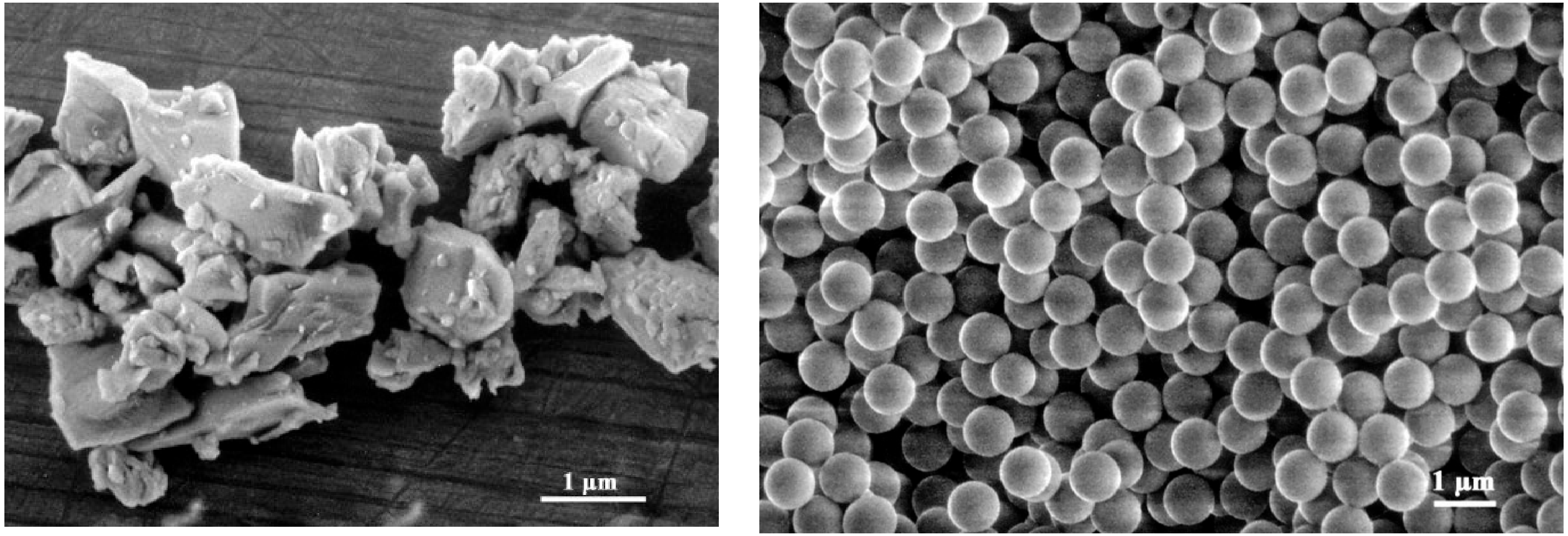
Elaboration of ceramics and colloids

Week 3

A. Testino

2.3 Raw materials and powder synthesis (p.81-127 *)



* Les Traité des Matériaux, Volume 16 « Les Céramiques »

2.3 Raw materials and powder synthesis

This week

next week(s)

* Les Traité des Matériaux, Volume 16 « Les Céramiques »

Summary

Properties of materials: atoms, bonds, packing. Basic concepts recall (*repetita iuvant)*

- **Ceramics**: natural or synthetic inorganic, non-metallic *polycrystalline* materials. Single crystals should not be considered ceramics. ***Ionic bonds***: metal – nonmetal (high electronegativity* difference). Cation and anion with high electrostatic force. ***Covalent bonds***: two nonmetals (similar electronegativity), shared electron pairs. In ceramic: ionic bond is predominant (due to oxygen..., metal oxides). *Properties*: high hardness, high melting points, low thermal expansion, and good chemical resistance, but brittleness. But properties depends on microstructure (grain size/shape, pores).

- **Glasses** are made of inorganic, non-metallic materials with an *amorphous* structure. Glass-ceramics: something in the middle. *Properties*: similar to ceramics in many aspects, but can be blown, drawn, laminated.

- **Metals.** ***Metallic bonds***: cations are surrounded by delocalized electrons. *Properties*: ductility, conductivity, etc.

- **Polymers.** ***Van der Waals bonds***: weak electrostatic forces permanent or induced polarization. E.g. hydrogen bond, interaction *between* polymeric chains (C-C, C-H, etc. bonds within the polymeric chain are covalent). *Properties*: elasticity, easily to melt, low strength, etc.

*Electronegativity: is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to cesium and francium which are the least electronegative at 0.7. (Oxygen: 3.5, metals: 1-2. Thus, any metal oxides…)

Introduction

- Raw materials, as supplied by powder producers, are often partially modified for ceramic manufacturing.
- The two main families of powders are Synthetic and Natural
- Synthetic are chemically modified products - expensive
- Natural come from the earth - sometimes with washing, grinding, classification
- Clays, quartz …… - cheap material
- Several manufacturing methods for synthetic
- More expensive powders does not imply an more expensive product: it depends on the whole manufacturing process:
  - – design
  - – forming
  - – sintering
  - – machining
  - – polishing
  - – market size
  - – added value

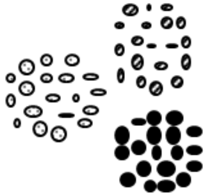
Silicon Carbide - synthetic

Refined quartz sand - 99.5% SiO_2

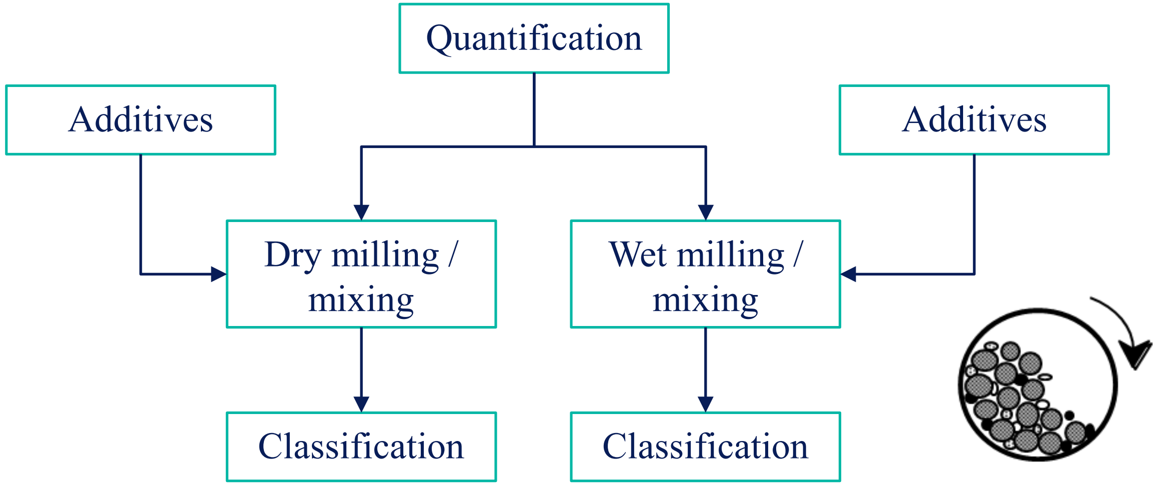
<1mm

Manufacture of Ceramics – Powders

Raw Materials



- High chemical purity;
- High reactivity: particle size in the µm range and a SSA of about 5-10 m^2/g;
- High homogeneity from both physical and chemical viewpoint;
- Constant quality of the raw materials (reproducibility is essential!)



Quantification

Additives

Additives

Dry milling / mixing

Wet milling / mixing

Classification

Classification

Two main families of synthetic powders / ceramics

- oxides (Al_2O_3, ZrO_2… ..)
- Ionic bonds…..

- non-oxides (SiC, TiN, Si_3N_4……)
- Covalent bonds….

e.g. Alumina, Al_2O_3

e.g. Silicon Nitride, Si_3N_4 (Kyocera)

* Les Traité des Matériaux, Volume 16 « Les Céramiques »

Market Global - Products Ceramics- growing market (billions of Euros)

Table 1 *: Evolution of the world market (expressed in billions of euros) of the main ceramic products*

Year **Products**	**1990**	**1992**	**1994**	**1996**	**1998**	**2000**	**2002**	**Evolution % 1990/2002**
Bricks	20.5	22.5	23.5	22.5	24.0	25.0	26.0	27
Floor and wall tiles	10.0	11.0	17.5	24.0	31.0	33.0	35.5	255
Table services	6.5	7.0	8.5	9.0	9.0	9.5	10.0	54
Sanitary	4.0	4.5	5.0	5.5	6.5	7.5	8.0	100
Refractories	12.0	12.5	12.5	12.0	12.5	12.5	12.5	4
Technical ceramics	15.0	17.5	19.0	24.0	29.0	32.0	**34.0**	127
Total	68.0	75.0	86.0	97.0	112.0	119.5	126.0	85
Progress (%)	100	110	127	143	164	176	185	7.1 ./. Year

Ceramic tiles market - 2017 - 13.1 trillion m^2 to 13.9 trillion m^2 in 2018 -

https://www.ceramica.info/fr/articoli/scenario-mondial-du-batiment-fevrier-2018/

Raw Materials

Table 2.6. Some compositions of raw materials with the main impurities and applications.

Raw material	**Compounds**		**Applications**
	Major	**Minor**	
Bauxite	Aluminum hydroxides (gibbsite) and oxide hydroxides (boehmite, diaspore)	Silica, iron oxide, titanium oxide, aluminosilicates	Abrasives, cements, refractories, chemicals
Clays - (aluminosilicates)	kaolin, montmorillonite, illite	quartz, micas, vermiculite, feldspar, carbonaceous materials	floor tiles, pottery, sanitary ware, paper, bricks, cements, porcelain, absorbents, refractories
Bentonite	montmorillonite	Many - various	drilling mud, pelletizing, sand stability
Kyanite	Kyanite	iron oxide, pyrite, micas	Bricks and refractories
Schists	Clay minerals (60%), silica (30%)	feldspar (5%) calcite and dolomite (5%), iron oxide (0.5%), organic materials (1%)	Bricks and refractories 

Clays

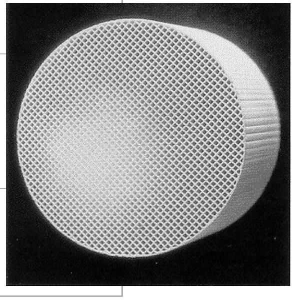
- Clays - rather than clay mineral – are less pure
- Clays - residual or sedimentary
- Residual
  - Found in their place of origin, i.e. in a parent rock
- Sedimentary
  - Transported by water elsewhere - finer - large particles lost during transport - less quartz - greater plasticity but
  - Contaminated with other fine particles difficult to separate
- Clays for:
  - pottery (2% iron oxides)
  - bricks (8% iron oxides) - red !!

Albion House - Liverpool

Refined Raw Materials

Table 2.7. The main refined materials used for ceramics (**and glasses**): chemical formulas and applications.
Silicates: They are the largest and most important class of minerals and make up approximately 90% of the Earth's crust

Refined minerals	Main components / chemical formula	Applications
Ball clay	Kaolinite $Al_4Si_4O_{10}(OH)_8$	Pottery, tiles, sanitary ware, porcelain
Feldspars - soda, - potash - calcium	albite - $Na_2O.Al_2O_3.6SiO_2$ orthoclase - $K_2O.Al_2O_3.6SiO_2$ anorthite - $CaO.Al_2O_3.2SiO_2$	Porcelain (fluxing agent), crockery, tiles and electrically insulating porcelain
Fluorspar	CaF_2	Glass, fiberglass, steel cleaner, filler rod, hydrofluoric acid
Kaolins *	kaolinite – $Al_4Si_4O_{10}(OH)_8$ Phyllosilicate	Paper, sanitary ware, tableware, fiberglass, refractories, filler, tiling
Quartz	SiO_2(99%)	Porcelain, refractories, enamels
Talc	$3MgO.4SiO_2.H_2O$	Porcelain, refractories, enamels, paint, paper, cosmetic plastics,
Sand	95-99.8% SiO_2	Glasses, fiberglass



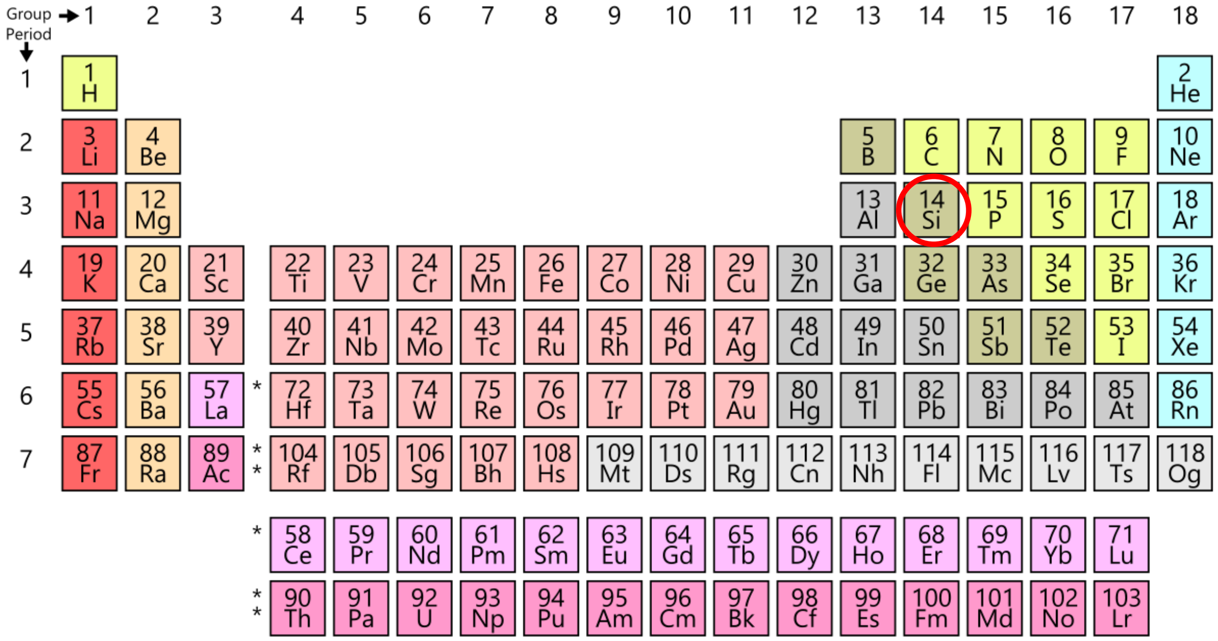
Support catalyst - car
Synthetic cordierite: 30% talc - 70% Kaolin (low thermal expansion)

water sapphires

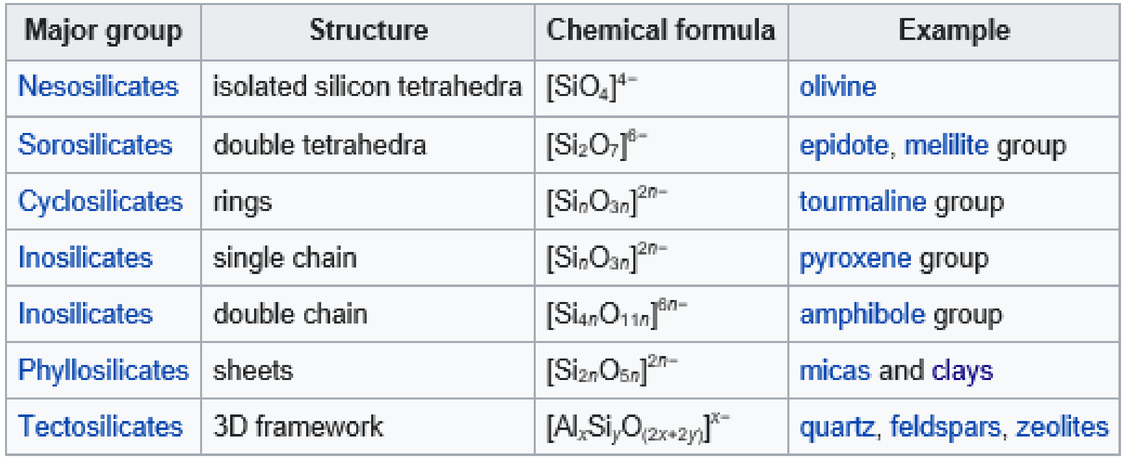
* - Kaolin - origin of the word – From Chinese provence - Kao Ling

Chemistry and (alumino)silicates…

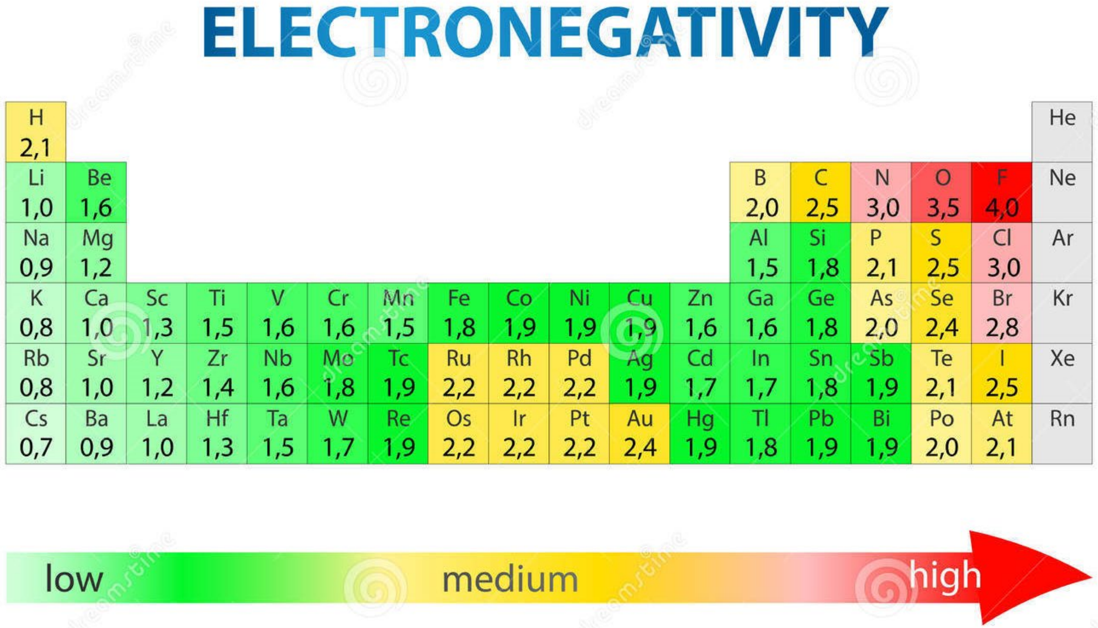
(90 percent of the Earth's crust)



Group → Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac **	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
*				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
**				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	



Major group	Structure	Chemical formula	Example
Nesosilicates	isolated silicon tetrahedra	$[SiO_4]^{4-}$	olivine
Sorosilicates	double tetrahedra	$[Si_2O_7]^{6-}$	epidote, melilite group
Cyclosilicates	rings	$[Si_nO_{3n}]^{2n-}$	tourmaline group
Inosilicates	single chain	$[Si_nO_{3n}]^{2n-}$	pyroxene group
Inosilicates	double chain	$[Si_{4n}O_{11n}]^{6n-}$	amphibole group
Phyllosilicates	sheets	$[Si_{2n}O_{5n}]^{2n-}$	micas and clays
Tectosilicates	3D framework	$[Al_xSi_yO_{(2x+2y)}]^{x-}$	quartz, feldspars, zeolites



ELECTRONEGATIVITY

H 2,1																	He
Li 1,0	Be 1,6											B 2,0	C 2,5	N 3,0	O 3,5	F 4,0	Ne
Na 0,9	Mg 1,2											Al 1,5	Si 1,8	P 2,1	S 2,5	Cl 3,0	Ar
K 0,8	Ca 1,0	Sc 1,3	Ti 1,5	V 1,6	Cr 1,6	Mn 1,5	Fe 1,8	Co 1,9	Ni 1,9	Cu 1,9	Zn 1,6	Ga 1,6	Ge 1,8	As 2,0	Se 2,4	Br 2,8	Kr
Rb 0,8	Sr 1,0	Y 1,2	Zr 1,4	Nb 1,6	Mo 1,8	Tc 1,9	Ru 2,2	Rh 2,2	Pd 2,2	Ag 1,9	Cd 1,7	In 1,7	Sn 1,8	Sb 1,9	Te 2,1	I 2,5	Xe
Cs 0,7	Ba 0,9	La 1,0	Hf 1,3	Ta 1,5	W 1,7	Re 1,9	Os 2,2	Ir 2,2	Pt 2,2	Au 2,4	Hg 1,9	Tl 1,8	Pb 1,9	Bi 1,9	Po 2,0	At 2,1	Rn

Electronegativity and

metals/non metals

C: 2.5	N:3.0
O: 3.5	H: 2.1
Si: 1.8	Al: 1.5

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Porcelain

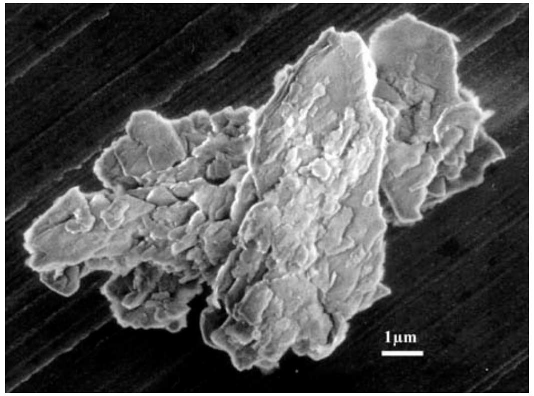
Porcelain: from old Italian word "porcellana"

Cowrie shell

since resemblance the shell surface.

Kaolin

(50-55%)

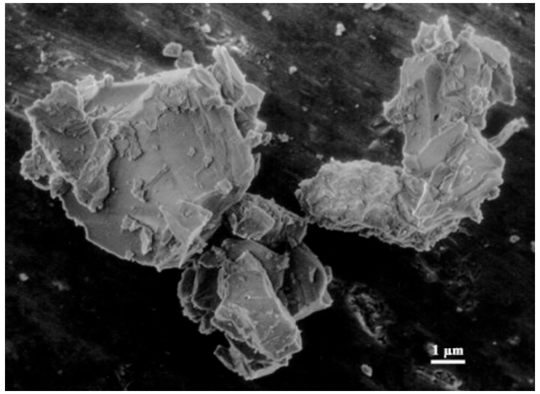


Feldspar

(25%)

glassy phase,

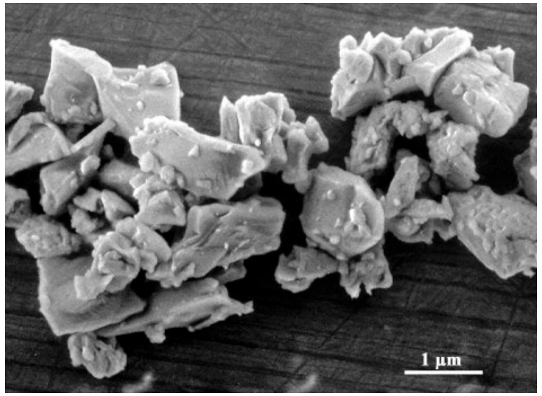
decrease firing temperature (flux)



Quartz

(20-25%)

thermal and dimensional stability

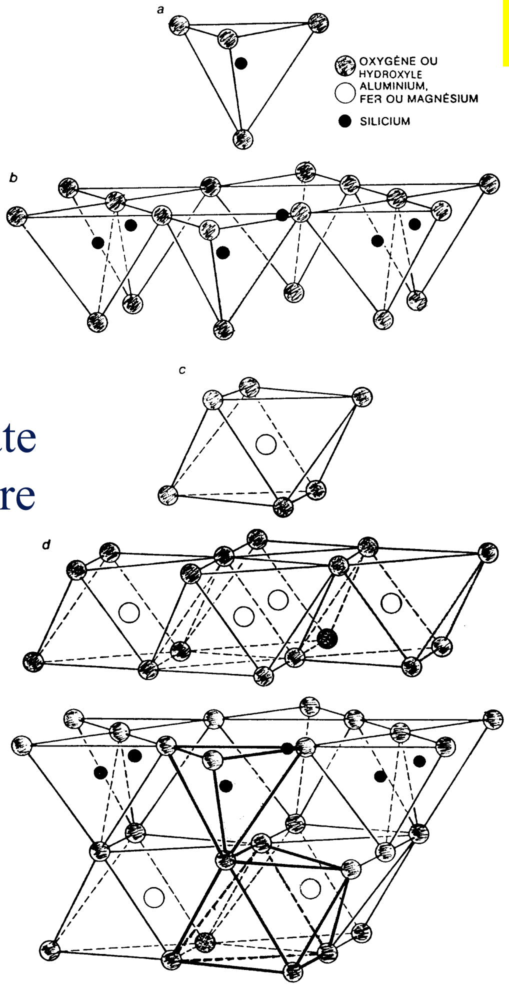


Porcelain

(hard)

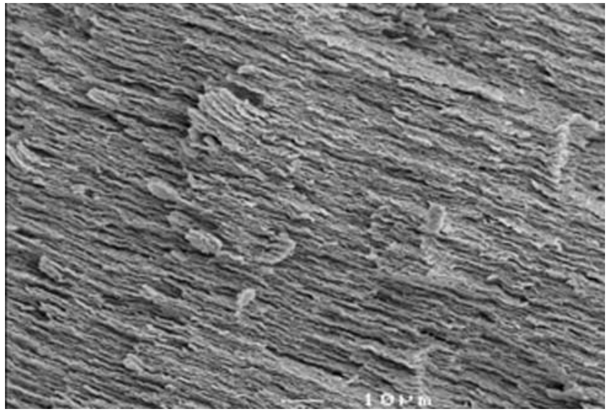
Kaolin

Alumino-silicate layered structure



Kaolin

Thin sheets



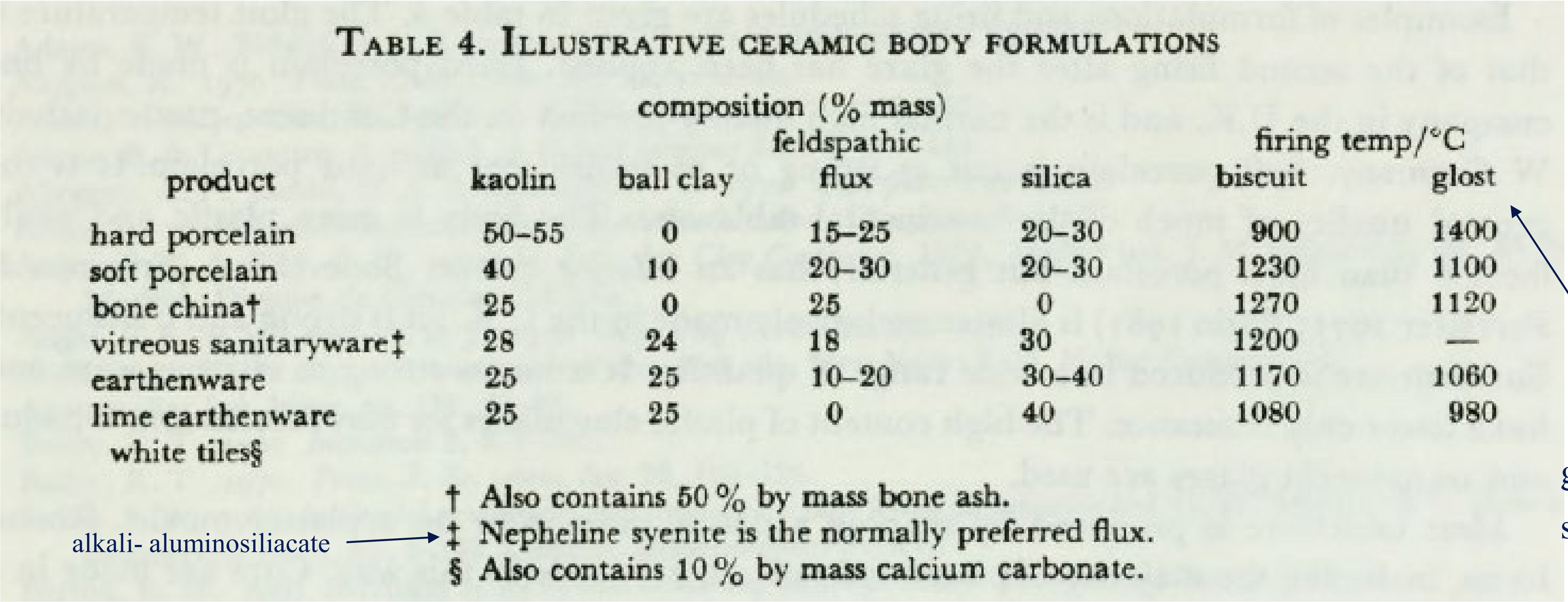


TABLE 4. ILLUSTRATIVE CERAMIC BODY FORMULATIONS

product	composition (% mass) kaolin	ball clay	feldspathic flux	silica	firing temp/°C biscuit	glost
hard porcelain	50–55	0	15–25	20–30	900	1400
soft porcelain	40	10	20–30	20–30	1230	1100
bone china†	25	0	25	0	1270	1120
vitreous sanitaryware‡	28	24	18	30	1200	—
earthenware	25	25	10–20	30–40	1170	1060
lime earthenware white tiles§	25	25	0	40	1080	980

† Also contains 50 % by mass bone ash.

‡ Nepheline syenite is the normally preferred flux.

§ Also contains 10 % by mass calcium carbonate.

alkali- aluminosiliacate

glaze firing or second firing

W.B. Jepson, " Kaolins: their properites and use"
Phil. Trans. R. Soc. Lond. A 311, 411-432 (1984)

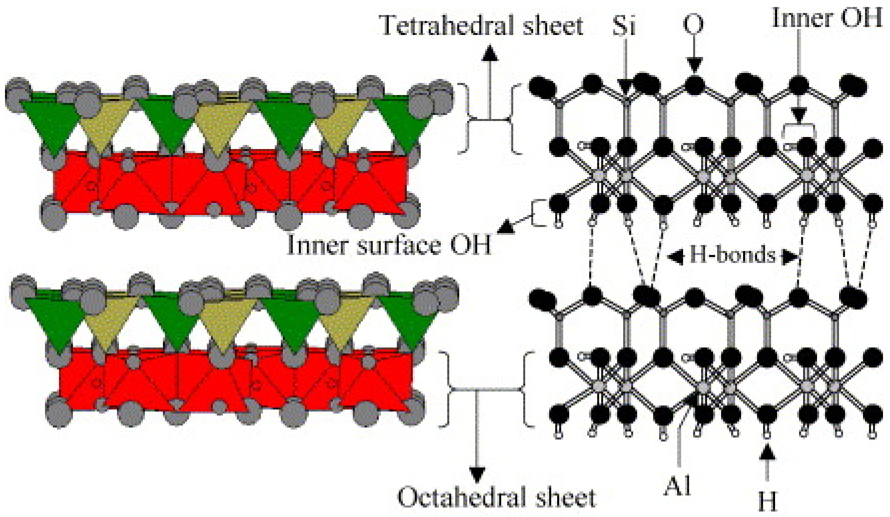
earthenware

soft/hard porcelain (different firing T, weaker / toughness)

Bone china strongest porcelain

Structure of clays 1:1 & 2:1

(a) **Kaolin** 1:1 structure

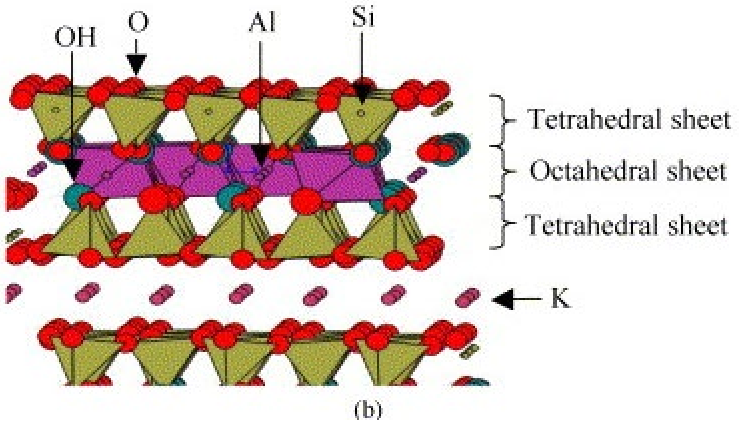


Kaolinite is a non-swelling clay. It is composed of layers that are linked together through hydrogen bonds between the hydroxyl surfaces of one layer with the oxygen atoms of the next layer. These bonds keep charge countering cations from entering the interlayer space. This unit repeats through out the structure of kaolinite to produce alternating layers in a 1:1 silicon to aluminum ratio*.

Substitution of Si^{4+} by Al^{3+} or Al^{3+} by Mg^{2+}

Need interlayer ion (e.g. K^+) to charge compensate for substitution

(b) **Montmorillonite.** 2:1 structure

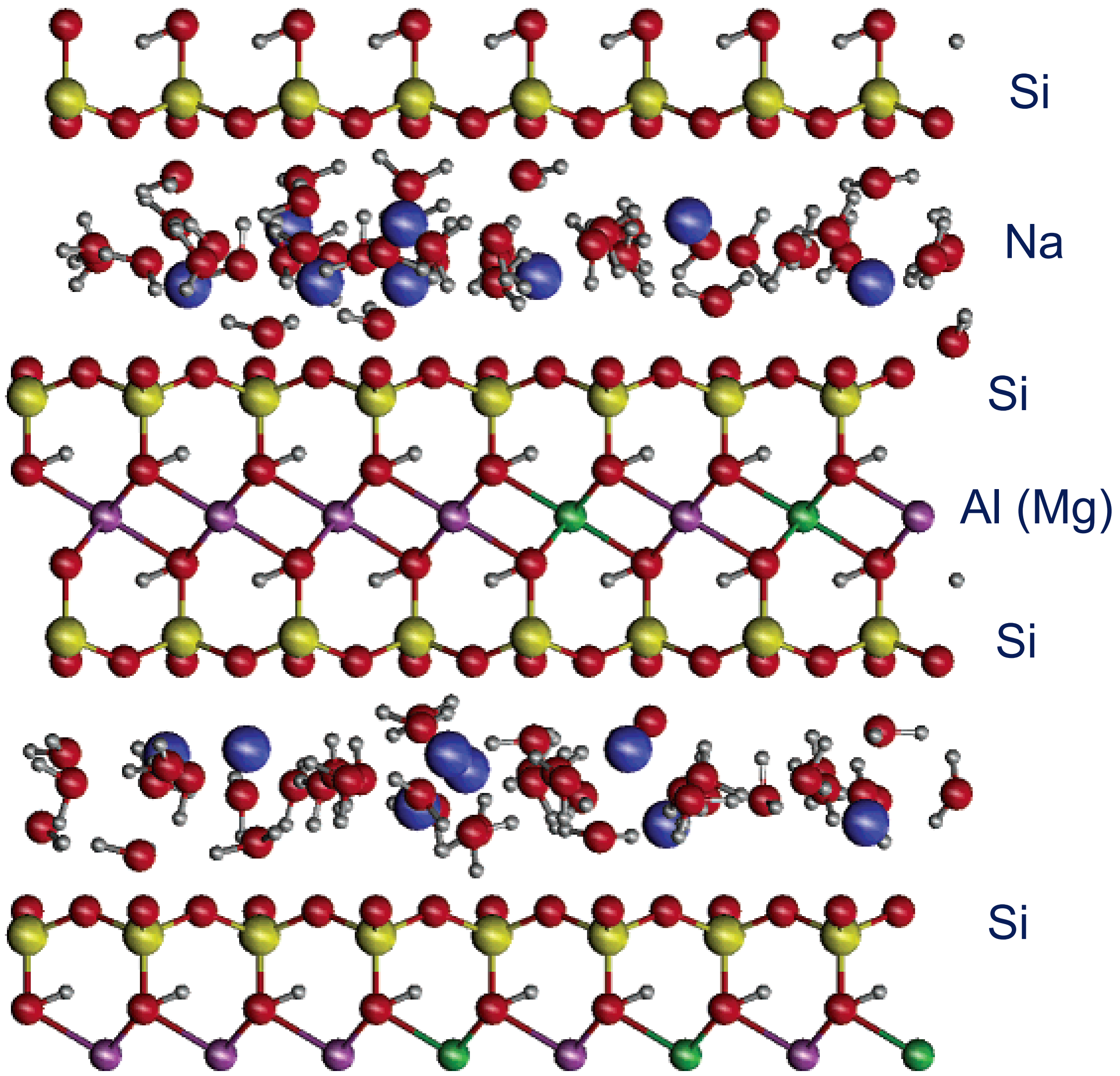


Montmorillonite is a swelling clay, the layers are ordered in a 2:1 silicon to aluminum ratio which are held together by van der Waals forces and / or interlayer charge-countering cations that can easily hydrate in the presence of water. The hydration energy is greater than the energy binding the layers, allowing the interlayer distance to increase in the presence of water due to the hydration of the cation and can result in a swelling of the structure*.

Konan eta l J.Coll.Interf.Sci 307 (1) 2007, 101–108

*Schuttlefield et al J.Geo.Phys.Res (2007)

Clay (2: 1) - Swelling Clays e.g. - Na Montmorillonite



Atomistic model of the one-layer hydrate of sodium montmorillonite

O: red,
H: white,
Si: yellow,
Na: blue,
Al: purple,and
Mg: green

This super cell simulation consists of two interlayer regions made up by 8 unit cells

Exchange of Na^+ with Li^+ – extra water of hydration interlayer spacing increased – pillared clays – catalysis

2.3.3 Chemical Synthesis Methods

Solid reagents
Thermal decomposition of solids
Solid-solid reaction
Solid-vapor reaction

- Thermal Decomposition of Solids
- Simple method - inexpensive
- Thermal decomposition of a metal salt (carbonate or nitrate). Salts are often a product of a precipitation reaction
- The particle size, purity, and shape of the final powders are highly dependent on the characteristics of the initial salt particles.
- There are two main factors to consider for the production of powders by thermal decomposition:
  - thermodynamics (TD) and
  - kinetics (K) of the reaction.

1

Thermal Decomposition of Solids

- Temperature at which decomposition becomes thermodynamically favorable depends on
  - the strength of the chemical bond of the solid in question and if
  - a gas is produced, the partial pressure of this gas in the surrounding atmosphere.

- Thermal decomposition of $MgCO_3$ is a good illustration of this type of reaction

$$MgCO_3 \rightarrow MgO + CO_2$$

- The enthalpy of reaction, ΔH_r^0 from $MgCO_3$ to MgO and CO_2 at 298 K is 105 KJ/mol (endothermic).
- Therefore, thermal energy will promote the decomposition of the compound.

Variation of the standard enthalpy, ΔH^0: it is the change in enthalpy when a substance(s) passes from its (their) initial to final state, in standard conditions. "Standard conditions" means in its (their) pure form at a given temperature and under a pressure of 1 bar.

Thermal Decomposition of Solids

$$\Delta_r G^0(T) = -RT \ln K_{eq}$$

System in equilibrium

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln Q_r$$

System out-of-equilibrium

$\Delta_r G$ is the free energy of reaction; $\Delta_r G^0$ standard free energy

R the gas constant, T the temperature (K) and

Q_r reaction quotient

a (activity) for liquids

f (fugacity) for gases

$a = 1$ for solids

$$Q_r = \frac{\prod_j (a_j)^{\nu_j}}{\prod_i (a_i)^{\nu_i}}$$

j : products

i : reagents

examples

$2A_{(aq)} + B_{(aq)} \rightarrow 3C_{(aq)}$

$$Q_r = \frac{(a_C)^3}{(a_A)^2 (a_B)}$$

$2A_{(s)} + B_{(aq)} \rightarrow C_{(g)}$

$$Q_r = \frac{f_C}{a_B}$$

Thermal Decomposition of Solids

influence of the atmosphere on the decomposition temperature of solids

$$MgCO_3 \rightarrow MgO + CO_2$$

$$Q_r = \frac{f_{CO_2}\cdot \overset{1}{a_{MgO}}}{\underset{1}{a_{MgCO_3}}} \cong p_{CO_2}$$

$$p_i = x_i \cdot p_t \qquad p_t = \sum_i p_i \qquad n_t = \sum_i n_i$$

$$x_i = \frac{n_i}{n_t} \qquad \sum_i x_i = 1$$

n_i: mol of *i*

x_i : molar fraction of *i*

p_i : partial pressure of *i*

p_t : total pressure

n_t: total mol

As in solution concentration is an approx. of activity, partial pressure is an approx. of fugacity

$$\Delta_r G(T) = \Delta_r G^0(T) + \mathrm{RT} \ln p_{CO_2}$$

$p_{CO_2} = 1;\ \ln 1 = 0$

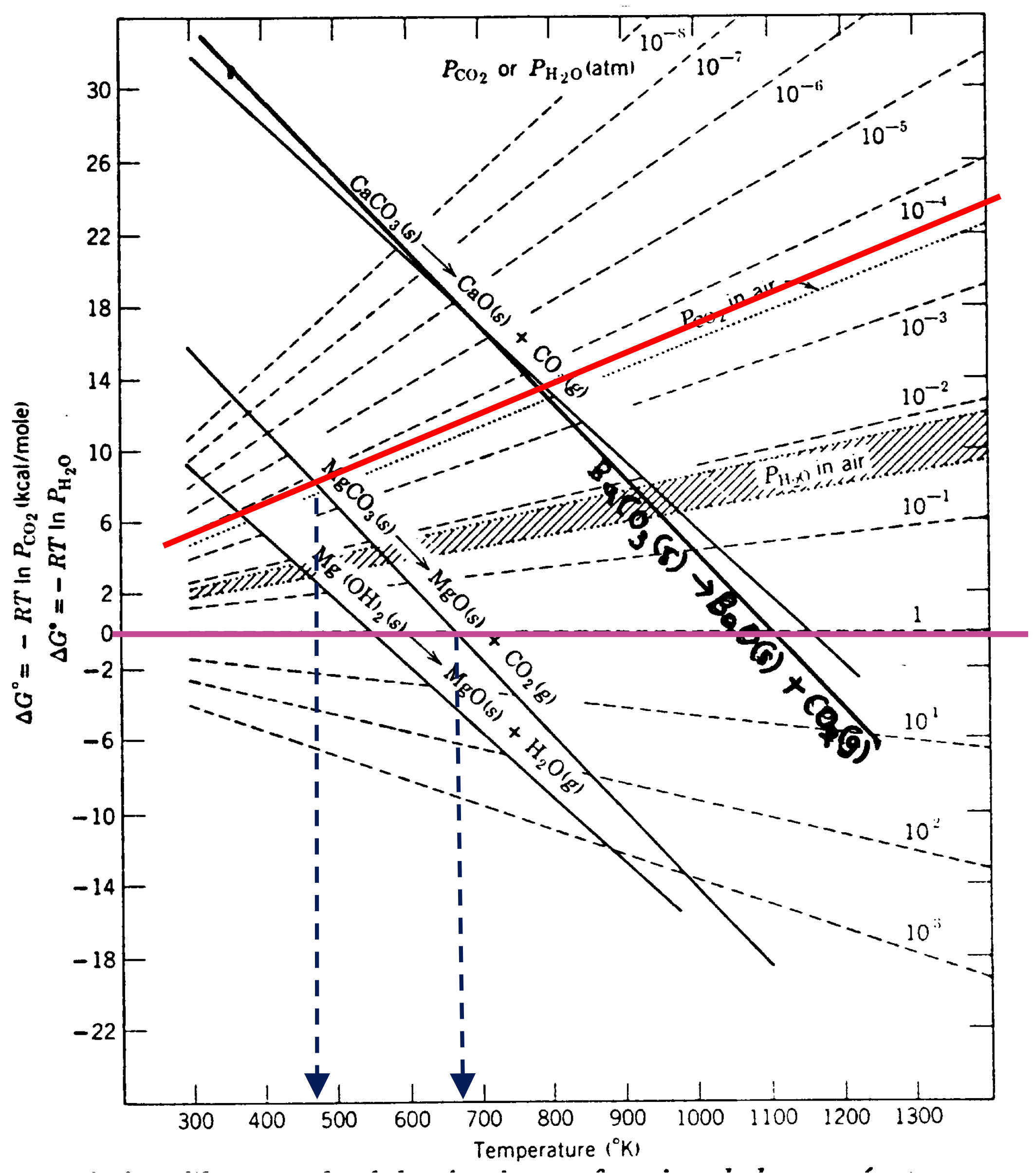
$\Delta_r G(T) = \Delta_r G^0(T)$

Reaction to take place spontaneously when $\Delta_r G < 0$

For a given system under a product gas atmosphere (standard conditions), there is only one equilibrium temperature. When decompositions are carried out in air: $P_{CO2} = 5 \times 10^{-4}$ bar.

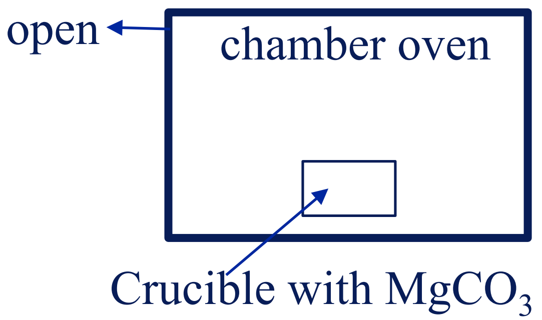
Large effect of atmosphere on decomposition temperature.

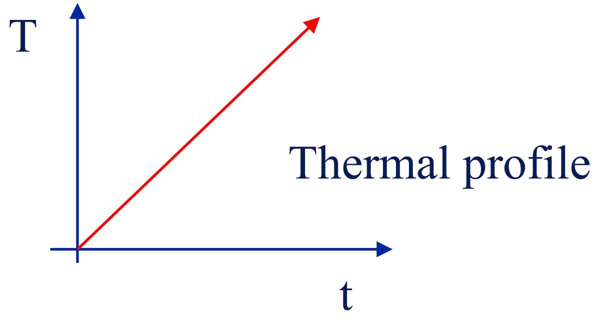
Thermal Decomposition of Solids



- $\Delta G_R = 0$ for $MgCO_3$ at 672 K,
- T> 672 K $MgCO_3$ will decompose spontaneously at atmospheric pressure ($p_{CO2} > 1$ bar)
- For air $p_{CO2} = 5 \times 10^{-4}$ bar, $MgCO_3$ starts to decompose at around 480 K

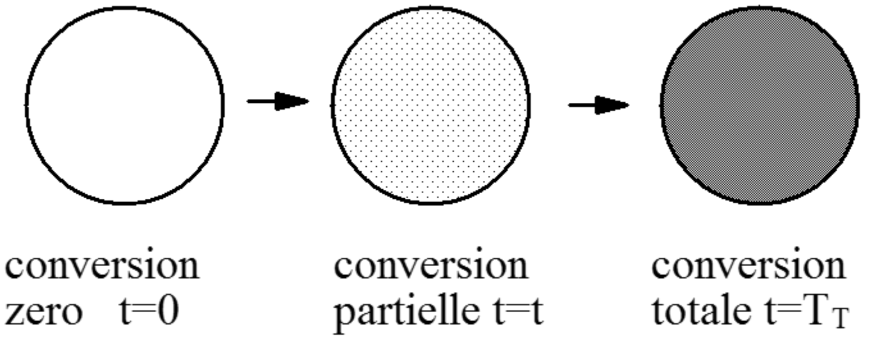
- Once the thermodynamic conditions are fulfilled, the transformation kinetics are governed by
  - Diffusion of the CO_2 produced from the interface through the formed product layer
  - Heat transport to the interface
  - Chemical reaction itself.



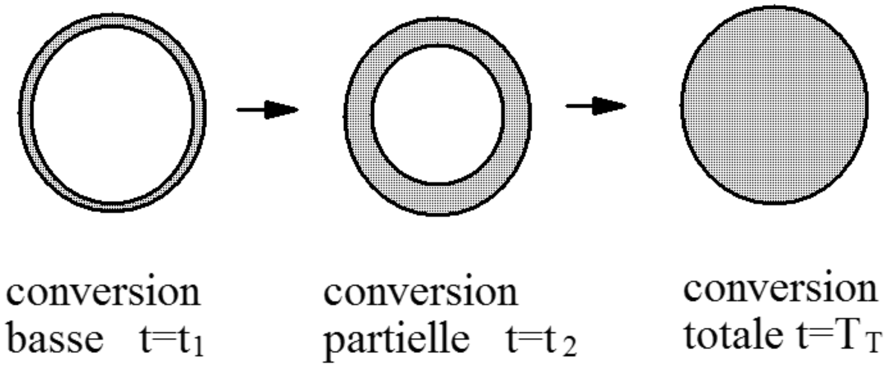


Thermal Decomposition of solids - Kinetics - models

(a) Conversion progressive



(b) Coeur rétrécissant

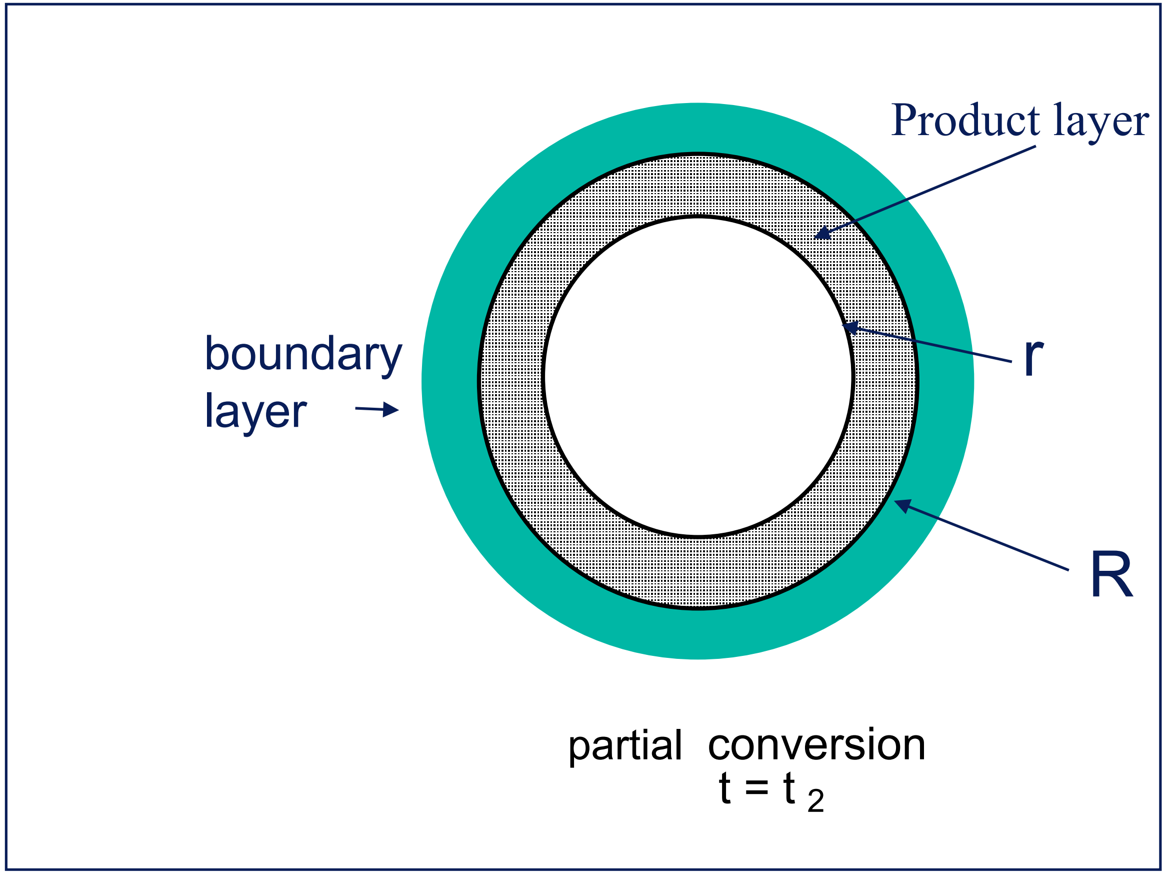


- **Gradual conversion**
- Porous Particles
- Product gas evacuated quickly
- Good heat conductor
- Gradients of T or Conc (gas) avoided

- **Shrinking core** – different possible rate limiting stages
- (i) Mass transfer of a reagent through a film (boundary layer)
- (ii) Diffusion through a product layer
- (iii) Surface chemical reaction (first order reaction)

Thermal Decomposition of solids - Kinetics

- X_B the volume fraction of the reacted core for a sphere
- R the initial radius of the particle, r the radius of the unreacted core at time t



$$X_B = 1 - \left(\frac{r}{R}\right)^3$$

Thermal Decomposition of Solids - Kinetics

- (i) Mass transfer of a reagent through a film (boundary layer)

$$t = T_F \cdot X_B$$

- (ii) Diffusion through a product layer

$$t = T_D\left[1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)\right]$$

- (iii) Surface chemical reaction (first order reaction)

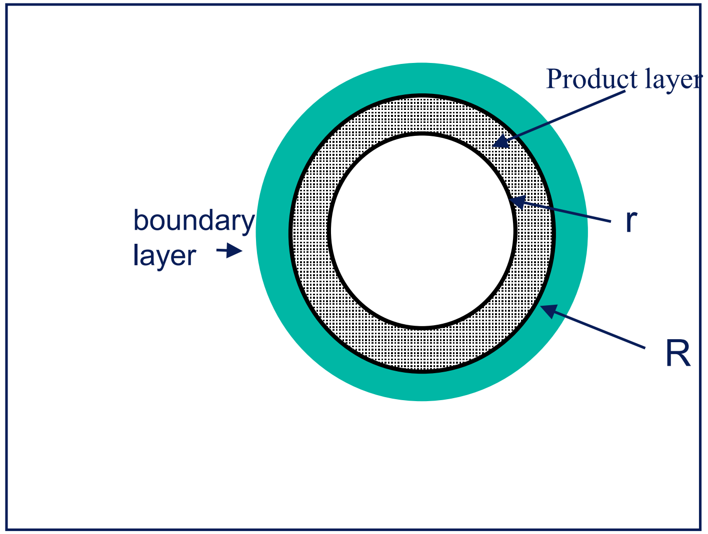
$$t = T_R\left[1 - (1 - X_B)^{1/3}\right]$$

- t is the reaction time,
- T is the total reaction time for a particle for each step
- X_B the volume fraction of the reacted core as a function of the total volume of the particle

Thermal Decomposition of Solids - Kinetics

- (i) Mass transfer of a reagent through a film

$$T_F = \frac{\rho_B \cdot R}{3 \cdot b \cdot k_l \cdot C_a}$$



- ρ_B the molar density of the reaction solid,
- b the stoichiometric coefficient of the reaction equation
  - 1 for $MgCO_3$ in the reaction of slide 19
- k_l the mass transfer coefficient of the gas through the film
- C_a the concentration of the gas in the atmosphere

If the gas is a reactant: $C_a = \frac{x_a}{m_V}$

If it is a product: $C_a = \frac{(1 - x_a)}{m_V}$

x_a: molar fraction of the considered gas

m_V: molar volume of gas,

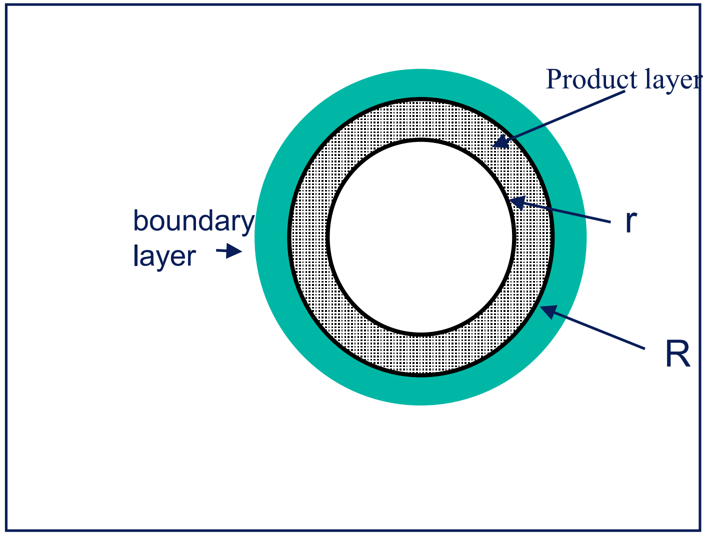
e.g. 22.414 L/mol at STP

MgO - Main application refractories 56% of magnesia in USA in 2004, other 44% being used in agricultural, chemical, construction, environmental, and other industrial applications (melting point 2852 ° C)

Thermal Decomposition of Solids - Kinetics

- (ii) Diffusion through a product layer
- The total reaction time, T_D,

$$T_D = \frac{\rho_B \cdot R^2}{6 \cdot b \cdot D_p \cdot C_a}$$

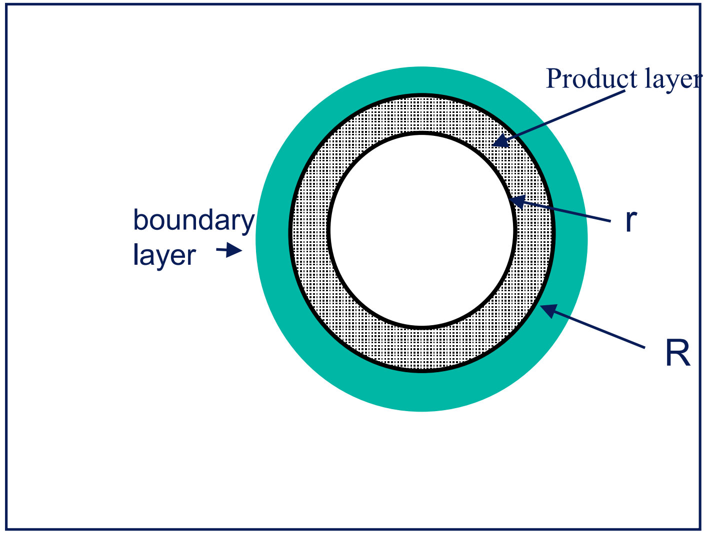


- where D_p is the effective diffusion coefficient of the reactive or product gas in the product layer.

Thermal Decomposition of Solids - Kinetics

- (iii) Surface chemical reaction (first order reaction)
- the total reaction time T_R is

$$T_R = \frac{\rho_B \cdot R}{b \cdot k_s \cdot C_a}$$



- k_s the first order rate constant for the chemical reaction.
- These expressions consider a single kinetically dominant mechanism.
- All these mechanisms can occur (series-parallel) and we can add to give a total reaction time T_T

$$T_T = T_F + T_D + T_R$$

$$T_T = \frac{\rho_B R}{b C_a}\left(\frac{1}{3k_l} + \frac{R}{6D_p} + \frac{1}{k_s}\right)$$

2

Dimensional check

$\rho_B: [mol\ L^{-3}]$

$R: [L\ ]$

$k: [L\ t^{-1}]$

$C_a: [mol\ L^{-3}]$

$D_p: [L^2\ t^{-1}]$

$$T_F = \frac{\rho_B \cdot R}{3 \cdot b \cdot k_l \cdot C_a}$$

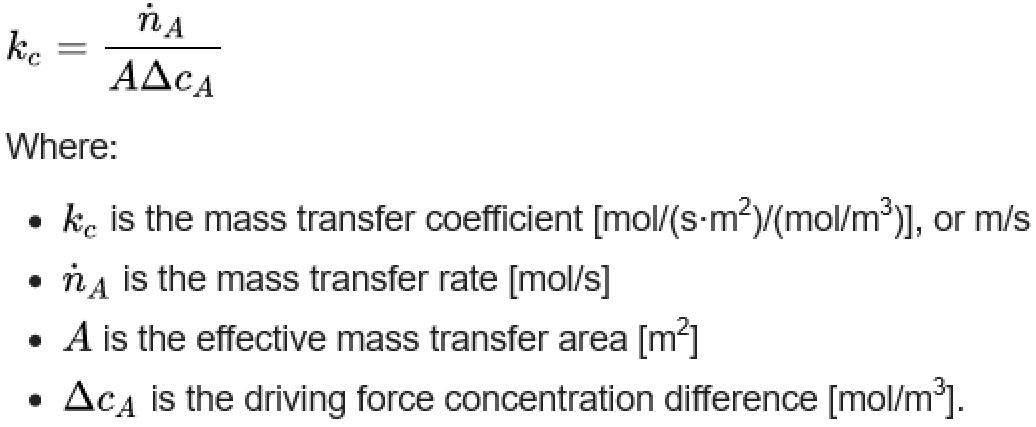
$$T_D = \frac{\rho_B \cdot R^2}{6 \cdot b \cdot D_p \cdot C_a}$$

$$T_R = \frac{\rho_B \cdot R}{b \cdot k_s \cdot C_a}$$

$$T_F: \frac{[mol\ L^{-3}][L]}{[L\ t^{-1}][mol\ L^{-3}]} = [t]$$

$$T_D: \frac{[mol\ L^{-3}][L^2]}{[L^2\ t^{-1}][mol\ L^{-3}]} = [t]$$

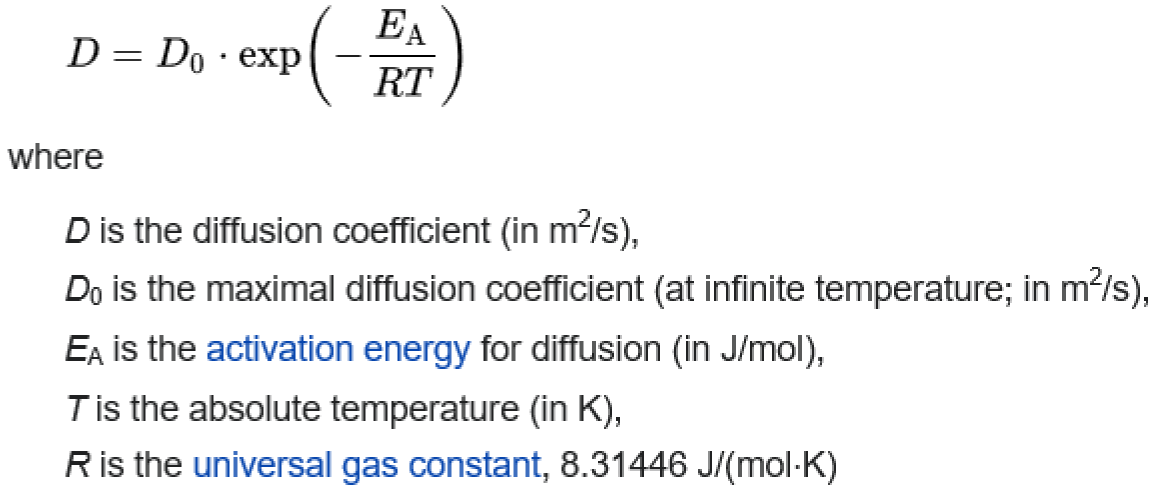
$$T_R: \frac{[mol\ L^{-3}][L]}{[L\ t^{-1}][mol\ L^{-3}]} = [t]$$



$$k_c = \frac{\dot{n}_A}{A \Delta c_A}$$

Where:

- k_c is the mass transfer coefficient [mol/(s·m^2)/(mol/m^3)], or m/s
- $\dot{n}_A$ is the mass transfer rate [mol/s]
- A is the effective mass transfer area [m^2]
- Δc_A is the driving force concentration difference [mol/m^3].



$$D = D_0 \cdot \exp\left(-\frac{E_A}{RT}\right)$$

where

D is the diffusion coefficient (in m^2/s),

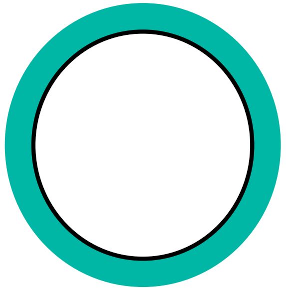
D_0 is the maximal diffusion coefficient (at infinite temperature; in m^2/s),

E_A is the activation energy for diffusion (in J/mol),

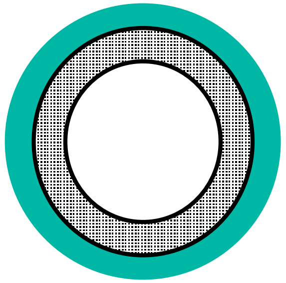
T is the absolute temperature (in K),

R is the universal gas constant, 8.31446 J/(mol·K)

Thermal Decomposition of solids - Limits of model



- Onset of reaction thin product layer and resistance is negligible.



- As the reaction progresses, the layer will thicken and its resistance will dominate.

- Whether or not the reaction is a limiting factor will depend on the thermodynamic chemical conditions at the interface.
- The temperatures are generally chosen so that they are not the limiting step.

Thermal decomposition of solids - Limits of model

- The hypothesis - well-defined reaction front - a limitation
  - If the reaction front is extended - an intermediate case between the continuous reaction model and the shrinking core can be applied.

- Another limiting factor is thermal gradients can form
  - if the reaction is strongly exothermic or
  - if the product is a poor conductor of heat.

- The hypothesis of spherical particles of the same size - again ...
  - The initial size distribution can be measured and taken into account but complicates the interpretation of the mechanism that seems to dominate the process.

- Despite these limitations, there are several examples where part of thermal decomposition is well described by the shrinking core model.
  - dehydration of kaolinite and gibbsite (Bayer process product),
  - thermal decomposition of $CaCO_3$ and $Mg(OH)_2$

Example exercises 2.3
- size - importance on relative resistance

3. Zinc blend particles having a radius R = 1 mm are calcined in a gas flow of 8% oxygen at 900 ° C and 1 atmosphere. The stoichiometry of the reaction is:

$2\ ZnS + 3\ O_2 \text{ ---> } 2\ ZnO + 2\ SO_2$

Assuming the reaction progresses according to the shrinking core model

(a) Calculate the time required for complete conversion of a particle and the relative resistance due to diffusion through the product layer during this operation.

(b) Do the same calculation for particles of radius R = 0.05 mm.

Assumption T_F negligible…..

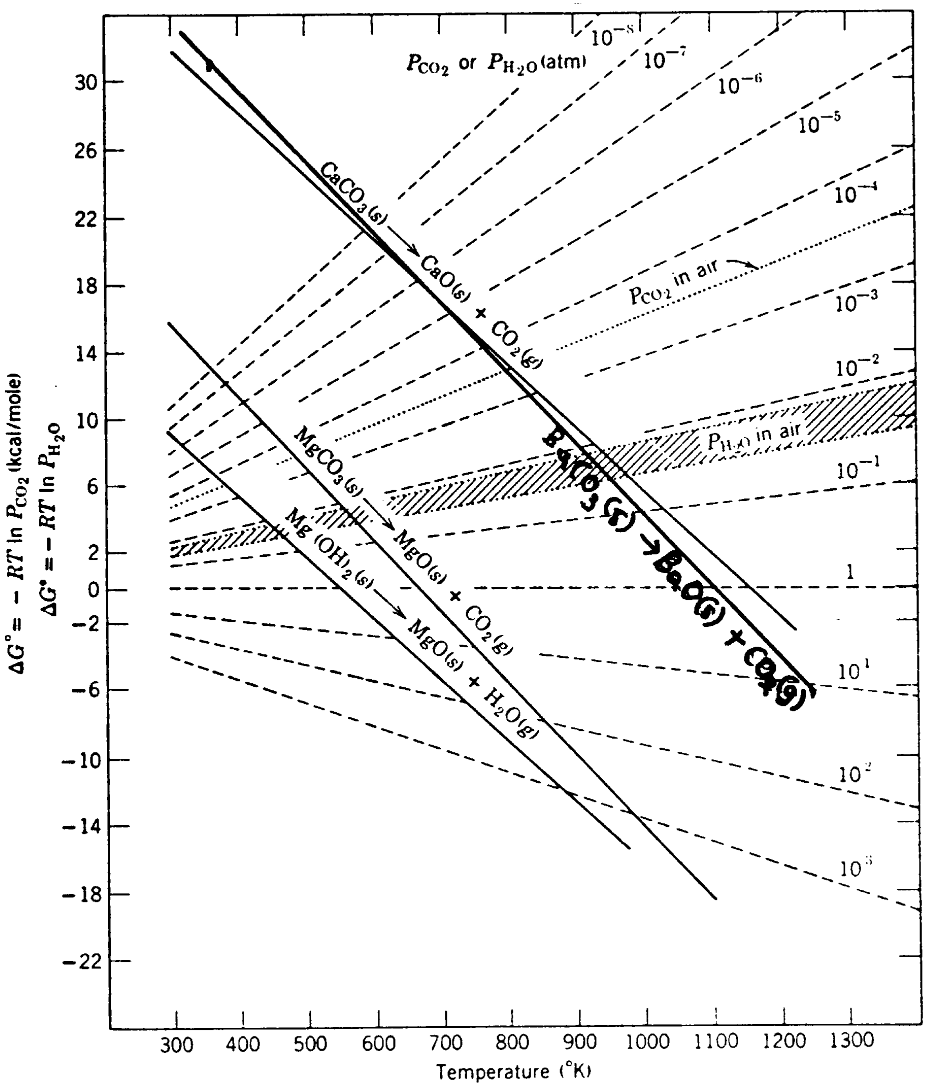
For R = 1mm T_D = 1600s, T_R = 3835 - 30% resistance is diffusion -

For R = 0.05mm T_D = 4s, T_R = 196s - 2% resistance is diffusion -

So we see that when the radius decreases, the reaction is quicker. But diffusion is less important as a resistance. The rate limiting step becomes the chemical reaction and even T_F should be reconsidered

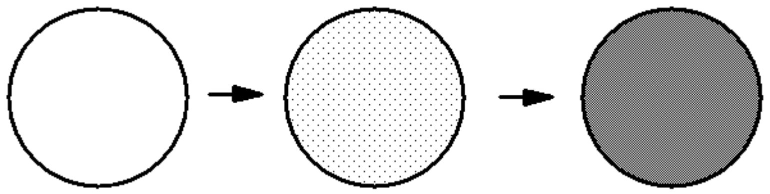
Thermal Decomposition of Solids -summary

Thermodynamics



Kinetics

(a) Conversion progressive

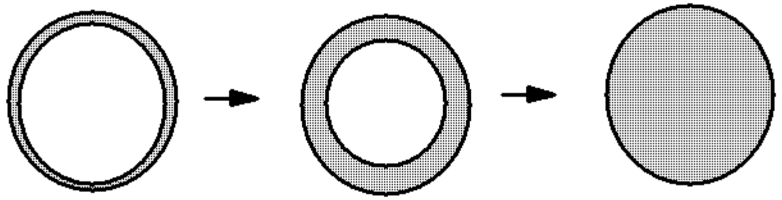


conversion zero t=0

conversion partielle t=t

conversion totale t=T_T

(b) Coeur rétrécissant



conversion basse t=t_1

conversion partielle t=t_2

conversion totale t=T_T

Thermal Decomposition of Solids – BaTi Oxalates

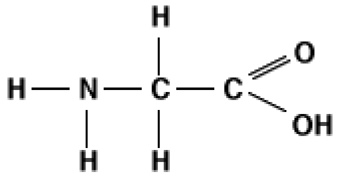
- $BaTiO(C_2O_4)_2.4H_2O \rightarrow BaTiO_3 + 4\ CO_2 + 4H_2O$
- Not a simple path of decomposition but three stages eq. 2.28 a, b, c

From 100 to 140 ° C $BaTiO(C_2O_4)_2.4H_2O \rightarrow BaTiO(C_2O_4)_2 + 4H_2O$ a

From 300 to 350 ° C $BaTiO(C_2O_4)_2 \rightarrow 0.5\ BaTi_2O_5 + 0.5\ BaCO_3 + 2CO + 1.5\ CO_2$ b

From 600 to 800 ° C $0.5\ BaTi_2O_5 + 0.5\ BaCO_3 \rightarrow BaTiO_3 + 0.5\ CO_2$ c

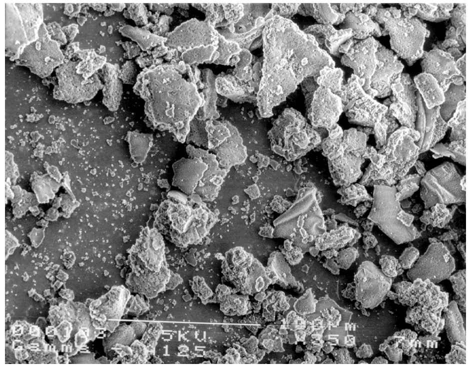
- The cations are initially mixed at the molecular level,
- The degree of segregation during the second stage and
- the stability of barium carbonate controls the kinetics and size or state of agglomeration of the final powder.
- Effect of grinding contamination - not always negative - M. Senna (Nylon - $BaTiO_3$£) - reduction of decomposition of carbonate around 550 ° C because of nylon
- Glycine simplest amino acid which has the same functional groups as nylon
- Acts as a catalyst and reduces the reaction temperature for step c….

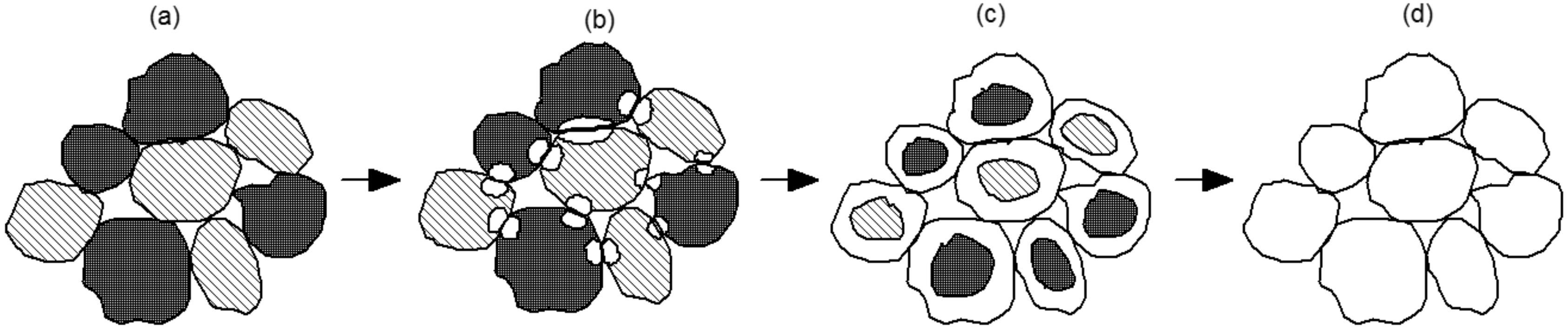


£ H. Oguchi, C. Ando, H. Chazono, H. Kishi and M. Senna "Effects of glycine on the solid-state synthesis of barium titanate micro-particles with high tetragonality "Journal of Physics IV (Proceedings) 128 33-39 (2005)

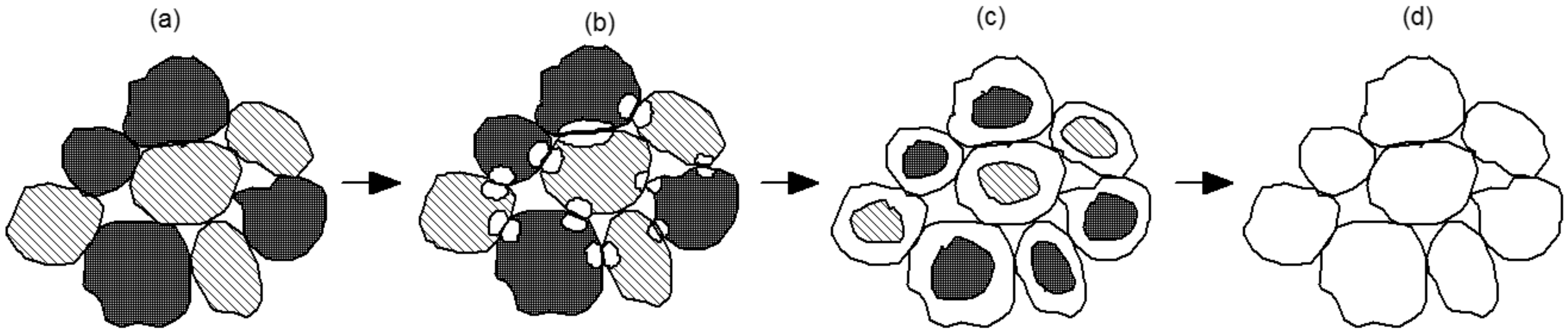
Solid-Solid Reaction

- Many ceramic powders are made by this method when a complex oxide formed from several cations is the end product.
- The traditional method
  - mix the powders containing the necessary cations,
  - often in the form of carbonates or oxides, then
  - heat for interdiffusion of the various ionic species.



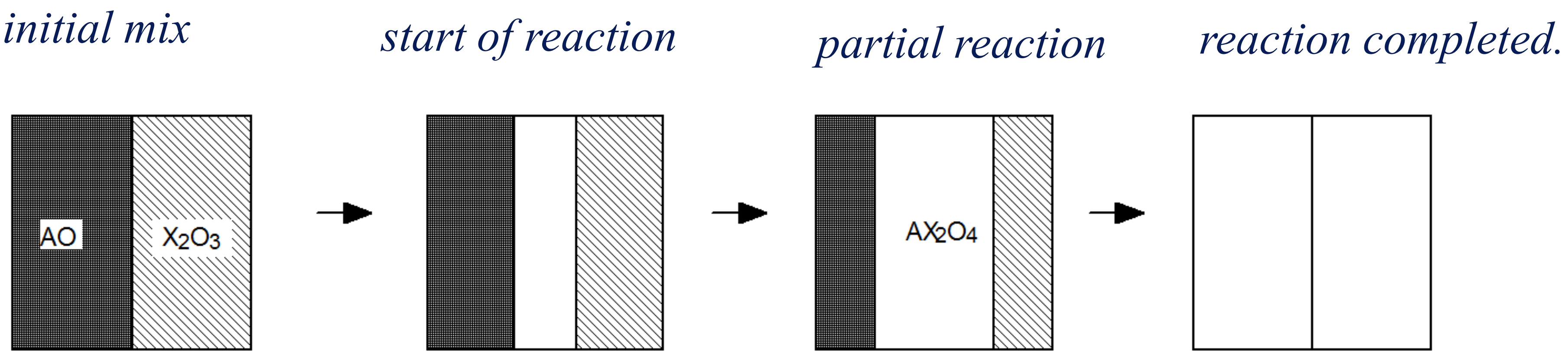


Solid-Solid Reaction – effects of size degree of mixing



- Two important parameters are
  - the degree of initial mixing and the particle sizes.
  - Influence diffusion lengths of various ions.
- Small size - mix is intimate – e.g by co-milling
- If particles too large - incomplete conversion – need a 2nd milling

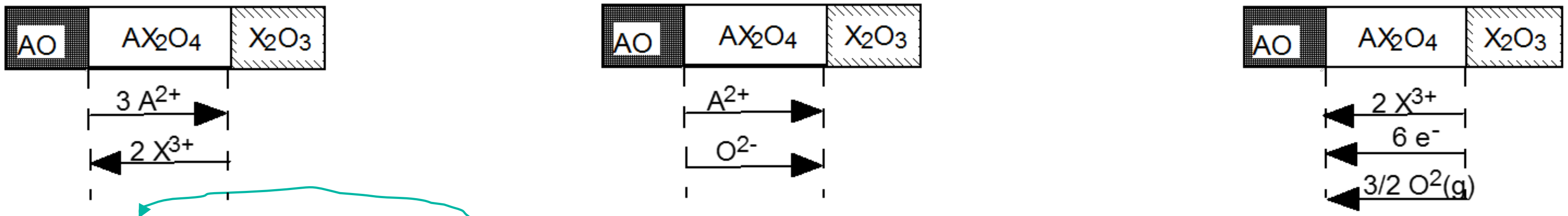
Solid-Solid Reaction - Interfaces - mechanisms



- In practice, the nucleation of a new phase at the interface is often faster than the transport of material to the interface.
- Transport speeds of various
  - cations,
  - anions (oxygen) (or even $O_{2\ (gas)}$) and
  - electrons
- Control the kinetics accordingly

Solid-Solid Reaction - Interfaces - mechanisms

$$AO + X_2O_3 = AX_2O_4$$



$$4AO + 2X^{3+} = AX_2O_4 + 3A^{2+}$$

$$4X_2O_3 + 3A^{2+} = 3AX_2O_4 + 2X^{3+}$$

$$A^{2+} + O^{2-} + X_2O_3 = AX_2O_4$$

$$AO + 2X^{3+} + 6e^- + \tfrac{3}{2}O_2(g) = AX_2O_4$$

- For the development of the kinetic expressions the following assumptions are made
  - the cations show similar diffusion rates
  - the product layer is uniform,
  - that the reactants and the products have the same molar volume

Solid-Solid Reaction - Kinetics of reaction

- For spherical particles - radius R and thin product layers,
- Reaction speed follow the parabolic equation

$$\left[1-(1-\alpha)^{1/3}\right]^2=\frac{K_e t}{R^2}$$

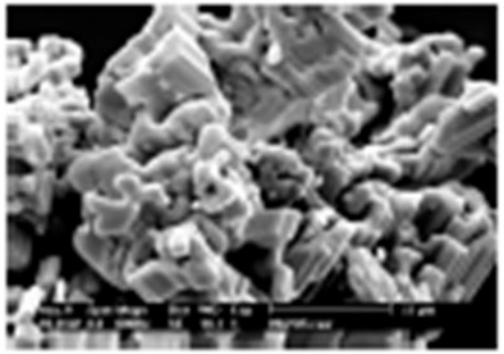
- α is the fraction of reactants already converted at reaction time t,
- K_e is the apparent rate constant which is assumed to follow an Arrhenius reaction as a function of temperature T,

$$K_e=K_0\cdot e^{-\frac{Q}{RT}}$$

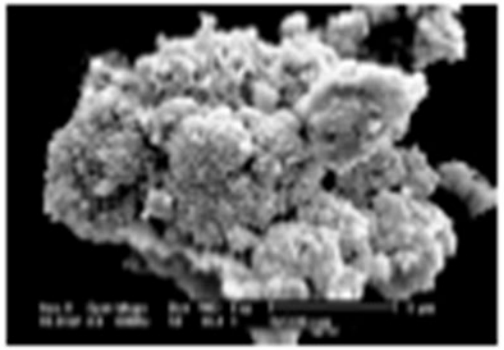
- K_0 the limiting speed constant which depends on the diffusion length and
- Q the apparent activation energy for diffusion

Limitations - Solid-Solid Reaction

- Often use high T for 24 hours – to get a complete reaction
- Induces sintering of the product and formation of aggregates
- Product must be milled to reduce size for shaping and sintering (risk of contamination)
- Despite these various limitations, this powder synthesis method has a low production cost and remains very popular.
- Especially for mixed components like $K_{0.5}Na_{0.5}NbO_3$ – e.g. Evelyn Hollenstein* – Laboratory of Ceramics – failed to produce a pure phase because of poor mixing – large size difference between powders.
- Pre-milling to render initial powders to about the same size K&Na carbonates and Nb oxide
  - Good phase produced
  - Li-Ta doped… first useful
  - Pb-free piezoelectric



K_2CO_3 20-50 µm



Nb_2O_5 2-3 µm

(*E. Hollenstein, M. Davis, D. Damjanovic and N. Setter, Appl. Phys. Lett.,**87**, 182905-1-3 (2005)
Piezoelectric properties of Li- and Ta-modified „$K_{0.5}$N / $A_{0.5}NbO_3$ ceramics (2019 843… citations…)

Synthesis of SiC - Acheson method (1890)

- Production via a carbothermal method
- Sand (50%) and carbon (coke 40%)
  - sawdust (7%) and salt (NaCl common salt) (3%).
- Heated in an electric arc furnace using graphite electrodes and temperature in excess of 2000 ° C
- The overall reaction seems simple

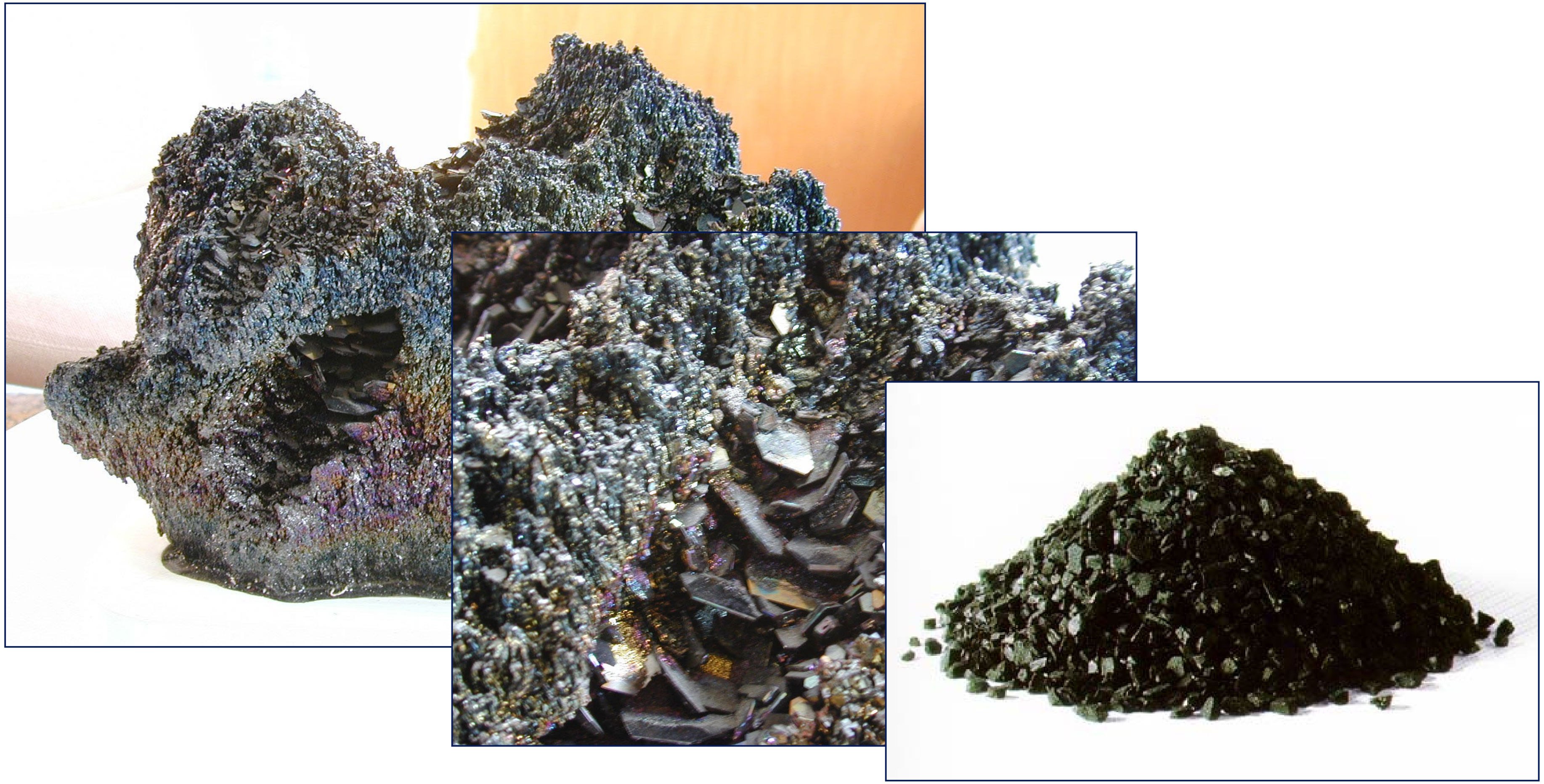
$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g)$$

- but intermediate steps involving liquid and vapor phases are part of a more complex mechanism

$$SiO_2(l) + C(s) = SiO(g) + CO(g)$$

$$SiO(g) + 2C(s) = SiC(s) + CO(g)$$

Synthesis of SiC - Acheson method



- Crystal aggregates are crushed, milled, and classified for use primarily as abrasive powders

Solid – Vapour Reaction

- There are two main categories:
- i) elementary solid reagents (metals) such as nitriding of Si

$$3Si + 2N_2 \rightarrow Si_3N_4$$

- ii) roasting of ores for example ZnS

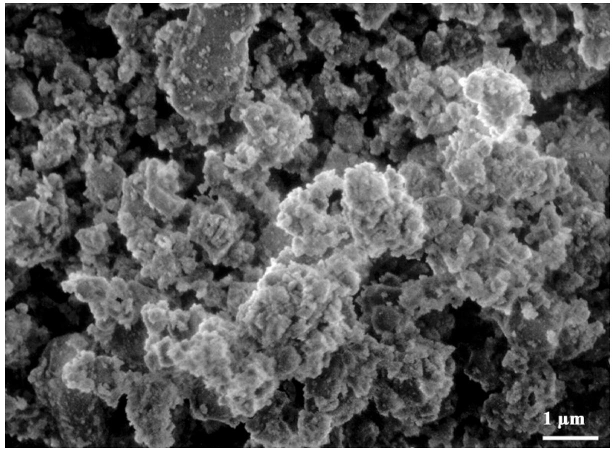
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

- Mechanisms and reaction rates will depend on the
  - particle size,
  - partial pressures of reactive and product gases
  - as well as rate-limiting steps of solid-vapour reactions

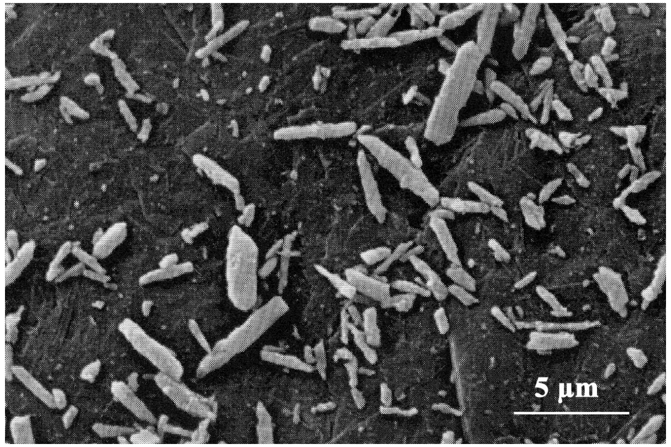
Solid – Vapour Reaction

- Example $3Si + 2N_2 \rightarrow Si_3N_4$
- two polymorphs of Si_3N_4 : polymorphs α (trigonal) and β (hexagonal) *

α



β



- Si purity of is important
- Impurities can:
  - influence the type of polymorph that will nucleate
  - produce a liquid phase - from which the β form precipitates.
- A certain amount of β is beneficial for the sintering of Si_3N_4 and so we don't need to produce a pure phase.

Si3N4 bearing parts

*Si3N4 γ (cubic) exists too only at high T and P