



# THE SOLUBLE SALTS IN THE BUILT HERITAGE



## Principal ions of the harmful soluble salts:

<b>Cations</b>	<b>Anions</b>
Na <sup>+</sup> (sodium)	CO <sub>3</sub> <sup>-</sup> (carbonate)
K <sup>+</sup> (potassium)	HCO <sub>3</sub> <sup>-</sup> (hydrogencarbonate)
Ca <sup>++</sup> (calcium)	SO <sub>4</sub> <sup>-</sup> (sulphate)
Mg <sup>++</sup> (magnesium)	NO <sub>3</sub> <sup>-</sup> (nitrate)
NH <sub>4</sub> <sup>+</sup> (ammonium)	Cl <sup>-</sup> (chloride)
	C <sub>2</sub> O <sub>4</sub> <sup>-</sup> (oxalate)



## Principal soluble salts in building stones (in CH):

	English	French	
<b>Chlorides</b>	halite sylvite	" sylvine	NaCl KCl
<b>Nitrates</b>	niter nitronatrite ammonium nitrate	salpêtre, nitre ", nitratine nitrate d'ammonium	KNO <sub>3</sub> NaNO <sub>3</sub> NH <sub>4</sub> NO <sub>3</sub> (pH<7)
<b>Sulphates</b>	thenardite mirabilite gypsum epsomite arcanite	thénardite " gypse " "	Na <sub>2</sub> SO <sub>4</sub> Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O CaSO <sub>4</sub> ·2H <sub>2</sub> O MgSO <sub>4</sub> ·7H <sub>2</sub> O K <sub>2</sub> SO <sub>4</sub>
<b>Carbonates</b>	calcite natron thermonatrite trona	" " " "	CaCO <sub>3</sub> (pH>7) Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O (pH>7) Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O (pH>7) Na <sub>3</sub> H(CO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O (pH>7)
<b>Oxalates</b>	weddellite whewellite	" "	Ca(C <sub>2</sub> O <sub>4</sub> )·2(H <sub>2</sub> O) Ca(C <sub>2</sub> O <sub>4</sub> )·(H <sub>2</sub> O)
<b>Complex salts</b>	ettringite darapskite	" "	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O Na <sub>3</sub> (SO <sub>4</sub> )(NO <sub>3</sub> )·H <sub>2</sub> O



## Origin of the soluble salts:

### Natural origins:

Sea water (all ions  $\neq$  NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>)

Groundwaters (all ions)

Fresh waters (all ions)

Organic origin (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, oxalates C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, HC<sub>2</sub>O<sub>4</sub><sup>-</sup>)

### Natural building materials:

→ ex. : sandstone of Berne (≈ 0.1% Ca<sup>2+</sup> et SO<sub>4</sub><sup>2-</sup>)



## Origin of the soluble salts:

### Restoration materials:

- cleaning products (formic acid, ammonium carbonate)
- conservation products (oxalates)
- additives of the conservation products (ammonia)

### Air pollution (sulphate, nitrogen oxides, etc.)

- dry deposition
- wet deposition



## Origin of the soluble salts:

### De-icing salts

- NaCl, CaCl<sub>2</sub>,...

### Alkali building materials

- Cement (Na<sup>+</sup>, K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>,...)
- Soluble glasses (Wasserglas) (K<sup>+</sup> ± Na<sup>+</sup> ± Li<sup>+</sup>)
- Trass (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>,...)

### Fireproof materials

- Boron salts
- Wasserglass



# The crystallization problem



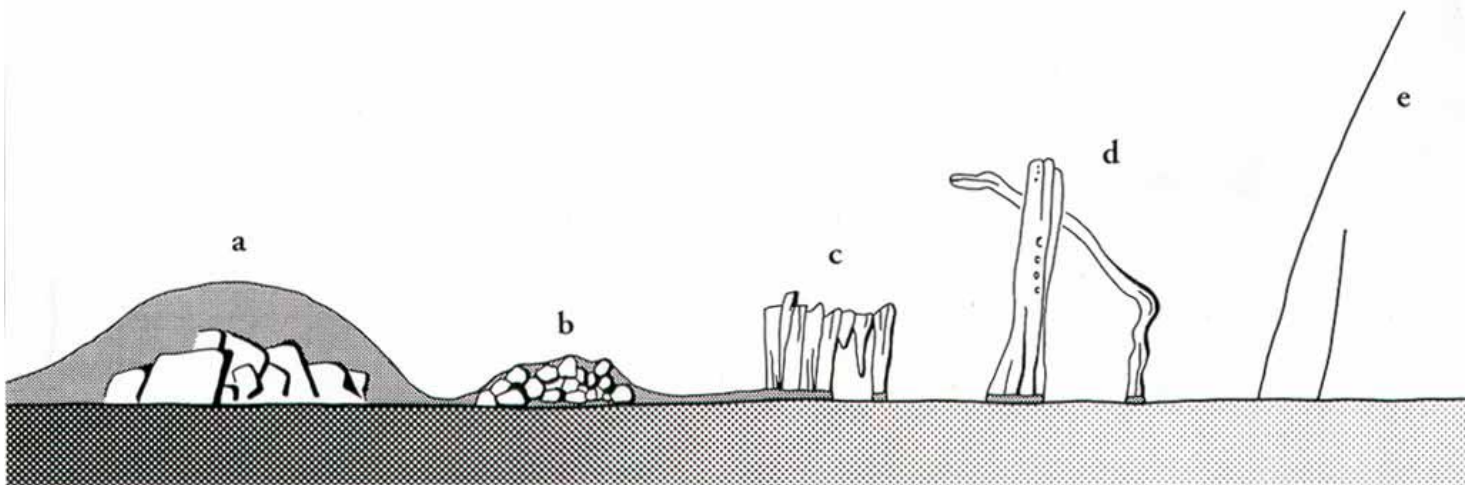




Nancy, 7.6.2008  
Black crust of gypsum on the  
Euville limestone



*Relationship between crystal morphology and the substrate humidity of a porous material*

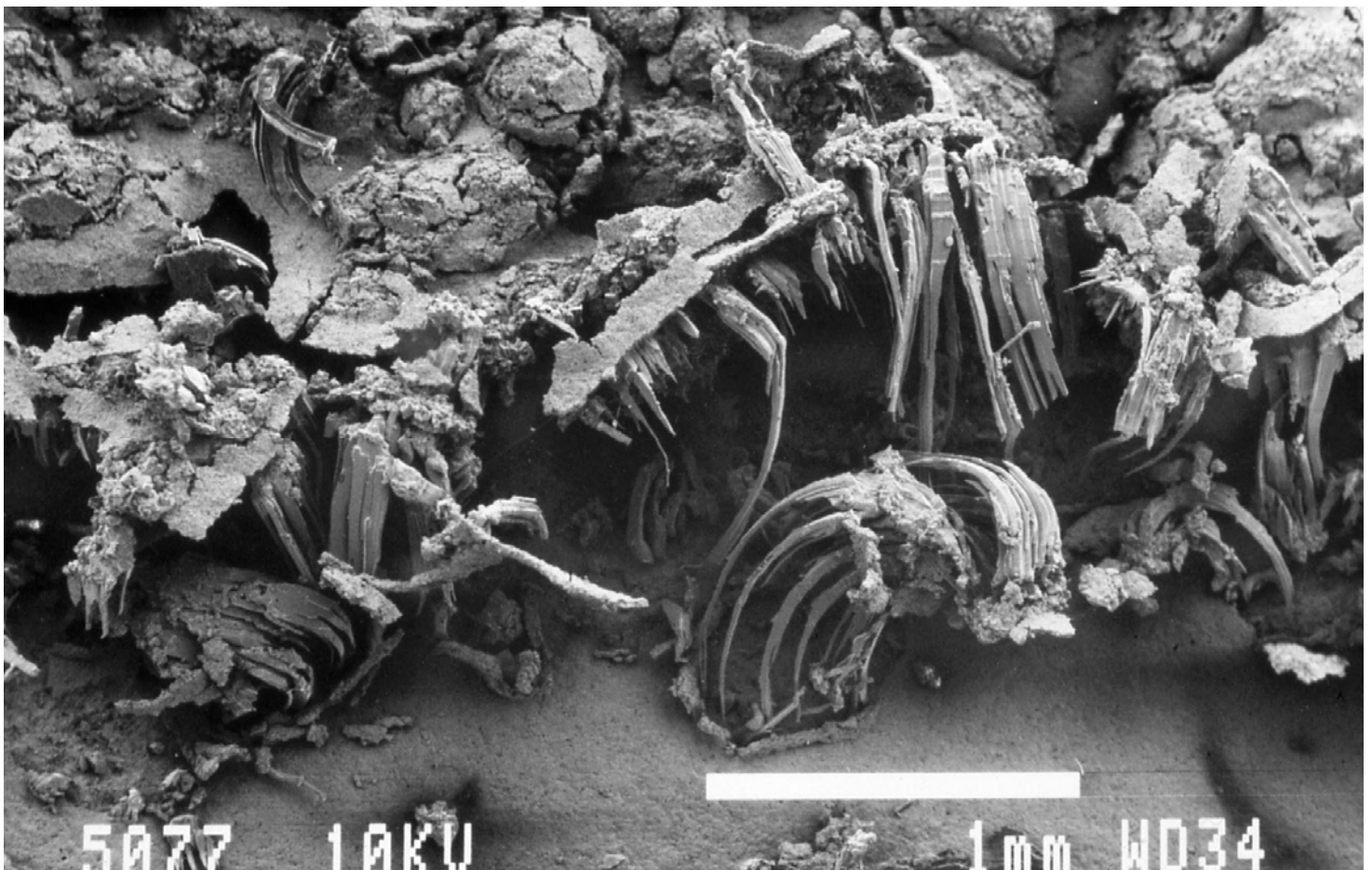


From: Arnold, A.; Zehnder, K. (1991): Monitoring wall paintings affected by soluble salts.- The Conservation of Wall Paintings. Proc. Symp. Courtauld Inst. Art & Getty Conservation Inst., London, July 13-16, 1987, 103-135.- The Getty Conservation Institute.





Nancy, rampart, 7.6.2008 (photo: C. Bläuer)

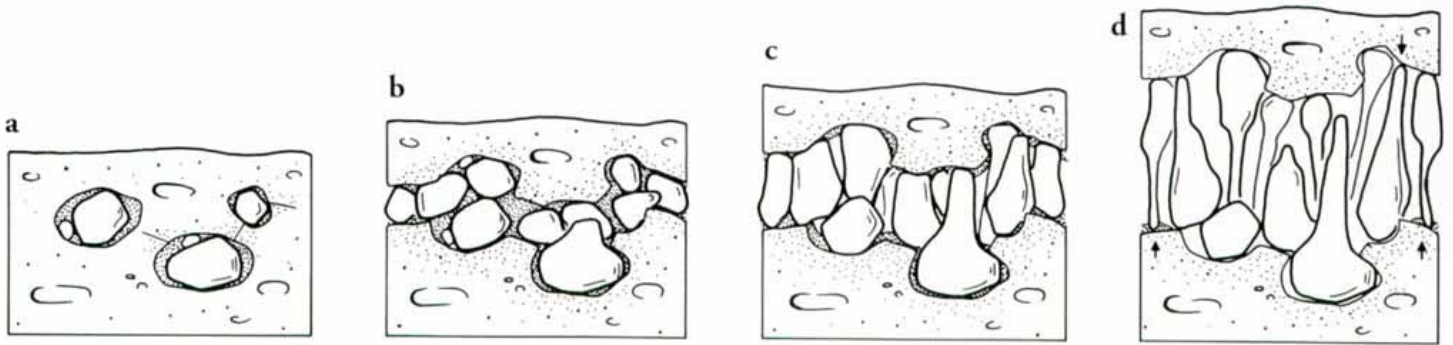


Paint layer on a ceramic with halite (NaCl) efflorescences (Laborexperiment)

Photo Konrad Zehnder



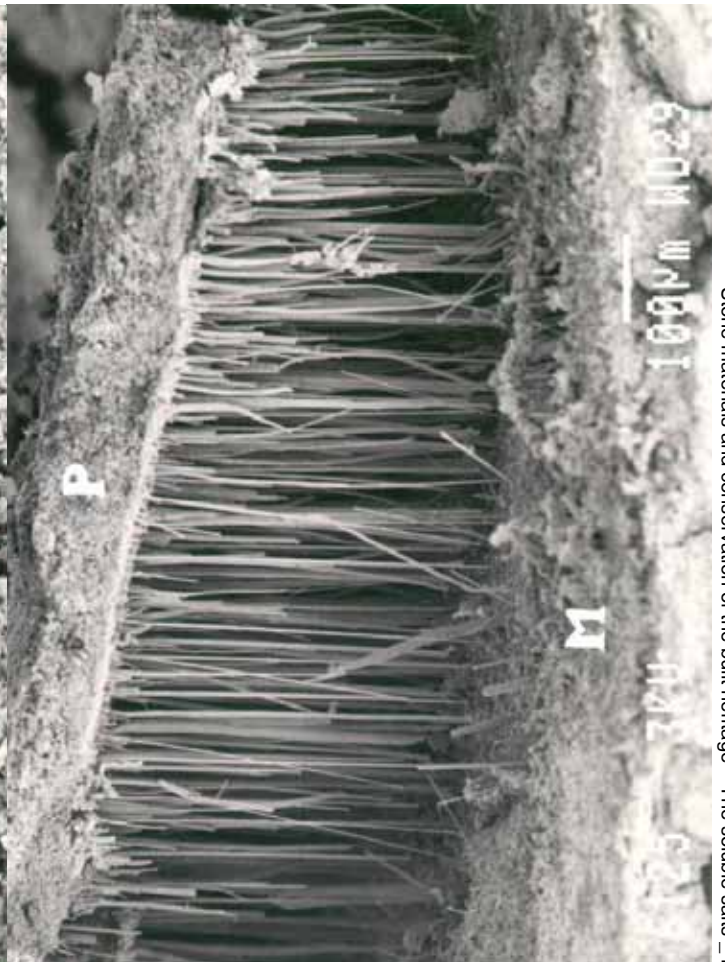
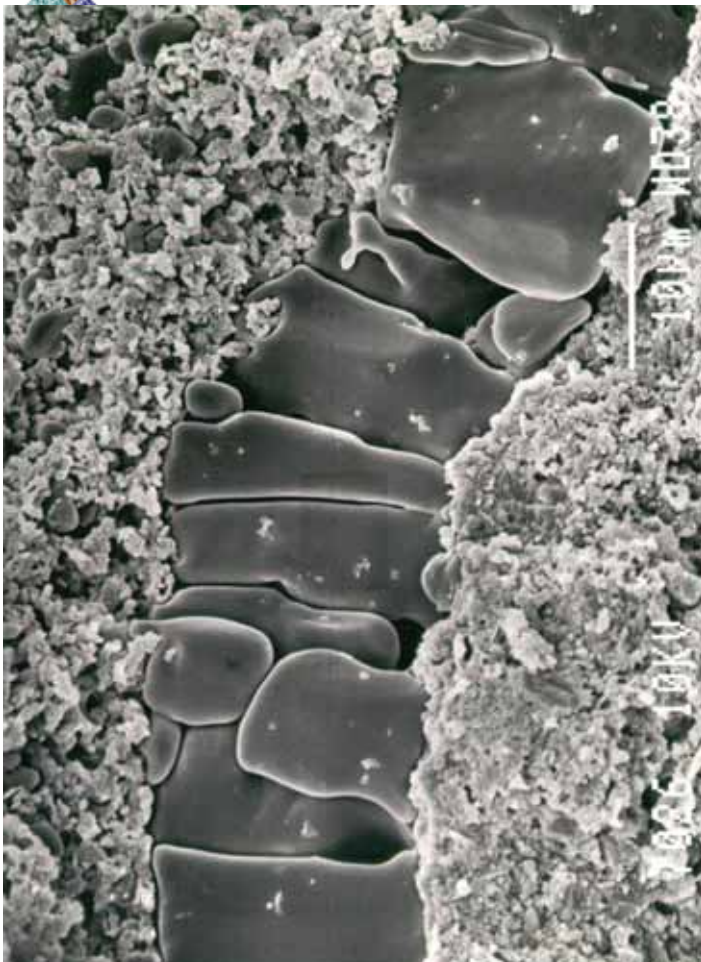
*Model of disruption process by crystallizing salts*



aus: Arnold, A.; Zehnder, K. (1991): Monitoring wall paintings affected by soluble salts.- The Conservation of Wall Paintings. Proc. Symp. Courtauld Inst. Art & Getty Conservation Inst., London, July 13-16, 1987, 103-135.- The Getty Conservation Institute.

soluble salts - BR /13

Photos: Konrad Zehnder

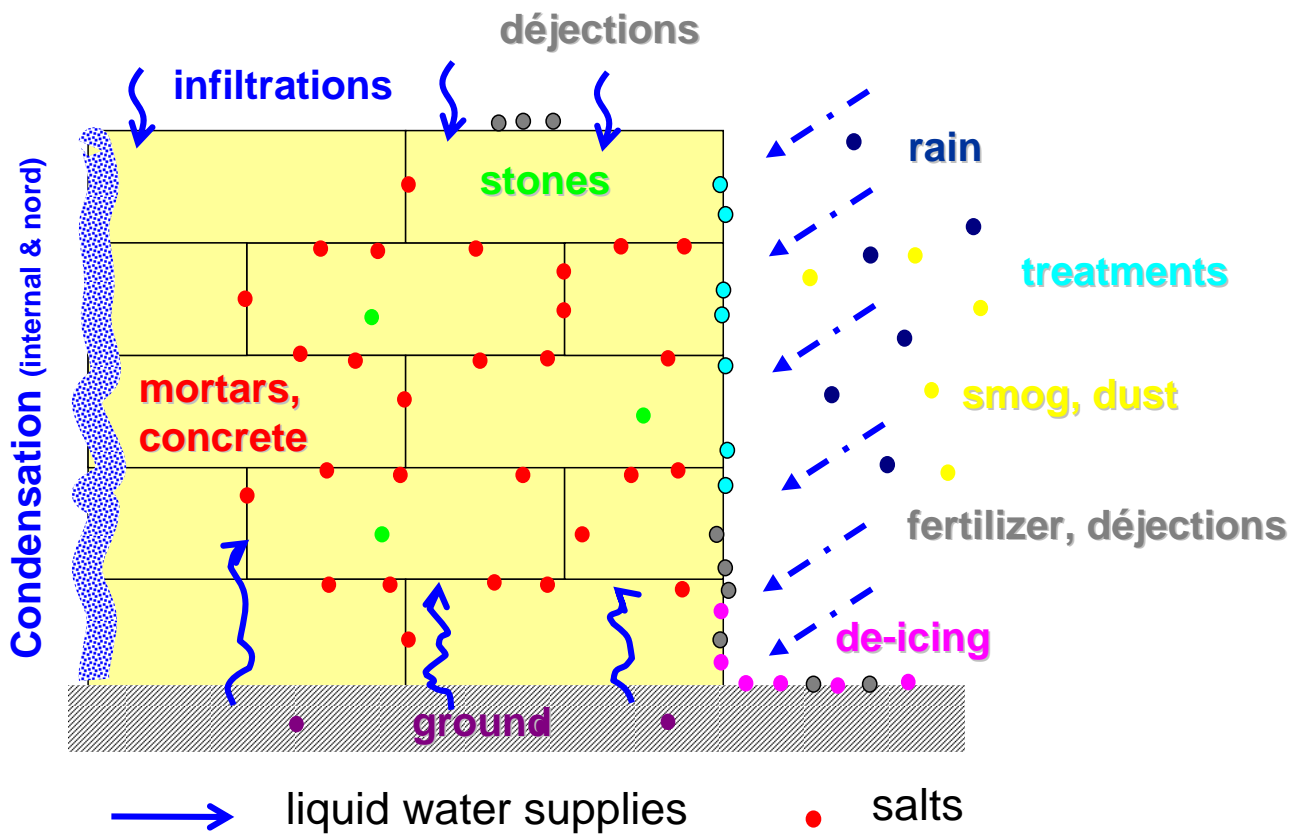


Stone materials and conservation of the built heritage - The soluble salts - BR /14

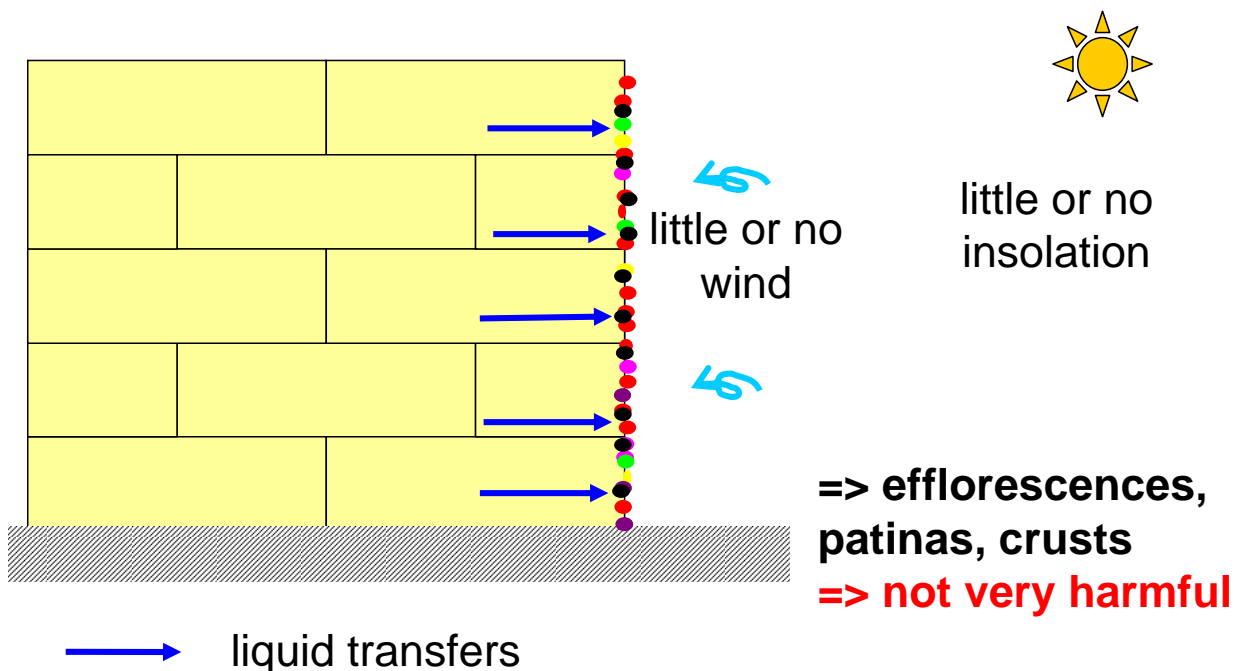
Nitronatrite ( $\text{NaNO}_3$ ) in ceramic (lab. experiment)



# Origin of salts and water in buildings



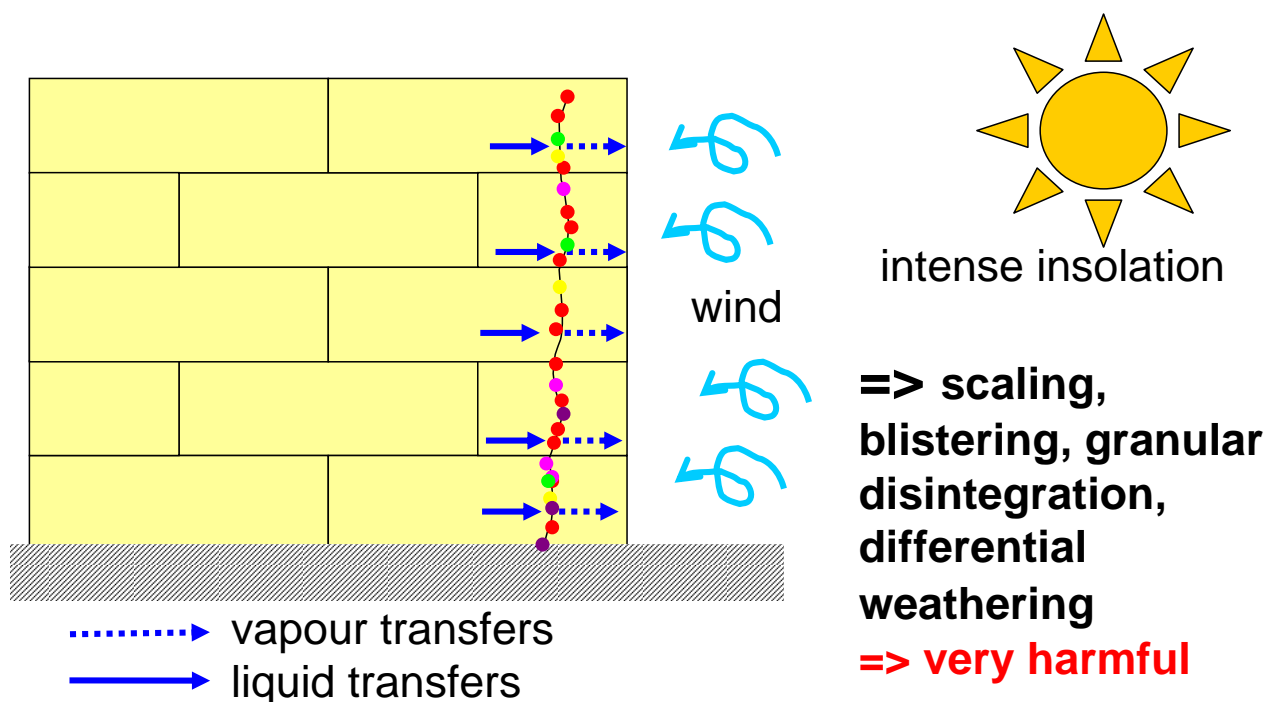
# Evolution of water and salts in case of slow drying







## Evolution of water and salts in case of fast drying



## The hygroscopicity (or deliquescence) problem

**Deliquescence humidity:** the relative humidity above which a material absorbs humidity from the air and dissolves



Fribourg, Notre-Dame basilica, 2.11.2008



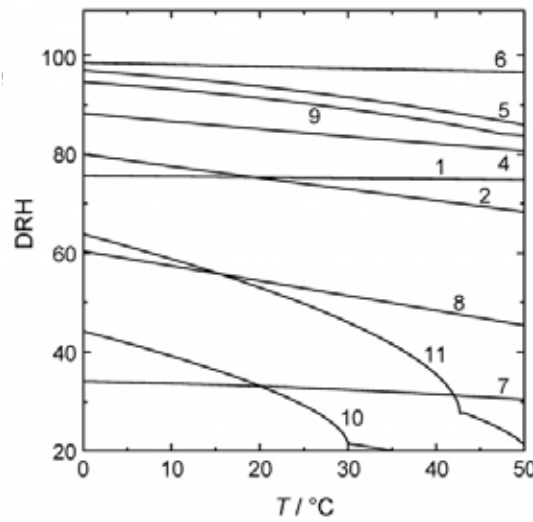
Kaysersberg castel, Alsace, France, 8.05.2008



© Vincent COURCELEAUD  
(<http://www.trekearth.com/gallery/Europe/France/East/Alsace/Kaysersberg/photo909171.htm>)



# Deliquescence humidity & temperature



- 1 NaCl
- 2 NaNO<sub>3</sub>
- 4 KCl
- 5 KNO<sub>3</sub>
- 6 K<sub>2</sub>SO<sub>4</sub>
- 7 MgCl<sub>2</sub>·6H<sub>2</sub>O
- 8 Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O
- 9 MgSO<sub>4</sub>·7H<sub>2</sub>O/MgSO<sub>4</sub>·6H<sub>2</sub>O
- 10 CaCl<sub>2</sub>·6H<sub>2</sub>O/CaCl<sub>2</sub>·4H<sub>2</sub>O
- 11 Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O/Ca(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O

Steiger, M.  
<http://www.saltwiki.net/>

Salz	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
NaCl	75.9	75.6	75.4	75.2	75.0	74.8
NaNO <sub>3</sub>	80.1	77.7	75.3	72.8	70.4	68.0
Na <sub>2</sub> SO <sub>4</sub>	98.8 <sup>(1)</sup>	97.8 <sup>(1)</sup>	95.6 <sup>(1)</sup>	90.1 <sup>(1)</sup>	87.9	88.4
KCl	88.3	86.7	85.0	83.5	82.1	80.7
KNO <sub>3</sub>	97.0	95.5	93.7	91.5	88.9	85.9
MgCl <sub>2</sub> ·6H <sub>2</sub> O	34.1	33.7	33.1	32.4	31.5	30.5
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	61.3	58.6	55.7	52.5	49.2	45.7
MgSO <sub>4</sub> ·7H <sub>2</sub> O	94.5	93.1	91.3	89.1	86.3	83.2 <sup>(2)</sup>
CaCl <sub>2</sub> ·6H <sub>2</sub> O	44.3	39.4	33.3	21.6 <sup>(3)</sup>	18.4 <sup>(3)</sup>	16.3 <sup>(4)</sup>
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	63.8	58.8	53.1	46.0	35.5	21.3 <sup>(5)</sup>

(<sup>1</sup>) Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, (<sup>2</sup>) MgSO<sub>4</sub>·6H<sub>2</sub>O, (<sup>3</sup>) CaCl<sub>2</sub>·4H<sub>2</sub>O, (<sup>4</sup>) CaCl<sub>2</sub>·2H<sub>2</sub>O, (<sup>5</sup>) Ca(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O



Formula	Molecular mass (g/mol)	% H <sub>2</sub> O (w)	Name FR	Name EN	solubility (g/l) / 20°C	Relative humidity of deliquescence or equilibrium (%)
(NH <sub>4</sub> ) <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	360.6	30.0	boussingaultite	boussingaultite	159 (0°C), 1300 (100°C)	
Ca(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	164.13	22.0	weddellite	weddellite	~ 0	
Ca(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	146.11	12.3	whewellite	whewellite	~ 0	
CaHCO <sub>3</sub> 2	130.11	0.0	formiate de calcium	calcium formate	162 (0°C)	
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	236.15	30.5	nitrocalcite	nitrocalcite	2660	56,5% (10°C), 53,6% (20°C), 50,5% (25°C)
Ca <sub>3</sub> Si(OH) <sub>6</sub> (CO <sub>3</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	622.61	34.7	thaumasite	thaumasite		
Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O	1255.09	37.3	ettringite	ettringite		
CaCl <sub>2</sub> ·6H <sub>2</sub> O	219.08	49.3	antarctite	antarctite	5360	33,7% (10°C), 30,8% (20°C), 22,4% (30°C)
CaCO <sub>3</sub>	100.09	0.0	calcite	calcite	0.014 (25°C)	
CaMg(CO <sub>3</sub> ) <sub>2</sub>	184.41	0.0	dolomite	dolomite	0,078 (18°C)	
CaMg <sub>2</sub> Cl <sub>6</sub> ·12H <sub>2</sub> O	517.59	41.8	tachyhydrite	tachyhydrite		
CaSO <sub>4</sub> ·0,5H <sub>2</sub> O	145.15	6.2	hémihydrate, bassanite	Plaster of Paris	3	
CaSO <sub>4</sub> ·2H <sub>2</sub> O	172.17	20.9	gypse	gypsum	2.14	
K <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	328.42	5.5	syngénite	syngenite	2.5	
K <sub>2</sub> Ca <sub>5</sub> (SO <sub>4</sub> ) <sub>6</sub> ·H <sub>2</sub> O	872.96	2.1	görgéyit	görgeyite		
K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	402.76	26.8	picromérite	picromerite	250	
K <sub>2</sub> SO <sub>4</sub>	174.5	0.0	sulfate de potassium	arcanite	111.5	98,2% (10°C), 97,6% (20°C), 97% (30°C)
K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>	332.42	0.0	glaserite	glaserite		
K <sub>3</sub> Na <sub>7</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	1135.3	9.5	humberstonite	humberstonite		
KAl <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>	414.21	0.0	alunite			
KCl	74.56	0.0	sylvine	sylvite	344	86,8% (10°C), 84,3% (25°C)
KHCO <sub>3</sub>	100.12	0.0	bicarbonate de potassium	Potassium bicarbonate	333	
KNO <sub>3</sub>	101.11	0.0	nitrate de potassium, salpêtre	niter	315	94,6% (20°C), 93,6% (25°C)
Mg(HCO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	150.37	24.0	formiate de magnésium	magnesium formate	140 (0°C)	
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	256.41	42.2	nitromagnésite	nitromagnesite	705	57,4% (10°C), 54,4% (20°C), 51,4% (30°C)
Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O	467.63	15.4	hydromagnésite	hydromagnesite		
MgCl <sub>2</sub> ·6H <sub>2</sub> O	203.31	53.2	bischoffite	bischoffite	543	33,5% (10°C), 33,1% (20°C), 32,4% (30°C)
MgCO <sub>3</sub>	84.32	0.0	magnésite	magnesite	0.106	
MgCO <sub>3</sub> ·3H <sub>2</sub> O	138.37	39.1	nesquehonite	nesquehonite	1.79 (16°C)	
MgCO <sub>3</sub> ·5H <sub>2</sub> O	174.4	51.7	lansfordite	lansfordite		
MgSO <sub>4</sub> ·6H <sub>2</sub> O	212.47	50.9	hexahydrate	hexahydrate	660	
MgSO <sub>4</sub> ·7H <sub>2</sub> O	246.48	51.2	epsomite	epsomite	710	90,1% (20°C) 94% (30°C)
MgSO <sub>4</sub> ·H <sub>2</sub> O	138.39	13.0	kiesérite	kieserite	684 (100°C)	
Na <sub>10</sub> Ca <sub>3</sub> (SO <sub>4</sub> ) <sub>8</sub> ·6H <sub>2</sub> O	1226.72	8.8	hydroglauberite	hydroglauberite		
Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	286.14	63.0	natron	natron	215.8	96,5% (15°C), 97,9% (20°C), 88,2% (25°C), 83,2% (30°C)
Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O	124	14.5	thermonatrite	thermonatrite	330	71% (35°C)
Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	334.48	21.5	blödite	astrakhanite		
Na <sub>2</sub> SO <sub>4</sub>	142.04	0.0	thénardite	thenardite	162	
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	322.19	55.9	mirabilite	mirabilite	900	93,6 (20°C) ; 90% (23°C) ; 87% (25°C)
Na <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	245.05	7.4	darapskite	darapskite		
Na <sub>3</sub> H(CO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	226.03	15.9	trona	trona	130 (0°C)	
NaCl	58.44	0.0	halite	halite	358	75,7 (10°C), 73,3 (25°C)
NaHCO <sub>3</sub>	84	0.0	hydrogénocarbonate de sodium	baking soda	96	
NaNO <sub>3</sub>	84.99	0.0	nitronatrite	nitratine	880	77,5% (10°C), 75,2% (20°C), 74,3% (25°C)
NH <sub>4</sub> NO <sub>3</sub>	80.04	0.0	nitrate d'ammonium, ammonitrate	Ammonium nitrate	1787	65% (20°C), 61,8% (25°C)