

ASSOCIATION FOR PRESERVATION TECHNOLOGY INT'L
STONE RESTORATION WORKSHOP

ATLANTA 2006

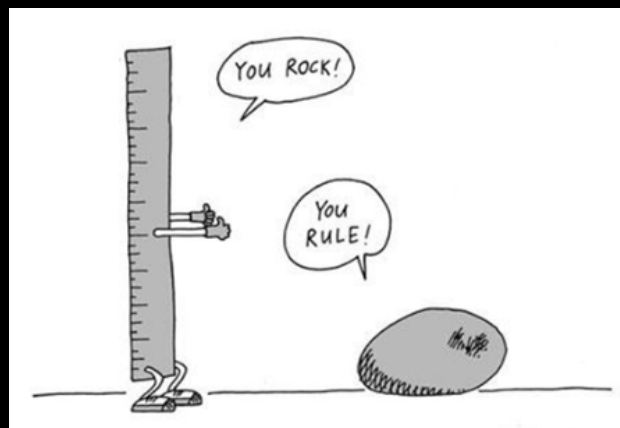
APTI Atlanta 2006



BASSETTI
ARCHITECTS

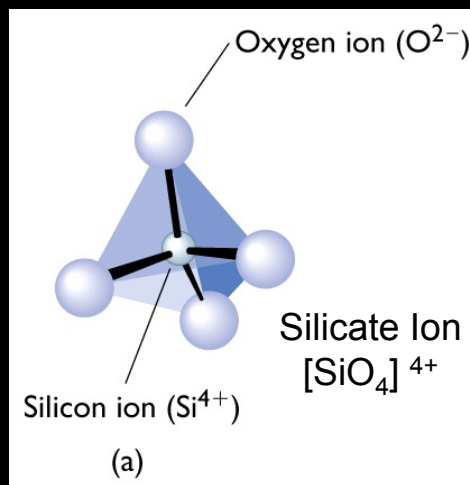
Stone Restoration Workshop

- *In-classroom seminar by:*
 - George Wheeler, PhD, Columbia University Historic Preservation Program
- *In-the-field Demonstrations and Hands-On Practice by:*
 - Frank Genello, American College of Building Arts
 - Simeon Warren, American College of Building Arts

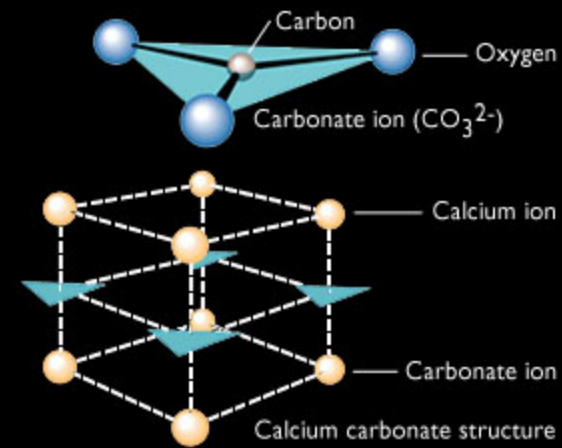


Mineralogy

- *Silicate vs. Carbonate Minerals*
 - *Two basic chemical compositions of all stone*
 - *Understanding the mineralogy of the stone is critical to*
 - *Understanding soiling problems*
 - *Proper cleaning of the material*

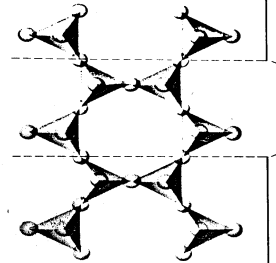
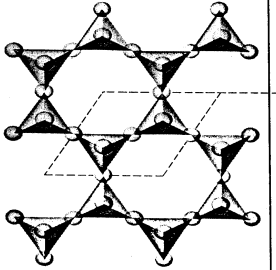
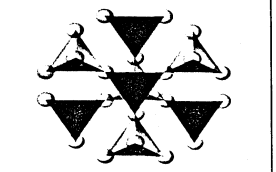




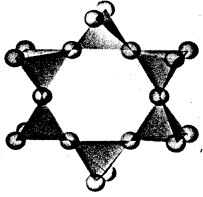
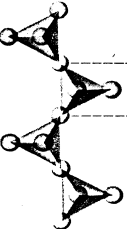
VS



Mineralogy

- *Molecular Structure of Silicate Minerals*

Inosilicates (double chain)		$(Si_4O_{11})^{-6}$	Amphibole Group tremolite actinolite hornblende
Phyllosilicates		$(Si_2O_5)^{-2}$	Serpentine Group antigorite chrysotile lizardite Clay Group kaolin illite montmorillonite talc Chlorite Group chlorite Mica Group muscovite biotite
Tectosilicates		$(SiO_2)^0$	quartz feldspars lazurite

Nesosilicates		$(SiO_4)^{-4}$	Olivine Group forsterite fayalite Garnet Group pyrope grossular almandine
Sorosilicates		$(Si_2O_7)^{-6}$	epidote
Cyclosilicates		$(Si_6O_{18})^{-12}$	beryl benitoite
Inosilicates (single chain)		$(SiO_3)^{-2}$	Pyroxene Group enstatite diopside augite jadeite

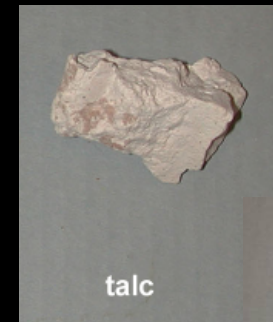
Mineralogy

- *Silicate rocks include:*
 - Quartz
 - Agates
 - Feldspars
 - Chlorite
 - Amphibole
 - Pyroxene
 - Olivine



Mineralogy

- *Silicate Stone With Increased Iron & Magnesium*
 - Chemically weaker stone
 - Mechanically weaker stone
 - Darker colors



Mineralogy

SILICATES				
Mineral (or Group)	Chemical Formulation	Weathering Product(s)		Hardness
		Mineral product	Dissolved Product	
<i>Quartz</i>	SiO ₂	quartz	silicic acid	7
<i>Feldspars</i>				
Alkali Feldspars				
Microcline	KAlSi ₃ O ₈	clay	silicic acid, potassium bicarbonate	6
Orthoclase	KAlSi ₃ O ₈	clay	silicic acid, potassium bicarbonate	6
Plagioclase Feldspars				
Albite	NaAlSi ₃ O ₈	clay	silicic acid, sodium bicarbonate	6
Anorthite	CaAl ₂ Si ₂ O ₈	clay	calcium bicarbonate	6
<i>Amphiboles</i>	(Mg,Fe) ₇ Si ₈ O ₂₂ (OH) ₂	goethite	silicic acid, magnesium bicarbonate	5-6
<i>Pyroxenes</i>	(Mg,Fe)SiO ₃	goethite	silicic acid, magnesium bicarbonate	5-6 (7)
<i>Olivines</i>	(Mg,Fe) ₂ SiO ₄	goethite	silicic acid, magnesium bicarbonate	5-6
Mineral (or Group)	Chemical Formulation	Weathering Product(s)		Hardness
		Mineral product	Dissolved Product	
<i>Serpentines</i>	Mg ₃ (Si ₂ O ₅)(OH) ₄			3-5
<i>Clays</i>	broad range of K, Na, Ca, Fe, Mg aluminosilicates			~2
<i>Micas</i>	broad range of aluminosilicates	clay, iron oxides		2-2.5
<i>Talc</i>	Mg ₃ Si ₄ O ₁₀ (OH) ₂			1
<i>Chlorites</i>	broad range of Fe, Mg, Mn aluminosilicates	iron oxides		2-3

Mineralogy

- *Non-Silicate (Carbonate) Rocks Include:*
 - Gypsum
 - Aragonite
 - Dolomites
 - Calcites
 - Pyrites
 - Hematites



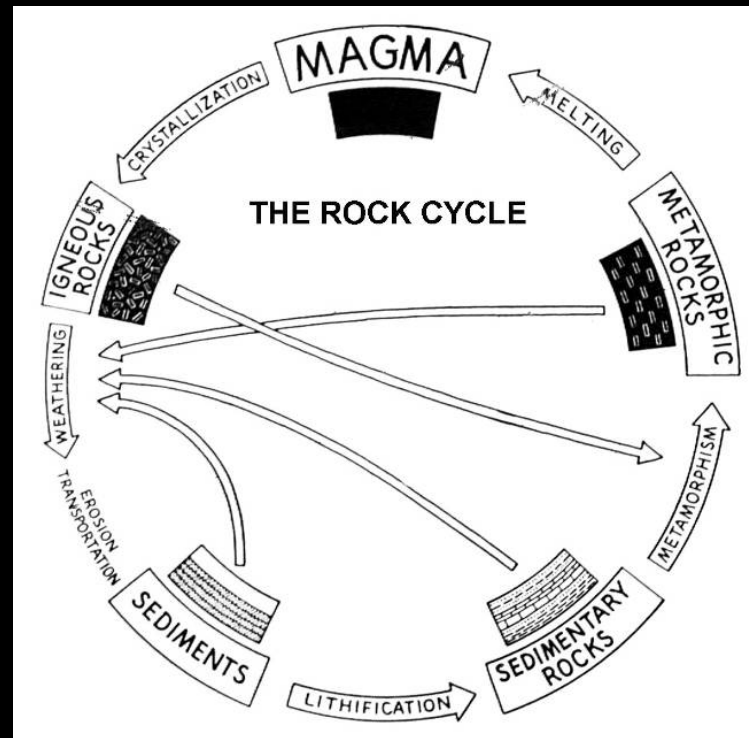
Mineralogy

- *Carbonate Minerals*
 - Can be detected by dropping acid on it and seeing if it reacts
 - $\text{CaCO}_3 + \text{HCl} \rightarrow \text{Ca}^{2+} + \text{CO}_2$

NON-SILICATES			
Mineral	Chemical Formulation	Solubility	Hardness
<i>Calcite</i>	CaCO_3	acid	3
<i>Aragonite</i>	CaCO_3	acid	3.5-4
<i>Dolomite</i>	$(\text{Ca}_{0.5}\text{Mg}_{0.2})\text{CO}_3$	acid	3.4-4
<i>Gypsum</i>	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	acid and water	2
<i>Pyrite</i>	Fe_2S	acid	6-6.5
<i>Hematite</i>	Fe_2O_3		5-6.5
<i>Goethite</i>	$\text{FeO} \cdot \text{OH}$		5-5.5
<i>Limonite</i>	$\text{FeO} \cdot \text{OH} \cdot n\text{H}_2\text{O}$		5-5.5
<i>Magnetite</i>	Fe_3O_4		6
<i>Pyrolusite</i>	MnO_2		1-2

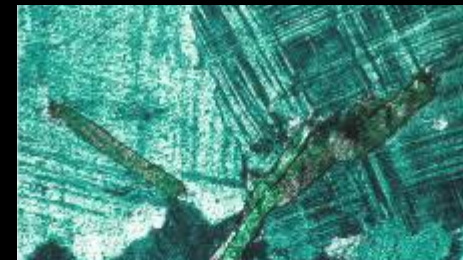
Rock Identification

- *Rock creation process – Circle of Life*



Rock Identification

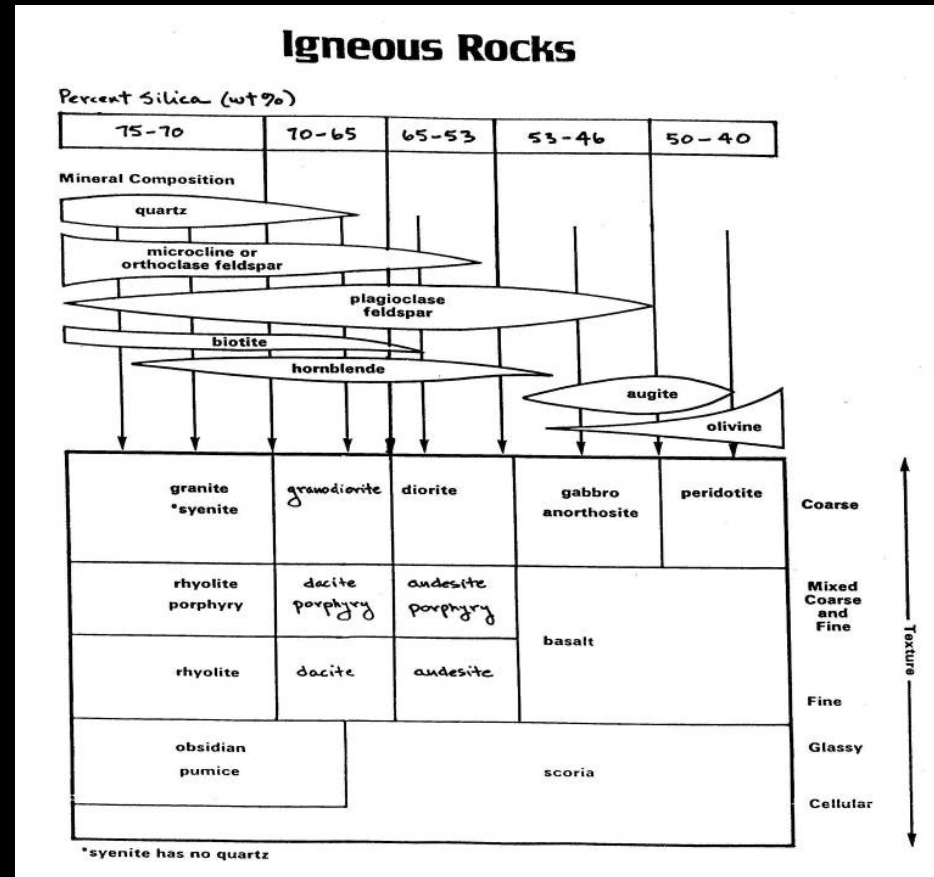
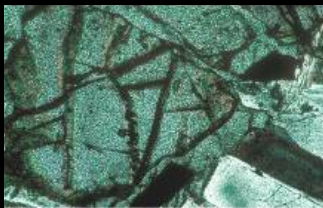
- *Volcanic Rocks vs. Plutonic Rocks*
 - Volcanic = porphyritic textures – fine ground mass with large individual grains – cooled quickly
 - Plutonic = All large grains – cooled very slowly



POP QUIZ!

Rock Identification

Igneous Rock Table



Rock Identification

Sedimentary Rock Table

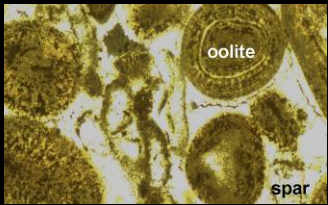
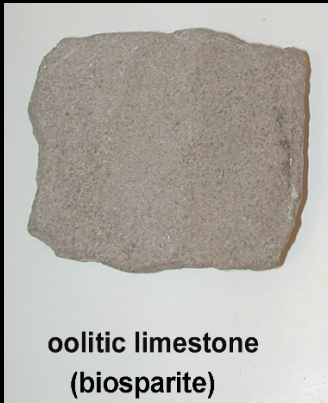


CLASSIFICATION OF SEDIMENTARY ROCKS

<i>Classified by Composition</i>	<i>Rock</i>	<i>Classified by Origin</i>	<i>Rock</i>
I. Clastic Sediments			
A. Coarse or mixed particles			
1. Rounded	Conglomerate Breccia	Glacial deposition Hillslope weathering	Tillite Talus breccia
2. Angular			
B. Medium to small particles			
1. Chiefly quartz	Sandstone Arkose		
2. Much feldspar as well as quartz			
C. Indistinguishable particles			
1. Fine quartz sand	Siltstone Mudstone & Shale Mudstone & Shale	Wind deposition	Loess
2. Mud (very fine quartz, and clay)			
3. Clay			
II. Nonclastic Sediments			
Calcium carbonate	Marl, Chalk, & Limestone	Hot-spring deposition Calcium carbonate Silica	Travertine Geyserite
Calcium magnesium carbonate	Dolomite		
Silica	Diatomaceous earth		
Vegetable carbon	Coal		
Salt	Rock salt		
Calcium sulfate	Anhydrite		
Hydrous calcium sulfate	Gypsum		
Phosphate	Phosphate rock		

Rock Identification

Metamorphic Rock Table



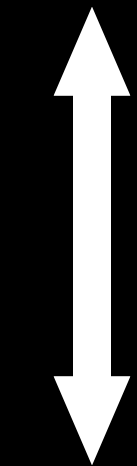
CLASSIFICATION OF SEDIMENTARY ROCKS

<i>Classified by Composition</i>	<i>Rock</i>	<i>Classified by Origin</i>	<i>Rock</i>
I. Clastic Sediments			
A. Coarse or mixed particles			
1. Rounded	Conglomerate Breccia	Glacial deposition Hillslope weathering	Tillite Talus breccia
2. Angular			
B. Medium to small particles			
1. Chiefly quartz	Sandstone Arkose		
2. Much feldspar as well as quartz			
C. Indistinguishable particles			
1. Fine quartz sand	Siltstone Mudstone & Shale Mudstone & Shale	Wind deposition	Loess
2. Mud (very fine quartz, and clay)			
3. Clay			
II. Nonclastic Sediments			
Calcium carbonate	Marl, Chalk, & Limestone	Hot-spring deposition	Travertine Geyserite
Calcium magnesium carbonate	Dolomite		
Silica	Diatomaceous earth	Calcium carbonate	
Vegetable carbon	Coal	Silica	
Salt	Rock salt		
Calcium sulfate	Anhydrite		
Hydrous calcium sulfate	Gypsum		
Phosphate	Phosphate rock		

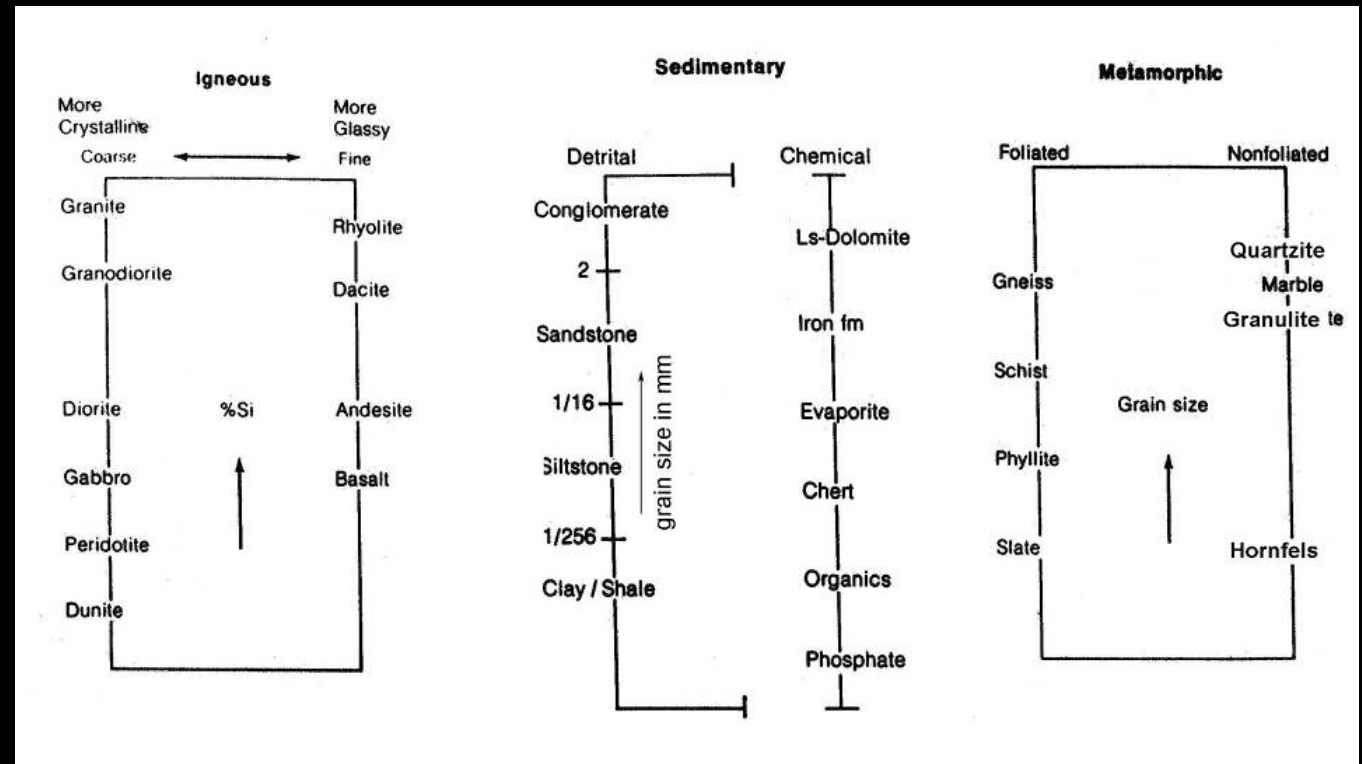
Rock Identification

- Overall Scheme for Rock Identification

Lighter



Darker

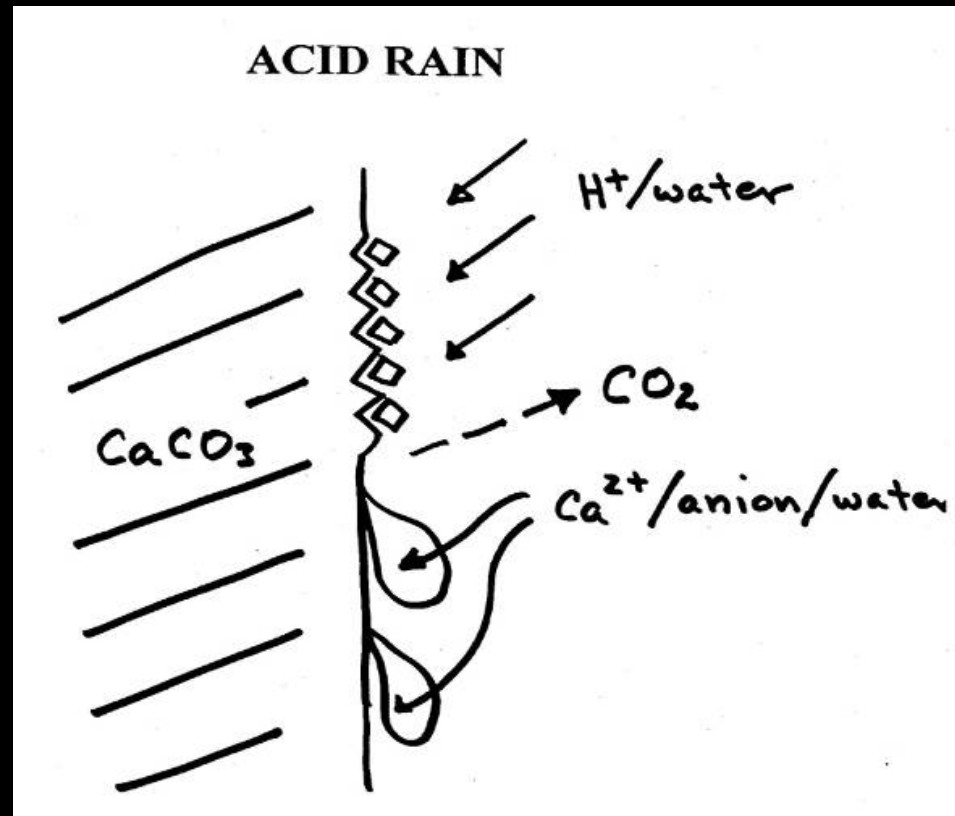


Types of Stone Deterioration

- *Acid rain*
- *Dry deposition*
- *Salt crystallization*
- *Freezing water*
- *Hygric swelling*
- *Biological effects (Biodeterioration)*
- *Thermal effects*

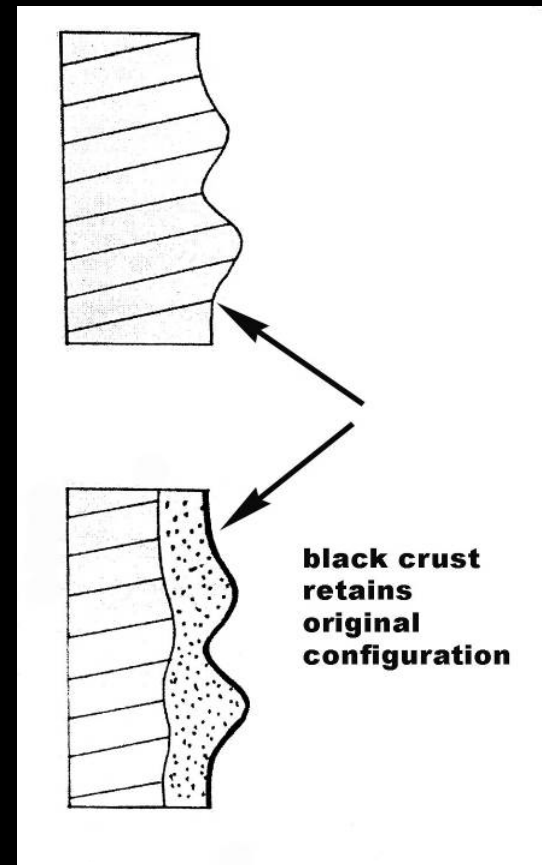
Types of Stone Deterioration

- *Acid Rain*
 - Acid dissolves carbonate rock



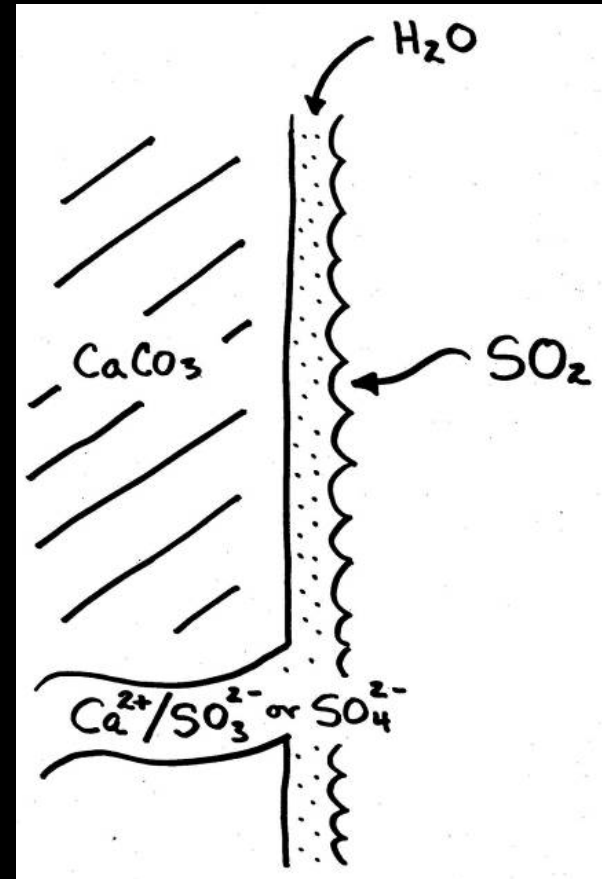
Types of Stone Deterioration

- *Gypsum Crusting*
 - Black from fly ash (not calcium)
 - May be on top of original surface or in place of original surface
 - Can merge with surface and then break off
 - Be careful to select the correct acid wash



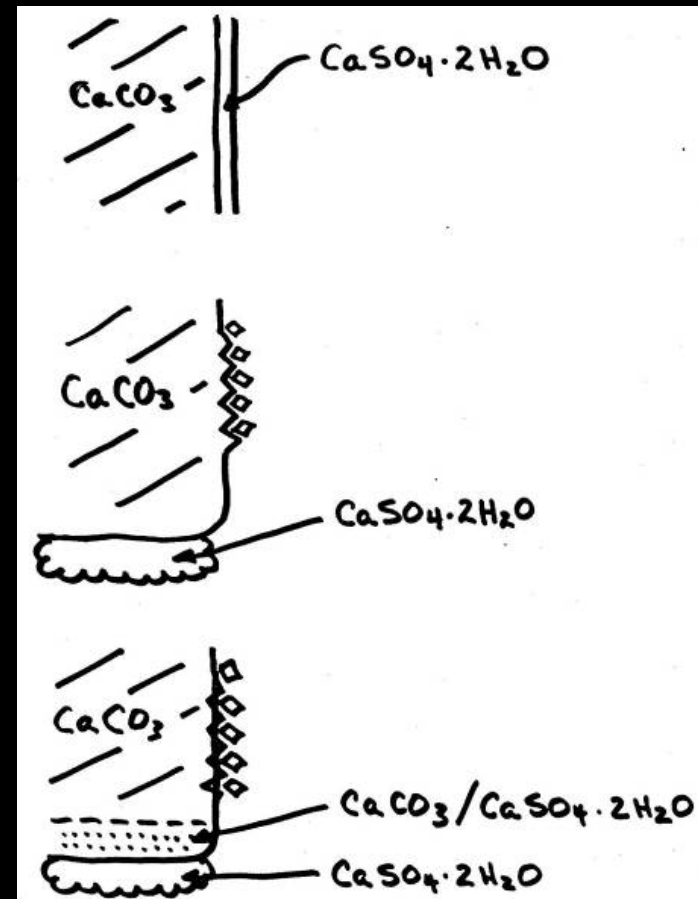
Types of Stone Deterioration

- *Dry deposition*
 - Dissolved material from acid rain is re-deposited as gypsum crusts elsewhere on the rock on top of original surface
 - Usually found in protected parts of the rock where rain will not wash away the gypsum
 - Gypsum can be re-absorbed back into surface of rock and will not come out



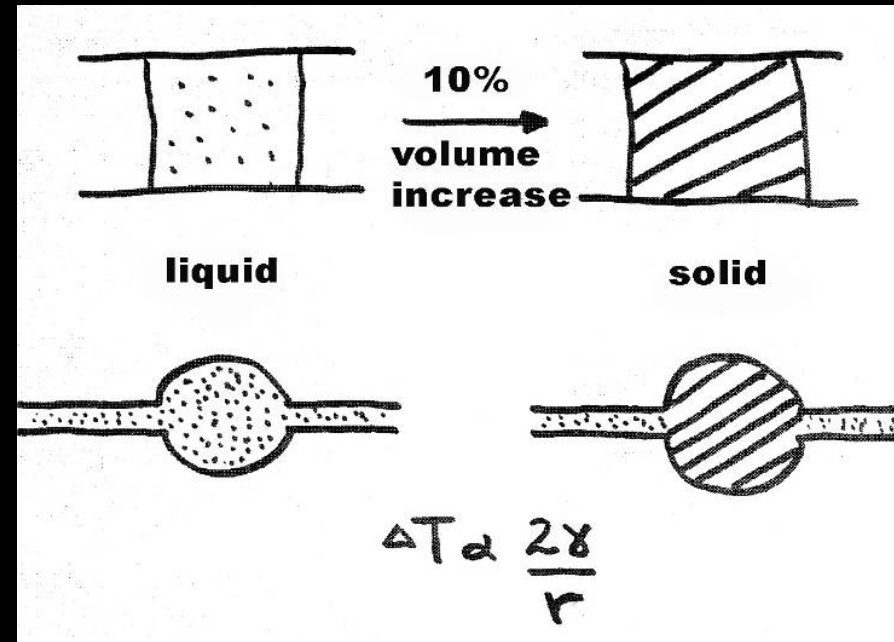
Types of Stone Deterioration

- *Salt Crystallization*
 - Salts are dissolved from within the rock, transit to the surface and then deposited when water evaporates
 - Efflorescence



Types of Stone Deterioration

- *Freezing water*
 - Freeze thaw cycling
 - Spalling



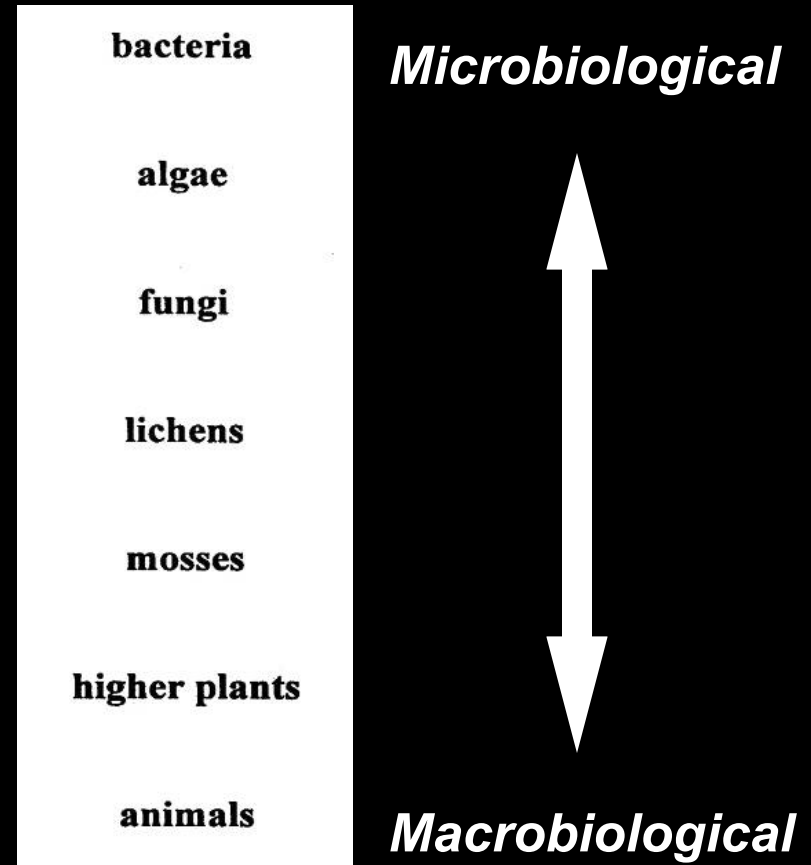
Types of Stone Deterioration

- *Hygric swelling*
 - Rock absorbs water and can then be subject to freeze/thaw cycles, salt crystallization, or other thermal effects
 - Clay in stone helps swelling
 - Egyptian Limestone (below, after 3 cycles)



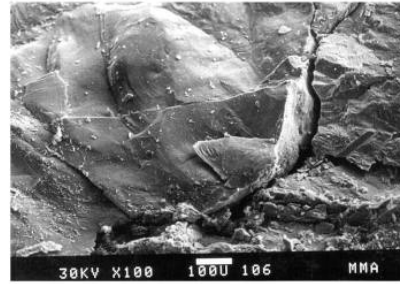
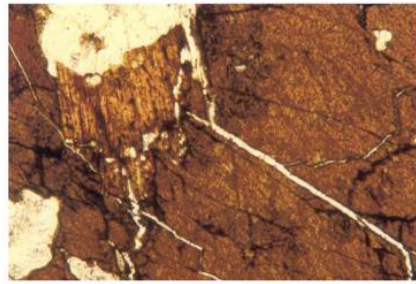
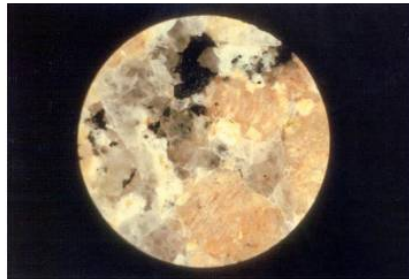
Types of Stone Deterioration

- *Biological Effects (Bio-deterioration)*
 - Plant life creates complex acids to dissolve and suck minerals out of rock
 - Plant life grows into crevices
 - Light, Nutritive input, temperature, and water affect bio-deterioration



Types of Stone Deterioration

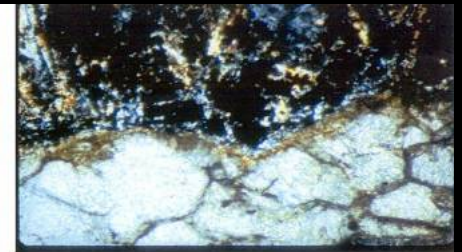
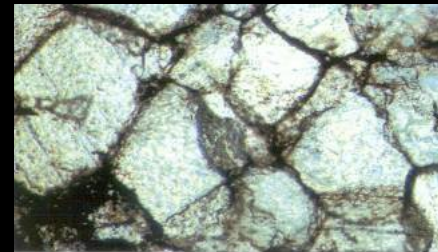
- *Thermal Effects*
 - Expansion and contraction creates weak planes in rock



Types of Stone Deterioration

- *Water is an AID to soiling in Silicate rocks*
- *Water PREVENTS soiling in Carbonate rocks*

Types of Stone Deterioration



POP QUIZ!

Cleaning Methods

CLEANING METHODS

Chemical

water
detergent
base-acid

Physical

water
steam
particulate
laser

Cleaning Methods

MARBLE, LIMESTONE, TRAVERTINE

⇒ **Calcium Carbonate (Calcite)**

SLIGHTLY soluble in water

READILY soluble acids

NOT soluble in bases like NaOH

Cleaning Methods

SANDSTONE, GRANITE, SCHIST

⇒ **Silicon Dioxide (Quartz)**

NOT *soluble in water*

ONLY *soluble in hydrofluoric acid*

READILY *in strong bases such as NaOH*

Cleaning Methods



POP QUIZ!

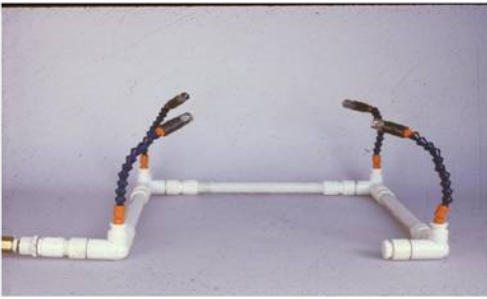
Water washing

- *Intermittent water spraying does least damage to delicate stone*
- *Intervelometers – photo equipment timer can turn water on or off for a few seconds throughout the day*
- *Irrigation sprinkler timers – not as sensitive*
- *Controlling the length of cleaning timing is critical*
- *Test water for contaminants and acidity*
- *5 micron filters required to remove iron in water*

Water washing

- *If stone is delicate, you may not want to try and wash out gypsum crusting that has been reabsorbed*
- *Partial Cleaning*
 - Not really possible with water except for reabsorbed gypsum
- ***Cold water is better for removing gypsum***
- ***Warm water is better for emulsifying hydrocarbons***

Water washing



Chemical Cleaning

- *Aesthetic concerns – can alter color of stone*
- *Material Science concerns – can remove excessive amounts of the stone or add materials that lead to later deterioration*
- *Very fast cleaning method – dwell time is critical and must be carefully controlled*
- *Difficult to isolate areas to be cleaned*



Chemical Cleaning

- *Alkaline Cleaners*

Alkaline cleaning agents

Agents based on:

Sodium hydroxide
(NaOH)

Potassium hydroxide
(KOH)

Ammonium hydroxide
(NH₄OH)

Sodium carbonate
(NaCO₃)

Sodium bicarbonate
(Na(CO₃)₂)

For cleaning

limestones

Must be followed by
neutralization with
acetic acid-based
compound

On sandstones, unglazed
terracotta and faience,
brick, unpolished
granite for the
degreasing and removal
of heavy soiling.

Followed by use of
hydrofluoric acid-based
compound

All have the potential for
depositing soluble salts
within masonry. This can
largely be overcome if
the products containing
them are used correctly
and on appropriate
surfaces

Must never be used
without neutralization

Chemical Cleaning

- *Acidic Cleaners 1*

Acidic cleaning agents

Agents based on:

Hydrofluoric acid (HF)
Ammonium bifluoride
(NH_4HF_2), also known
as ammonium hydrogen
fluoride

For cleaning sandstones,
unpolished granite,
brickwork and unglazed
terracotta and faience

NH_4HF_2 releases HF in
contact with water
Must not be used on
glazed surfaces
Must not be used on
limestone, marble and
lime-based mortars or
renders
Use on calcareous and
argillaceous sandstones
must be controlled
carefully

Agents based on:

Acetic acid
(CH_3COOH)

For neutralizing
limestone and marble
surfaces after use of
alkaline cleaning. Used
with other acids
in efflorescence
treatments

Chemical Cleaning

- *Acidic Cleaners 2*

Agents based on:

Hydrochloric acid (HCl)
(muriatic acid)

For removing cement
splashes and calcium
carbonate (lime)
deposits

Included with glycolic
acid in efflorescence
treatments and
limestone neutralizers

Other ingredients
include:

Phosphoric acid
(H₃PO₄)
(orthophosphoric acid)

Included with HF
formulations to
counteract attack on iron
constituents in masonry,
usually sandstones

Sulphuric acid (H₂SO₄)

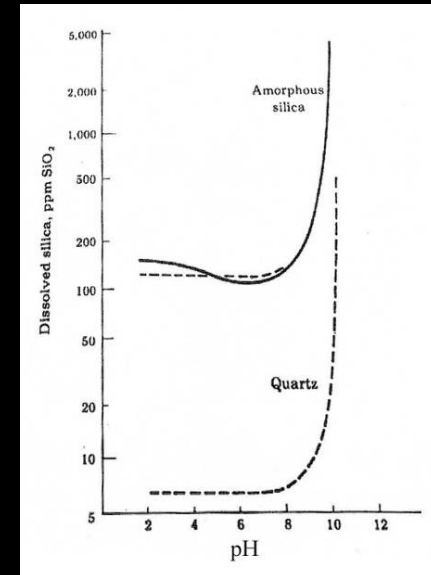
Included in some
formulations as a minor
ingredient

Chemical Cleaning

- In all cases, salts must be cleaned out after neutralizing wash

RINSE, RINSE, RINSE!

- Don't use alkaline cleaners on quartz containing stone due to high solubility of quartz in alkali solutions.
- USE ACIDIC solutions on quartz!



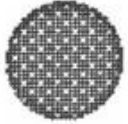



Chemical Cleaning

- *Advantages of Chemical Cleaning*
 - Speed of execution

Chemical Cleaning

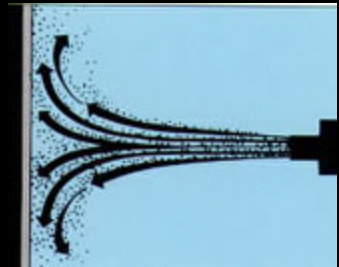
- *Disadvantages of Chemical Cleaning*
 - Usually requires pressure washing for adequate removal of chemical residues
 - Usually requires acids either as a cleaning agent or neutralizing agent that can attack the substrate
 - With speed of execution comes limited control
 - Can leave residues that lead to efflorescence and possibly salt damage
 - Can alter color of stones by changing oxidation state of iron oxide compounds
 - Can deposit fine white particles on surface

Abrasive Cleaning

FACTORS AFFECTING ABRASIVE CLEANING		
	MORE DAMAGE	LESS DAMAGE
PARTICLE SIZE		
PARTICLE SHAPE		
PARTICLE HARDNESS	HIGHER	LOWER
PRESSURE OF DELIVERY	HIGHER	LOWER
MEDIUM OF DELIVERY	AIR	WATER

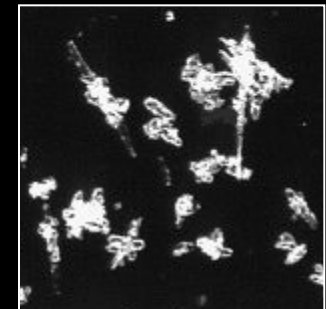
Abrasive Cleaning

- *Façade Gommage or Thomann Hanry*
- Medium glass beads or aluminum oxide
- Size 15-90 microns
- Shape round-to-angular
- Pressure 35-50 psi
- Delivery air
- Working Distance approximately 10 inches
 perpendicular to surface
- Containment can be difficult on non-flat surfaces (vacuum)
- No competitive bidding – only one contractor can provide services



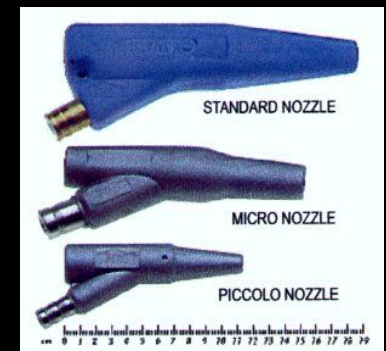
Abrasive Cleaning

- *Armex*
 - Medium
 - Size
 - Shape
 - Pressure
 - Delivery
 - Working Distance
- | |
|-------------------------|
| sodium bicarbonate |
| 60-600 microns |
| angular |
| 40-50 psi |
| air and water |
| approximately 12 inches |
| 60 degrees to surface |
- Not as effective as other abrasive techniques
 - May leave sodium bicarbonate residue (results in sodium sulfate salts)



Abrasive Cleaning

- *Jos Quintec*
- Medium dolomite
- Size 60-600 microns with 75% between 70 & 270 microns
- Shape round-to-angular
- Pressure 30 psi
- Delivery air and water
- Working Distance approximately 12 inches, vortex yields 45 degree angle to surface
- Containment is a major problem
- Can be used by any trained contractor – competitive bidding easy
- Multiple nozzle sizes and shapes

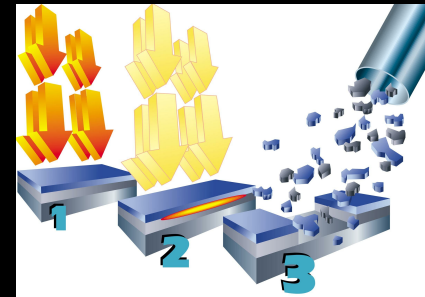


Abrasive Cleaning - Summary

- Can be used on different stone (and other masonry) types in juxtaposition
- Cannot not be easily used on fragile stone surfaces
- Containment is often a problem
- Can be difficult to achieve uniform cleaning at times
- Does not remove subsurface materials
- Can easily be used in conjunction with other techniques
- Requires trained operators
- Dry techniques eliminate risk of staining
- Wet techniques can mobilize salts
- Soft pointing may be damaged during cleaning
- Resoiling rates may be higher than for other techniques
- Localized cleaning can easily be carried out
- Cleaning is non seasonal
- Cannot remove sub-surface soiling (migration of gypsum into stone)

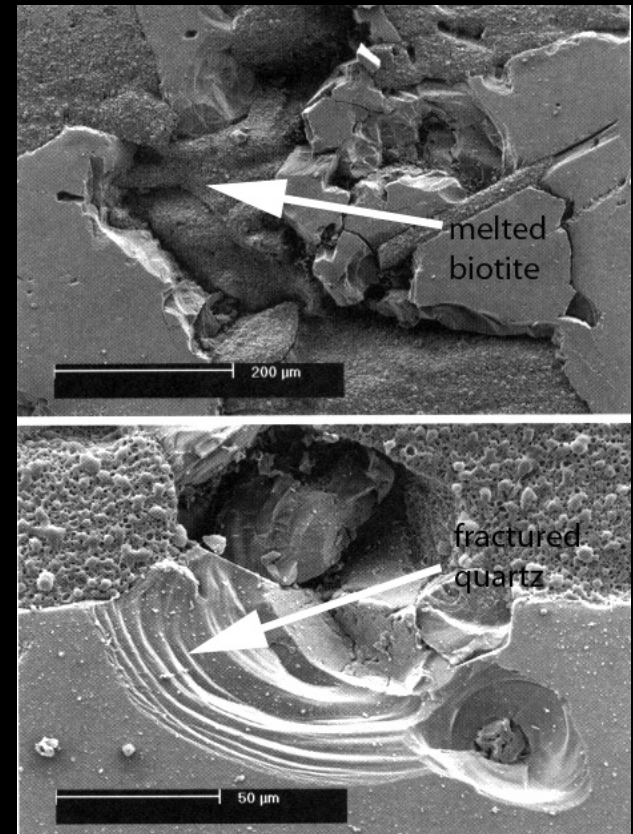
Laser Cleaning

- *Advantages*
 - Not a particle so it can be used on very delicate stone
 - Only works on dark soiling on light colored stone
 - dark absorbs laser energy
 - if used on dark stone, it will damage the stone
 - Physically the most gentle of all cleaning methods
 - Partial cleaning possible – control over small areas
 - Laser cleaning leaves “patina” of gypsum or oxalates



Laser Cleaning

- *Disadvantages*
 - Primary risk is yellowing of the stone
 - Sources include patina inherent to object, alteration of structure of the marble, transformation of iron minerals or organics in soiling.
 - Slow – lasers do not cover a large area
 - Can only be used on a narrow range of stone types
 - Expensive
 - Does not remove subsurface gypsum
 - Requires a skilled Operator



Stone Consolidation

- *What Types of Stone Benefit from Consolidation?*
 - *Limestone*
 - *Marble*
 - *Sandstone*

COMMON ROCKS IN SCULPTURE & MONUMENTS

LIMESTONE	SEDIMENTARY
MARBLE	METAMORPHIC OF LIMESTONE
SANDSTONE	SEDIMENTARY
ALABASTER	SEDIMENTARY
GRANITE	IGNEOUS, PLUTONIC
DIORITE	IGNEOUS, PLUTONIC
GABBRO	IGNEOUS, PLUTONIC
RHYOLITE	IGNEOUS, VOLCANIC
BASALT	IGNEOUS, VOLCANIC
GNEISS	METAMORPHIC OF GRANITE

Stone Consolidation

- *Characteristics of the ideal Consolidant*
 - *Low VOC is not common*
 - *There is no such thing as “reversible” – removal damages stone*
 - *Consolidant can be applied to all substrates, but may not work equally well*

IDEAL CONSOLIDANT

light stable

low VOC

low toxicity

easy application

reversible

retains appearance

"works!?" on all stones equally well

Stone Consolidation

- *Types of Consolidants*
 - *Epoxies are not used much anymore*
 - *Toxicity of barium is a problem in environment*
 - *Calcium hydroxide = lime method*

Organic Monomers or Resins

epoxies
acrylics

Biom mineralization

calcium carbonate

Inorganic Salts

barium hydroxide

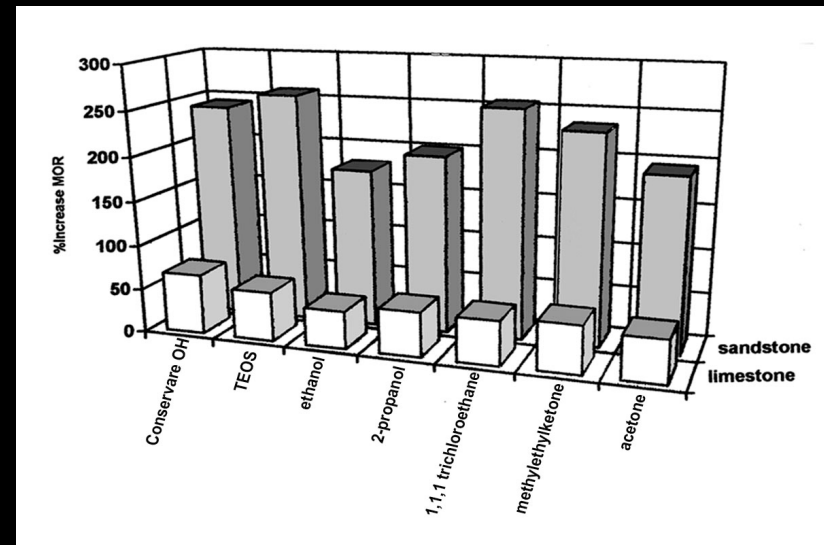
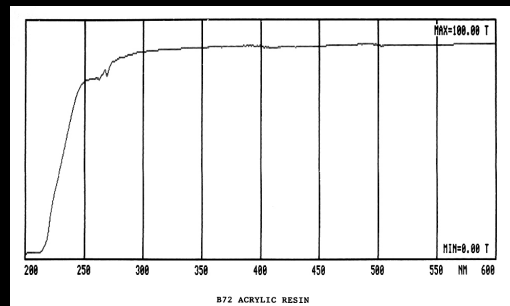
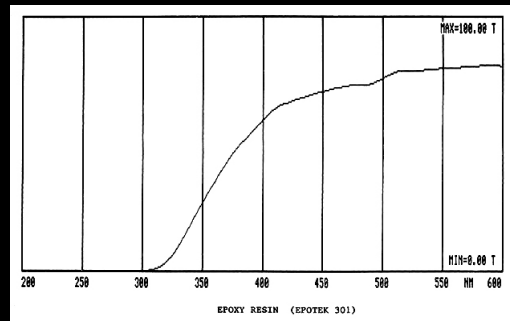
calcium hydroxide

Alkoxysilane Monomers, Oligomers, or Resins

MTMOS
MTEOS
TEOS
Silicone Resin

Stone Consolidation

- Consolidants can strengthen the face of stone, but are subject to UV light degradation



Adhesives and Pinning

- *Stone Adhesives include:*
 - *Acrylics*
 - *Methyl methacrylate (MMA)*
 - *Acryloid B-72 (ethyl methacrylate and methyl acrylate co-polymer)*
 - *Acryloid B-48N (methyl methacrylate co-polymer)*
 - *Addition of Poly Vinyl Acetates (PVAC)*
 - *Epoxies*
 - *Manufacturers include Akemi and Sikadur*
 - *Polyesters*
 - *Manufacturers include Akemi and Sebralit*

Adhesives and Pinning

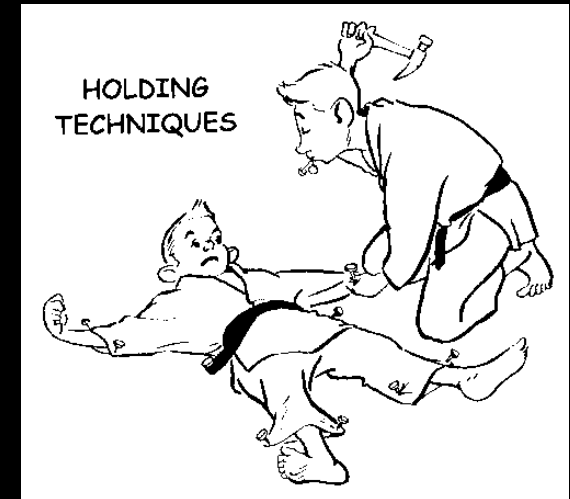
Mechanical aids to reconstructing stone include:

- *Staples*
- *Dowels*
- *Drilled in anchors*
- *Carbon Fiber Reinforcement*
- *Strong-back support of masonry*
- *Teflon*
- *Nylon*
- *Brass*
- *Aluminum*



Adhesives and Pinning

- *Considerations in Pinning Materials*
 - *Material Properties (strengths and weaknesses)*
 - *Installation techniques*
 - *Aesthetic effects*
 - *Coefficients of Expansion (stone versus pins)*
 - *Titanium = Limestone & Marble*
 - *Steel = Concrete and cement mortars*
 - *Aluminum and organic resins are higher than stone, typically*
 - *pH ranges affect steel corrosion*
 - *Low pH = more acidic = more corrosion*



Compensating for Loss of Material

Usually employed when:

- There is a structural necessity
- To alleviate further damage
- Provide visual integration



Compensating for Loss of Material

Two basic methods:

- Replacement
 - In-kind
 - Near in-kind
 - In pre-cast imitation
- Repair
 - Surface
 - Composite (plastic)



Compensating for Loss of Material

Technical Considerations In Choosing A Compensation Method:

- Is it reversible?
- Does it damage the original?
- Does it require removal of the original materials?
- Equal to or less than the strength of the original materials?
- Is it easy to work?
- Is it stable?
- Is it transferable to all cases?
- Is it cost effective?
- Does it satisfy aesthetic requirements?

Compensating for Loss of Material

Additional Considerations

- What is the scale of the loss?
- What is the environment of the loss?
- What are the available resources (materials, craftsman, etc)?
- Additional outdoor considerations include:
 - Durability of the method
 - Good weathering properties
 - No salt content
 - Same properties as stone (thermal expansion, water absorption, exchange, strength, etc.)

Compensating for Loss of Material

Disadvantages of Replacement Option:

- May not be a fulfilling aesthetic
- Usually requires removal of the original materials
- Not a simple process
- Can be expensive

Compensating for Loss of Material



dutchmen

In-Kind Replacement with Dutchmen



Compensating for Loss of Material

Two approaches to
Composite Stone Fill
(Patching):

- Integral Solution
 - Color, texture, and volume all in one material
- Multi-layer solution
 - Bulk material to create volume plus a refined surface



Compensating for Loss of Material

Advantages of Stone Patching:

- Quick
- Inexpensive
- Relatively easy to match shape and color of original material

Disadvantages of Stone Patching:

- Inorganic based products – may introduce salts, weak adhesion, variable opacity, may require retouching
- Solvent based products – toxicity, working properties, shrinkage, stability
- Thermoplastic resin based – strength, working properties

Compensating for Loss of Material

Components of a Stone Patching Material:

- Binder
 - Cement, Lime, Pozzolans, Plaster, wax, resins
- Filler
 - Stone Dust, Microballoons, Fumed Silica, Frit, Wax, Minerals, Crushed Stone
- Color
 - Dry Pigment, Glass, Stone Dust

Compensating for Loss of Material



In The Field Hands On Experience

- *Carving stone*
- *Cutting out a Dutchman*
- *Installing marble wall cap*

- *Some photos...*

ASSOCIATION FOR PRESERVATION TECHNOLOGY INT'L
STONE RESTORATION WORKSHOP
ATLANTA 2006

THANK YOU!

QUESTIONS?