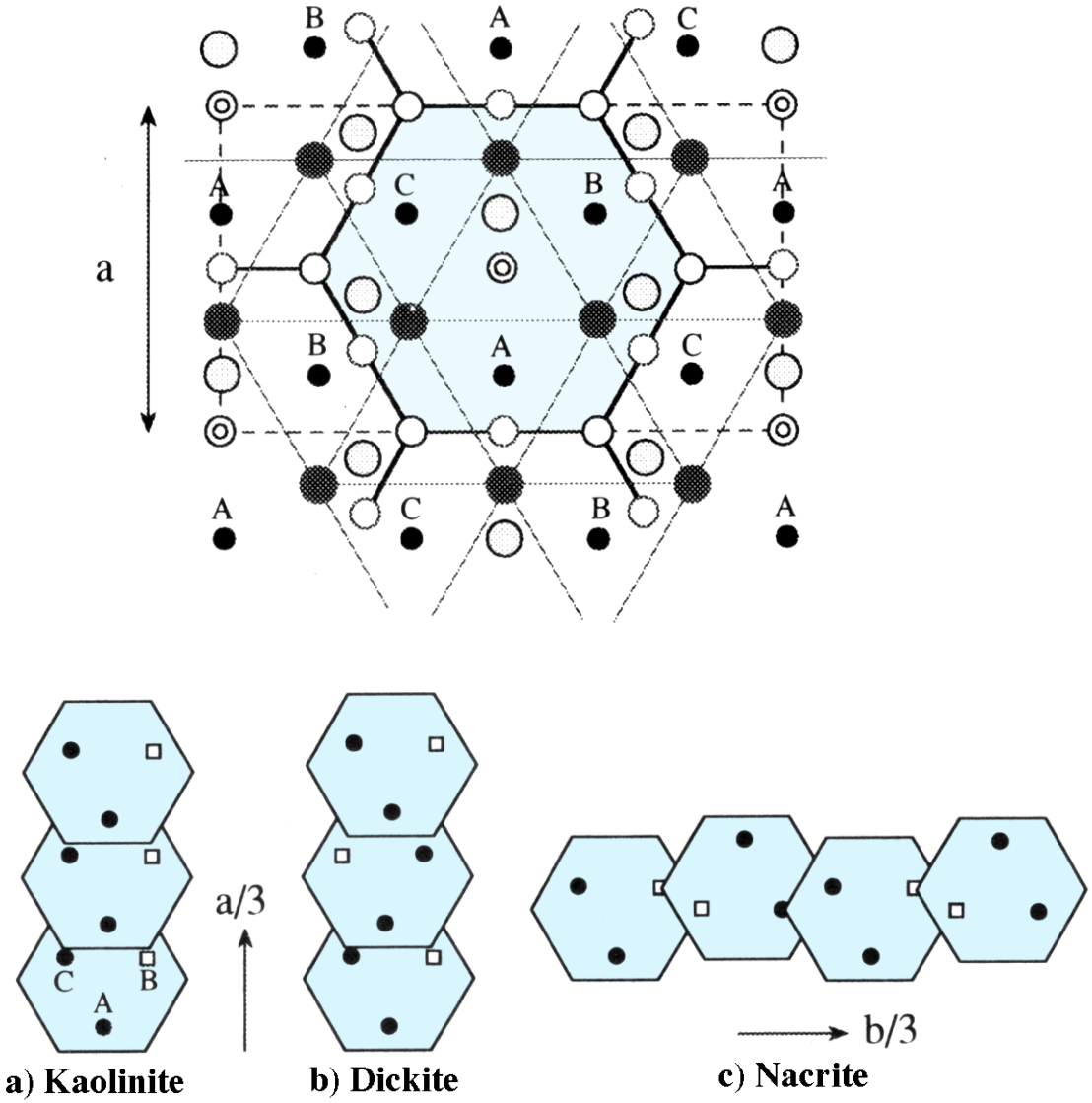


XRD profiles of clay minerals

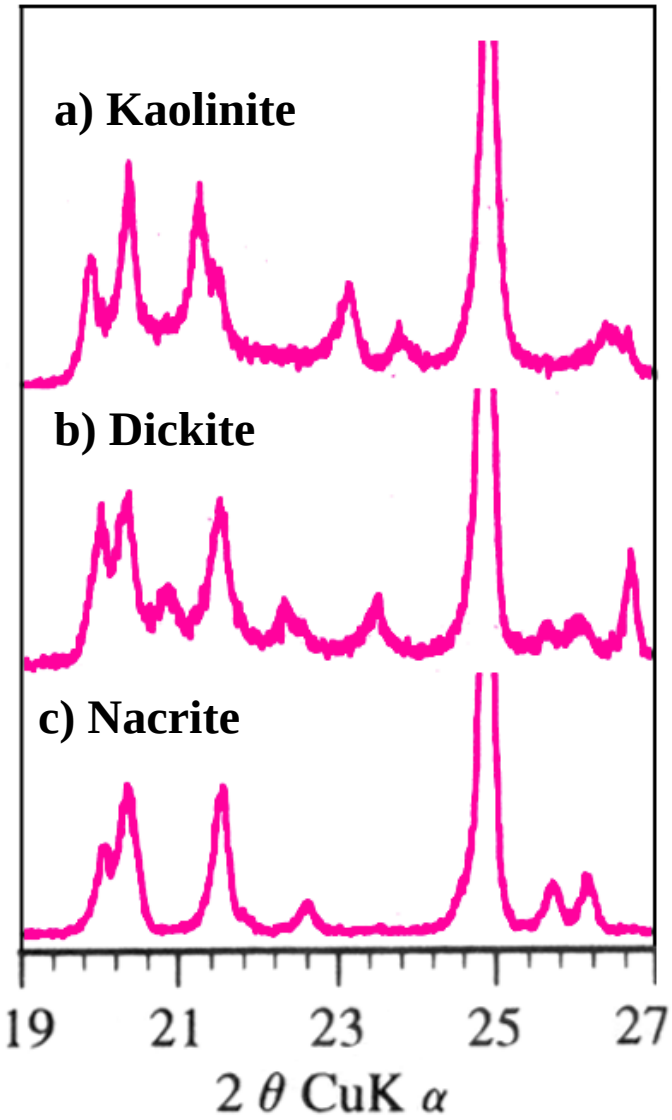


Dioctahedral type: b = 8.94～9.00Å	Dioctahedral type: d(060) = 1.49～1.50Å
Trioctahedral type: b = 9.18～9.24Å	Trioctahedral type: d(060) = 1.53～1.54Å

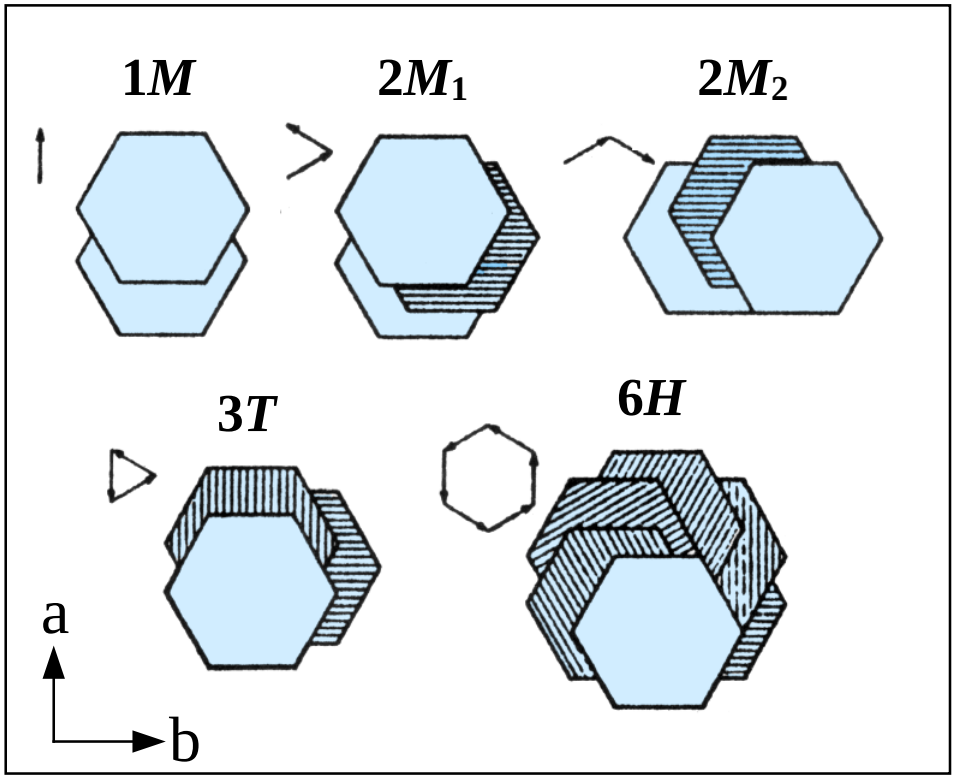
カオリン鉱物のポリタイプ



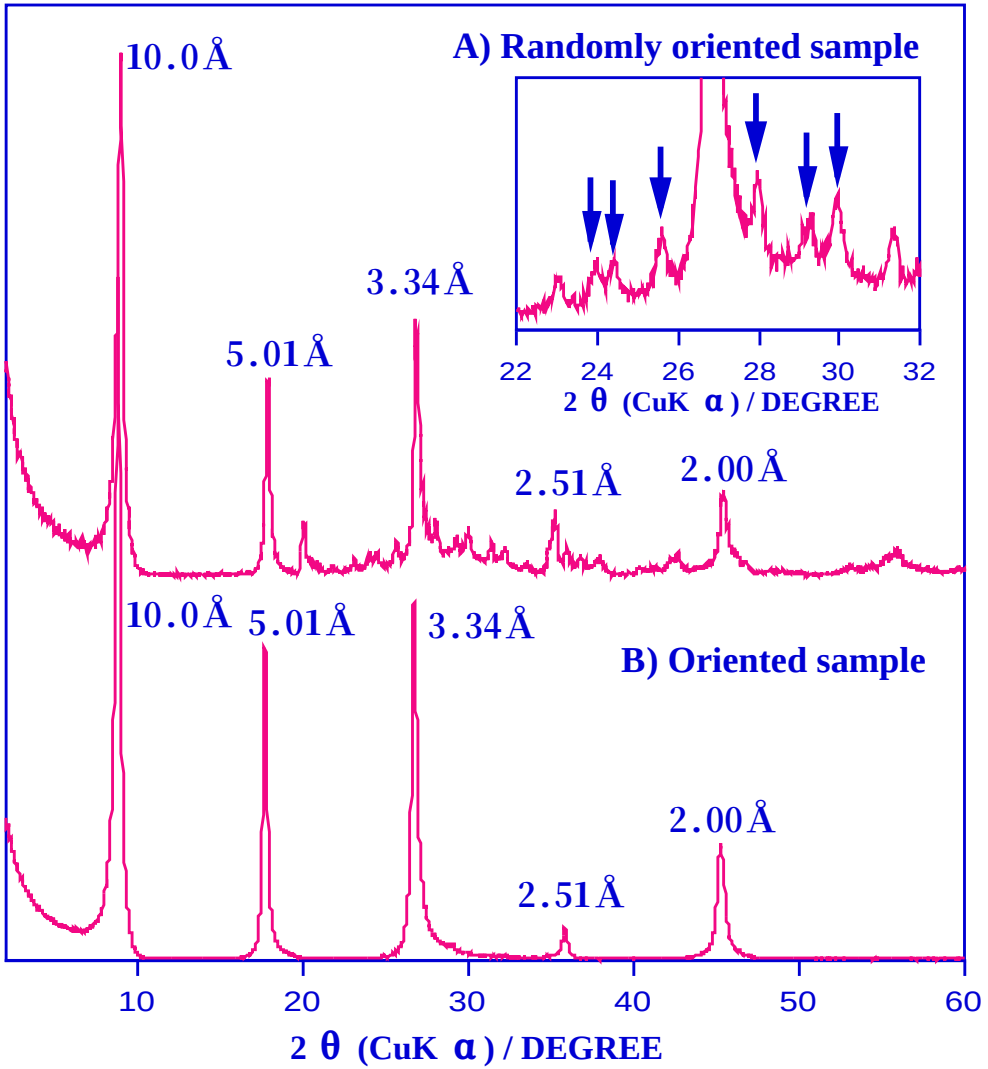
XRD profiles of kaolin minerals



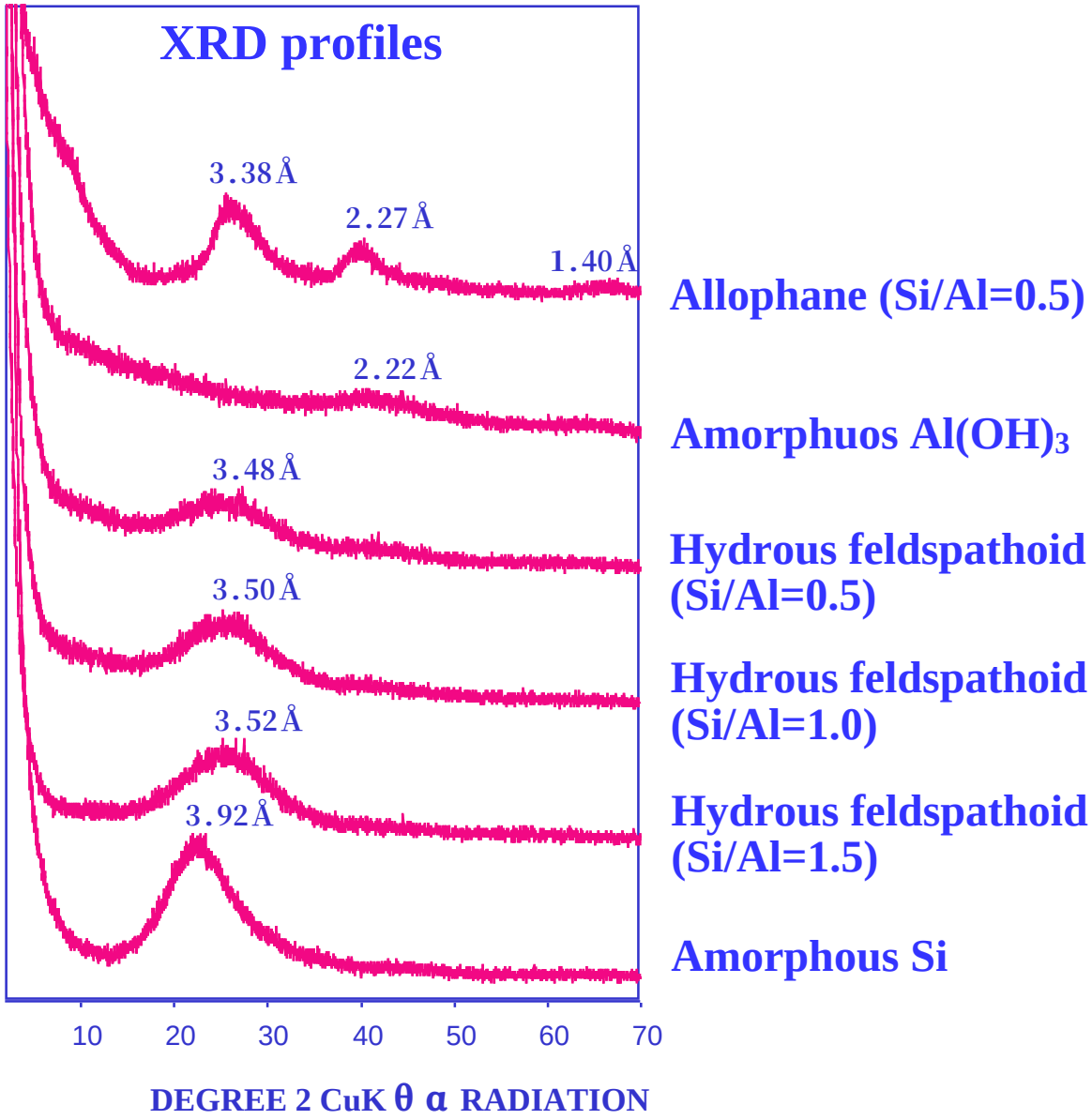
雲母のポリタイプ



XRD profiles of $2M_1$ illite



アロフェンおよび関連物質のX線回折



Allophane (Si/Al=0.5)

Amorphuos $Al(OH)_3$

Hydrous feldspathoid (Si/Al=0.5)

Hydrous feldspathoid (Si/Al=1.0)

Hydrous feldspathoid (Si/Al=1.5)

Amorphous Si