Materials Properties, Use and Conservation: Construction Materials and Binders

Calcic binders

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CIBA Centro per i Beni Culturali
Diagnostica . Rilievo . Tecnologie

Binders classification

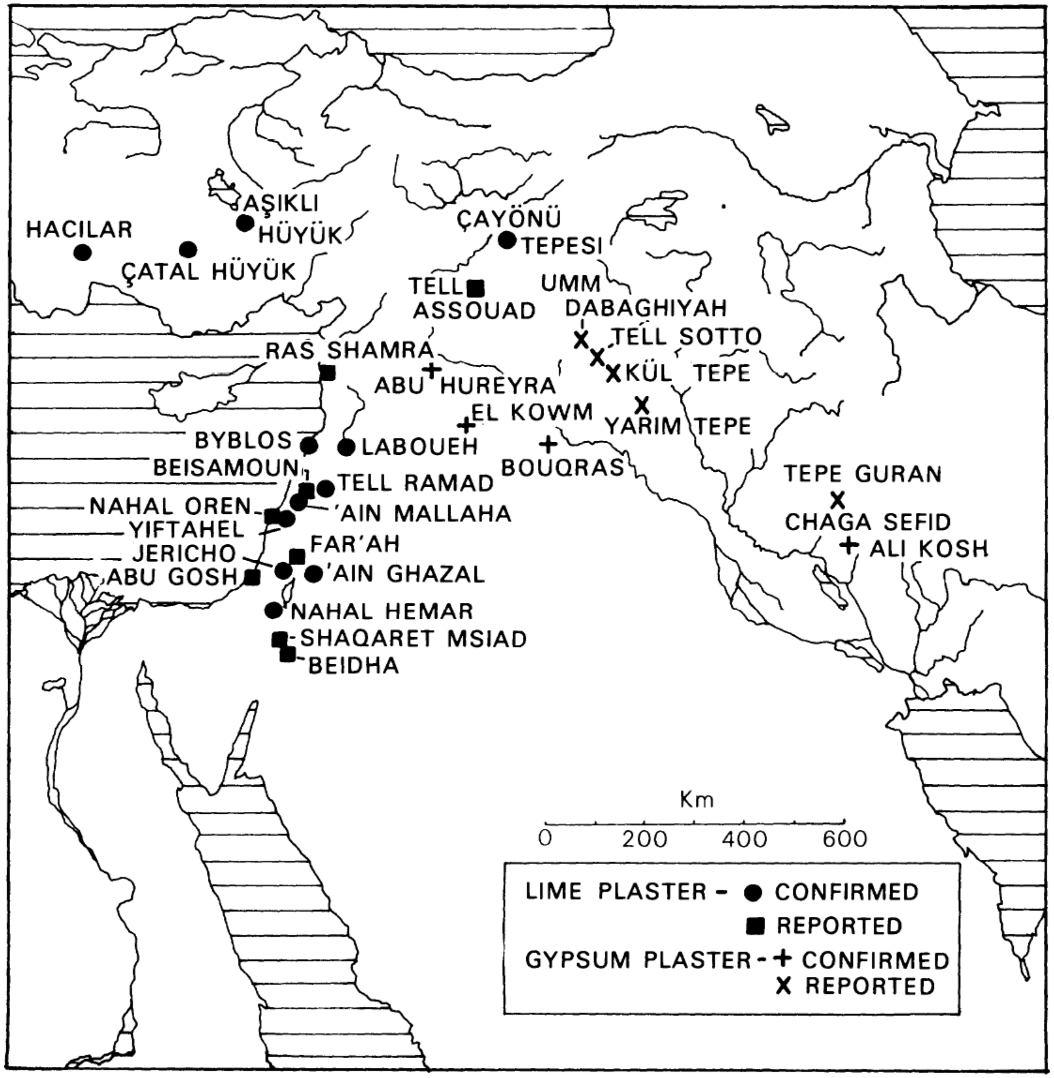
Table 3.6. Main classes of binding compounds produced by pyrotechnology.

Starting reactive material	***Production process***	***Material-water mixture***	***Final product***	***Mineral phases in the hardened aged material***
Lime-plaster (quicklime)	Calcinations of limestone	Slaked lime (lime putty)	Lime plaster	Calcite
		Slaked lime + fine aggregate	Lime mortar	Calcite + aggregate
		Slaked lime + fine aggregate + pozzolan	Hydraulic mortar (Roman opus caementitium)	Calcite, zeolites, C-S-H + aggregate
	Calcination of dolomite	Slaked magnesia-lime	Dolomitic or magnesian plaster	Calcite, brucite, periclase
Gypsum-plaster (plaster of Paris)	Calcination of gypsum	Bassanite (± anhydrite)	Gypsum plaster	Gypsum
		Bassanite + fine aggregate	Gypsum mortar	Gypsum + aggregate
Portland-clinker	Calcinations of limestones+clay	Portland cement paste	Portland cement	Portlandite, C-S-H, calcite
		Portland cement paste + fine aggregate	Portland cement mortar	Portlandite, C-S-H, calcite + aggregate
		Portland cement paste + fine and coarse aggregate	Concrete	Portlandite, C-S-H, calcite + aggregate
		Cement paste + fine aggregate + pozzolan	Pozzolanic Portland cement mortar	Portlandite, C-S-H, calcite, Ca-aluminosilicates

Calcic binders

Calcic binders

Figure 14. Geographical distribution of lime plaster and gypsum plaster in the Pre-Pottery Neolithic.



W. David Kingery, Pamela B. Vandiver, Martha Prickett

The Beginnings of Pyrotechnology, Part II: Production and Use of Lime and Gypsum Plaster in the Pre-Pottery Neolithic near East
Journal of Field Archaeology, Vol. 15, No. 2, pp. 219-244

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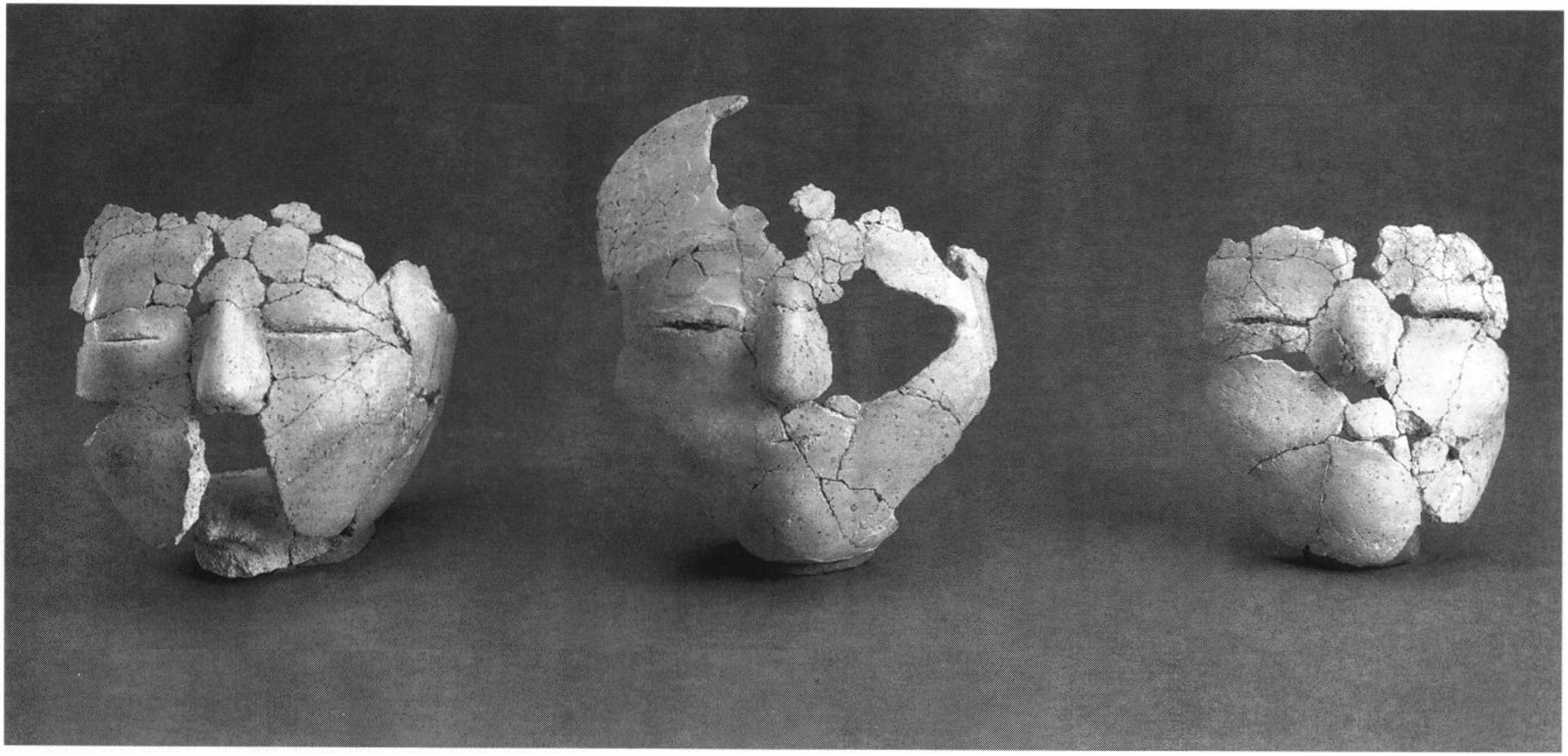


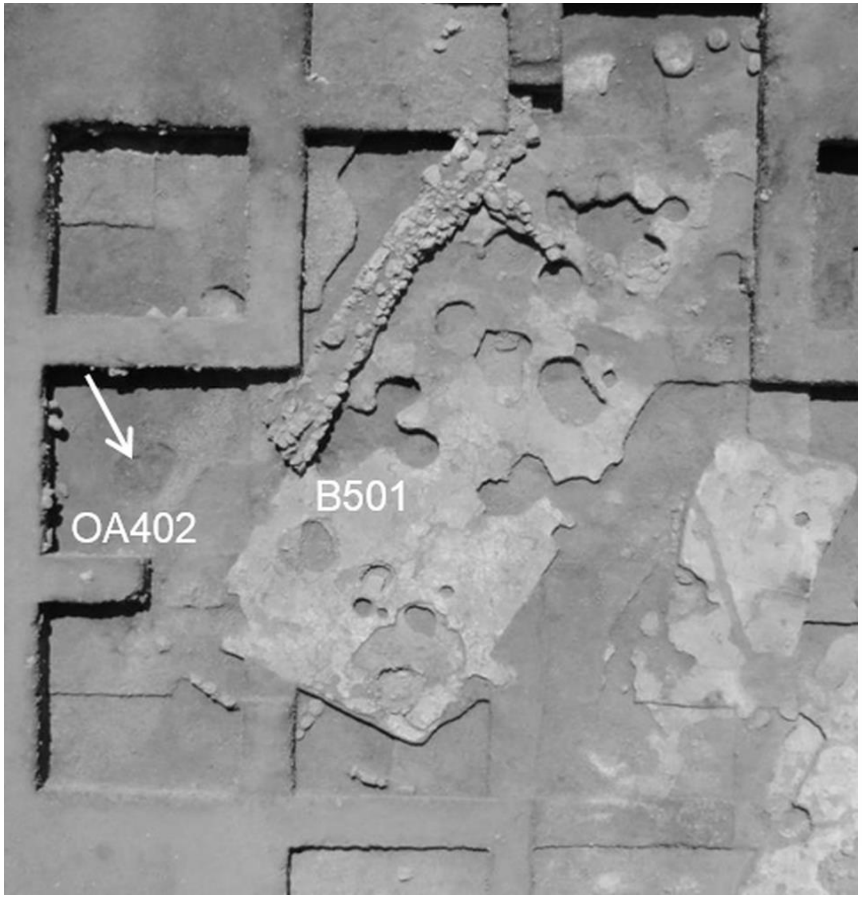
Fig. 1 : *Faces 1, 2, and 3, left to right (J. Tsantes, Smithsonian Institution).*

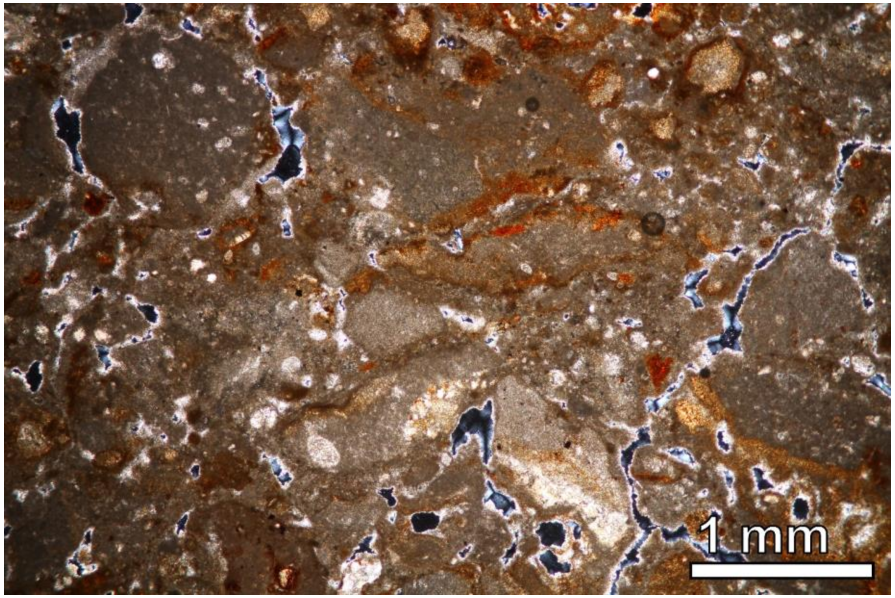
THREE LATE EIGHTH MILLENNIUM PLASTERED FACES FROM 'AIN GHAZAL, JORDAN

P.S. GRIFFIN, C.A. GRISSOM and G.O. ROLLEFSON

Paléorient, Année 1998, Volume 24, Numéro 1
p. 59 - 70

Yiftahel (Israel)
7000 b.C.





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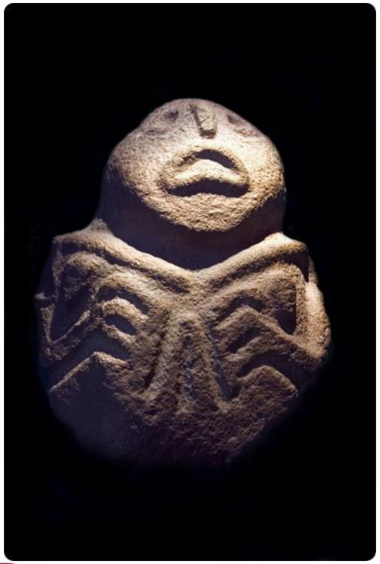
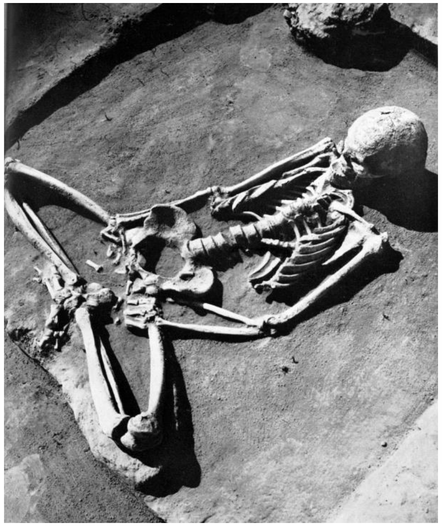
Lepenski Vir, right bank of Danube, Serbia
Lepenski Vir culture, 5600 b.C.





Calcic binders

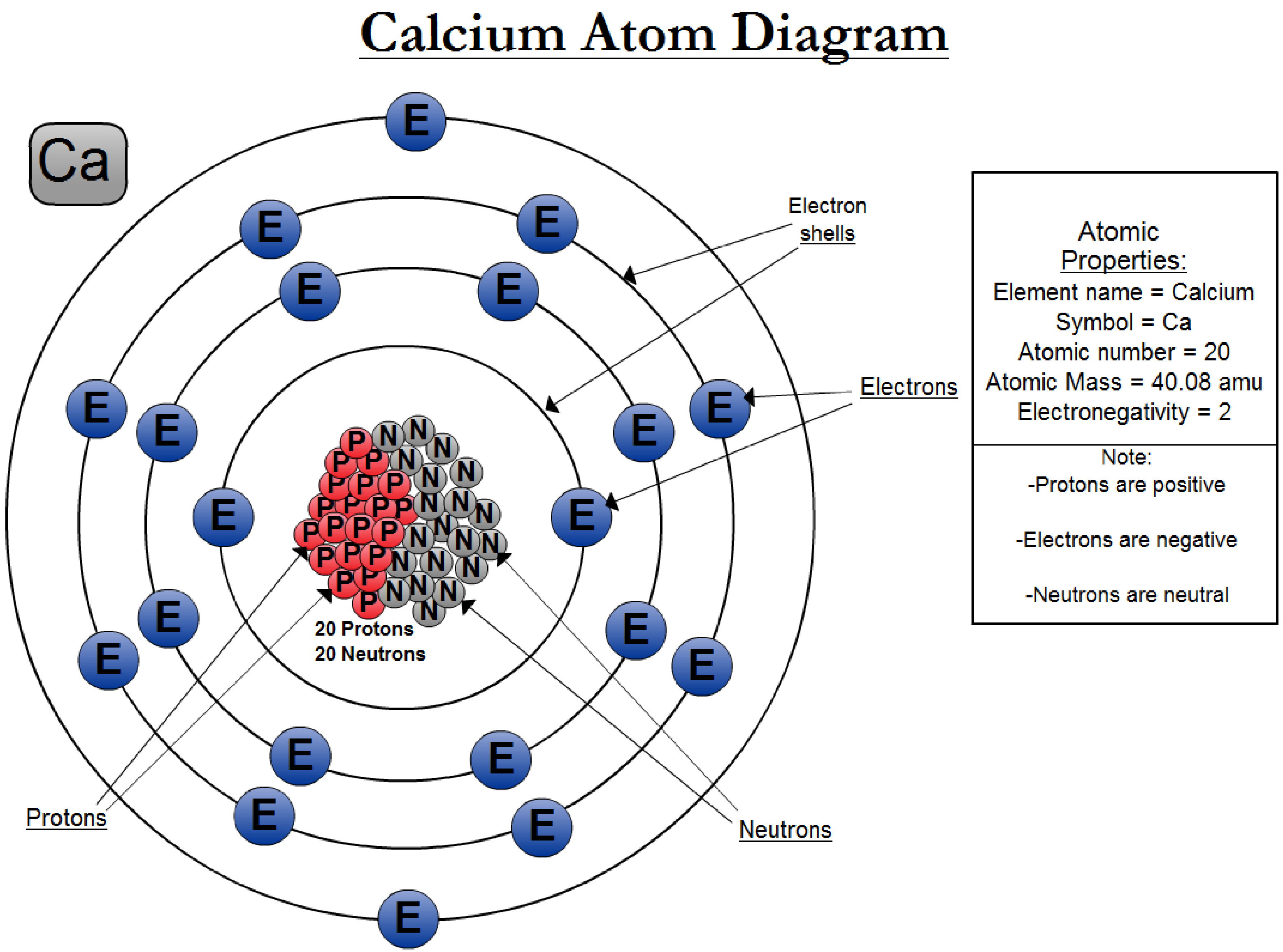
Periodic table of the elements

- Alkali metals
- Alkaline-earth metals
- Transition metals
- Other metals
- Other nonmetals
- Halogens
- Noble gases
- Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
- Actinoid elements

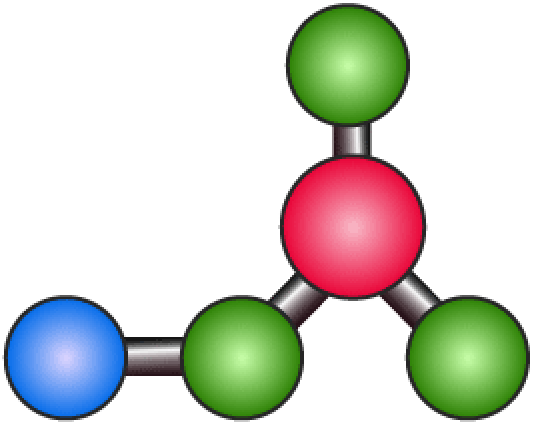
period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	**20 Ca**	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 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

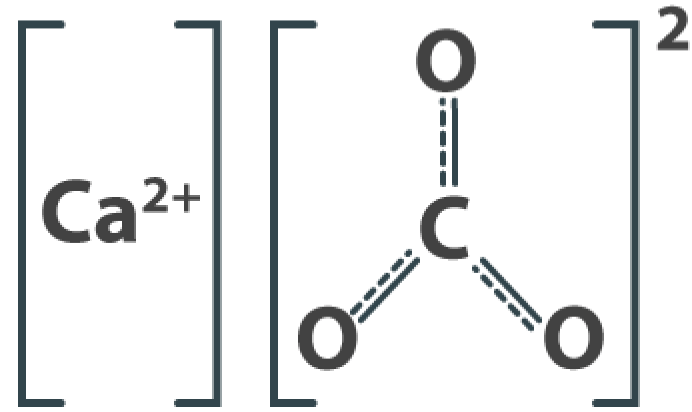
lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

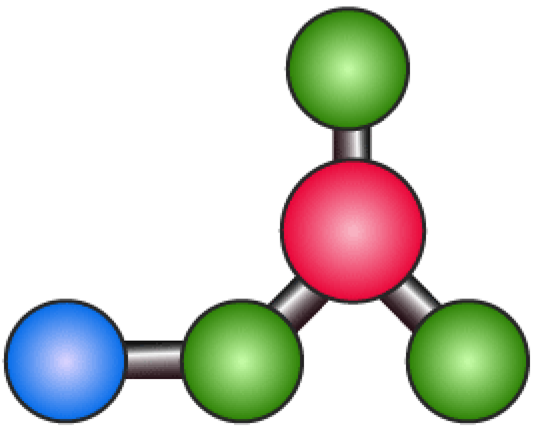

Calcium Atom Diagram
Ca
Electron shells
Electrons
20 Protons
20 Neutrons
Protons
Neutrons
Atomic Properties:
Element name = Calcium
Symbol = Ca
Atomic number = 20
Atomic Mass = 40.08 amu
Electronegativity = 2
Note:
-Protons are positive
-Electrons are negative
-Neutrons are neutral

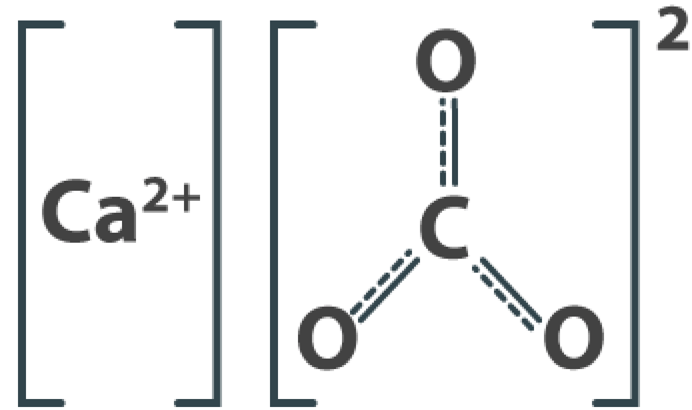
Calcite - $CaCO_3$

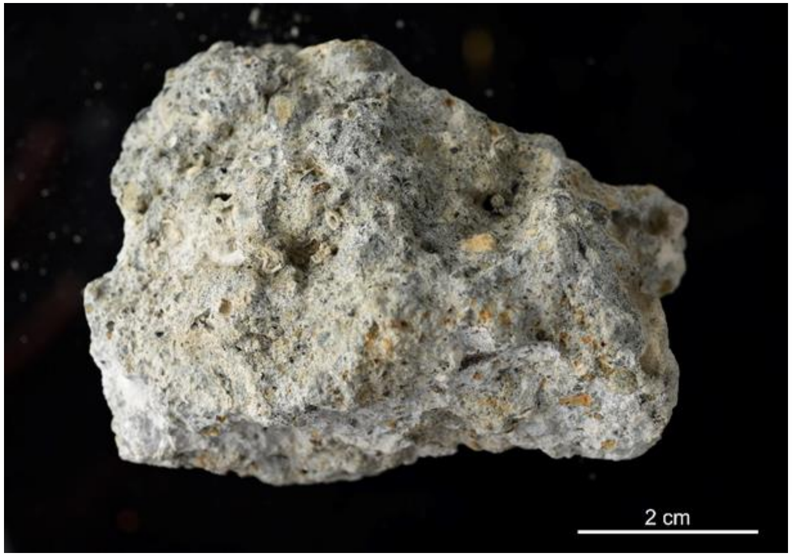


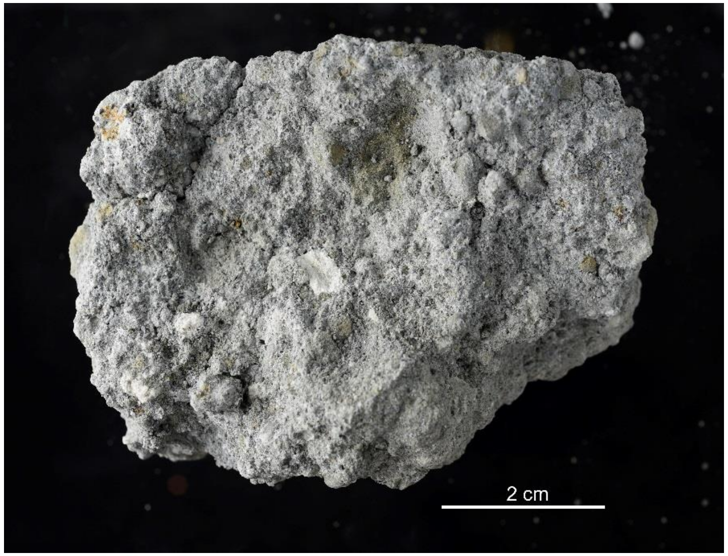


Calcite - $CaCO_3$

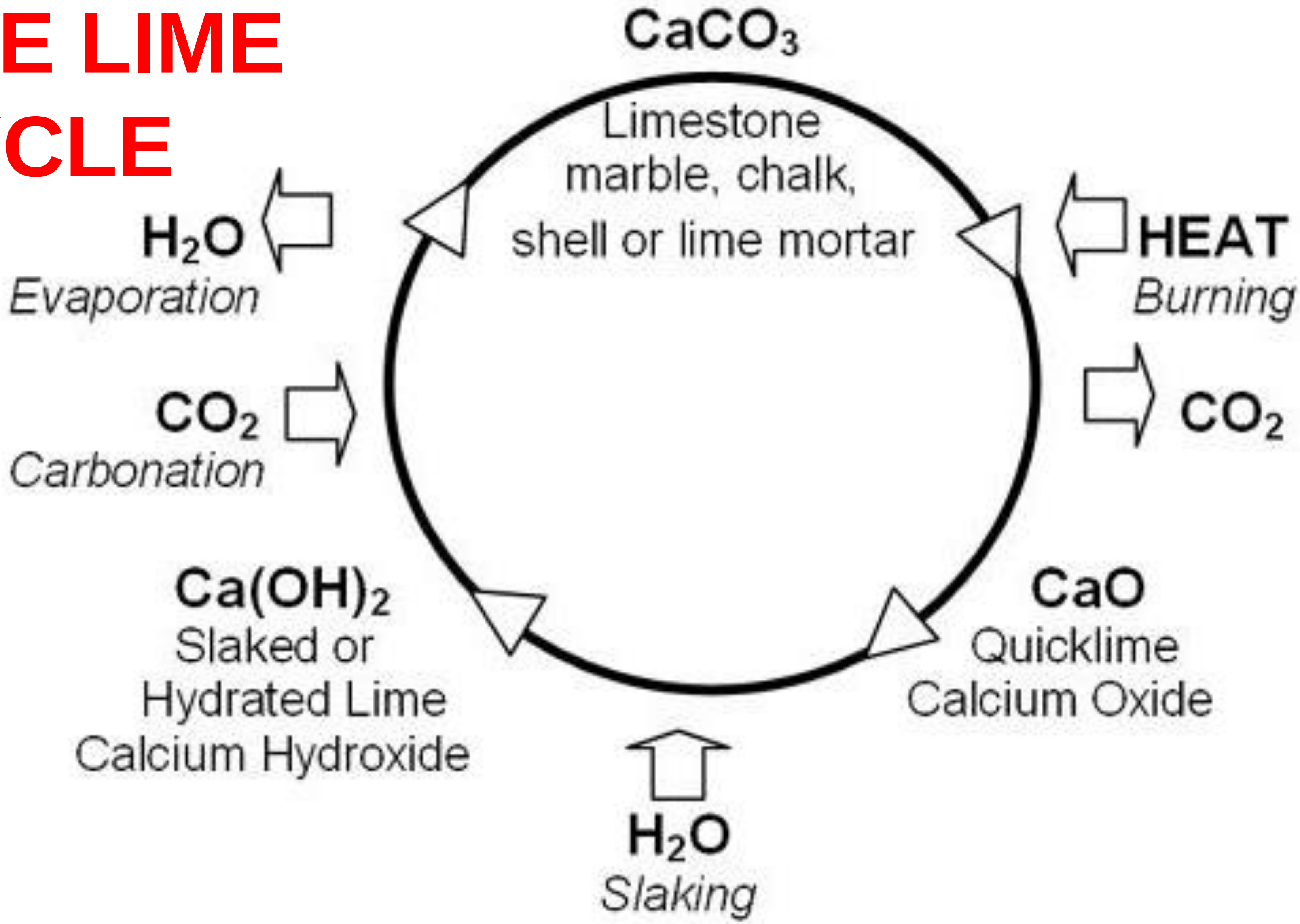




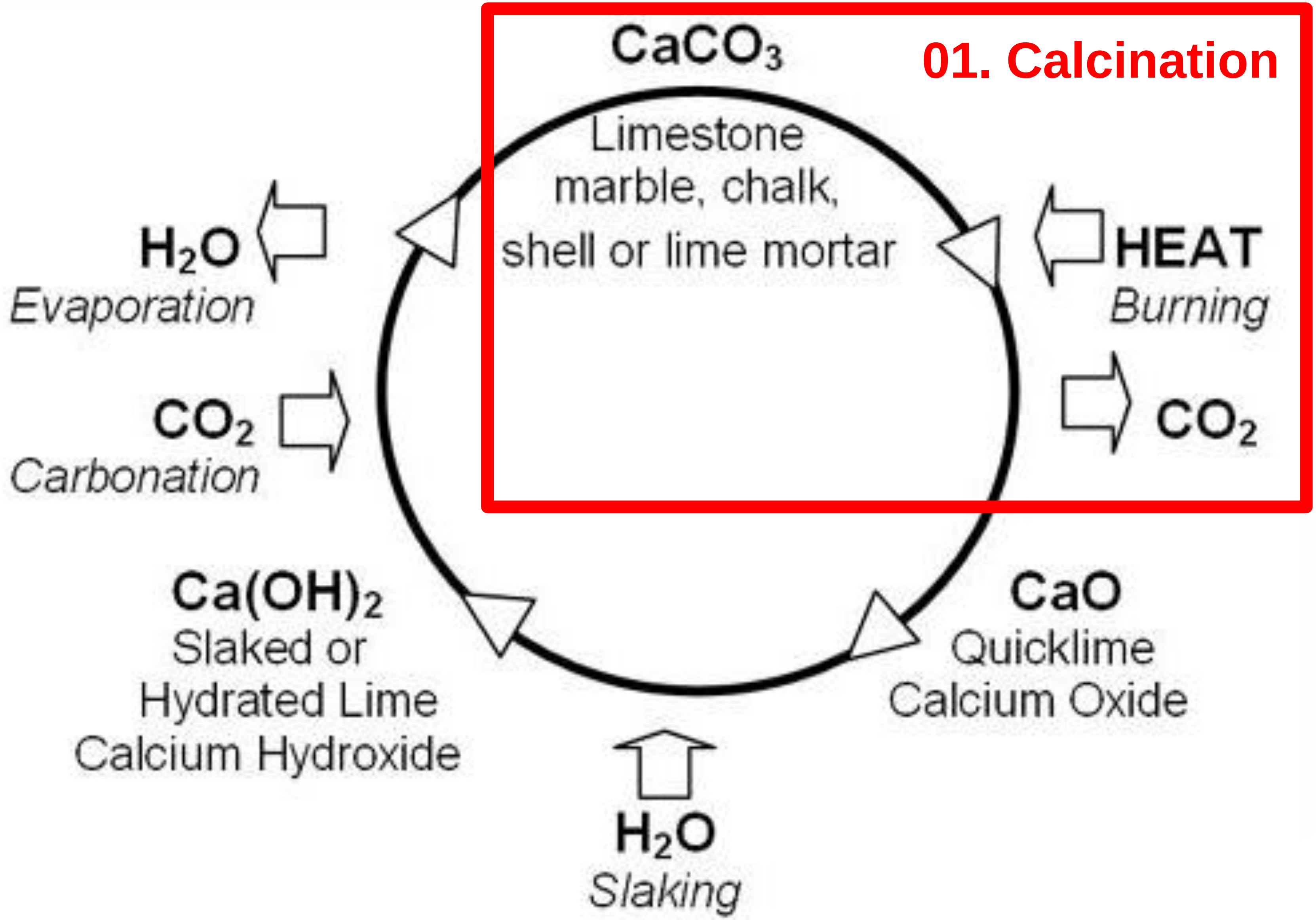




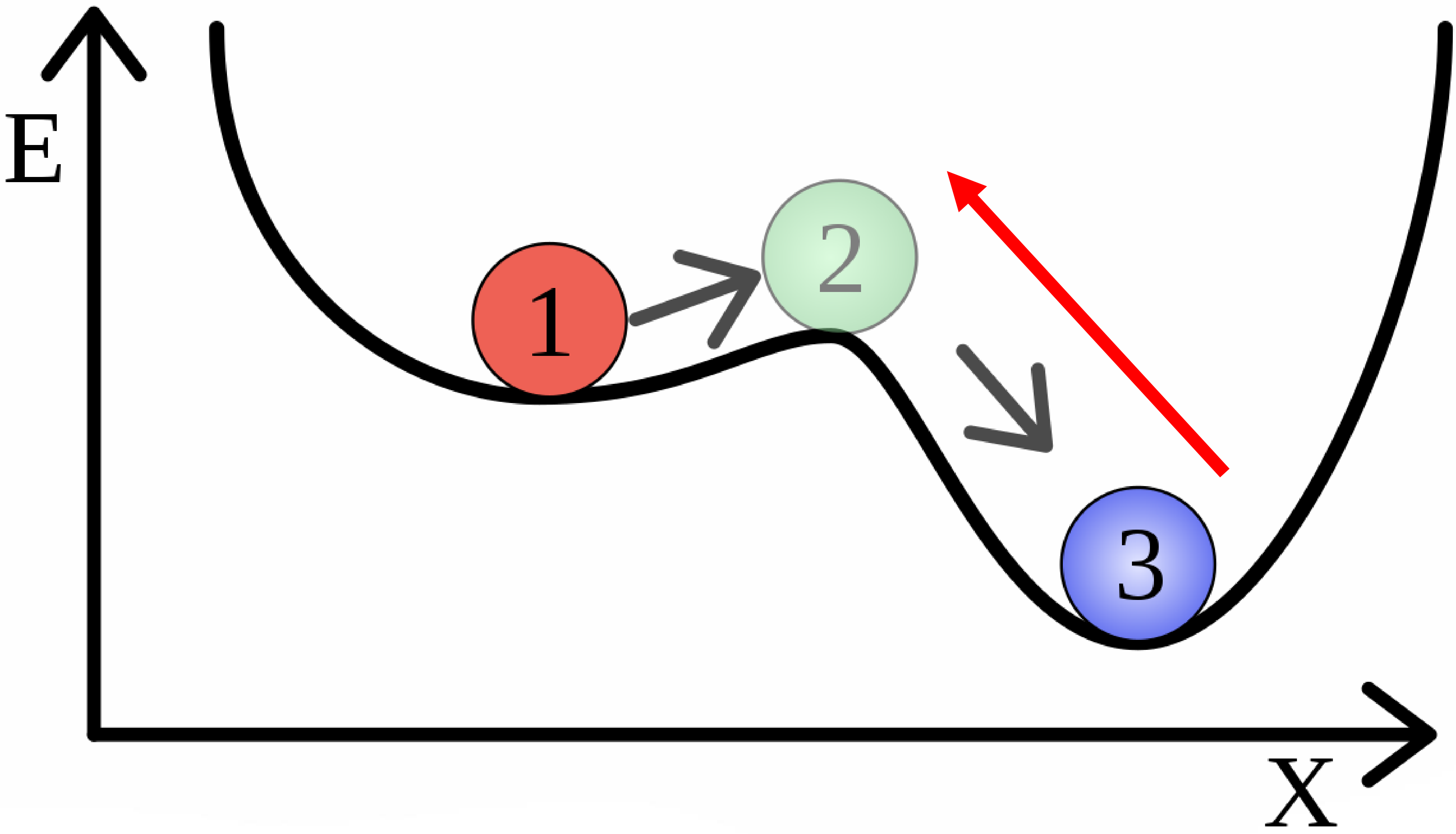
THE LIME CYCLE



Calcic binders



Calcic binders



Calcination

$CaCO_3$(calcite) + heat → **CaO**(quicklime) + **CO_2**(carbon dioxide)

$\Delta G°_r \approx 177.1$ (kJ/mol) (25 °C) → 848 °C

Calcic binders

Prissé-la-Charrière, Niort, Francia, 200 b.C **- 70** AD

Several ancient lime-kilns have been excavated from Roman (Dix 1982, Coulson et al. 1986), to Late Classic Maya (Abrams and Freter 1996), to more recent times (Williams 2004). An accurate description of lime burning operations in Roman times are supplied by Marcus Porcius Cato (Cato the Elder: On agriculture, XXXVIII).

An illustration of the lime kiln at Crypta Balbi. From Manacorda 2001, p. 52.

Calcic binders

Hoi Han Wan, Hong Kong (600-900 AD**)**

Former lime making industry, in which shells and corals were baked to form lime

FIGURE 1. Ruins of old lime kiln at the south Cool-Cave Valley deposit on the east side of State Highway 49. *Photo by Mary R. Hill.*

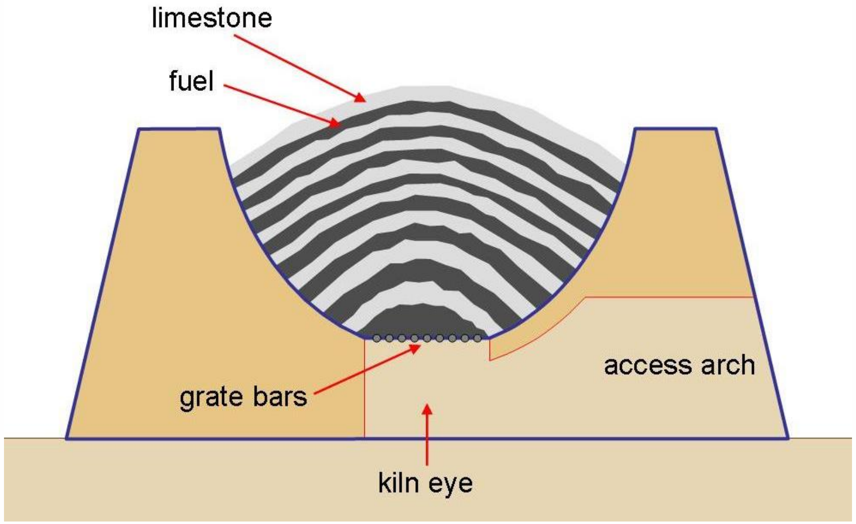
Cool-Cave Valley, California (1880-1930)

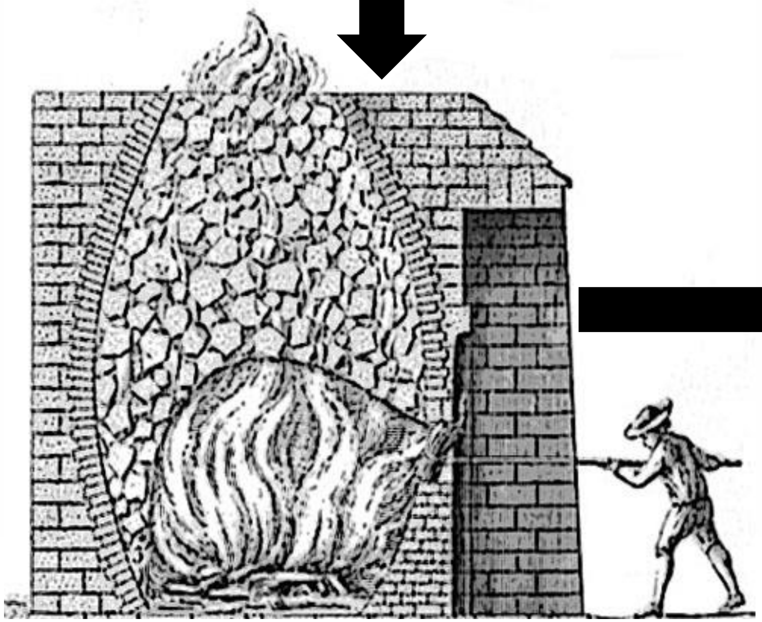
Limekilns Aberthaw, Barry Island, South Wales (1888 – 1926)

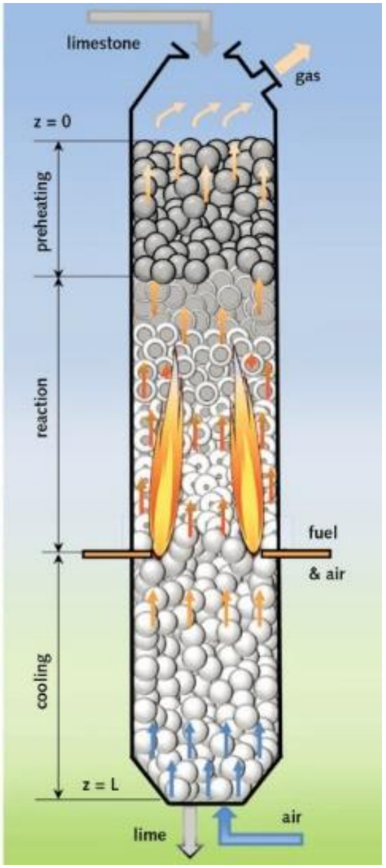
Calcic binders

- The temperature to produce CaO must be above 898 °C, though the decomposition reaction of the carbonate can proceed also at slightly lower temperatures (780-800 °C) in reducing conditions.
- Operational temperatures of lime-kilns are in the range 920-1000 °C in order to speed up the decarbonation reaction.
- Excessive temperatures are avoided because they produce unreactive "dead-burned" lime.

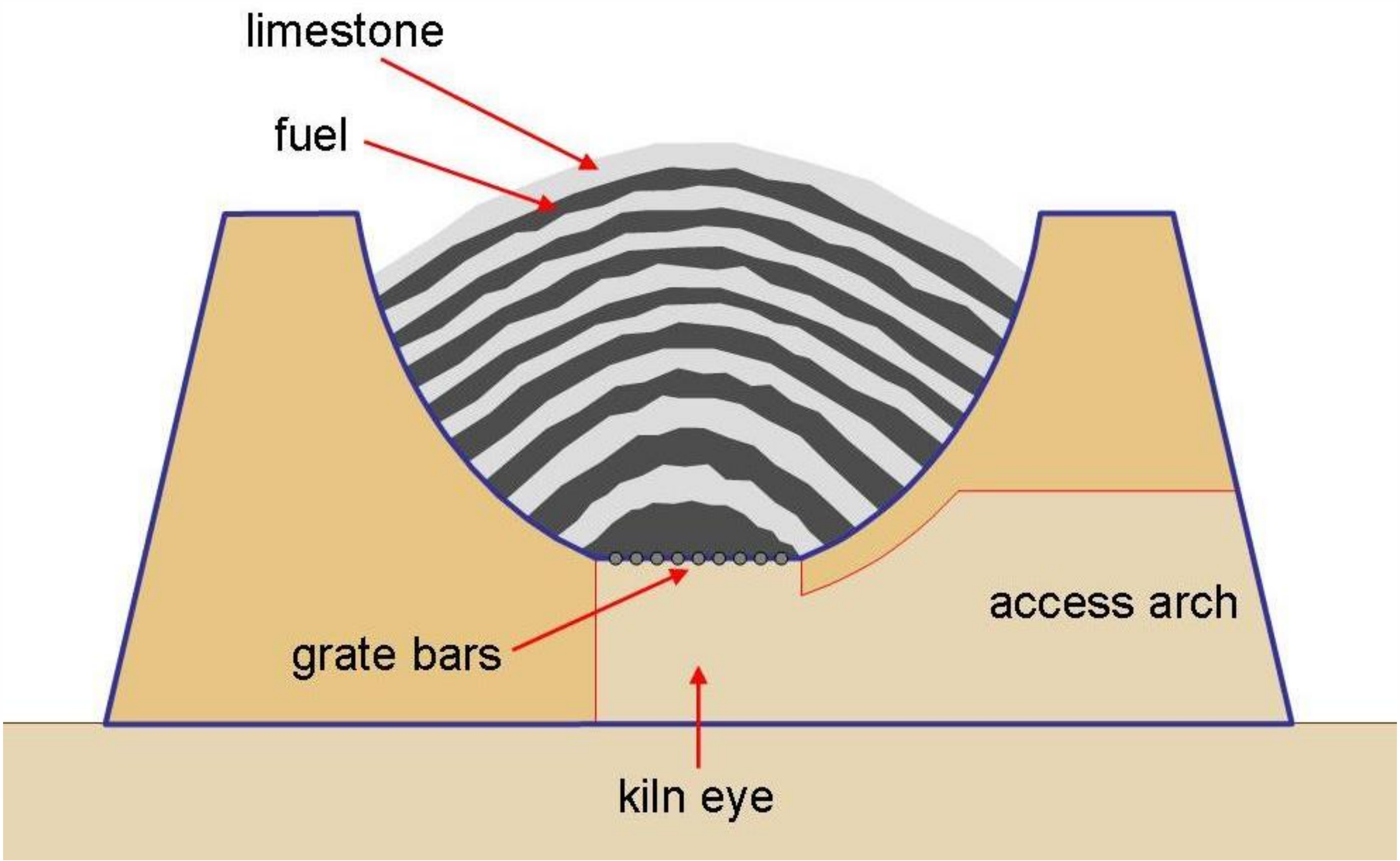
Calcic binders







Calcic binders



Calcic binders

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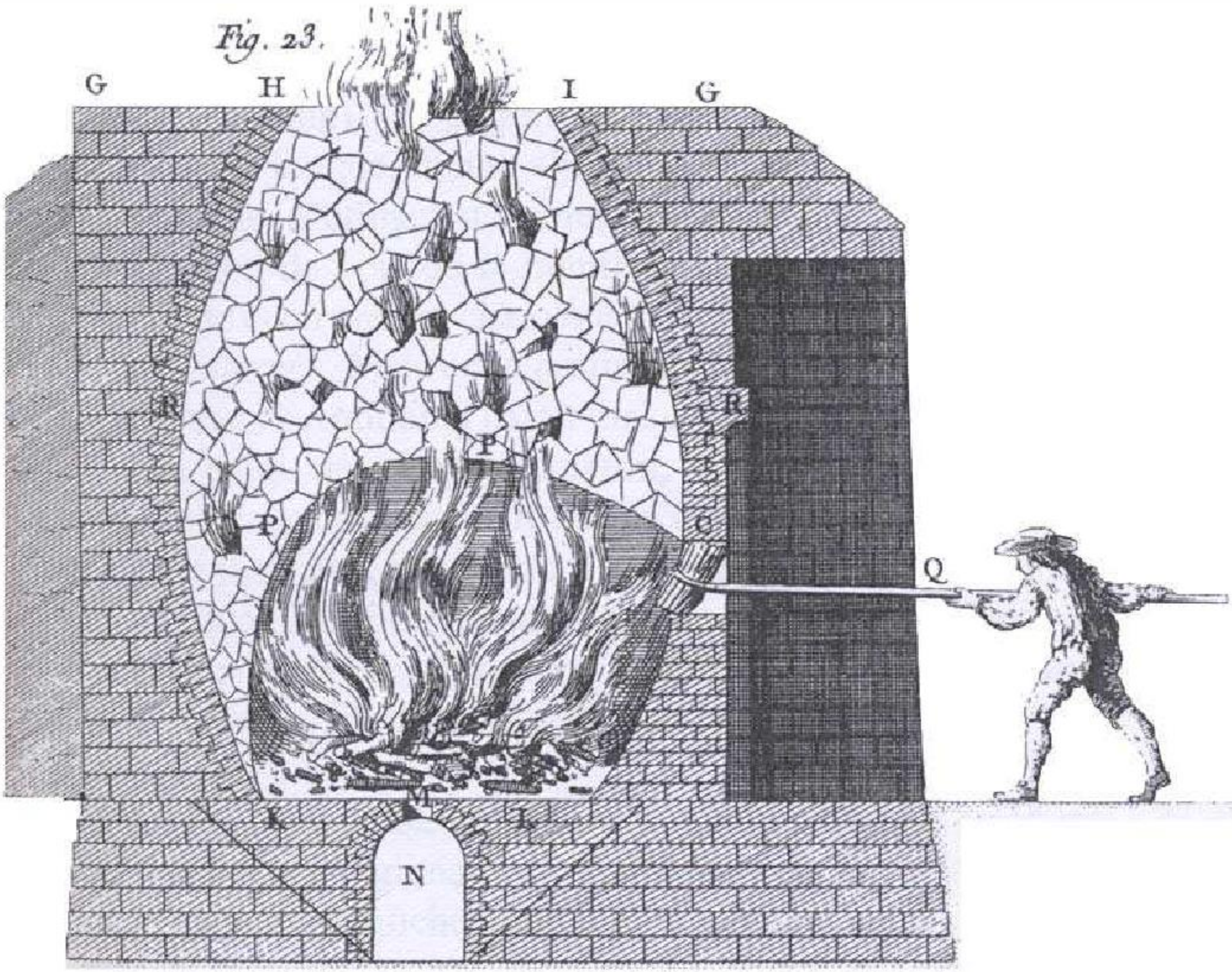

Calcic binders

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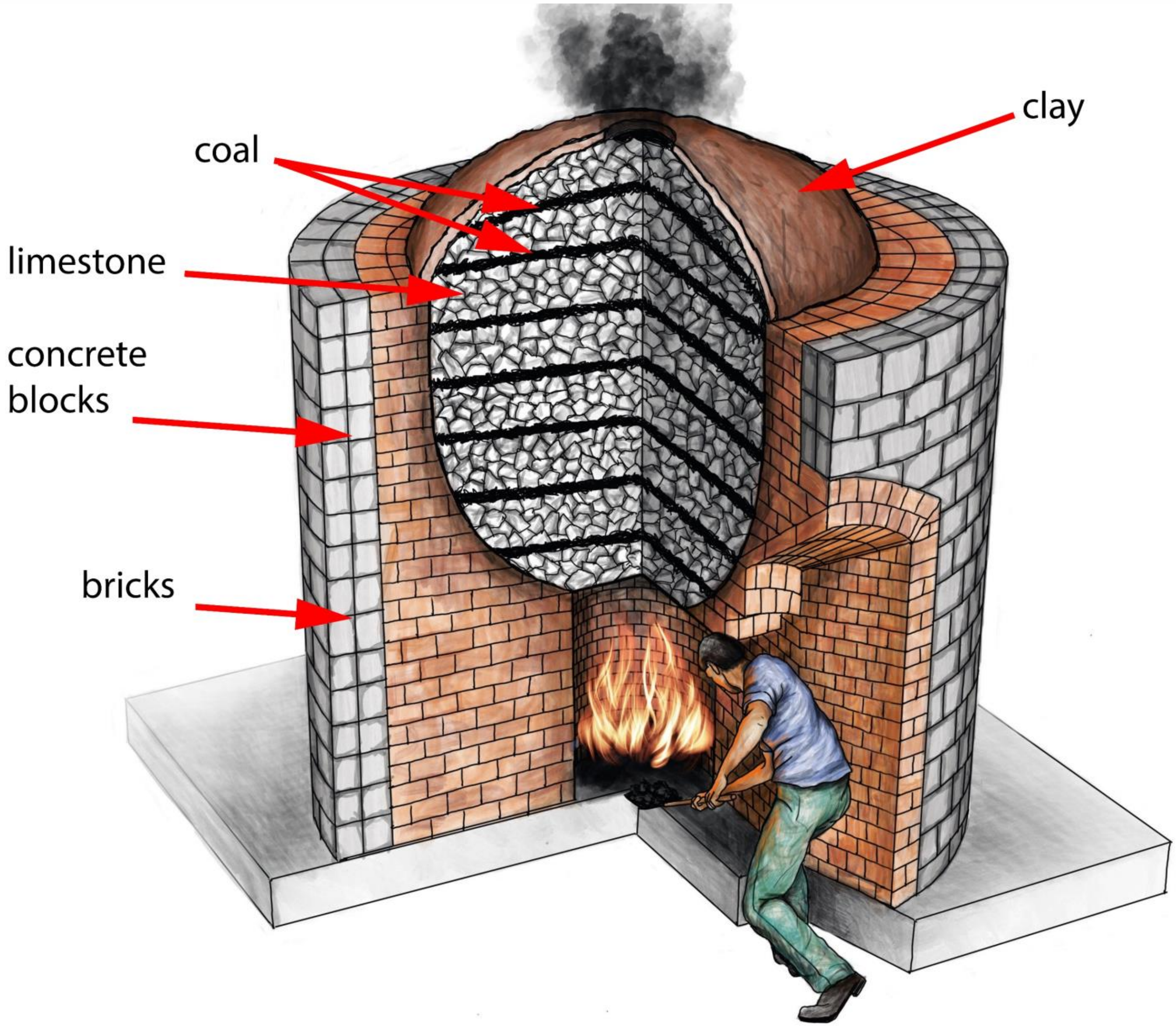


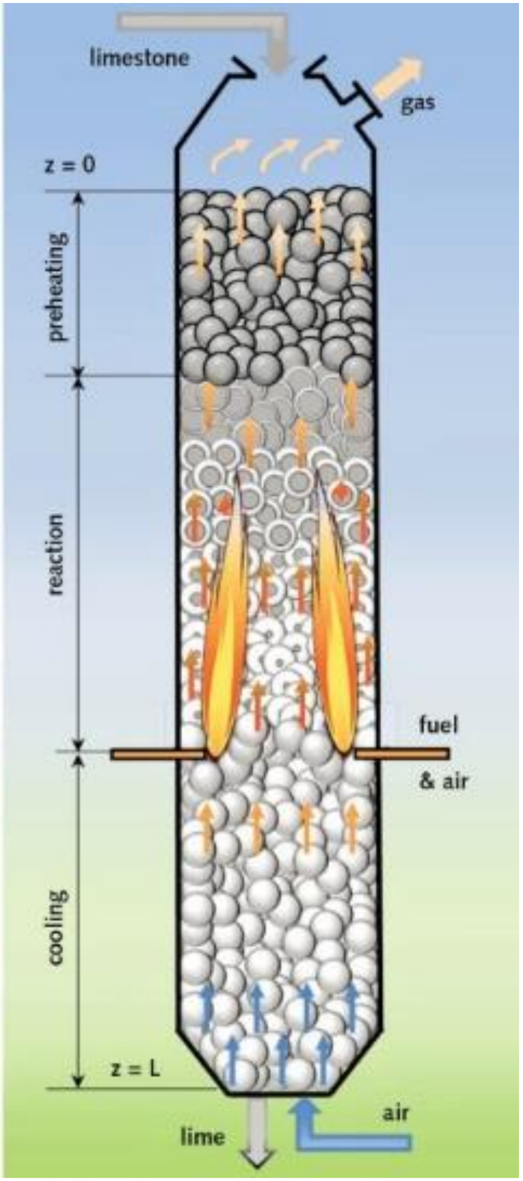
Calcic binders

Lime Kiln as it may have looked when in use

In ancient times production was carried out on a batch basis with each cycle averaging 15 days. The cycle is as follows:

- •3 days for loading (4 persons required);
- •3 days for calcining;
- •4 days for cooling;
- •3 days for discharging;
- •1 day for cleaning the kiln.

Calcic binders



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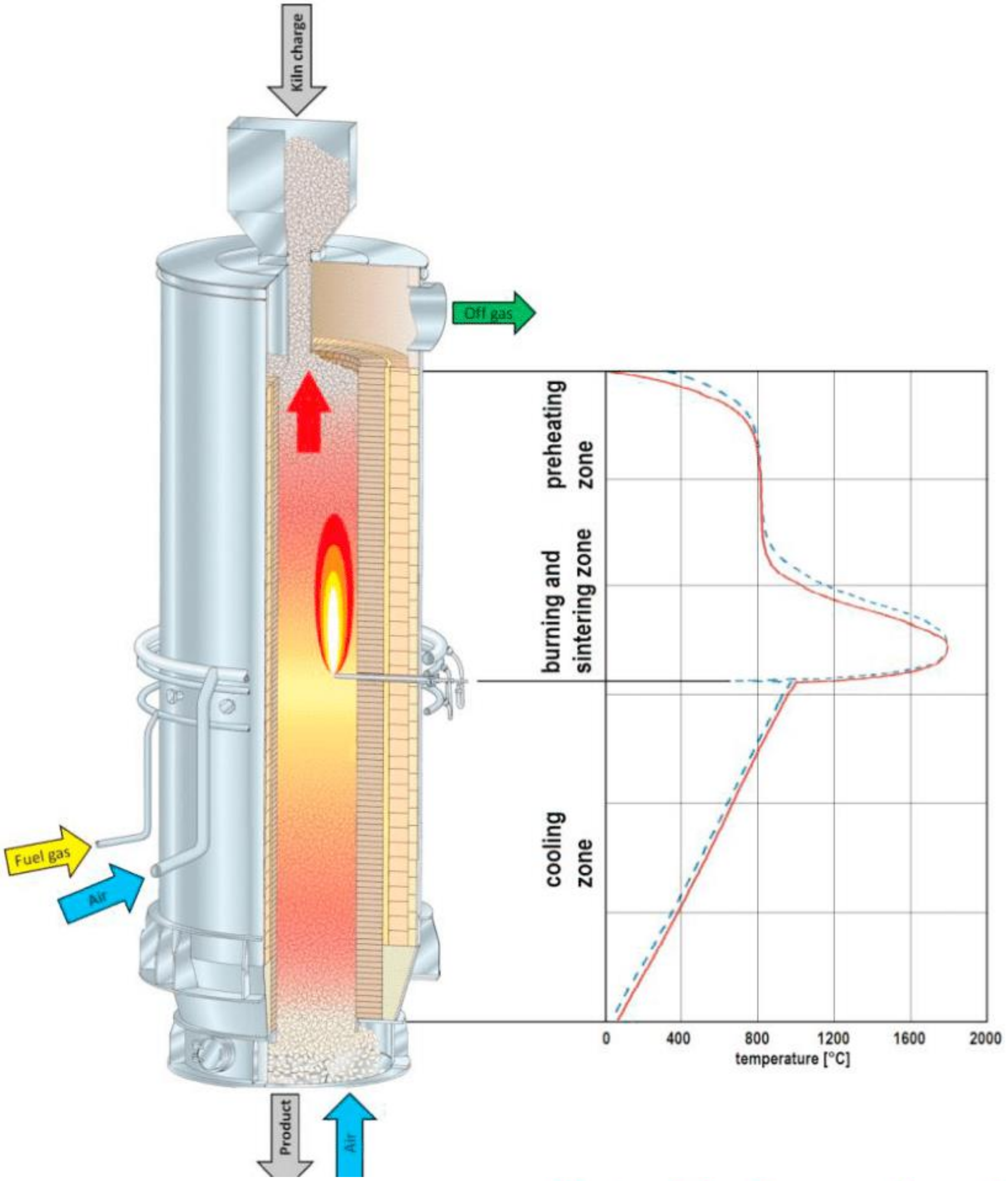

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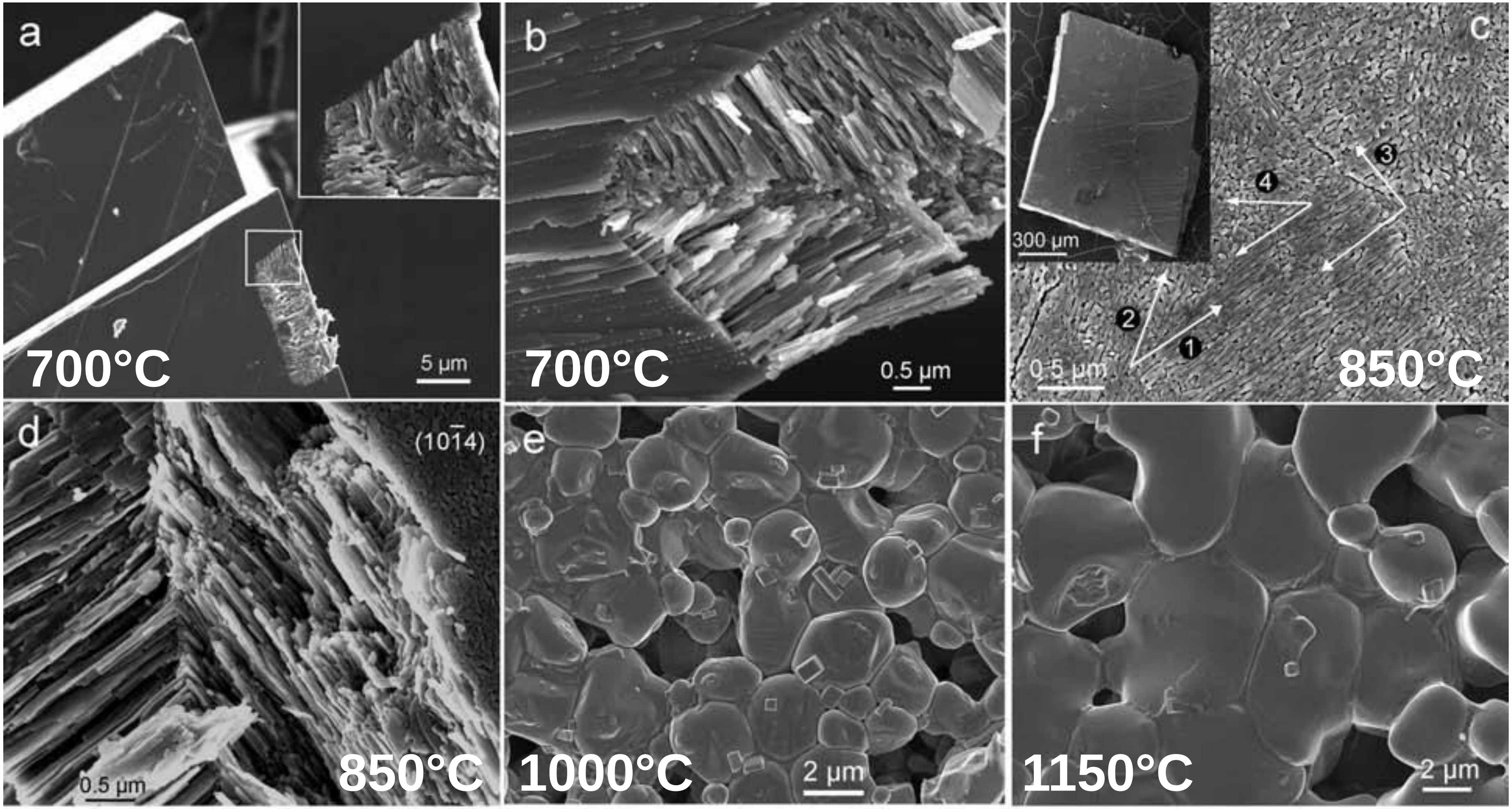

Rodriguez-Navarro et al. (2009)

Calcic binders

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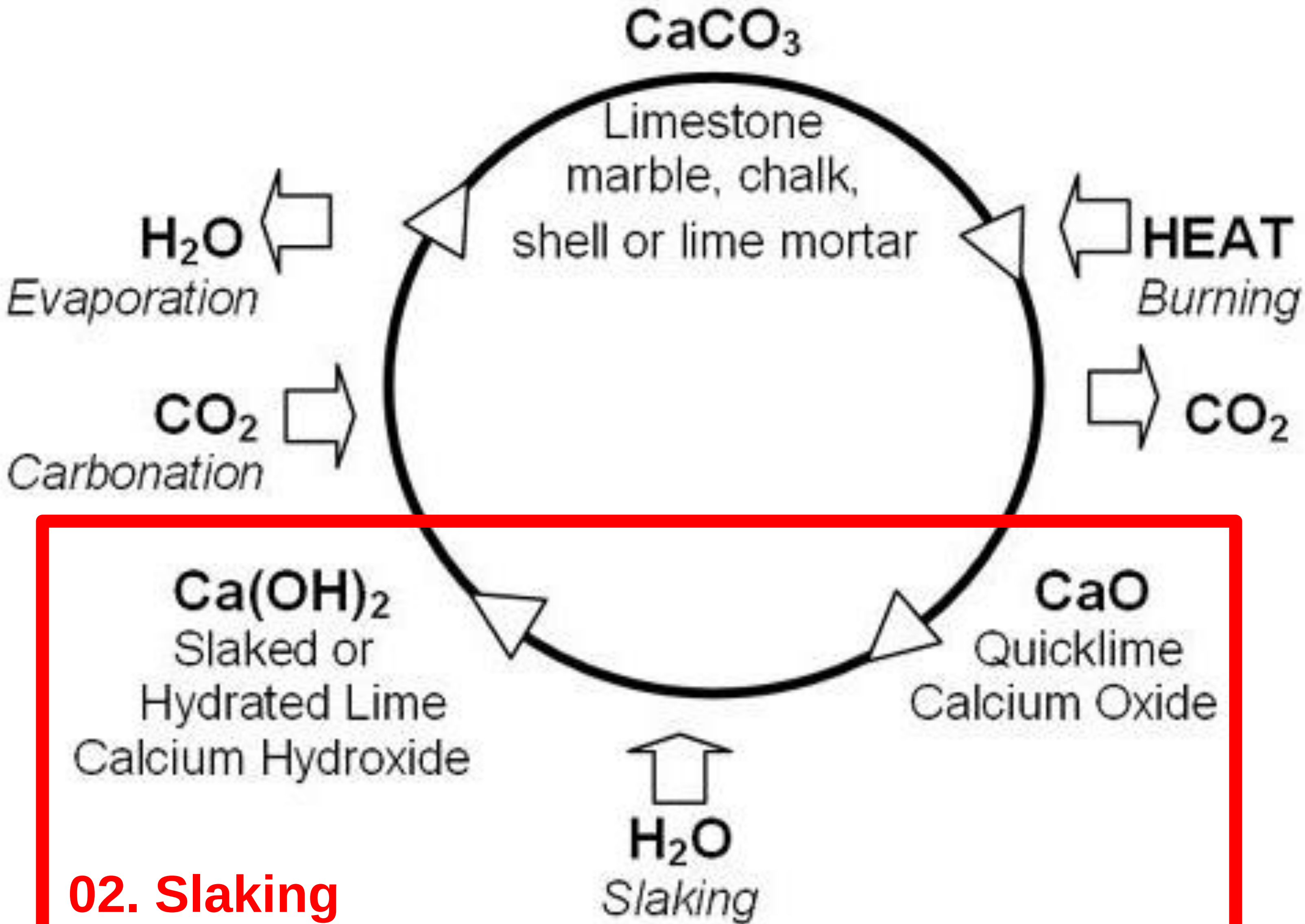
•The quality of the binder depends on a variety of parameters, including the composition, porosity and impurity content of the fired limestone, the maximum temperature and the time-temperature path of the firing, and the conditions of slaking.

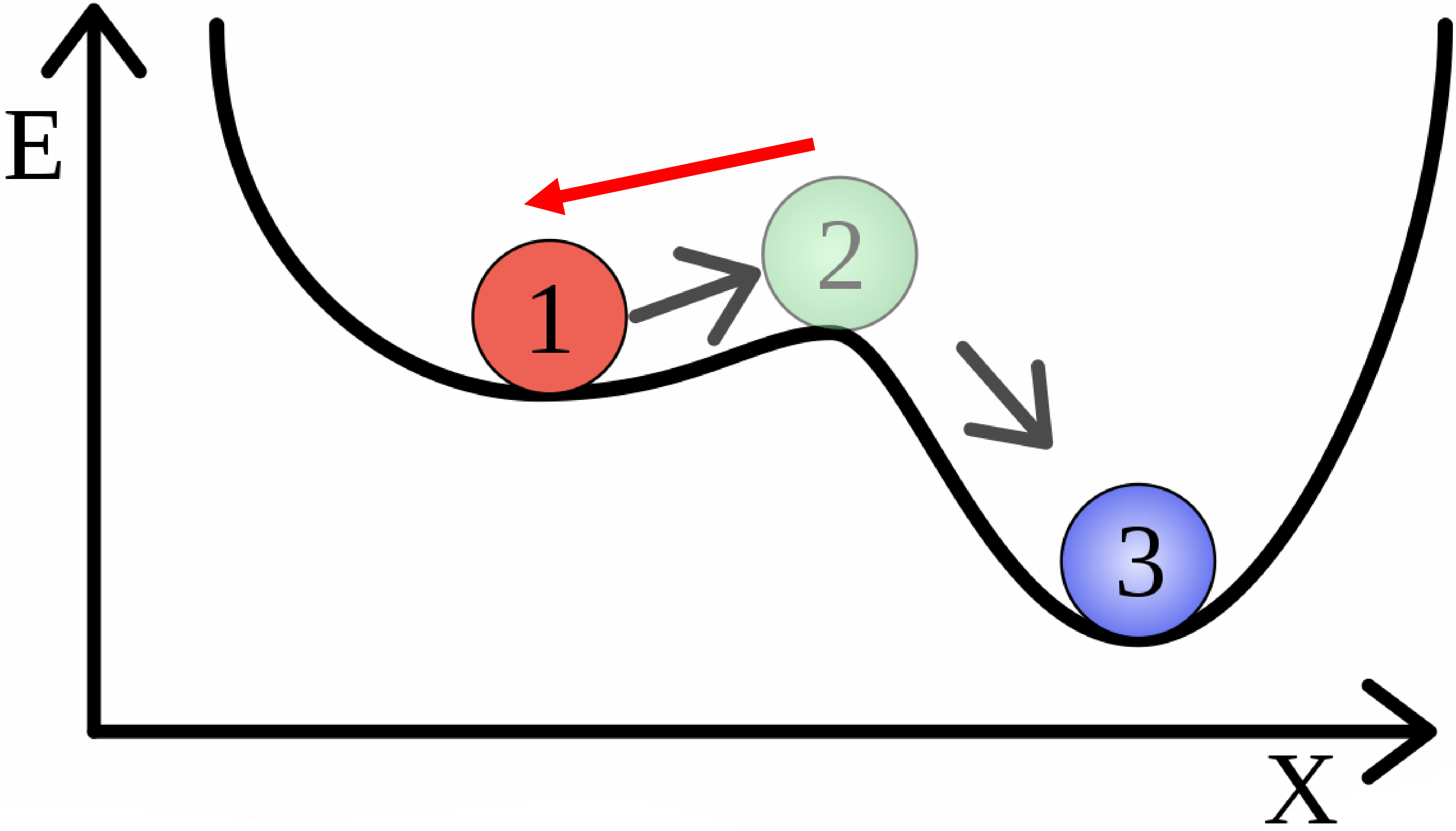
• The starting limestone should have a non carbonate mineral content (usually silicates and clays) lower than 5-10 wt %, and the carbonate should be pure calcium.

Calcic binders



02. Slaking

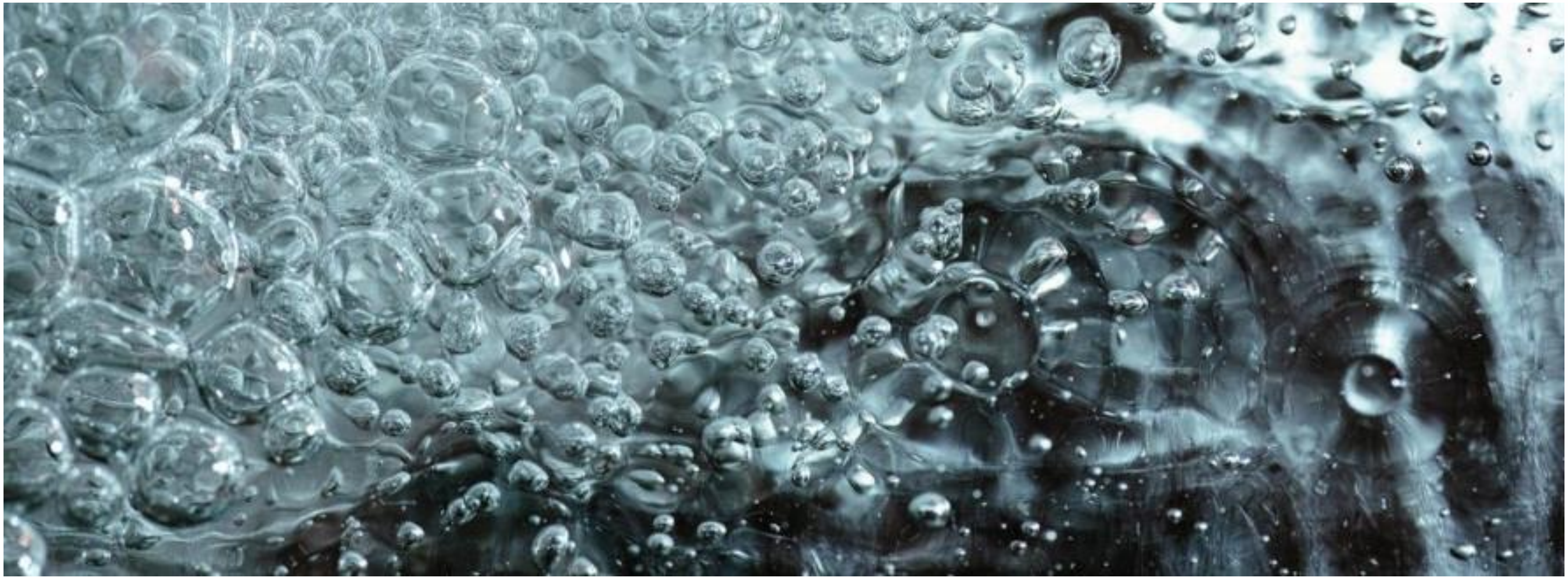
Calcic binders



Slaking

CaO(quicklime) + **H_2O** → **$Ca(OH)_2$**(slaked lime - portlandite) + heat

$\Delta G°_r \approx -57.9$ (kJ/mol)



Calcic binders

Calcic binders

• The fired blocks are ground to obtain the fine **powdered quicklime**, which however is rather unstable in normal humidity conditions and tends to hydrate to portlandite (calcium hydroxide, $Ca(OH)_2$).

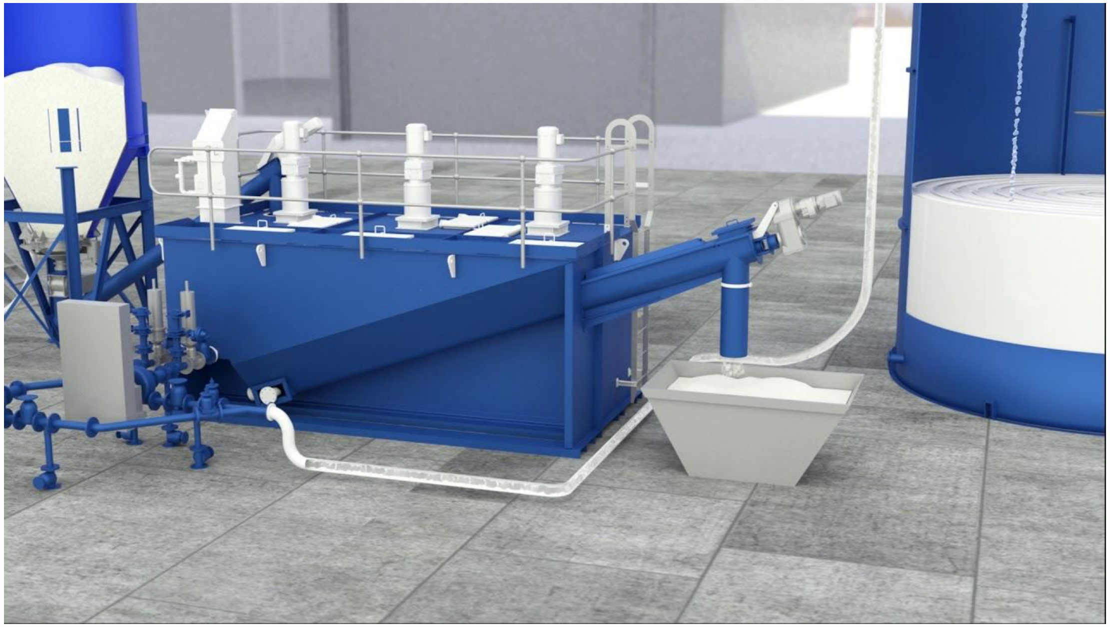
• If the CaO powder is mixed with an **exact** (i.e stoichiometric) amount of water (lime/water = 75.7/24.3 = 3.12 by weight) the product is fine dry powder and the process is called ***dry hydration***, because there is just the right amount of water to produce portlandite.

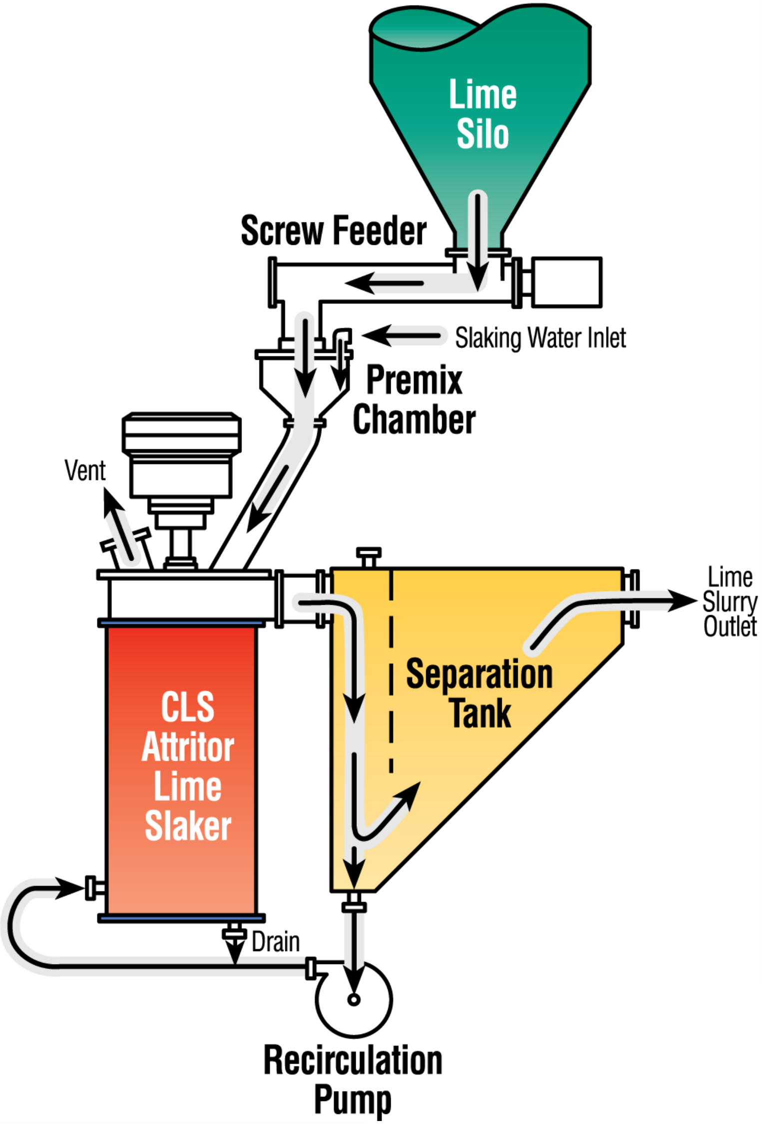
• If the CaO powder is mixed with **excess** water then a smooth paste is obtained in a slurry form, and the process id referred to as ***lime slaking***.

• The portlandite paste (***slaked lime*** or ***lime putty***) can then be used as a binder and an architectural component (filler, adhesive, cracks sealer, floor consolidant, surface smoother, etc.) or as a raw material for modelling objects, vessels, and even artwork.

Calcic binders

Calcic binders



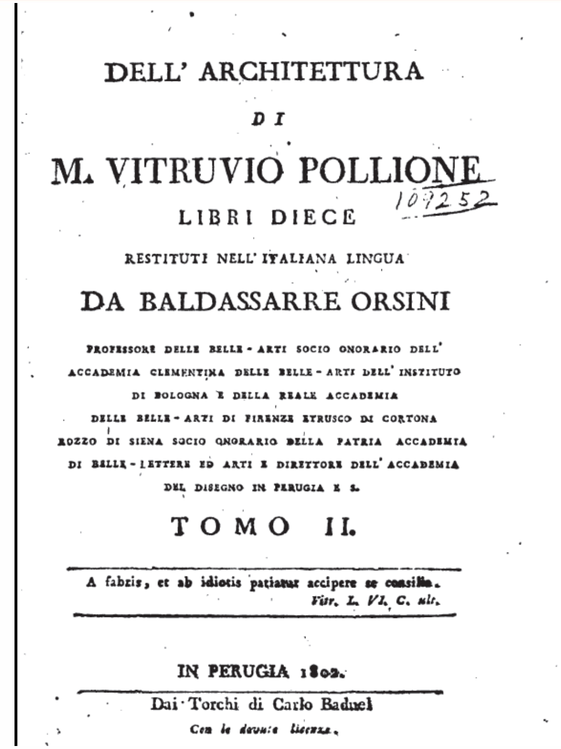


Calcic binders

• In early Roman times there was the widespread belief that aging of the slaked lime was crucial to the quality of the plaster.

• **Vitruvius** (*De architectura*, Book VII) had realized the importance of properly mixing the lime with a hoe to ensure good homogeneity and above all slaking for a sufficient time in pits.

• Similarly, **Plinius** (*Naturalis Historia*, Book V) claimed that lime putty needed to mature for at least three years to produce a good binder. Long homogeneous mixing and aging definitely helped in producing a slaked compound with a very fine grain size and little porosity, and this is one of the "secrets" of the excellent quality of Roman mortars, which are still astonishingly solid and hard.



DELL' ARCHITETTURA

DI

M. VITRUVIO POLLIONE

LIBRI DIECE

RESTITUTI NELL' ITALIANA LINGUA

DA BALDASSARRE ORSINI

PROFESSORE DELLE BELLE - ARTI SOCIO ONORARIO DELL' ACCADEMIA CLEMENTINA DELLE BELLE - ARTI DELL' INSTITUTO DI BOLOGNA E DELLA REALE ACCADEMIA DELLE BELLE - ARTI DI FIRENZE ETRUSCO DI CORTONA ROZZO DI SIENA SOCIO ONORARIO DELLA PATRIA ACCADEMIA DI BELLE - LETTERE ED ARTI E DIRETTORE DELL' ACCADEMIA DEL DISEGNO IN PERUGIA E S.

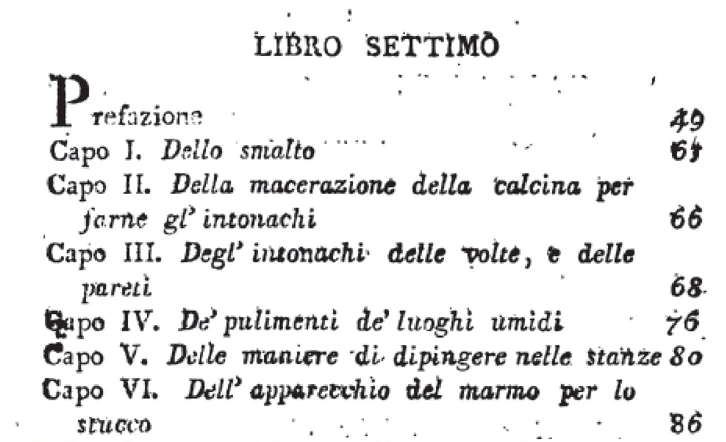
TOMO II.

A fabris, et ab idiotis patiatur accipere se consilia.
Vitr. L. VI. C. ult.

IN PERUGIA 1802.

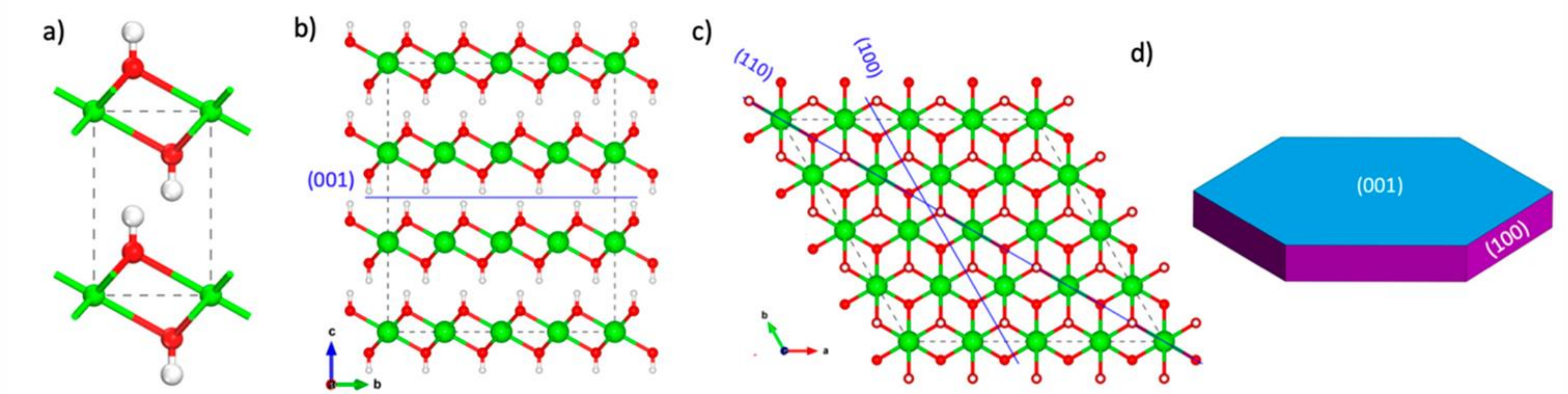
Dai Torchi di Carlo Baduel

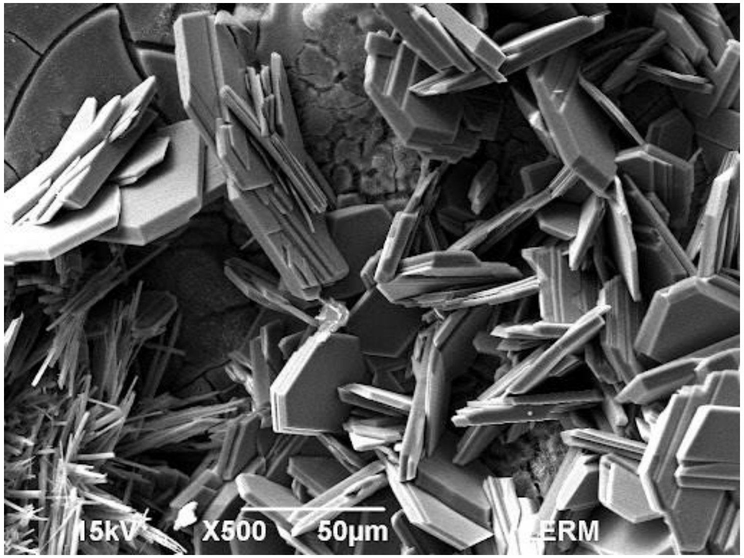
Con le dovute licenze.



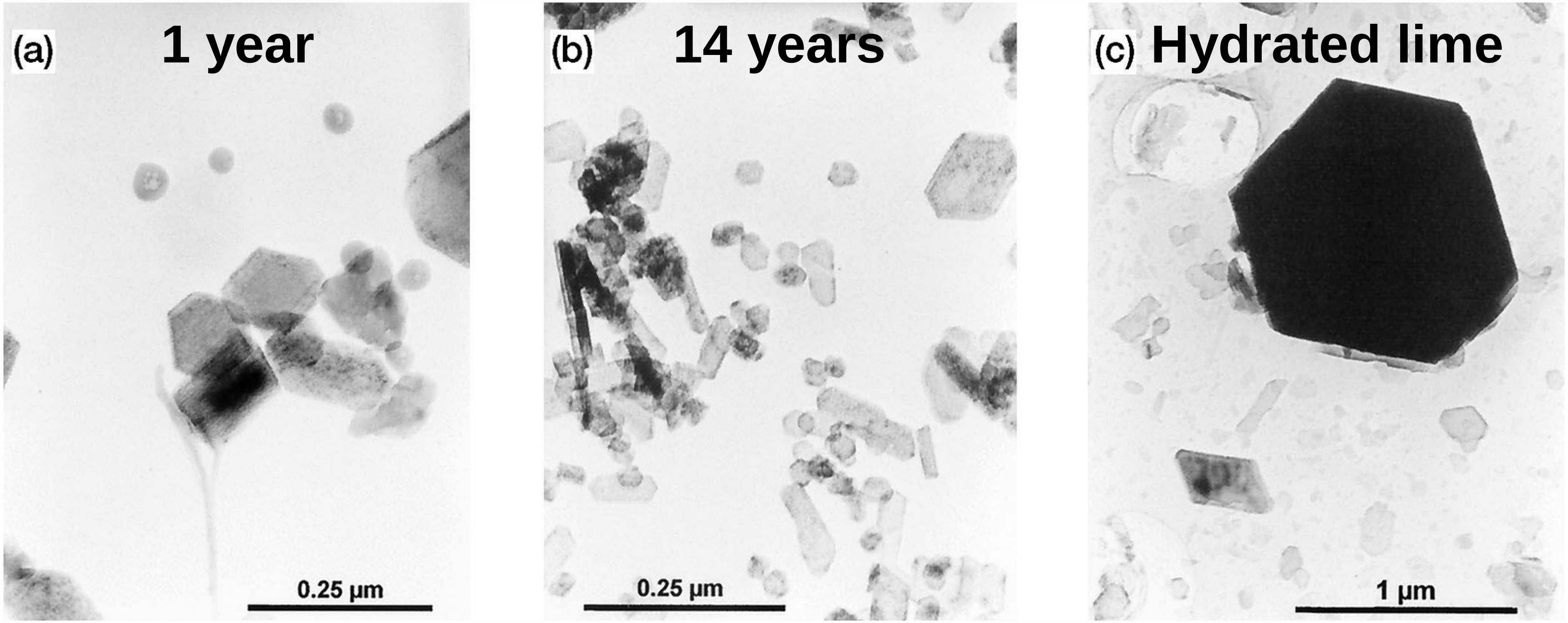
LIBRO SETTIMO

Portlandite crystal structure



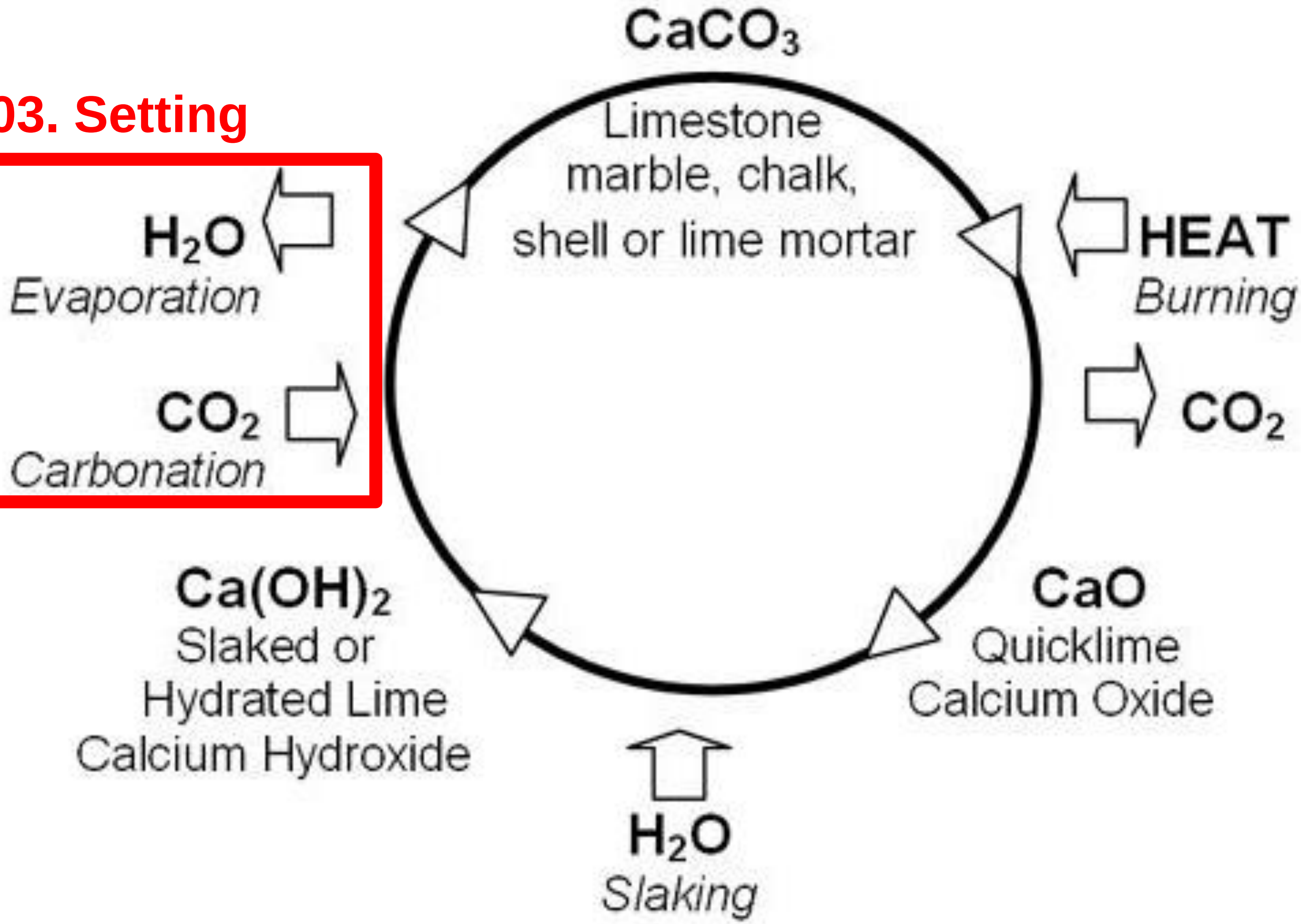


Calcic binders

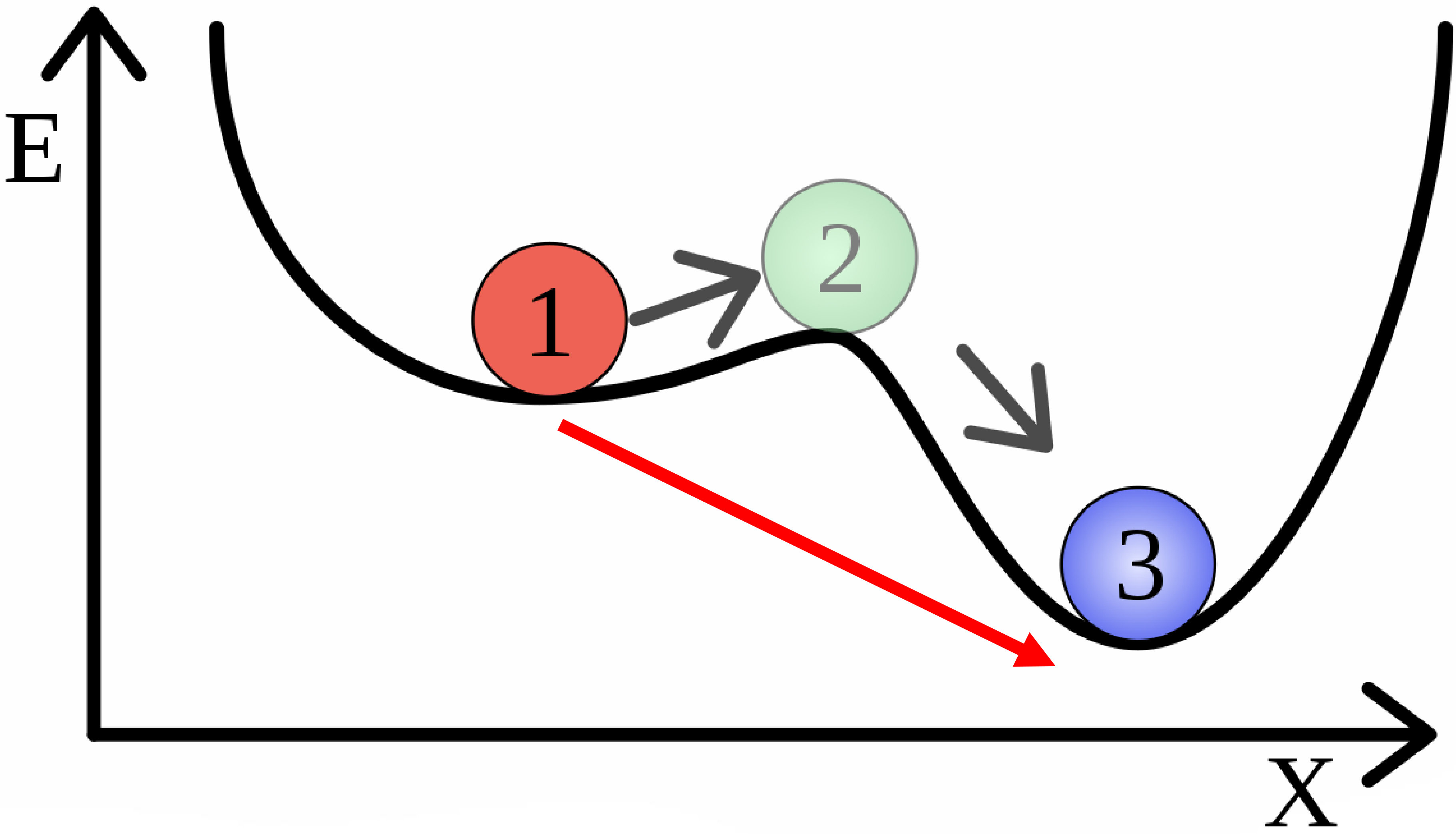


Cazalla et al. (2000)

03. Setting


CaCO3
Limestone
marble, chalk,
shell or lime mortar
H2O
Evaporation
CO2
Carbonation
HEAT
Burning
CO2
Ca(OH)2
Slaked or
Hydrated Lime
Calcium Hydroxide
CaO
Quicklime
Calcium Oxide
H2O
Slaking

Calcic binders



Setting

$Ca(OH)_2$ (slaked lime) + CO_2 (carbon dioxide) → $CaCO_3$ (calcite) + H_2O + heat

Solubility $Ca(OH)_2$: 1.73 g/L
(Solubility NaCl: 360 g/L)

↓

Slaked lime poorly soluble!

Release of hydroxyl ions during $Ca(OH)_2$ dissolution → pH

12.5

Reaction paths

$$CO_{2(g)} \leftrightarrow CO_{2(aq)};$$

Rate-controlling step

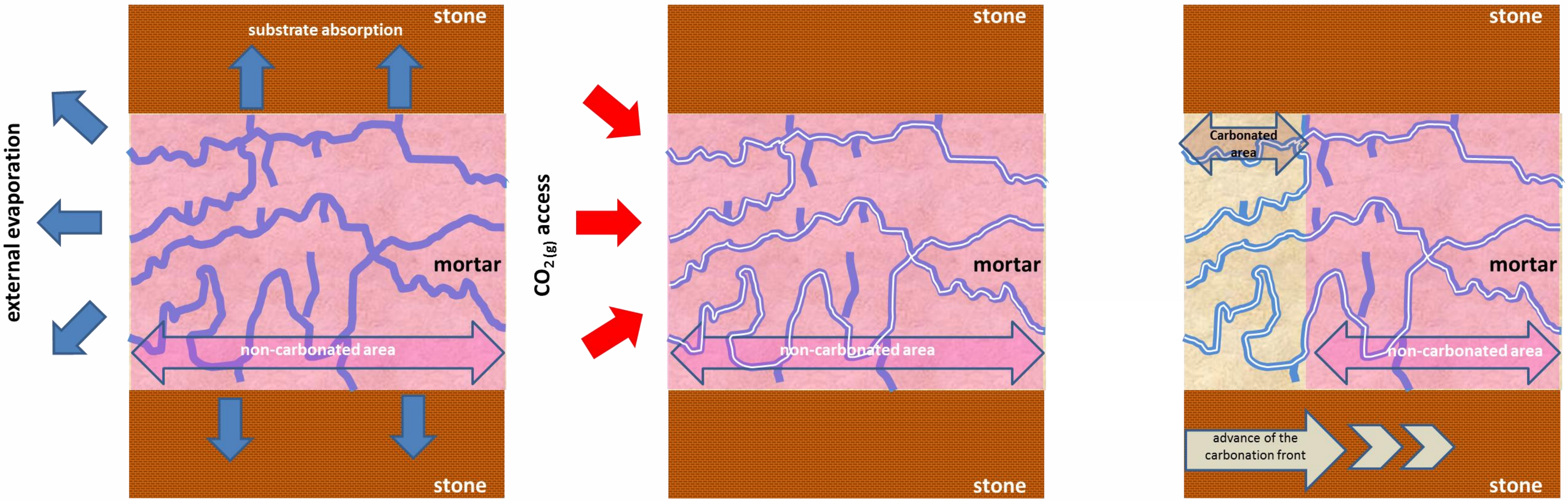
$$CO_{2(aq)} + OH^{-}{}_{(aq)} \leftrightarrow HCO_3{}^{-}{}_{(aq)};$$

Instantaneous reaction

$$HCO_3{}^{-(aq)} + OH^{-}{}_{(aq)} \leftrightarrow CO_3{}^{2-}{}_{(aq)} + H_2O_{(l)};$$

$$Ca^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \leftrightarrow CaCO_{3(s)}.$$

Progression of carbonation



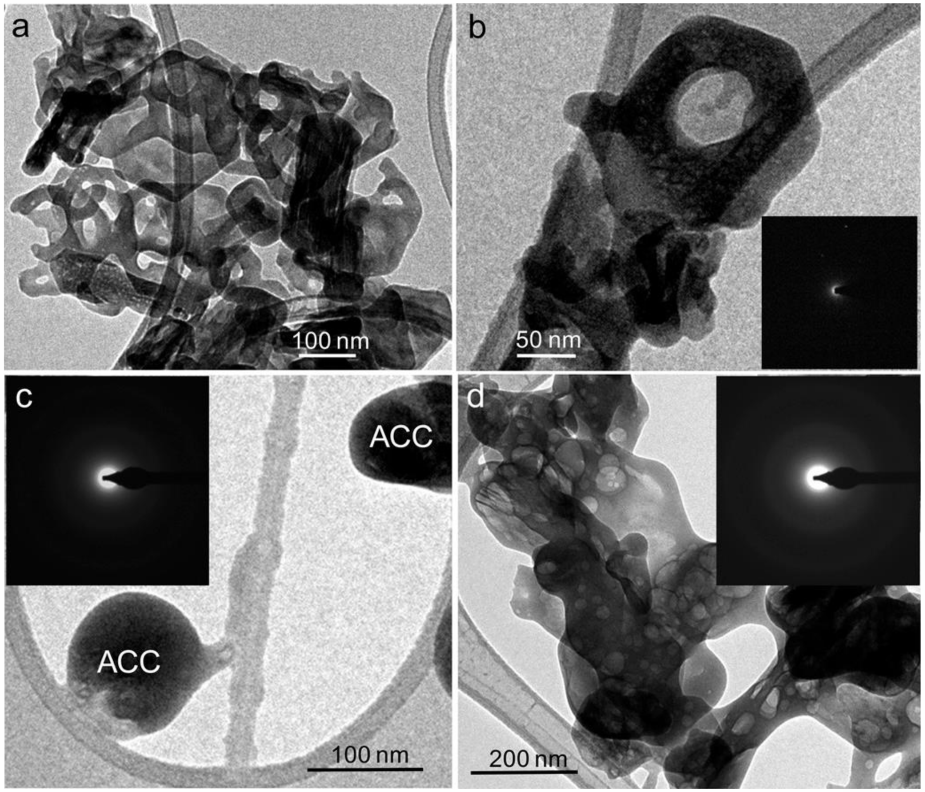
Step 1. Fresh mortar: porous network, pores saturated with mixing water. Drying

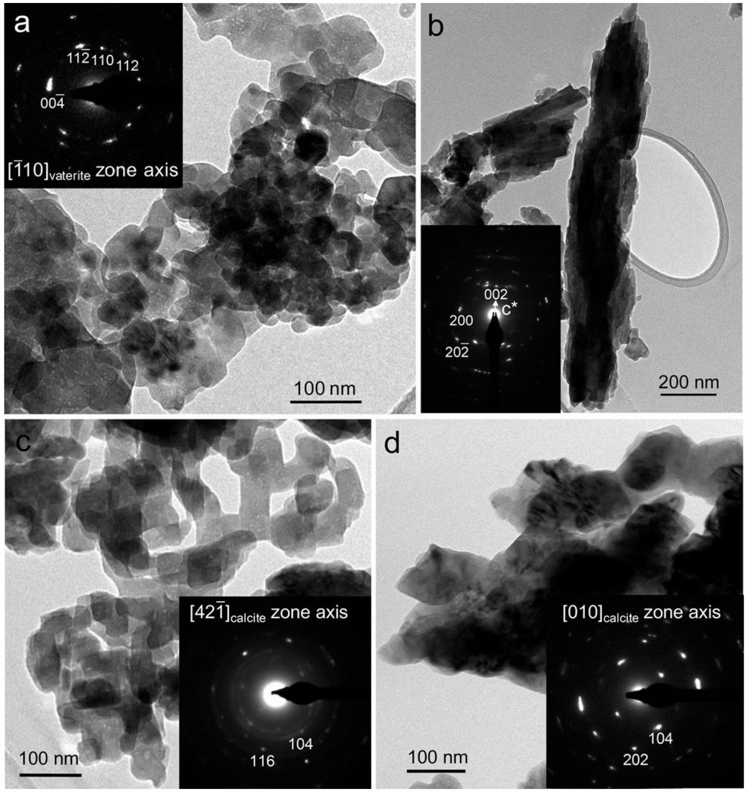
Step 2. Fresh mortar: porous network, pores with an adsorbed layer of water. Atmospheric CO_2 access and dissolution in the water

Step 3. First stages of the carbonation: advance of the front of carbonation

Crystallization sequences

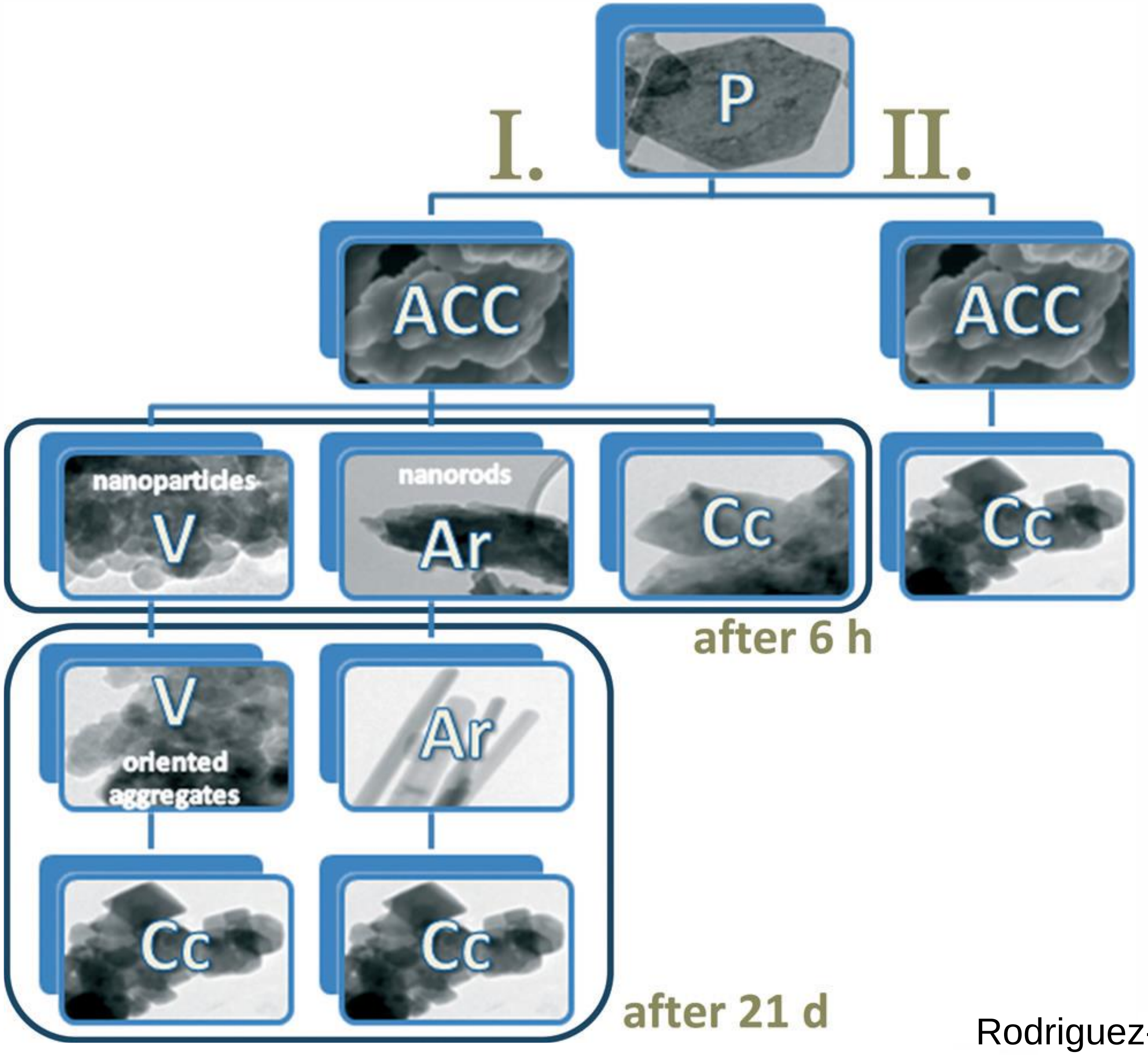
Amorphous calcium carbonate (AAC) → $CaCO_3$ metastable polymorphs (aragonite, vaterite) → Calcite





Rodriguez-Navarro et al. (2016)

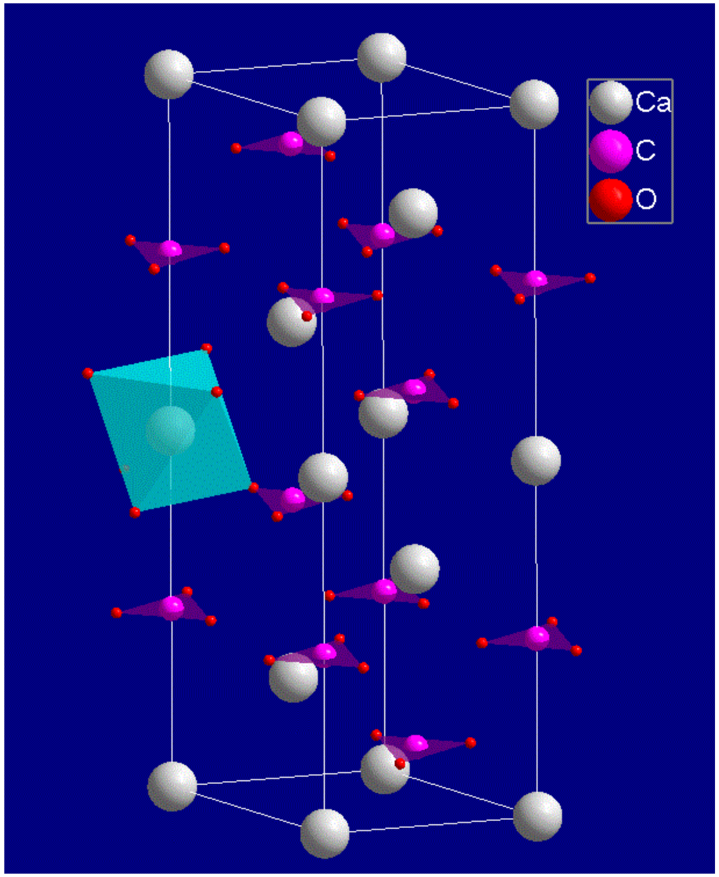
Crystallization sequences



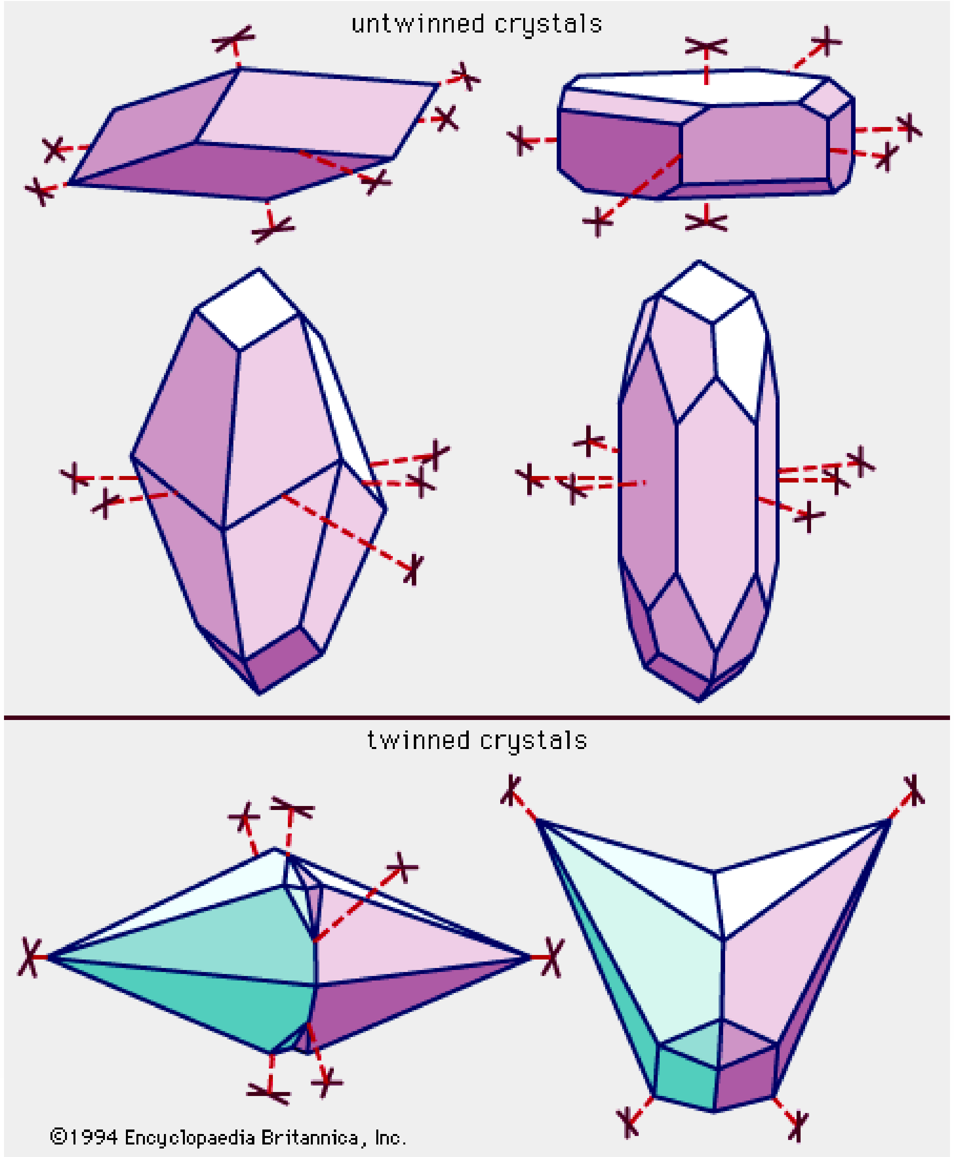
Rodriguez-Navarro et al. (2016)

Calcic binders

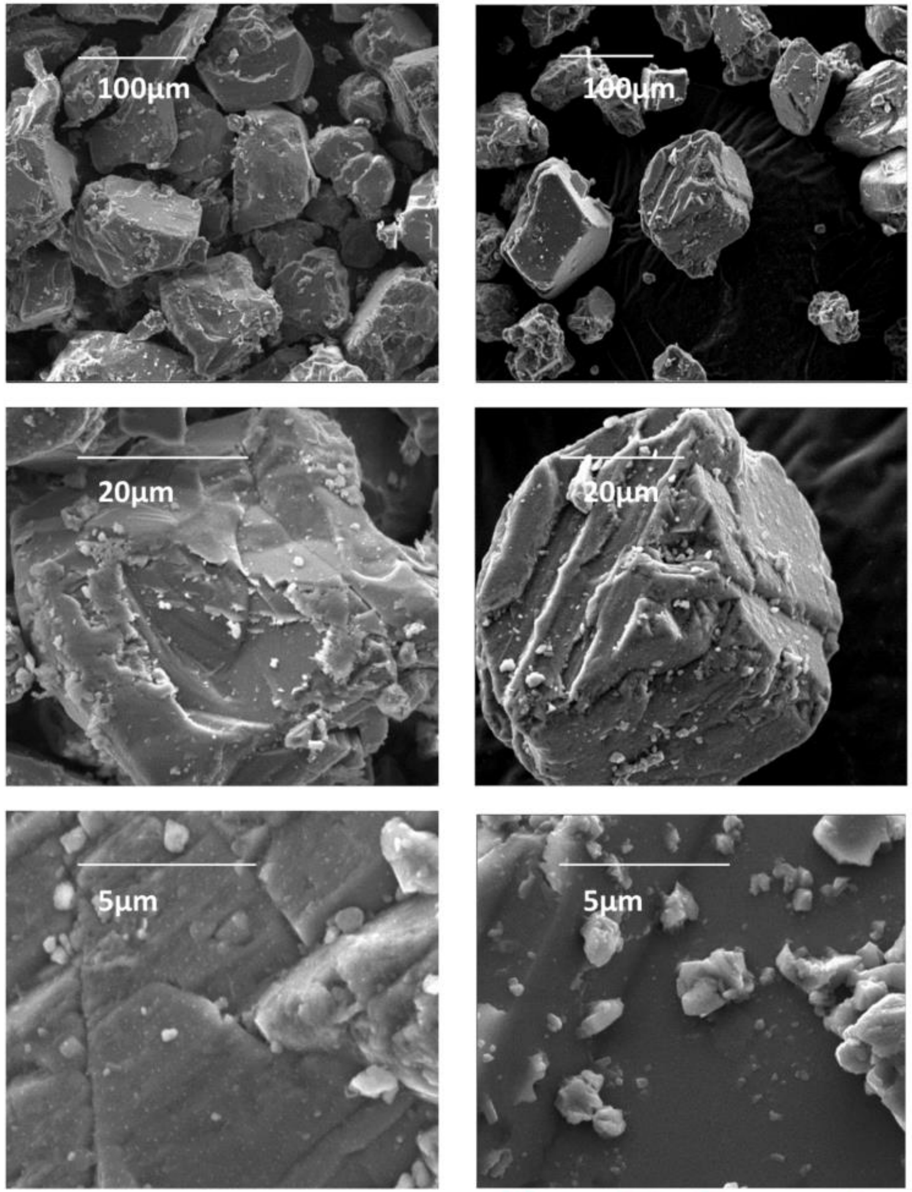
CALCITE STRUCTURE



Layers of carbonate ions and Ca^{2+} ions in octahedral coordination



Calcic binders



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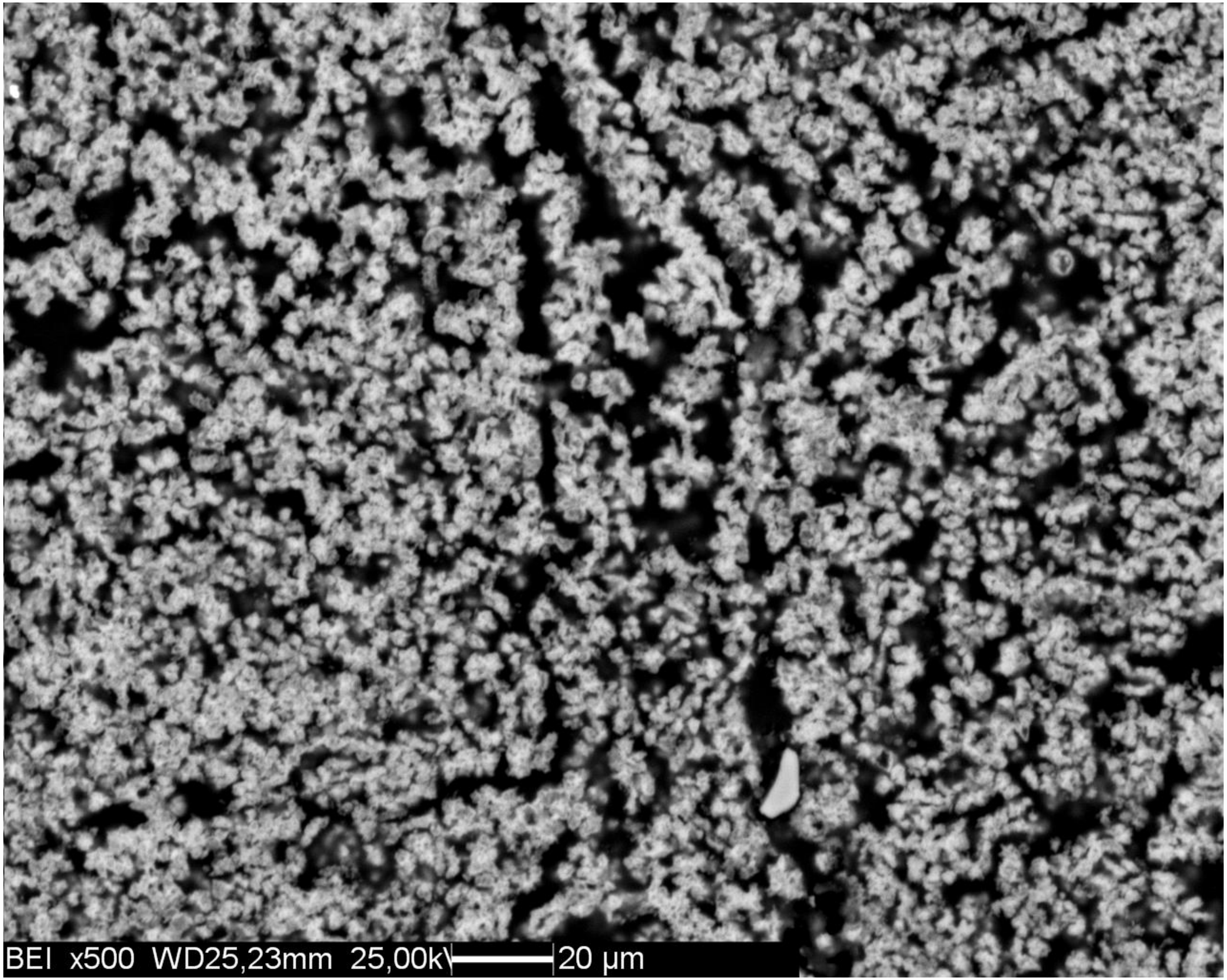
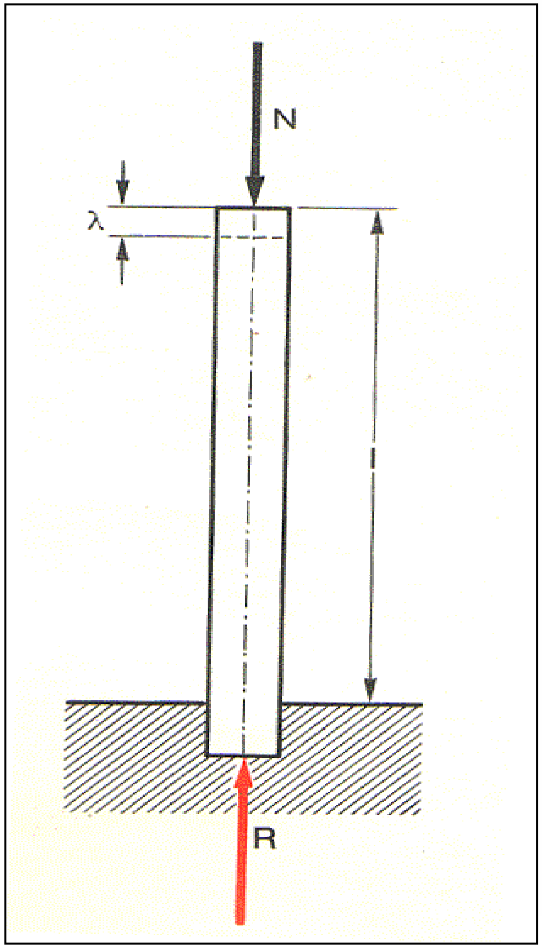
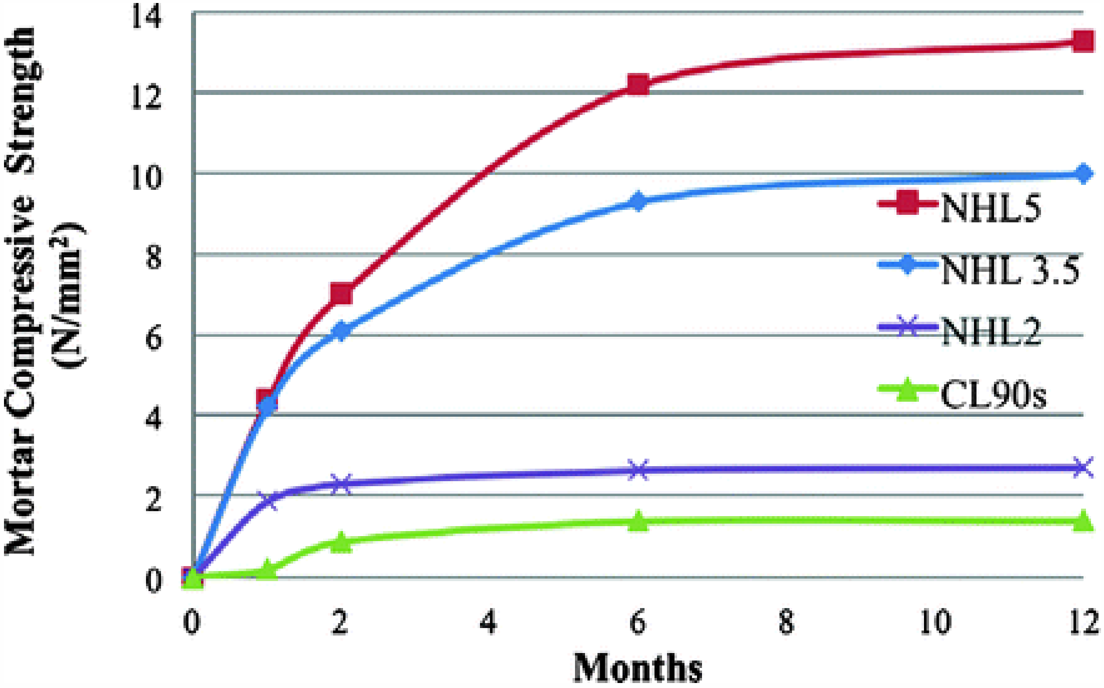


Compressive strength of lime





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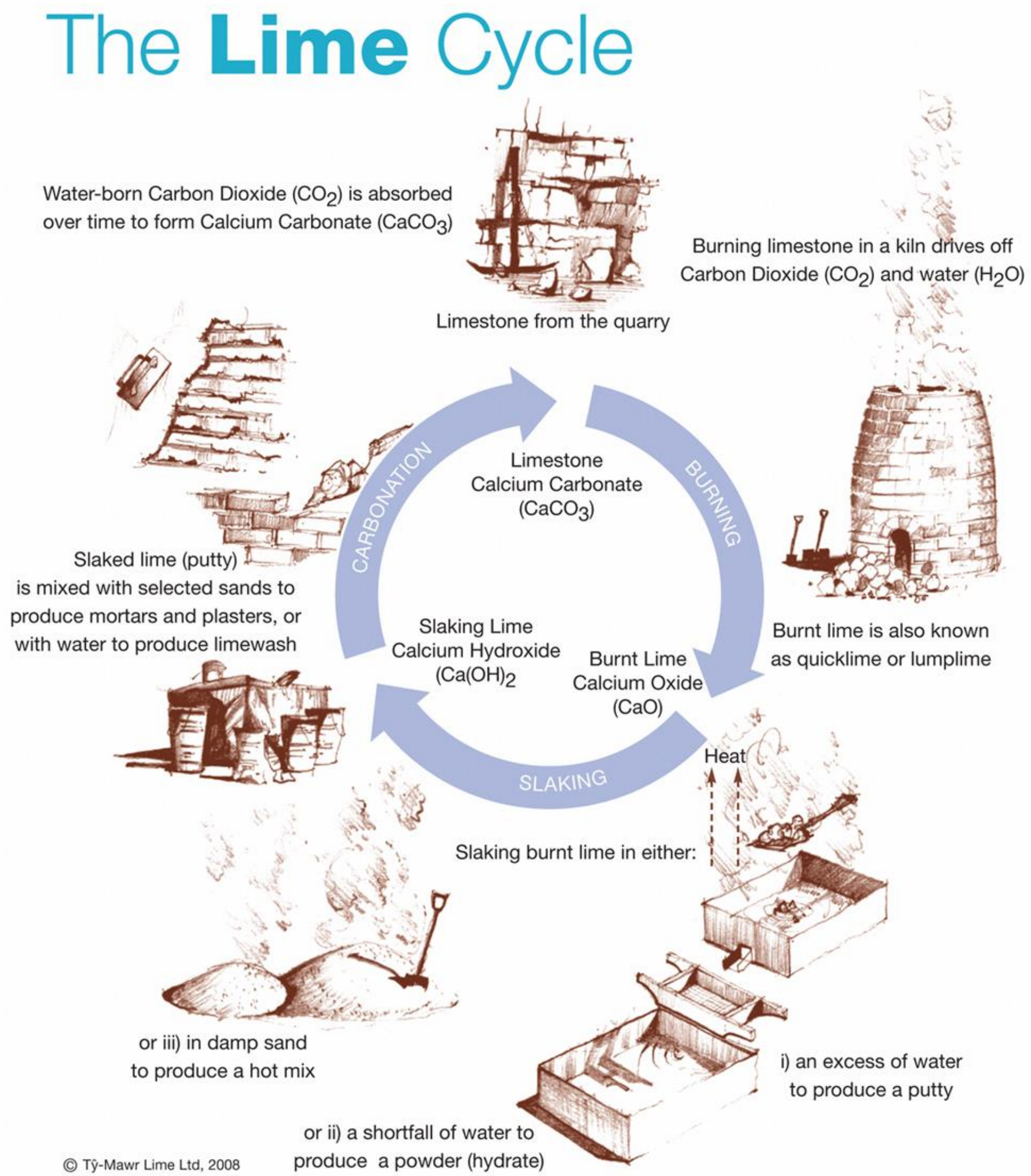

THANK YOU FOR YOUR ATTENTION!