

# **Layered Compounds**

## **Two-dimensional layers**

**Graphite**

**Clay Minerals**

**Layered Double Hydroxides (LDHs)**

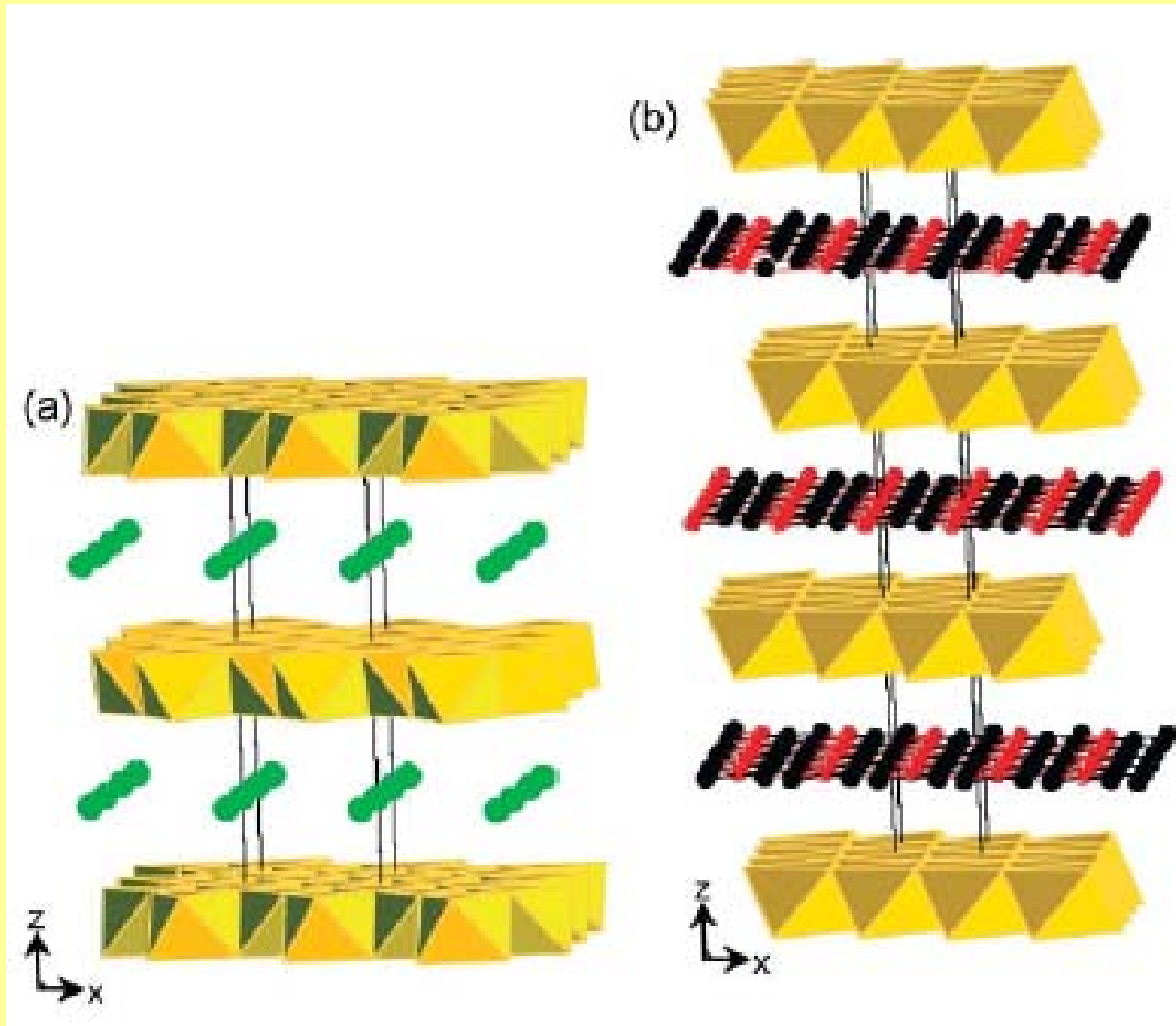
**Layered  $\alpha$ -Zirconium Phosphates and Phosphonates**

**Layered Manganese Oxides**

**Layered Metal Chalcogenides**

**Alkali Silicates and Crystalline Silicic Acids**

# Layered Compounds

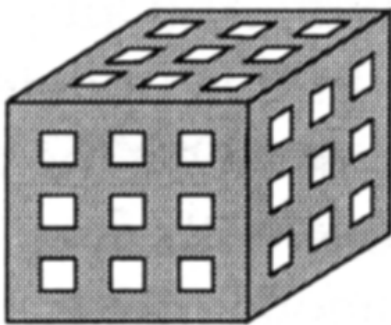


# Host-Guest Structures

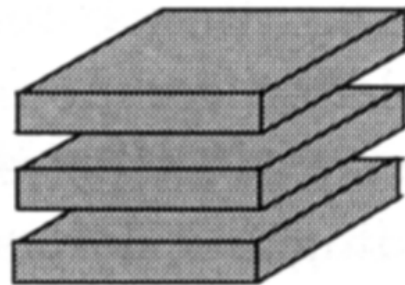
**TOPOTACTIC SOLID-STATE REACTIONS = modifying existing solid state structures while maintaining the integrity of the overall structure**

## Host dimensionality

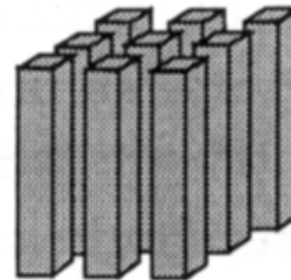
**3D**



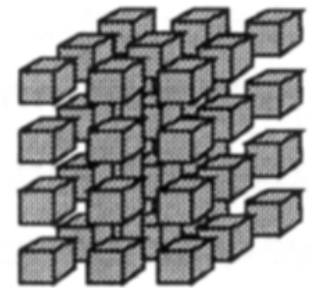
**2D**



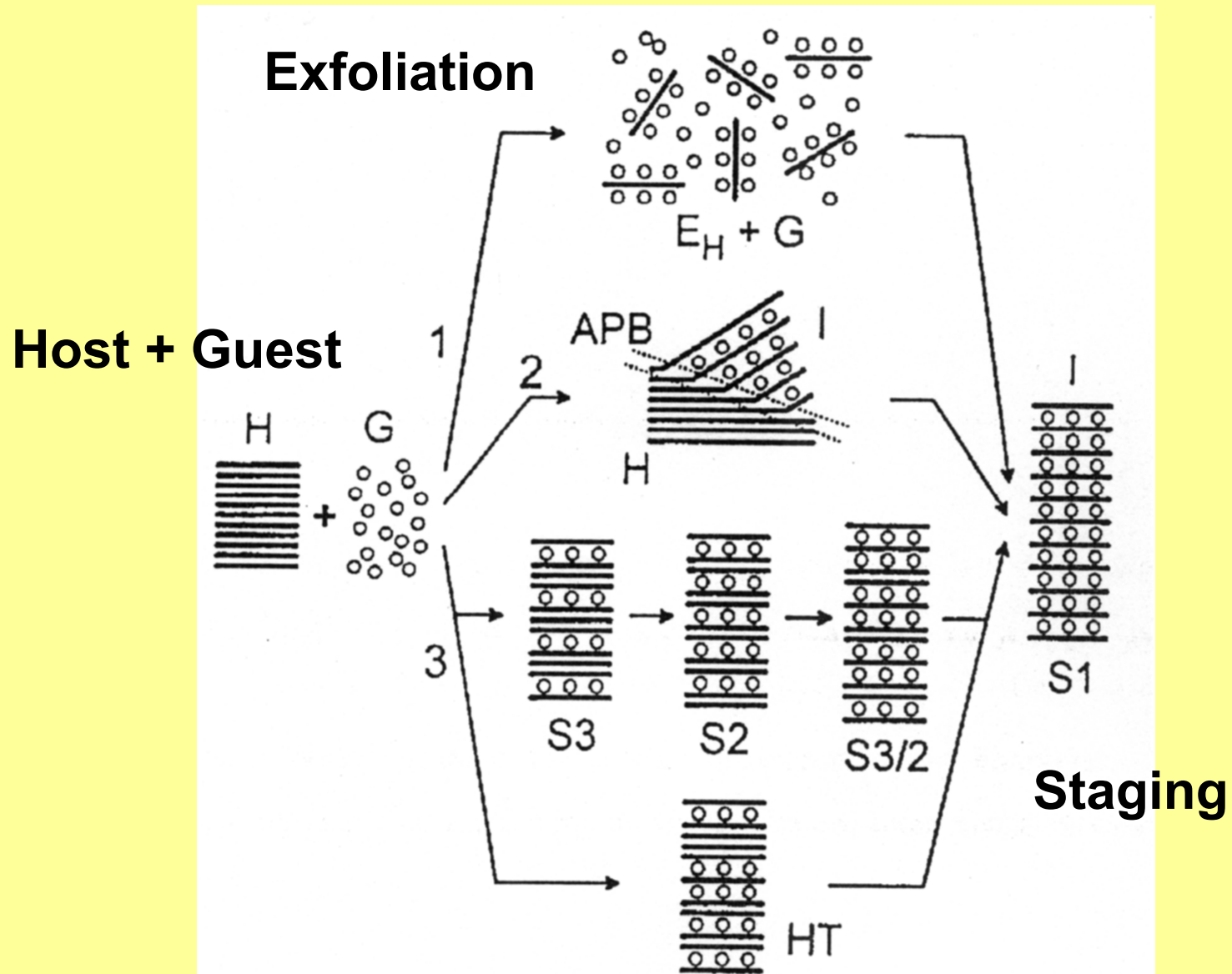
**1D**



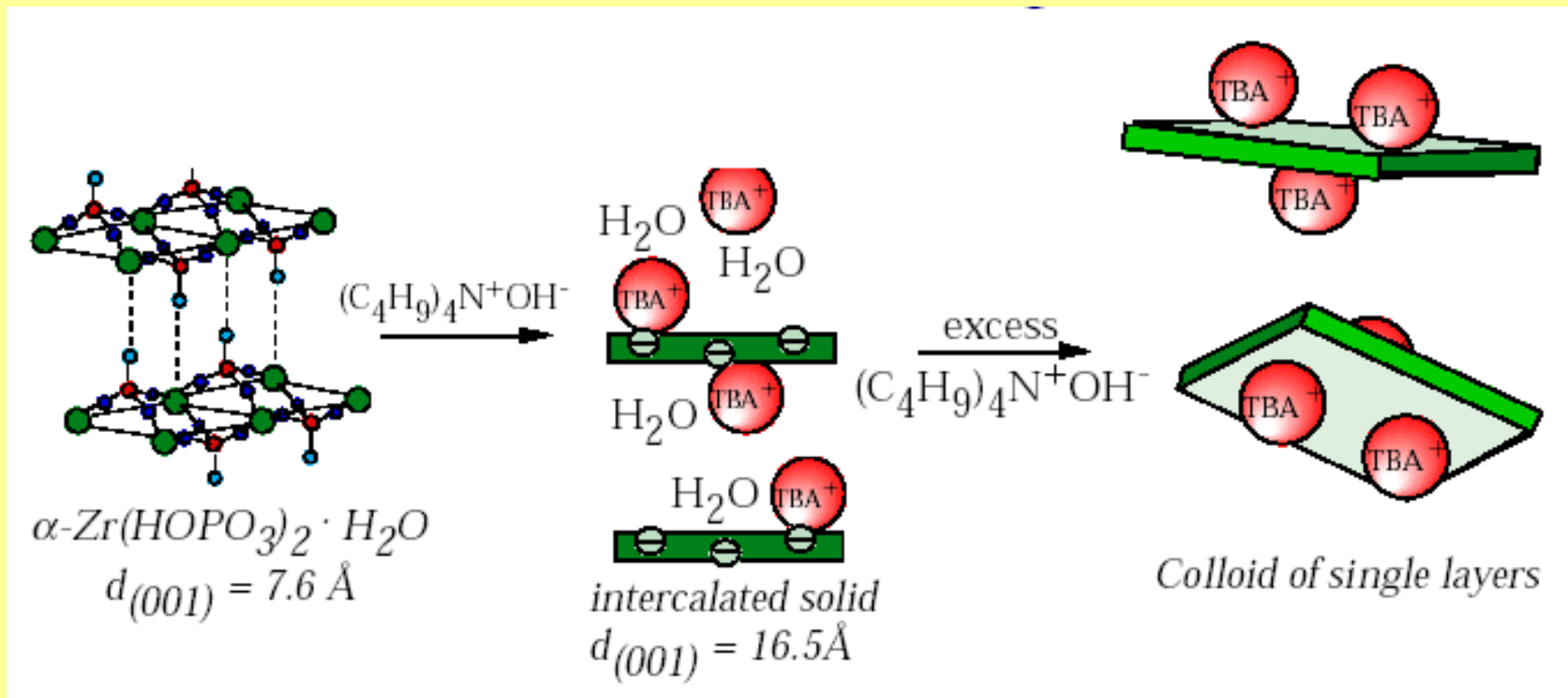
**0D**



# Host-Guest Structures

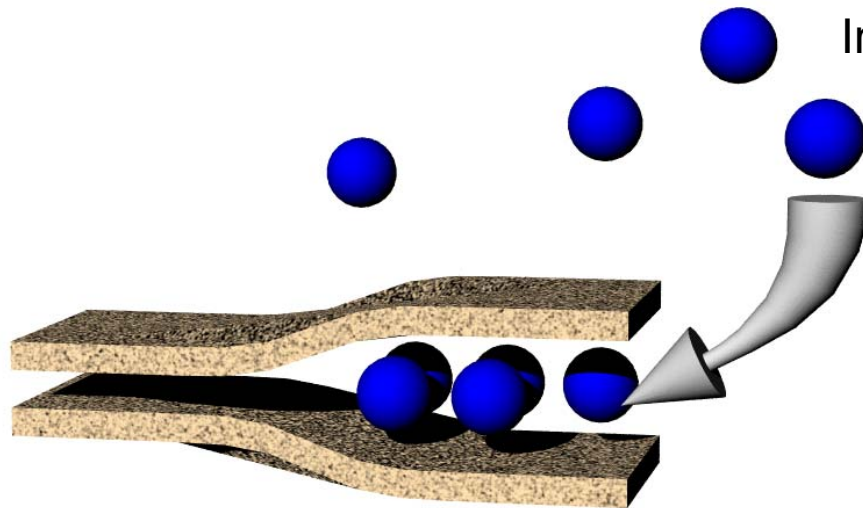


# Exfoliation

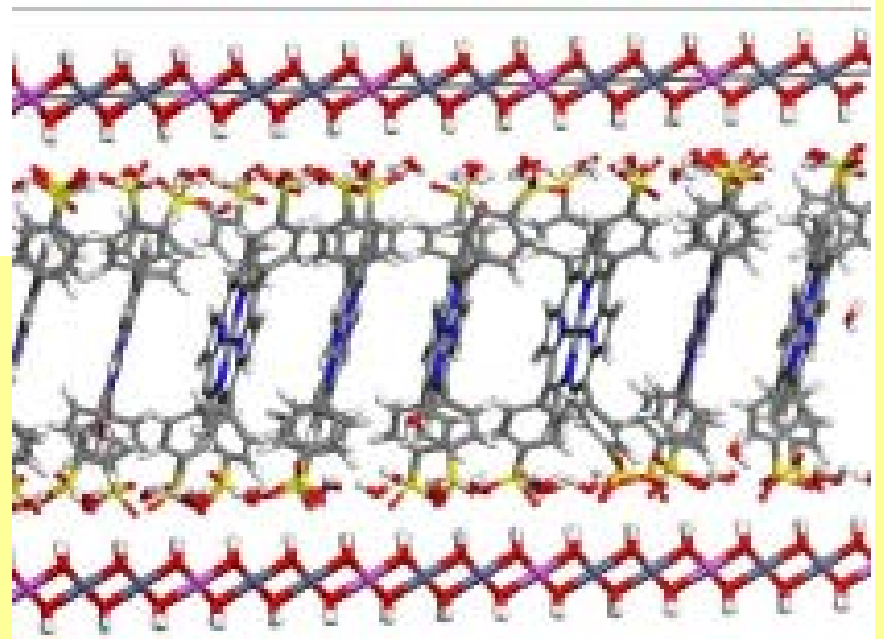


# Intercalation

Intercalation

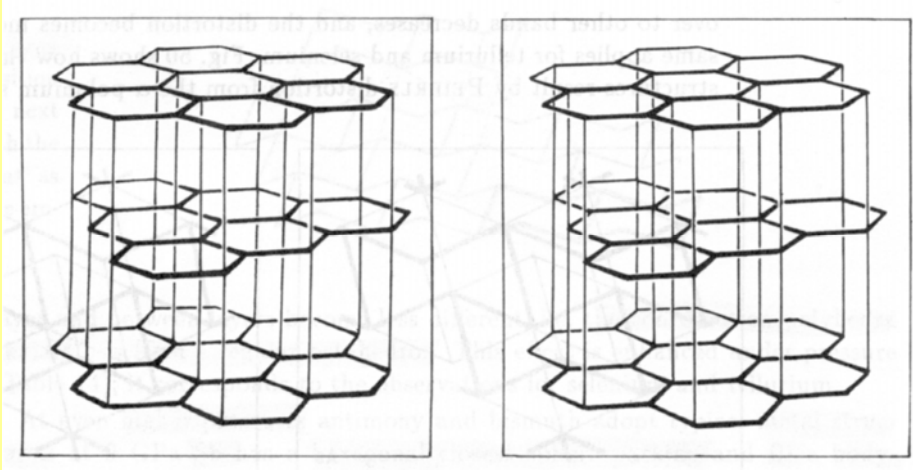


Insertion of molecules between layers



# Graphite

**ABABAB**

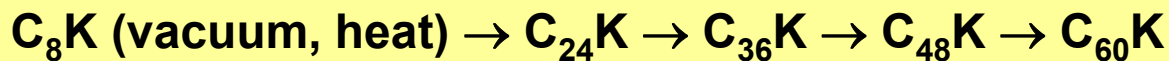


**Graphite  $sp^2$  sigma-bonding in-plane p-p-bonding out of plane  
Hexagonal graphite = two-layer ABAB stacking sequence**

**SALCAOs of the p-p-type create the valence and conduction bands of graphite, very small band gap, metallic conductivity properties in-plane,  $10^4$  times that of out-of plane conductivity**

# Graphite

## GRAPHITE INTERCALATION



**C<sub>8</sub>K potassium graphite ordered structure**

**Ordered K guests between the sheets, K to G charge transfer**

**AAAA stacking sequence**

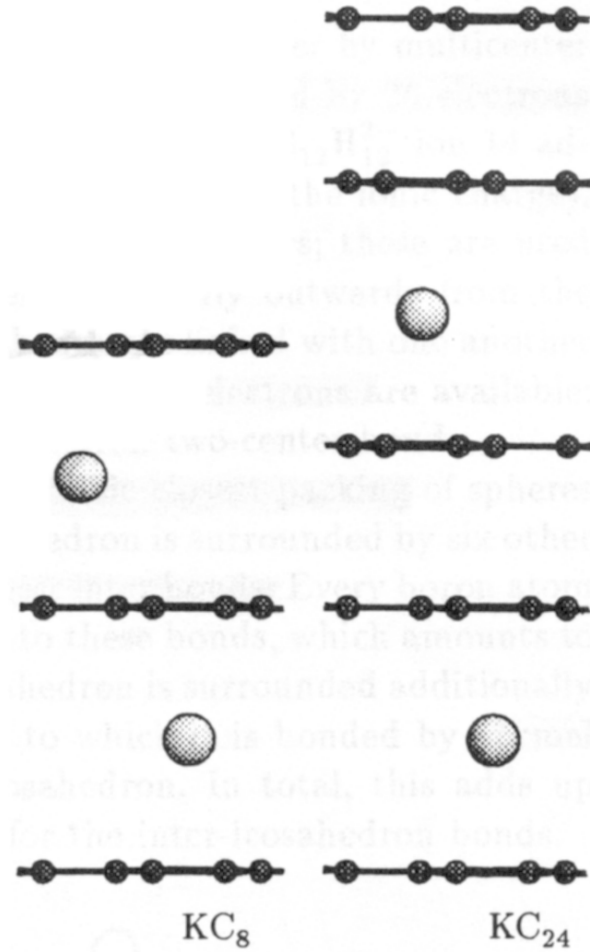
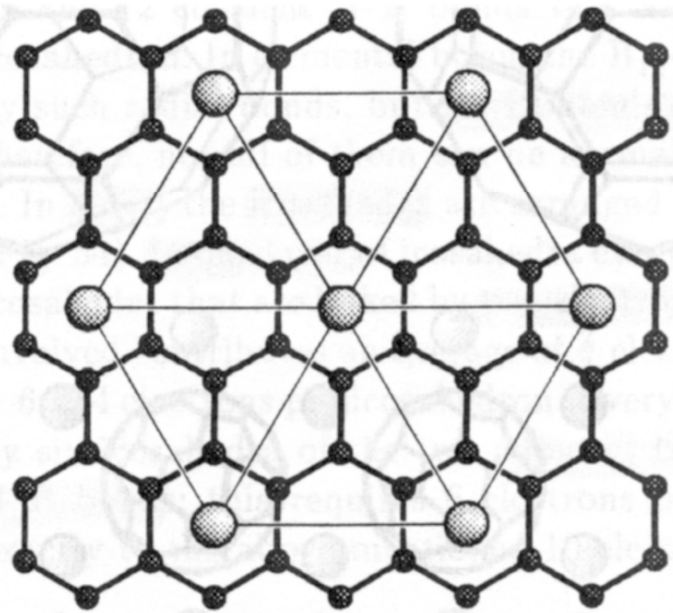
**reduction of graphite sheets, electrons enter CB**

**K nesting between parallel eclipsed hexagonal planar carbon six-rings**

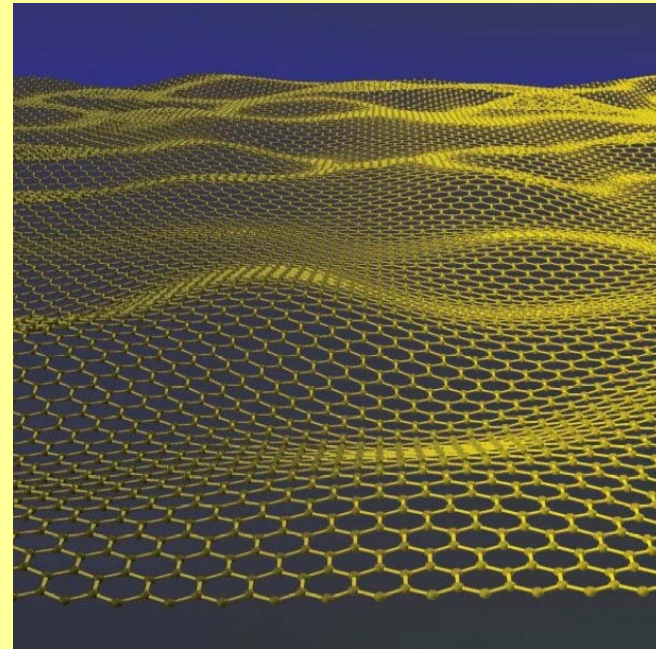
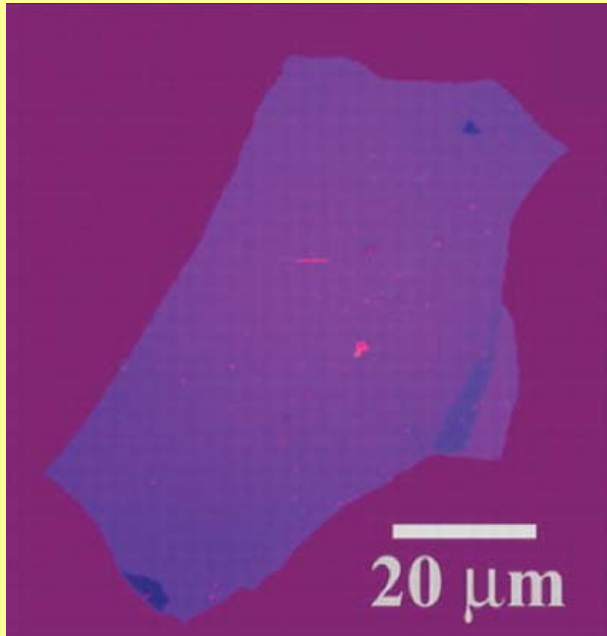


# Graphite

## Intercalates



# Graphene



**High electric conductivity (metallic)**

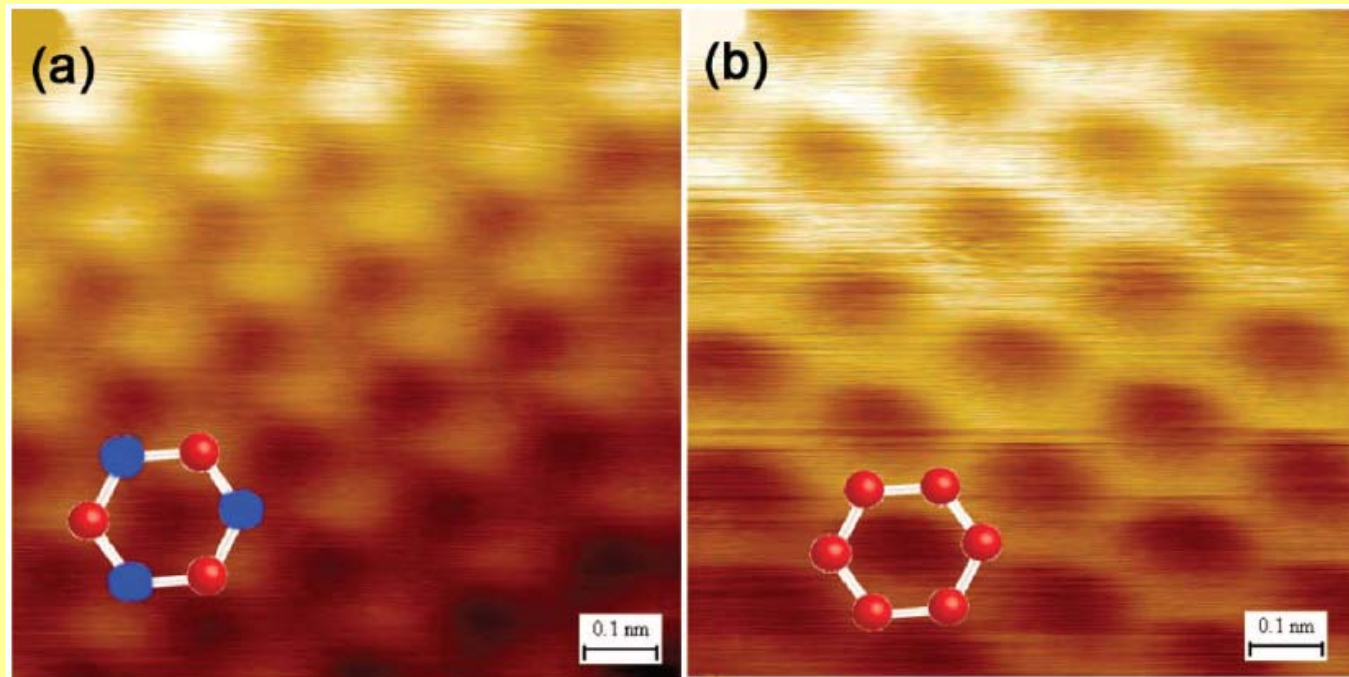
**Optically transparent – 1 layer absorbs 2.3% of photons**

**High mechanical strength**

# Graphene

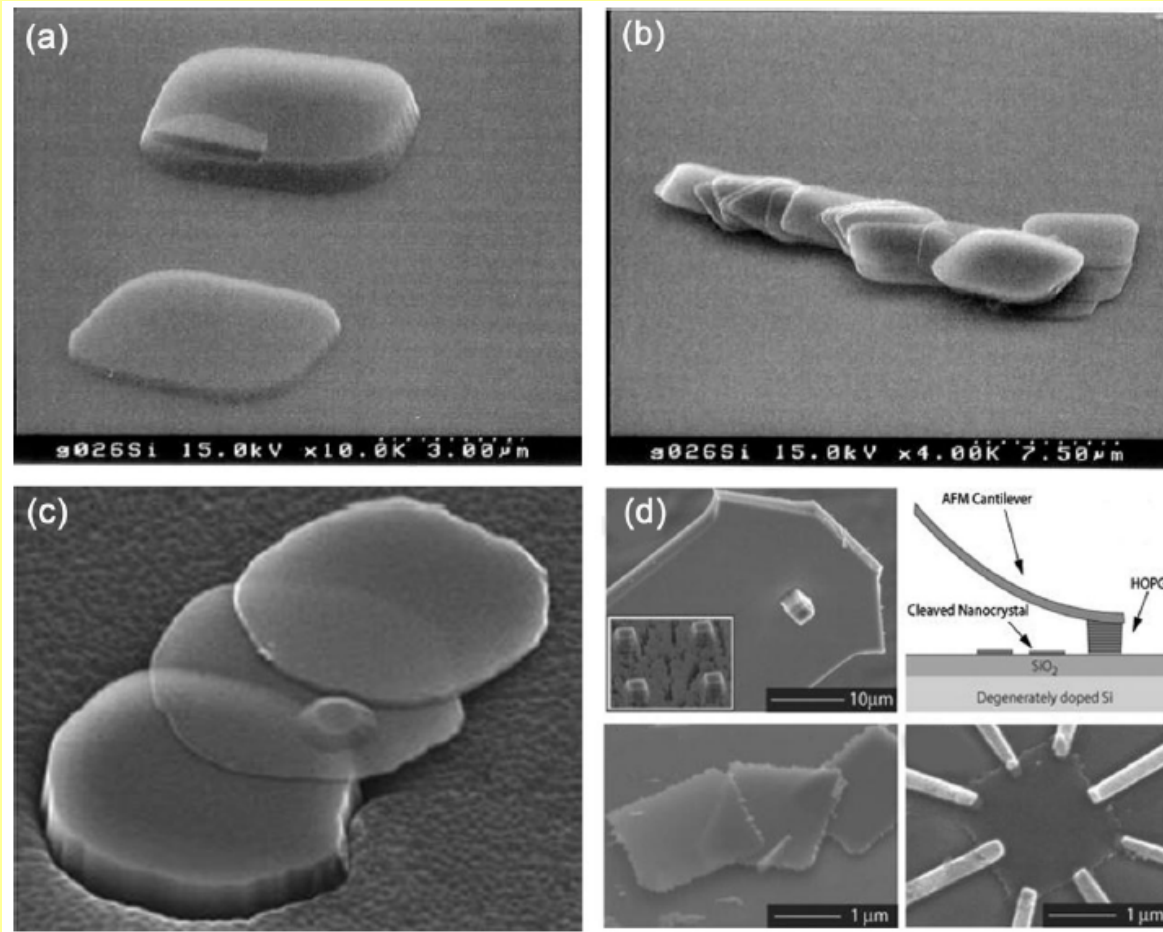
Preparation:

- Scotch tape – layer peeling, flaking
- SiC pyrolysis – epitaxial graphene layer on a SiC crystal
- Exfoliation
- CVD from  $\text{CH}_4$  on Ni, Cu surfaces



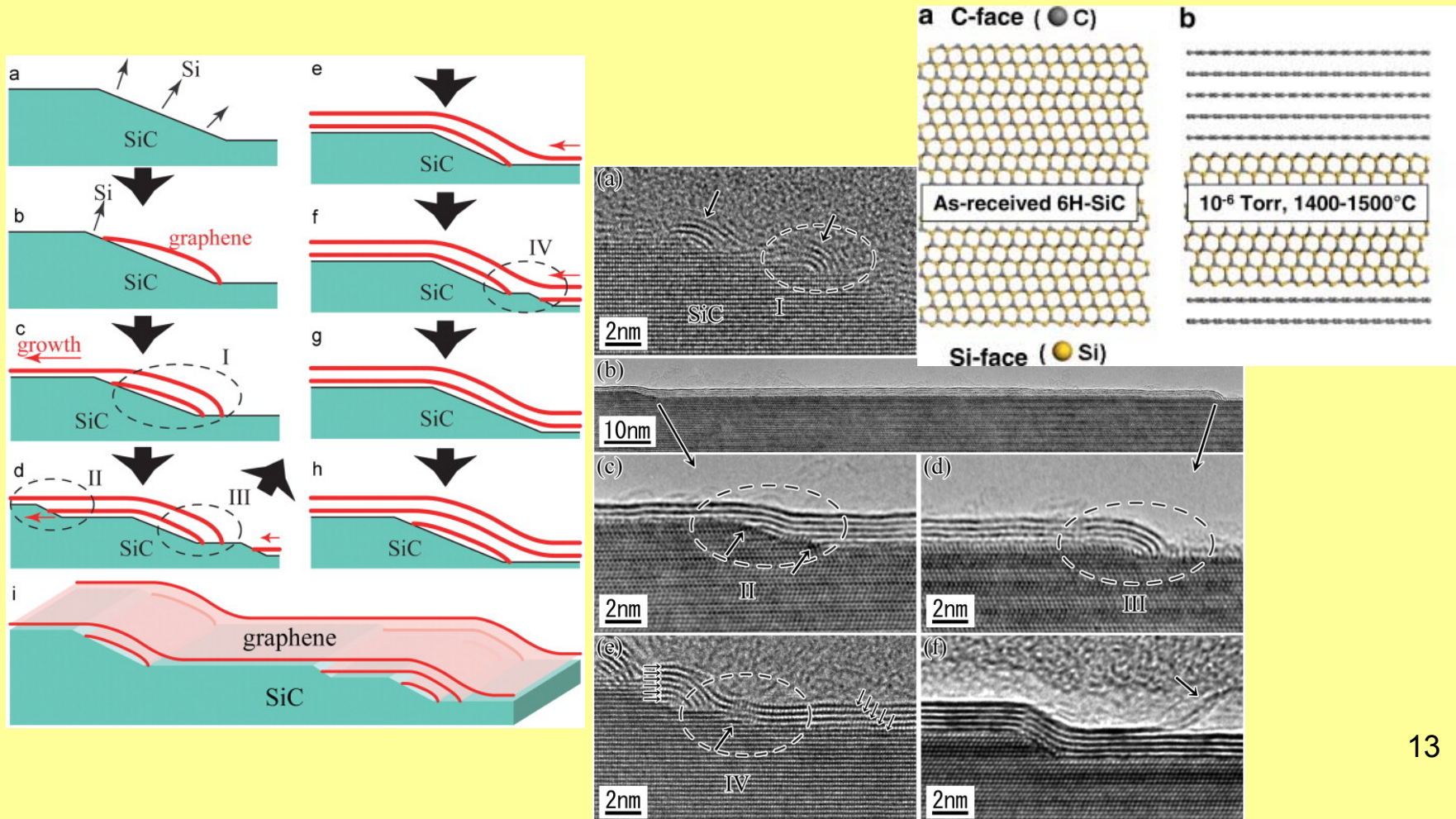
# Scotch tape – Layer peeling

## Mechanical exfoliation



# SiC pyrolysis

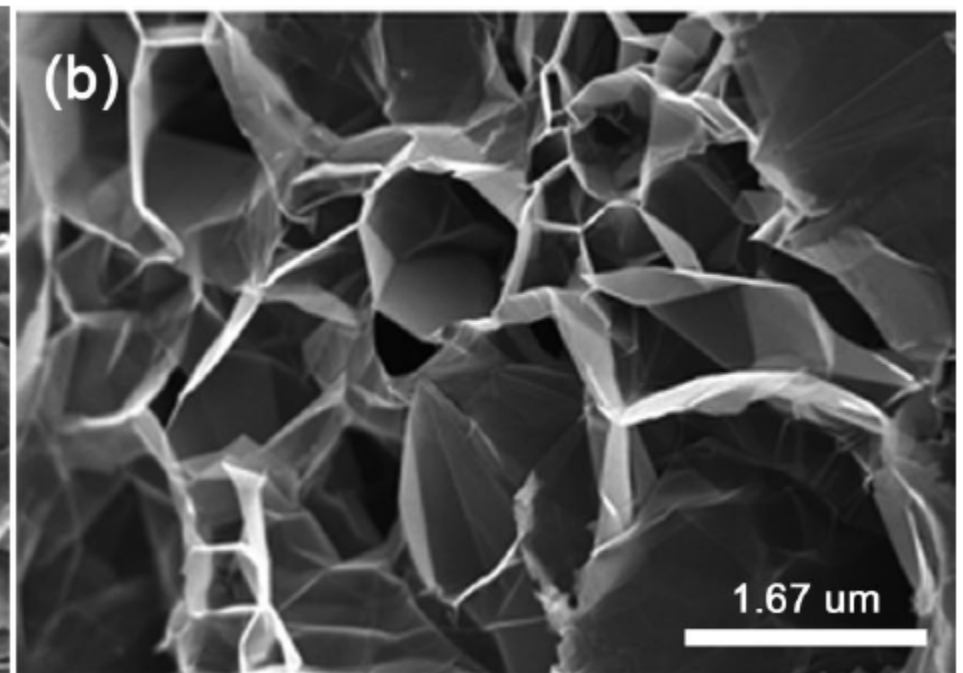
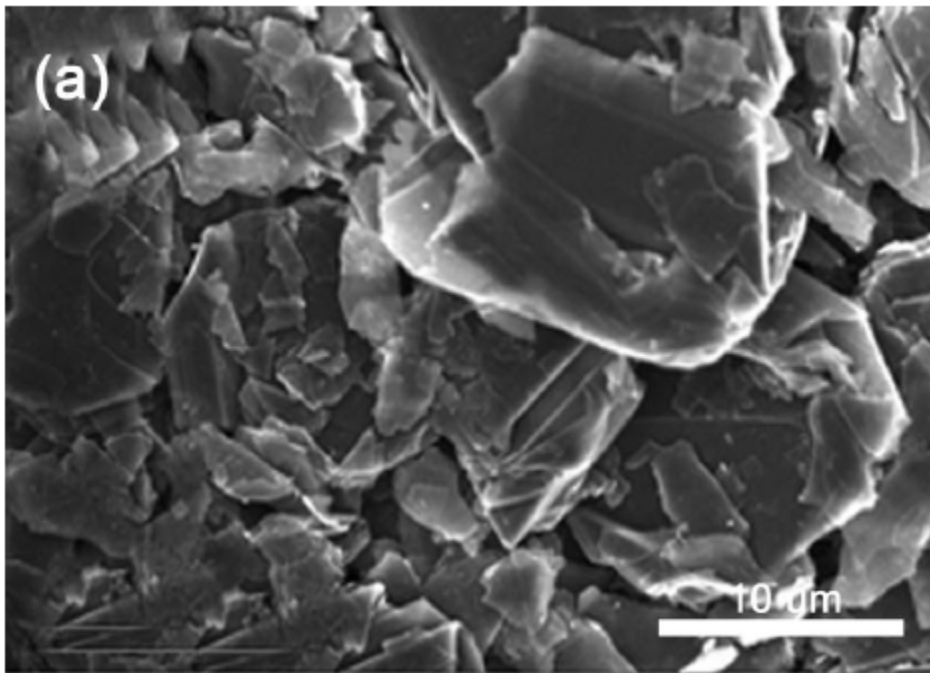
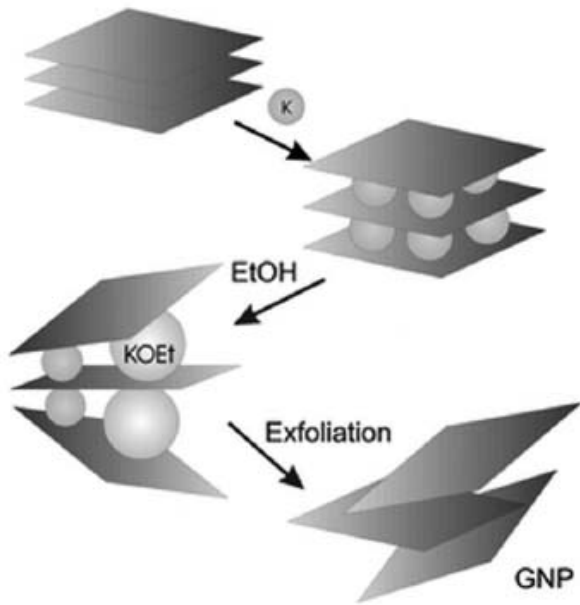
- Annealing of the SiC crystal in a vacuum furnace (UHV  $10^{-10}$  Torr)
- Sublimation of Si from the surface at 1250 - 1450 °C
- The formation of graphene layers by the remaining carbon atoms



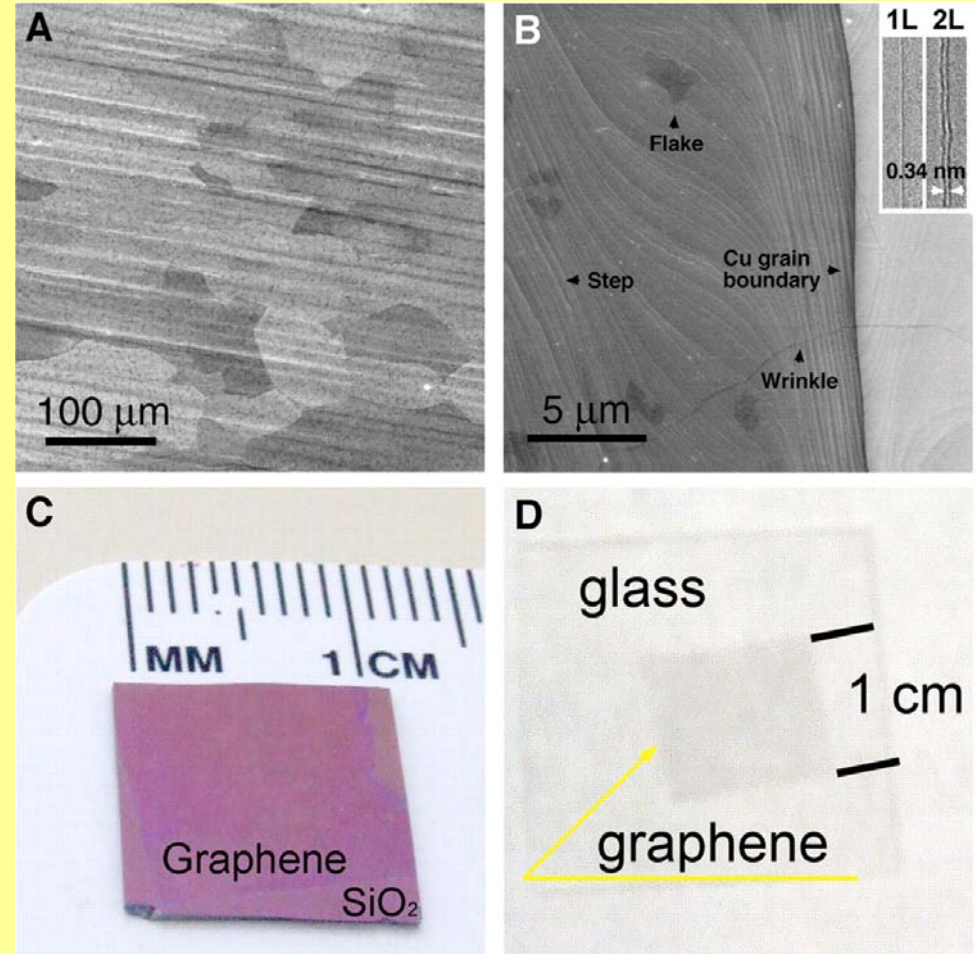
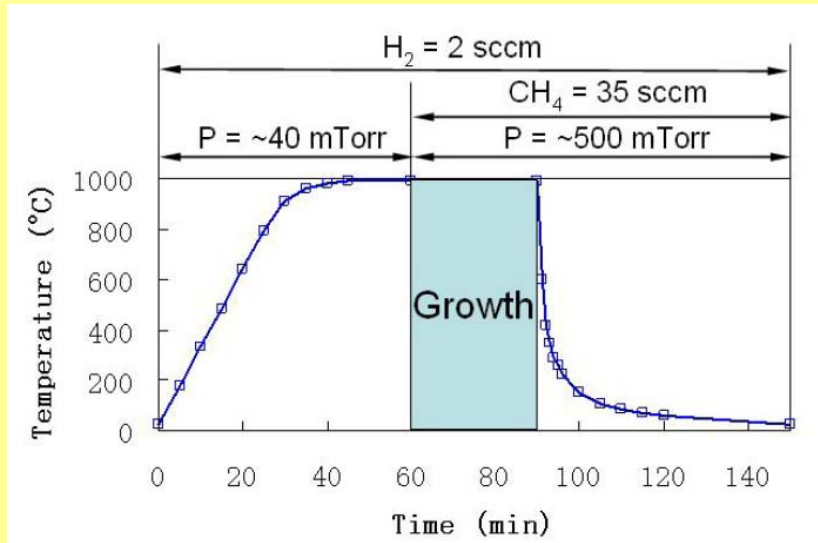
# Exfoliation

Chemical exfoliation (surfactant)

Sonochemical exfoliation



# CVD from CH<sub>4</sub> / H<sub>2</sub> on Metal Surfaces

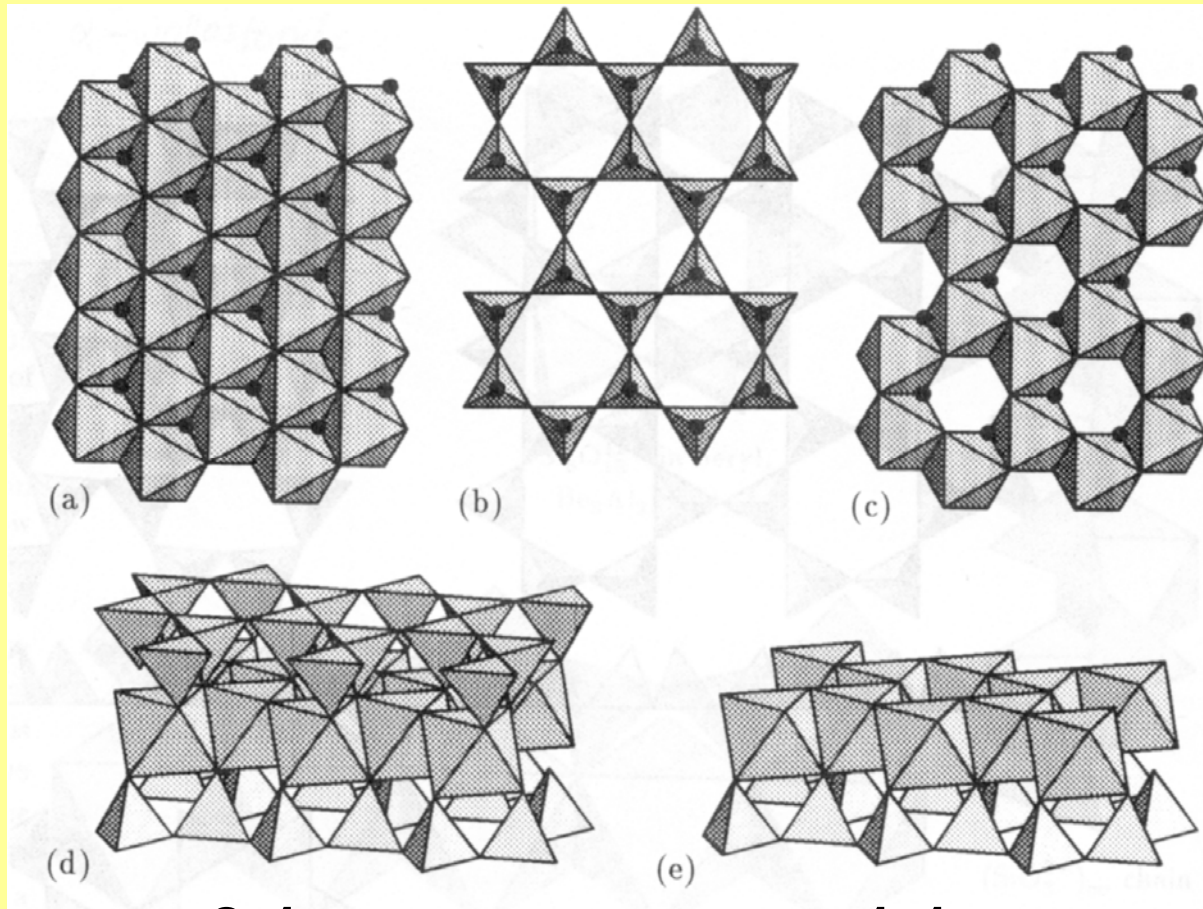


(A) SEM - graphene on a copper foil

(B) High-resolution SEM - Cu grain boundary and steps, two- and three-layer graphene flakes, and graphene wrinkles. Inset (B) TEM images of folded graphene edges. 1L, one layer; 2L, two layers.

Graphene transferred onto  
(C) a SiO<sub>2</sub>/Si substrate  
(D) a glass plate

# Clay Minerals



**2:1**

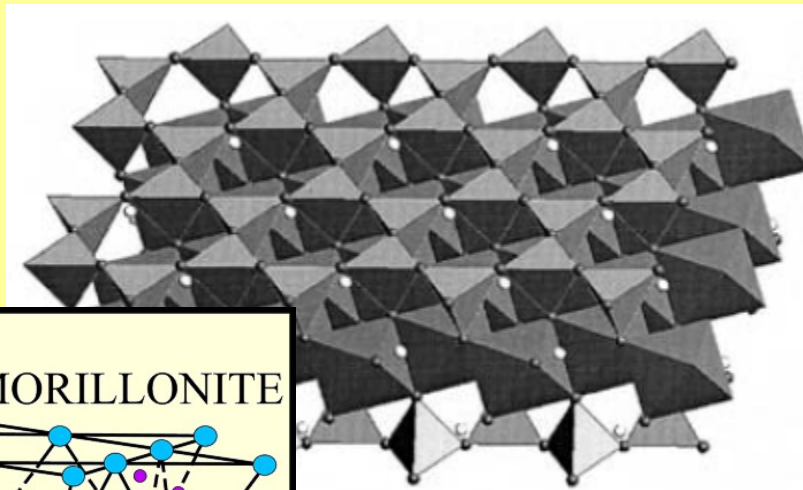
**montmorillonite**

**1:1**

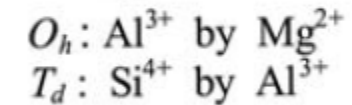
**kaolinite**



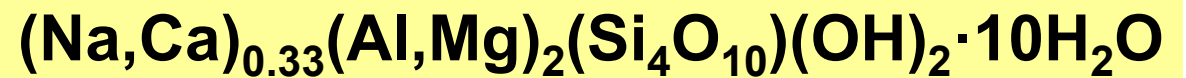
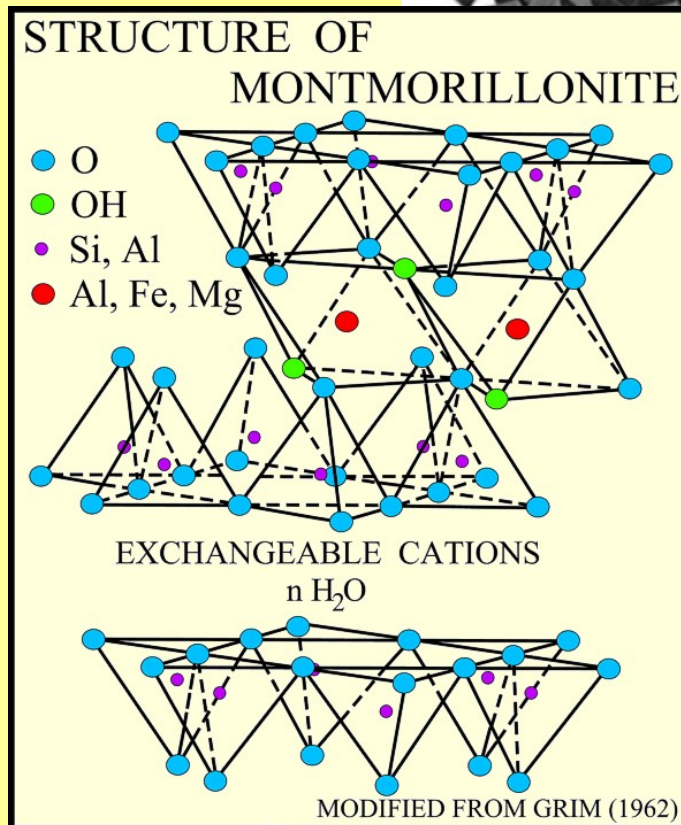
# Montmorillonite



- Dioctahedral clay mineral
- $T_d-O_h-T_d$  sandwich
- Isomorphous substitution



- Net negative charge
- Interlayer cations



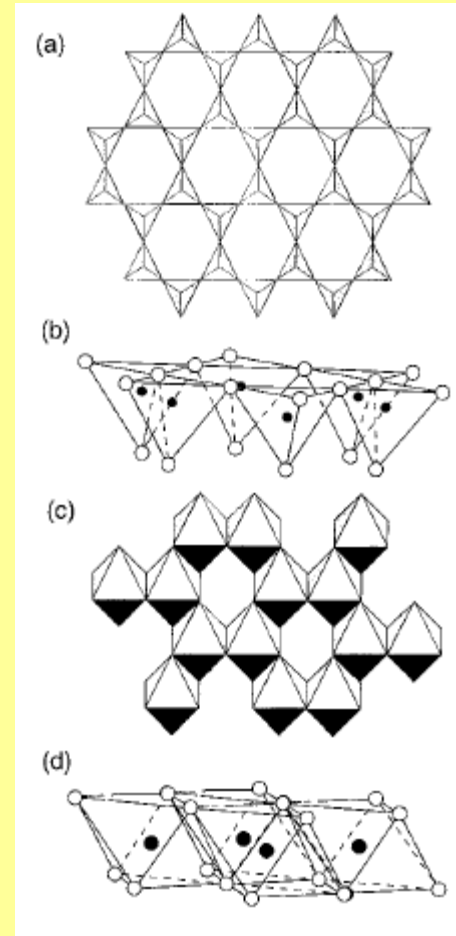
# Clay Minerals

A clay  $[\text{Si}_4\text{O}_{10}]^{4-}$  tetrahedral (T) sheet in (a) top view and (b) side view

A clay octahedral (O) sheet (c) top view and (d) side view

The  $[\text{Al}_4\text{O}_{12}]^{12-}$  dioctahedral top view is shown in (c)

$[\text{Mg}_6\text{O}_{12}]^{12-}$  trioctahedral top view would show a continuous sheet of octahedral units



# Clay Minerals

## $N_2$ sorption isotherms

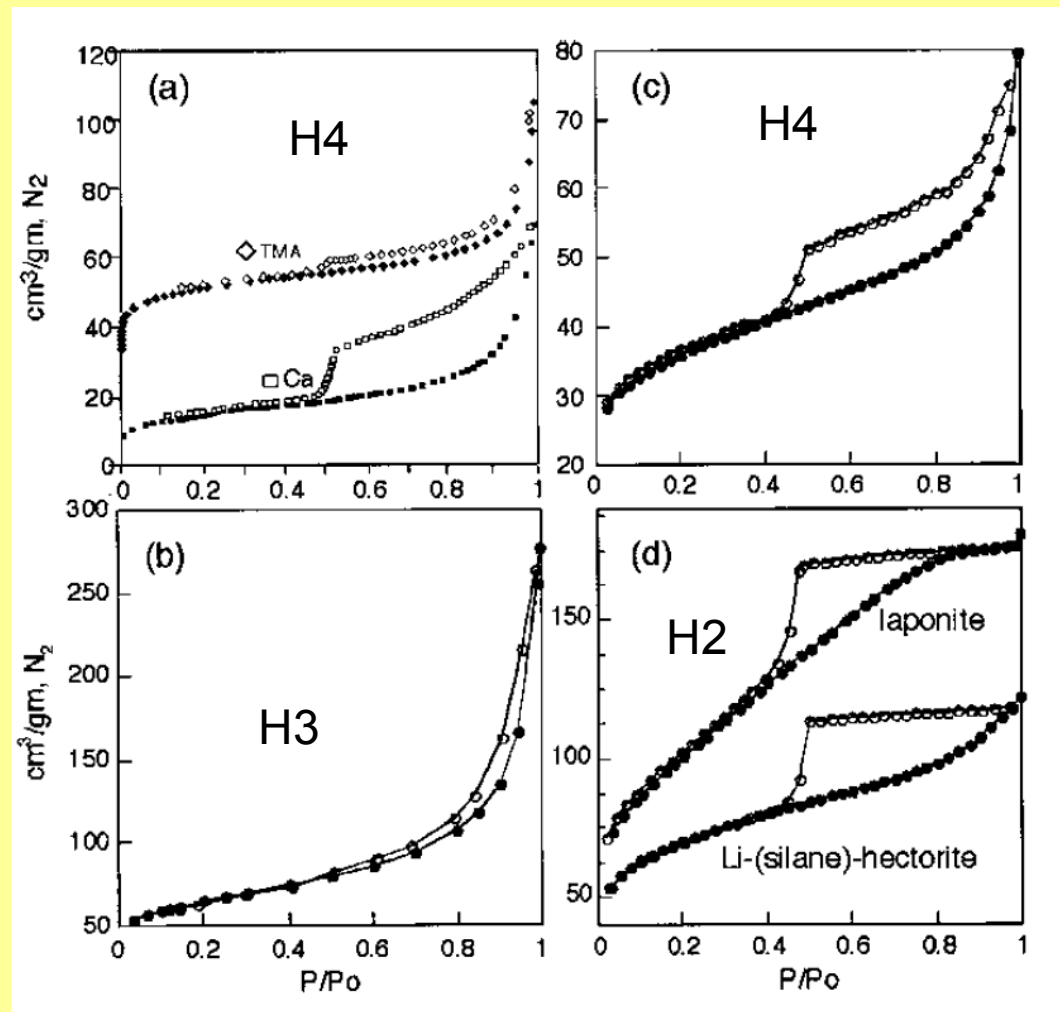
(a) TMA- and Ca-montmorillonite

(b) An Italian sepiolite

(c) Natural SHCa-1 Na-hectorite

(d) synthetic laponite and Li-(silane)-hectorites

Closed symbols = adsorption  
Open symbols = desorption



# Surface Area

the most important parameters of clays with respect to catalytic applications

**TABLE 3** N<sub>2</sub> BET Surface Areas of Various Clay Minerals

Clay	Outgassing conditions	S. A., m <sup>2</sup> /g
Kaolinite <sup>a,b</sup>	200 °C, overnight, <10 <sup>-2</sup> torr	8.75
Na,Ca-montmorillonite <sup>a,c</sup>	same	31.0
Ca-montmorillonite <sup>a,d</sup>	same	80.2
Ca-montmorillonite <sup>a,e</sup>	same	93.9
Na-hectorite <sup>a,f</sup>	same	64.3
Laponite <sup>g</sup>	105 °C, overnight, 10 <sup>-3</sup> torr	360
Sepiolite <sup>h</sup>	96 °C, 3 h	378
Palygorskite <sup>h</sup>	95 °C, <70 h	192

nonpolar guest molecules N<sub>2</sub> do not penetrate the interlayer regions

Na<sup>+</sup> forms of smectites and vermiculites – no penetration

larger ions (Cs<sup>+</sup> and NH<sub>4</sub><sup>+</sup> keep the basal planes far enough) - limited penetration

# Layered Double Hydroxides

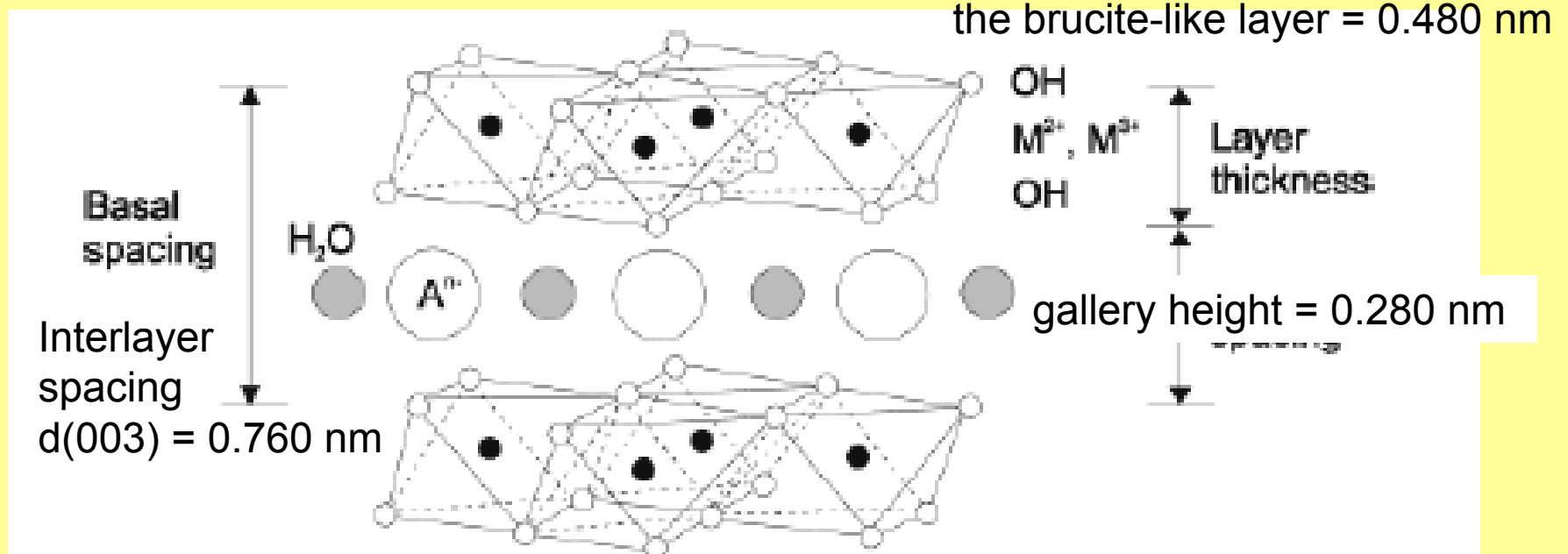
LDH = layered double hydroxides

HT = hydrotalcites

Natural mineral hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$

Brucite layers,  $\text{Mg}^{2+}$  substituted partially by  $\text{Al}^{3+}$

Layers have positive charge

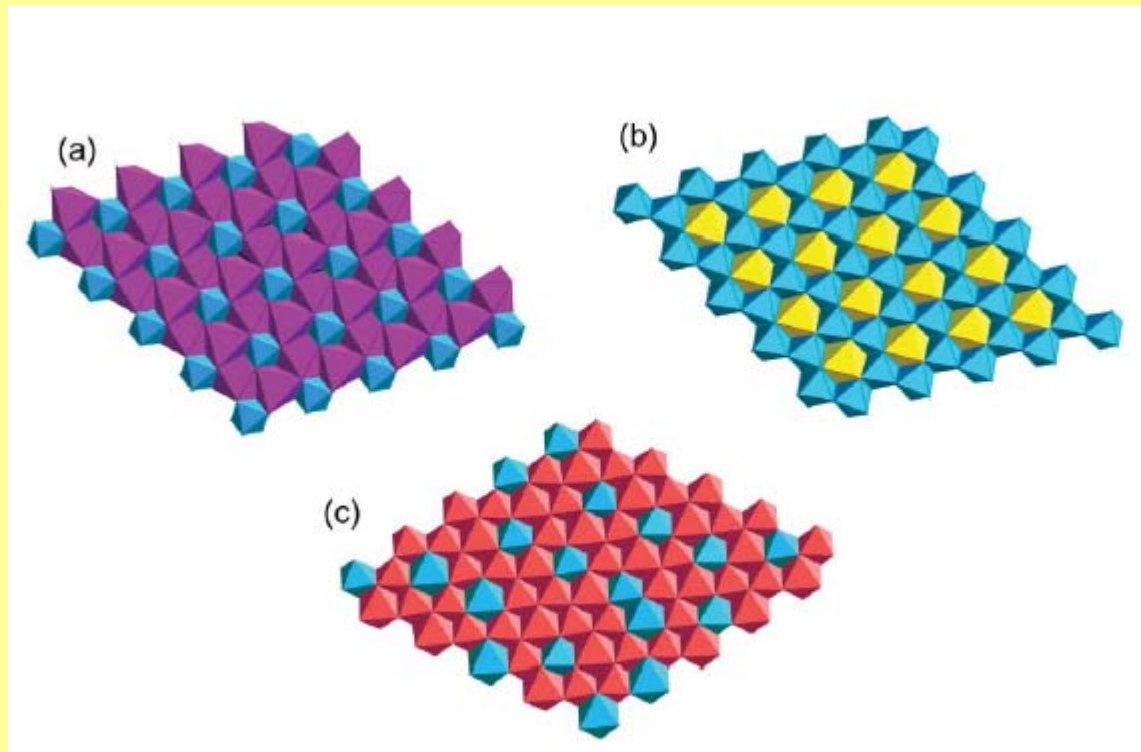


Hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$

# Hydrotalcites

Brucite layers,  $\text{Mg}^{2+}$  substituted partially by  $\text{Al}^{3+}$

Layers have positive charge



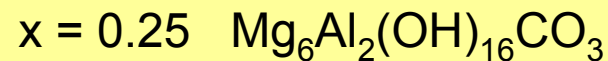
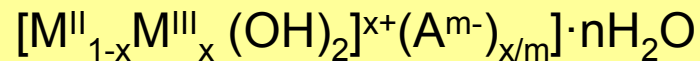
(a)  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (b)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}$  (c)  $[\text{Mg}_{2.25}\text{Al}_{0.75}(\text{OH})_6]\text{OH}$

# Hydrotalcite

The layered structure of LDH is closely related to brucite  $\text{Mg}(\text{OH})_2$

a brucite layer,  $\text{Mg}^{2+}$  ions octahedrally surrounded by six  $\text{OH}^-$   
the octahedra share edges and form an infinite two-dimensional layer  
the brucite-like layers stack on top of one another  
either rhombohedral (3R) or hexagonal (2H) sequence

Hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$  - 3R stacking



# Hydrotalcite

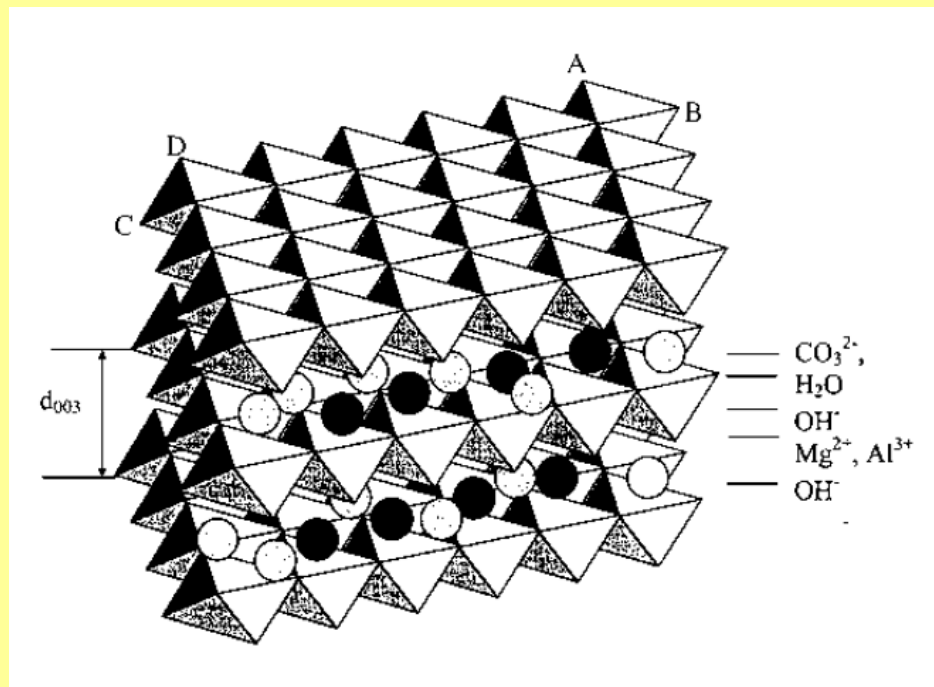
The interlayer spacing  $c'$  is equal to  $d_{003}$ ,  $2d_{006}$ ,  $3d_{009}$ , etc.;

$$c' = (d_{003} + 2d_{006} + \dots + nd_{00(3n)}) / n$$

The cell parameter  $c$  is a multiple of the interlayer spacing  $c'$

$c = 3c'$  for rhombohedral (3R)

$c = 2c'$  for hexagonal (2H) sequences





# Hydrotalcite

Hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$  - 3R stacking

unit cell parameters

$$a = 0.305 \text{ nm} \quad c = 3d(003) = 2.281 \text{ nm}$$

the interlayer spacing:  $d(003) = 0.760 \text{ nm}$

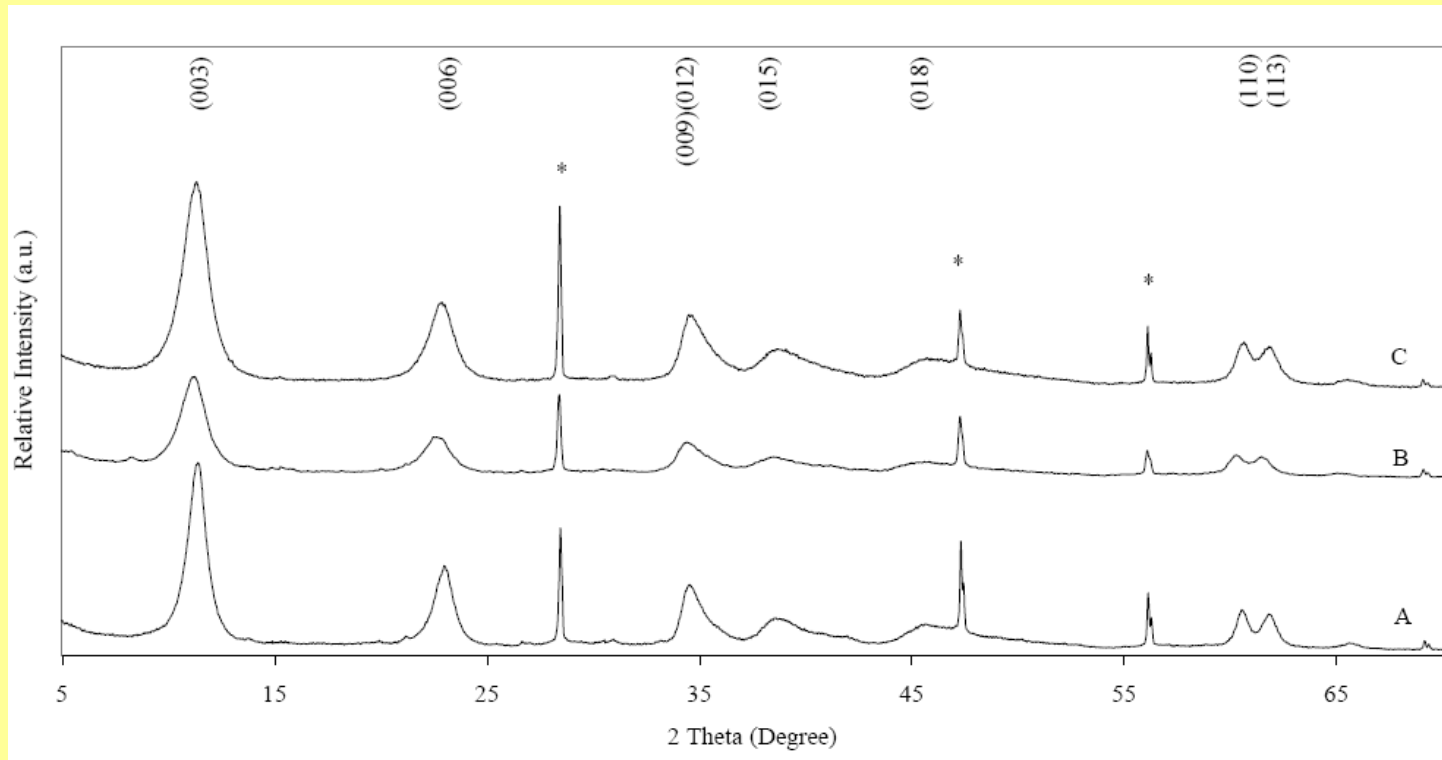
the spacing occupied by the anion (gallery height) =  $0.280 \text{ nm}$

a thickness of the brucite-like layer =  $0.480 \text{ nm}$

the average M—O bond =  $0.203 \text{ nm}$

the distance between two nearest  $\text{OH}^-$  ions in the two opposite side layers =  $0.267 \text{ nm}$  shorter than  $a$  ( $0.305 \text{ nm}$ ) and indicative of some contraction along the  $c$ -axis.

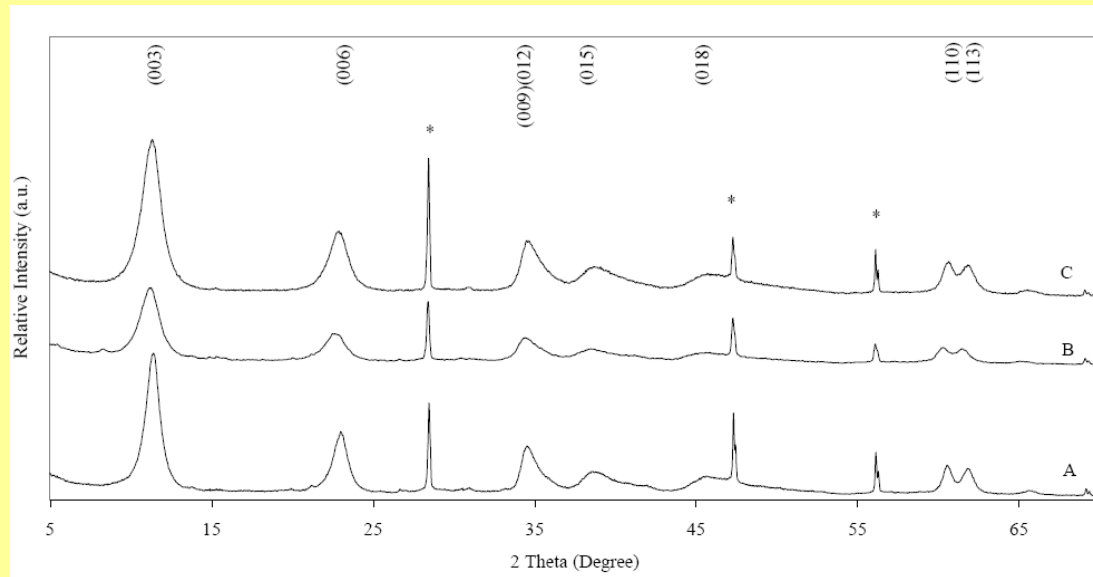
# XRD Patterns of LDH



**XRD patterns of layered double hydroxides synthesized by coprecipitation method with various cations composition:  
A – Mg/Al; B- Mg/Co/Al; C- Mg/Ni/Al**

**\* = Reflections from Si crystal used as a reference**

# XRD Patterns of LDH



rhombohedral structure  
the cell parameters  $c$  and  $a$

The lattice parameter  $a = 2d(110)$  corresponds to an average cation–cation distance

The  $c$  parameter corresponds to three times the thickness of  $d003$

$$c = 3/2 [d003 + 2d006]$$

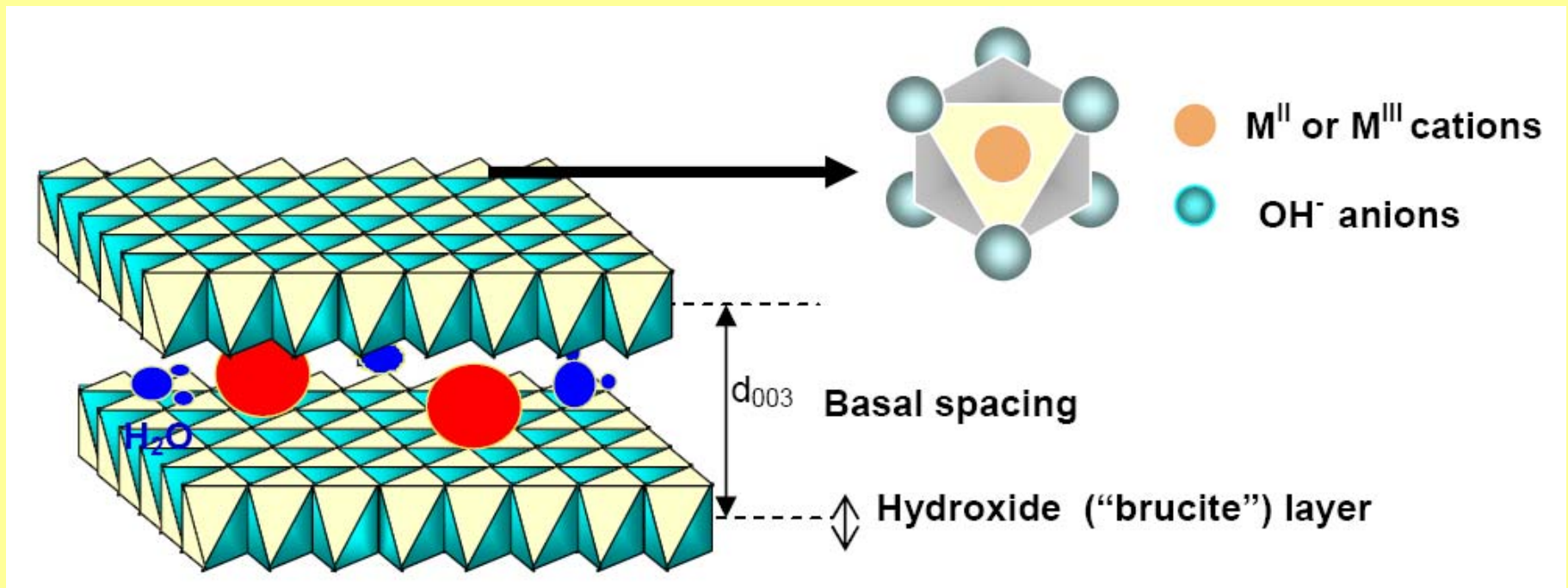
# Layered Compounds

LDH = layered double hydroxides

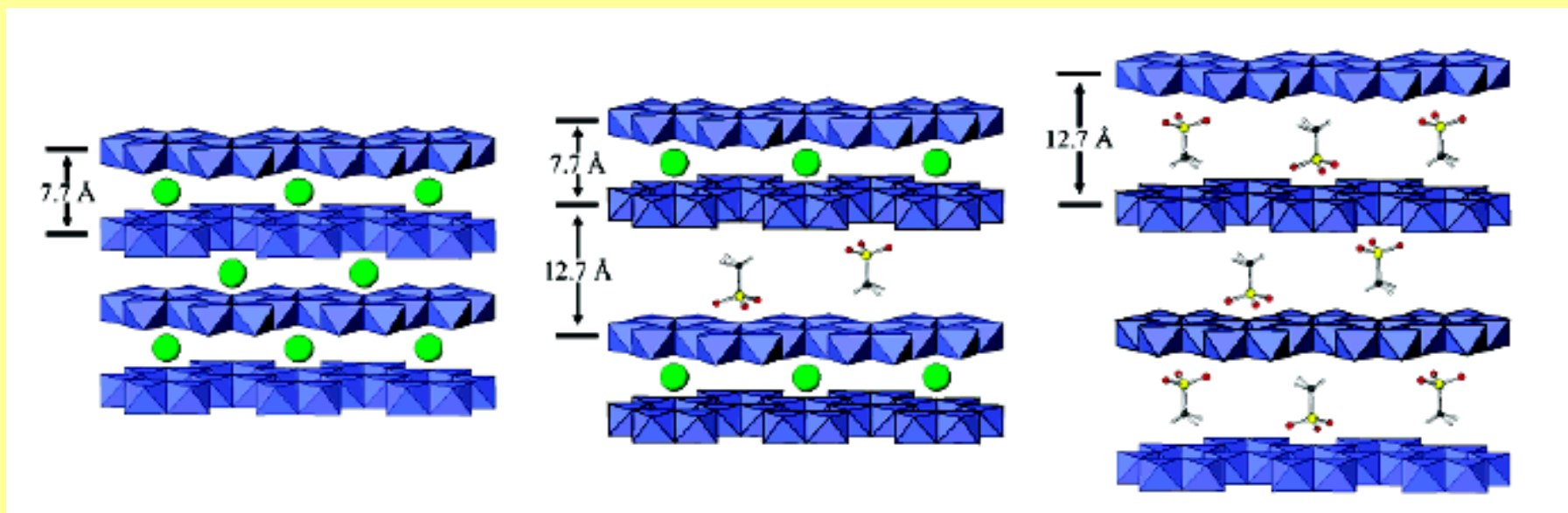
hydrotalcites

mineral  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$

Brucite layers,  $\text{Mg}^{2+}$  substituted partially by  $\text{Al}^{3+}$



# Intercalation to LDH



the intercalation of methylphosphonic acid into Li/Al LDH

(a)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot\text{H}_2\text{O}$

(b) second-stage intermediate, alternate layers occupied by Cl and MPA anions

(c) first-stage product with all interlayer regions occupied by MPA.

# Intercalation to LDH

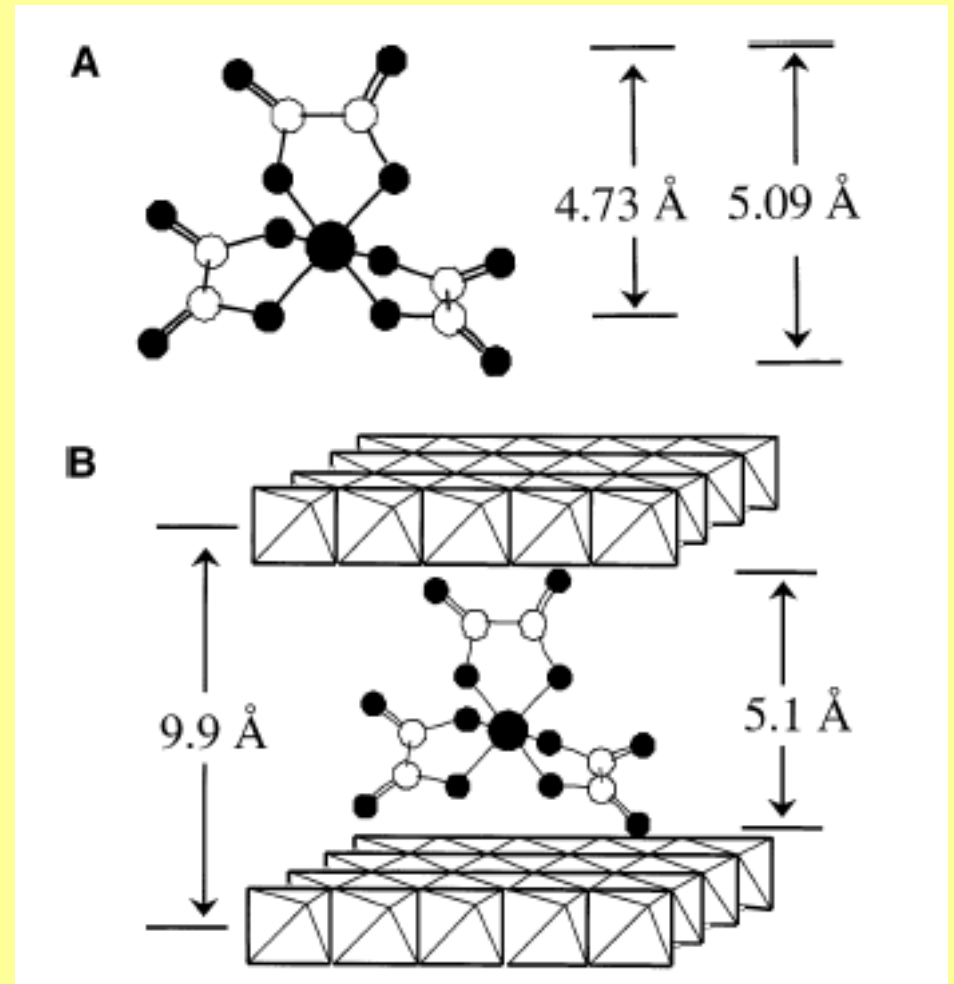
LDH = layered double hydroxides

hydrotalcites  
mineral  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$

Brucite layers,  $\text{Mg}^{2+}$  substituted  
partially by  $\text{Al}^{3+}$

Layers have positive charge

Intercalate anions  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

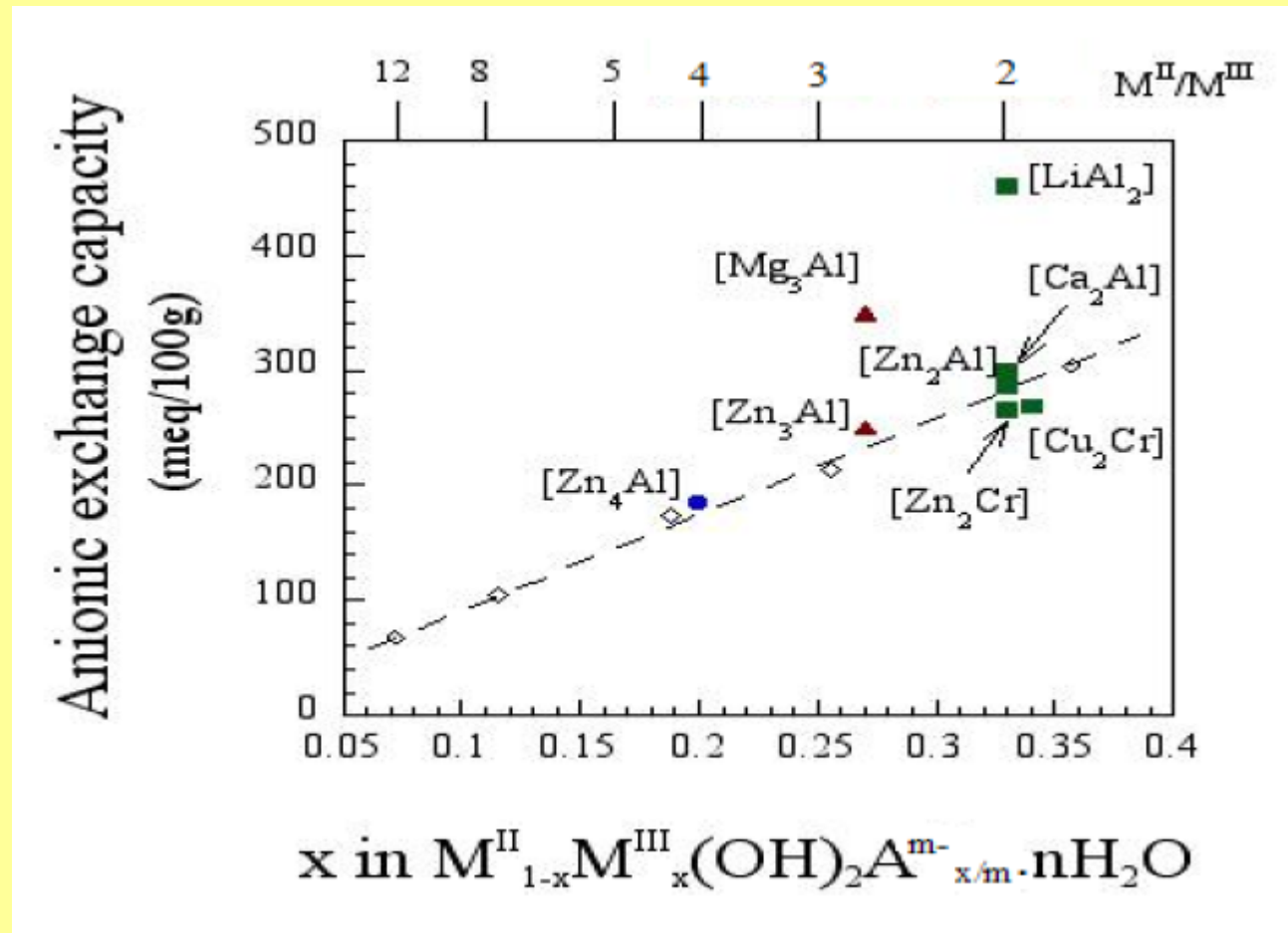


# Memory Effect

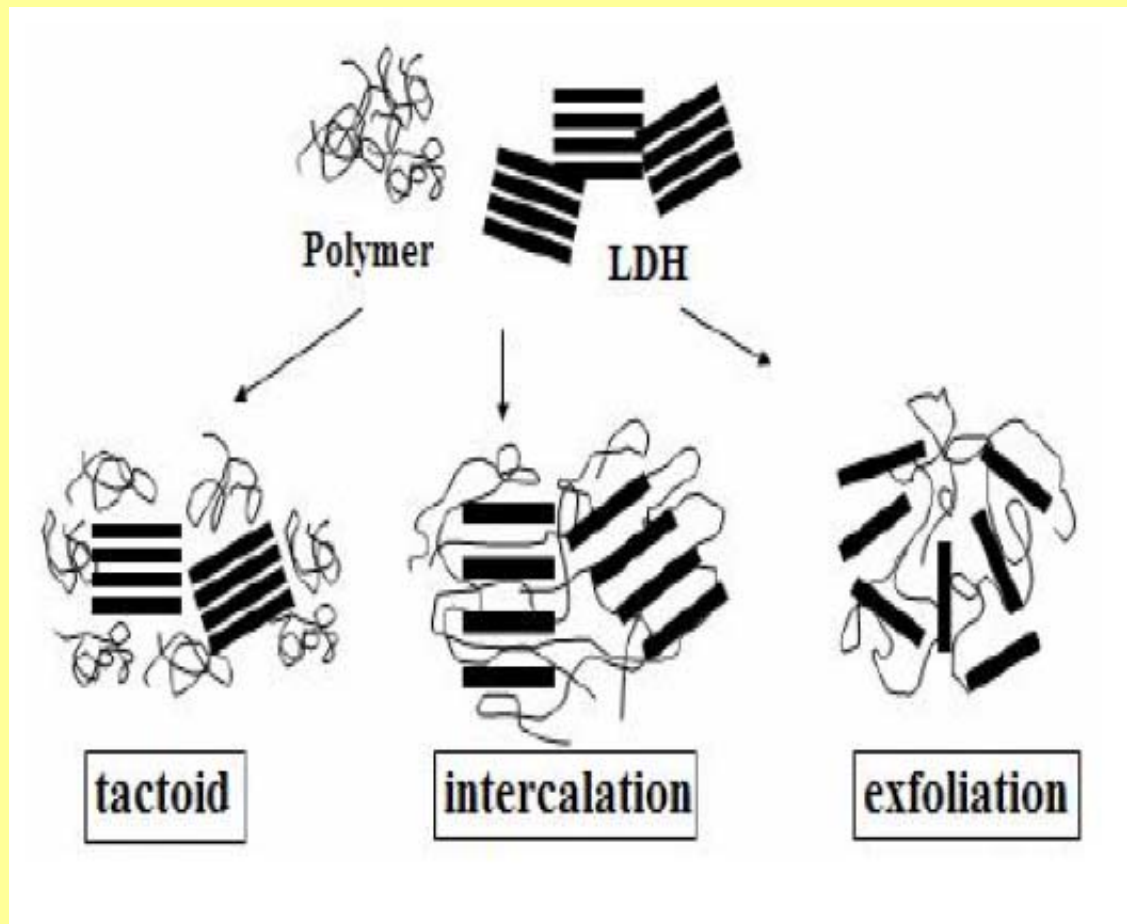
# Calcination to Spinel



# The anionic exchange capacity (AEC)



# Types of the composite structures

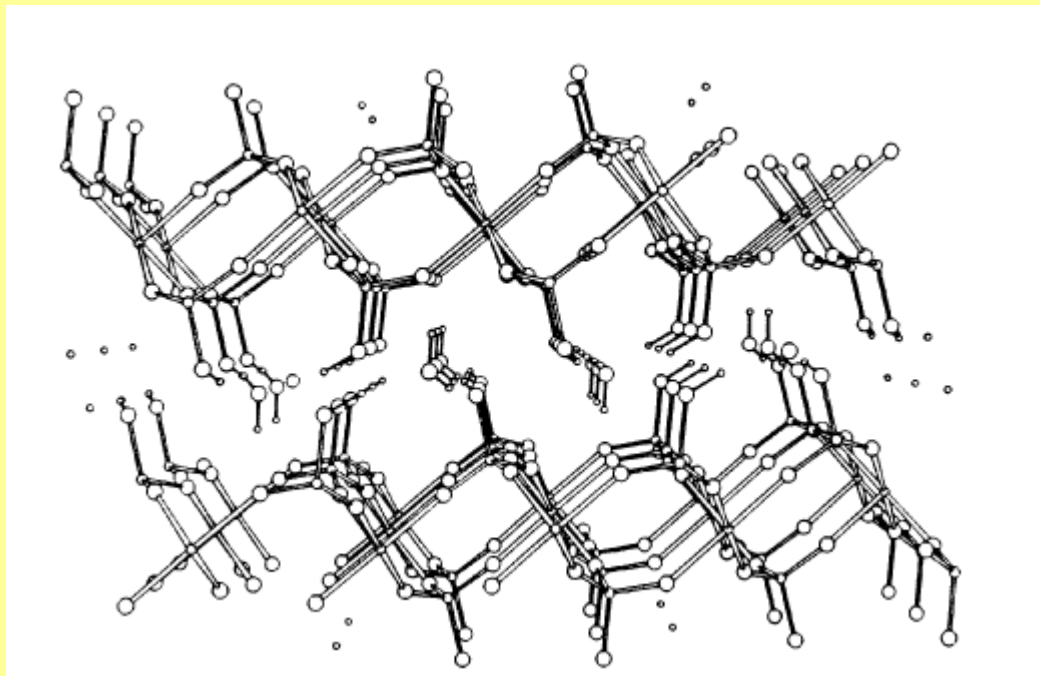


# Layered Compounds

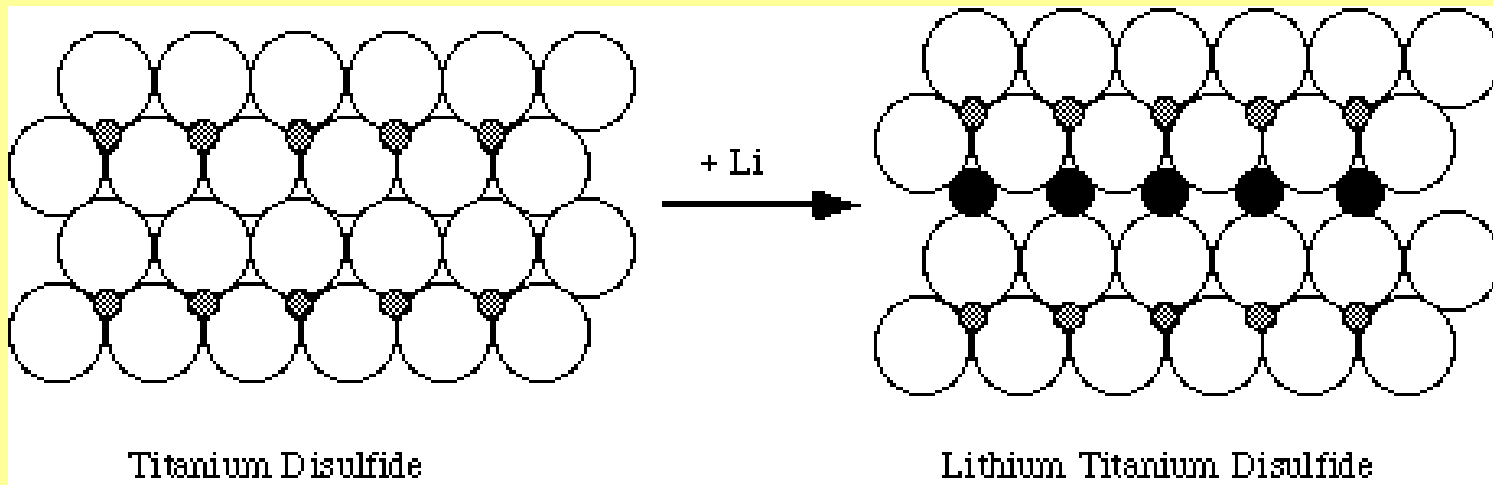
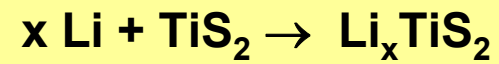
$MPS_3$  (M = V, Mn, Fe, Co, Ni, Zn)

$TiS_2$

$\alpha\text{-Zr(HPO}_4)_2 \cdot \text{H}_2\text{O}$

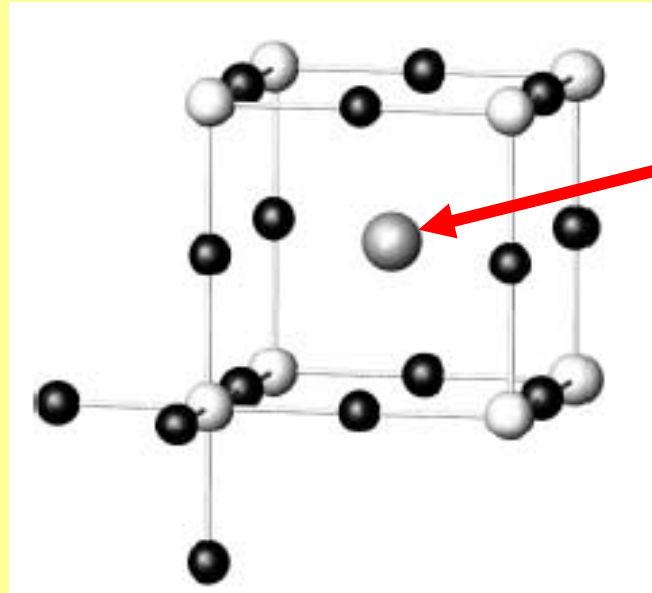


# Layered Compounds



# 3D Intercalation Compounds

$\text{Cu}_3\text{N}$  and  $\text{Mn}_3\text{N}$  crystallize in the (anti-)  $\text{ReO}_3$ -type structure



the large cuboctahedral void in the structure can be filled

By Pd to yield (anti-) perovskite-type  $\text{PdCu}_3\text{N}$

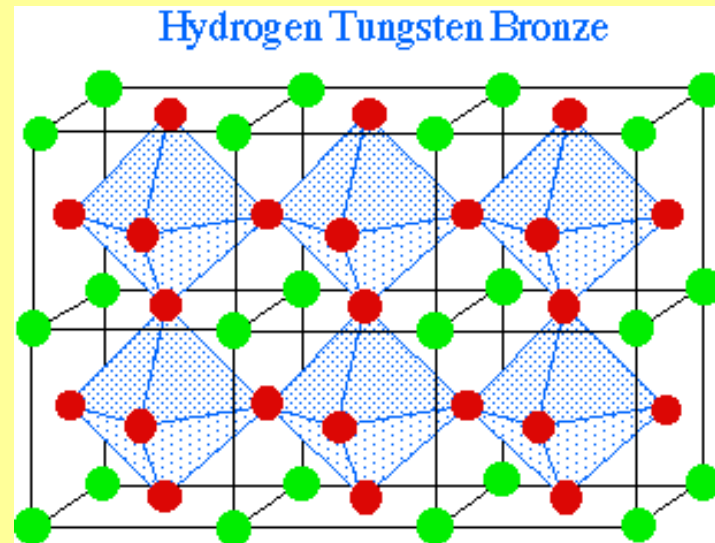
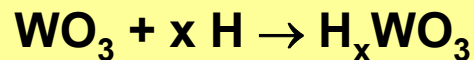
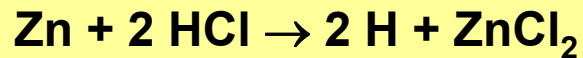
By  $M = \text{Ga}, \text{Ag}, \text{Cu}$  leading to  $\text{MMn}_3\text{N}$

# 3D Intercalation Compounds

Tungsten trioxide structure

=  $\text{WO}_6$  octahedra joined at their corners

= the perovskite structure of  $\text{CaTiO}_3$  with all the calcium sites vacant



The color and conductivity changes are due to the intercalation of protons into the cavities in the  $\text{WO}_3$  structure, and the donation of their electrons to the conduction band of the  $\text{WO}_3$  matrix. The material behaves like a metal, with both its conductivity and color being derived from free electron behavior.

The coloration reaction used in electrochromic displays for sun glasses, rear view mirrors in cars

# 0D Intercalation Compounds

