Weathering and Weathering Rates of Natural Stone

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ABSTRACT / Physical and chemical weathering were studied as separate processes in the past. Recent research, however, shows that most processes are physicochemical in nature. The rates at which calcite and silica weather by dissolution are dependent on the regional and local climatic environment. The weathering of silicate rocks leaves discolored margins and rinds, a function of the rocks' permeability and of the climatic parameters. Salt action, the greatest disruptive factor, is complex and not yet fully understood in all its phases, but some of the causes of disruption are crystallization pressure, hydration pressure, and hygroscopic attraction of excess moisture.

The decay of marble is complex, an interaction between dissolution, crack-corrosion, and expansion-contraction cycles triggered by the release of residual stresses. Thin spalls of granites commonly found near the street level of buildings are generally caused by a combination of stress relief and salt action. To study and determine weathering rates of a variety of commercial stones, the National Bureau of Standards erected a Stone Exposure Test Wall in 1948. Of the many types of stone represented, only a few fossiliferous limestones permit a valid measurement of surface reduction in a polluted urban environment.

Introduction

The fact that weathering affects stone used in buildings and monuments has long been known; we have records of replacement of stone blocks and emergency treatment of stone surfaces with waxes and linseed oil since the Middle Ages. A statue at Herten, Westphalia, photographed in 1908 and again in 1968 (Fig. 1A and B), is carved from soft glauconitic Baumberg sandstone. The rate of weathering has accelerated exponentially since the erection of the sandstone statue in 1702 (Fig. 1C, and Winkler, 1981). Remnants of the statue, which is beyond recognition today, are now stored in a basement for the record. Other similar pairs of time-lapse photos are on record. Air pollution has accelerated, mostly because of carbonic and sulfuric acids that result from industrial and automotive combustion, leading to the phenomenon popularly called "acid rain," but it should be noted that air pollution has been with us for millions of years as a result of forest fires, volcanic eruptions, and salt spray from the ocean and desert flats. Likens (1976) has stated that the acidity of rain has increased in the last decade from near pH = 5.0 to 4.5 or even lower, but I question the validity of these figures; it is extremely difficult to measure the pH of rainwater which was originally distilled water and which has picked up a few H^+ ions on its travel from the cloud base to the ground, reaching a theoretical pH = 5.6 after reaching equilibrium with the 0.03% CO_2 of the pure atmosphere. Were the measurements taken at the beginning of the rain, when atmospheric pollutants were at maximum concentration, at a later stage, or averaged?

Weathering, General Classification

Weathering is generally classified in most geology textbooks as (1) *physical weathering:* frost action, insolation, salt weathering as crystallization and hydration pressures, plant root action, and fires; and (2) *chemical weathering:* dissolution of carbonates and sulfates, solubilization by leaching of elements from silicates and sulfides, followed by oxidation and hydration.

On both natural outcrops and urban buildings, the process turns out to be more complex, and not readily separable into physical and chemical components. Where can we draw the line between crystallization and hydration pressure, as these are physicochemical processes? There is also evidence of chemical reactions between salts in the masonry and the masonry substance (Arnold 1981) leading to new compounds. Today we still do not understand the physical behavior and the chemical effect of water trapped in capillaries under pressure in most types of stone.

Dissolution of Carbonates

Pure limestones, limestone-marbles, dolomites, and crystalline marbles dissolve in pure water without leaving a residue. The rate of dissolution per unit of time depends on the acidity of the precipitation, the wind direction, the surface angle to the horizon, and other factors. To measure the rate of surface reduction, unweathered reference points, such as patches or veins of unweathered quartz or hornblende, possibly still showing the original surface finish, are needed. The writer has performed such surface reduction

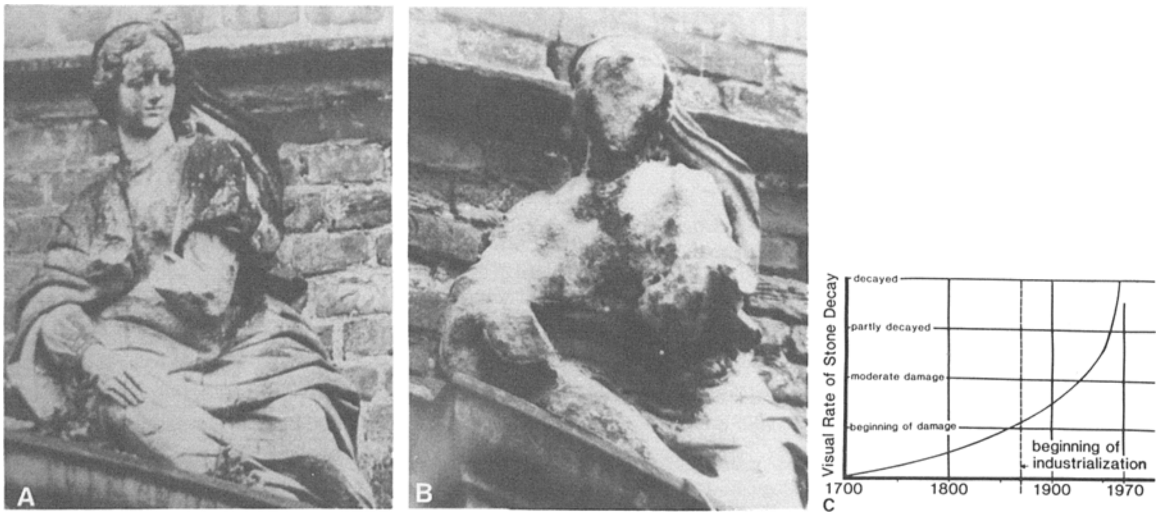
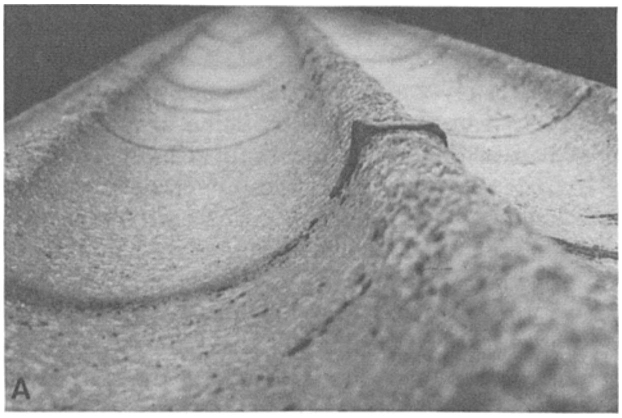


Figure 1. Time-lapse photos of a sculpture at Herten Castle near Recklinghausen, was built of soft and porous glauconitic Baumberg sandstone in 1702. **A.** Photo taken in 1908; **B.** Photo taken in 1968 shows almost complete obliteration of details. **C.** Visual semi-quantitative presentation of stone decay of statue pictures in A–B.



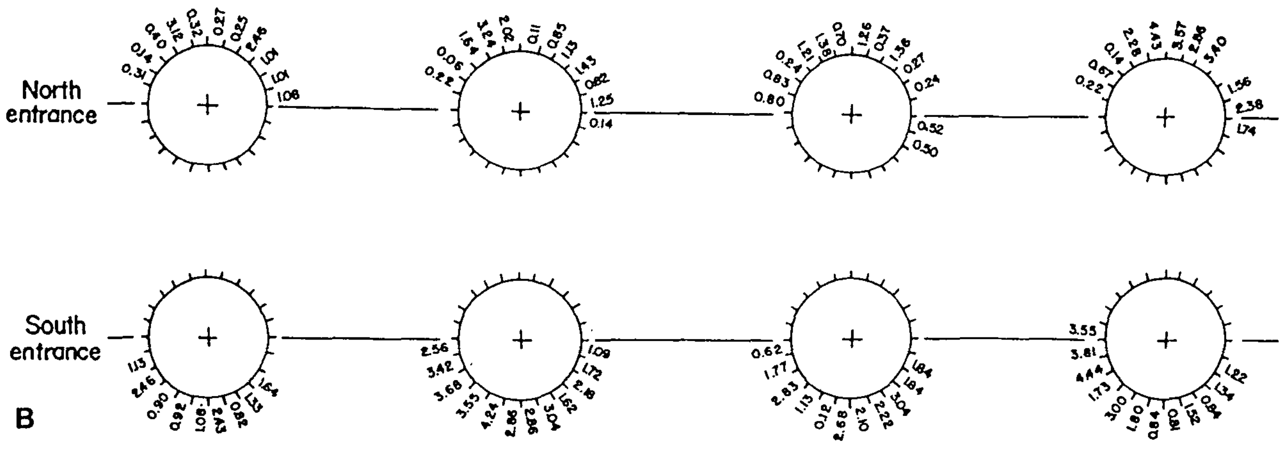


Figure 2A. Weathered ribs of columns of coarse-grained Georgia marble. Unweathered hornblende band indicates surface reduction of over 3 mm. South side of Chicago Field Museum Natural History. **B.** Surface reduction of marble ribs, expressed in mm, against unweathered patches of hornblende. Figures measured with a depth micrometer.

measurements on coarse-grained Georgia marble in the strongly weathered columns of the Chicago Field Museum of Natural History with a needle-pointed depth micrometer combined with techniques of macrophotogrammetry, and on fine-grained Vermont marble in the columns of the Lincoln monument in Grant Park, Chicago (Figs. 2 and 3). Although the fronts of the Field Museum columns were strongly

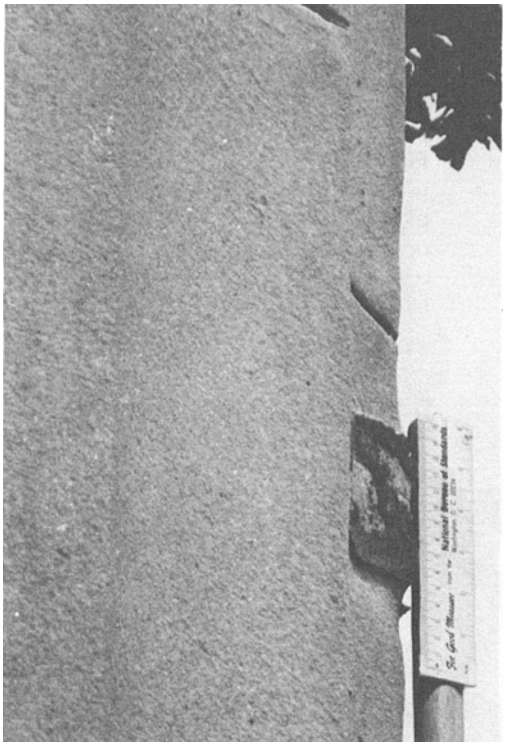


Figure 3. Surface reduction of fine-grained Vermont-type marble against an unweathered patch of hornblende; a reduction of about 4 mm in 60 y of exposure. Column of Lincoln Monument, Grant Park, Chicago.

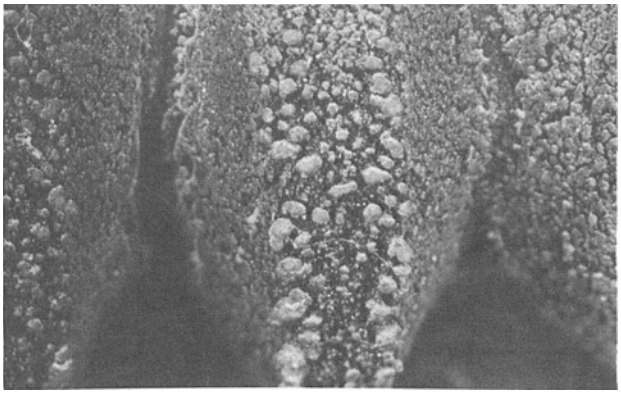


Figure 4. Pustules of gypsum on black soot 3 mm in size protecting Indiana limestone beneath. Chicago Museum of Science and Industry.

scared by 60 y of exposure to 76 cm of mean annual precipitation, the back sides of the columns still show the original finish, despite free access to fog and air pollutants. A similar observation was made on columns of red limestone-marble outside the church of San Vitale of Ravenna, over 1000 y older than the columns of the Field Museum; at Ravenna the weather side was deeply etched, whereas the side averted from the rain still shows the original crude polish; moist air and fog were unable to corrode the carbonate rocks in either case. Gypsum is frequently found on limestone surfaces that have recrystallized in the presence of SO_2 where protected from the washing action of rain. Many such secondary gypsum deposits are intermixed with black soot crusts (Fig. 4). Gypsum is about 20 times more soluble than calcite at temperatures near 40°C, whereas at low temperature and pH of the solvent, acid rainwater, the maximum solubility of calcite in nature is near 0.02% (Fig. 5A).

Dissolution of Silica

At near 60°C and pH = 7 the solubility of silica as amorphous opal is comparable to that of calcite; it rapidly increases beyond pH = 9 (Fig. 5B). Silica as grain cement in sandstones is susceptible to dissolution near a hot and sundrenched alkaline desert floor, and also on buildings where silica can migrate from inside the rock and stone outward toward the stone surface, leading to scaling of a thin hardened crust while crumbling occurs beneath (Fig. 6).

Honeycomb Weathering

Honeycomb formation is based on the relocation of calcite and/or silica toward exposed surfaces while the stone behind the surfaces, now deprived of a part of its grain cement, crumbles away, often a process accelerated by salt action. At Sacred Heart Church, Notre Dame, Indiana, siliceous sandstone making up columns is crumbling beneath the overhang with the help of salt used for de-icing at the south entrance (Fig. 7). Honeycombs have developed above the arched entrance by a combination of solar exposure on the south side of the building, alkaline solutions, and salts.

In another type of honeycomb, calcite was introduced into calcite-free red Buntsandstein on the east face of the Muenster of Freiburg, West Germany; calcite was supplied by moisture moving outward through mortar joints, covering the area below with a dripstone-like crust (Fig. 8).

Weathering of Silicate Minerals

The weathering of silicate minerals cannot be measured in terms of surface reduction, but it can be judged by the width of the weathered rims and rinds. The iron of gray to bluish-gray sandstones, granites,

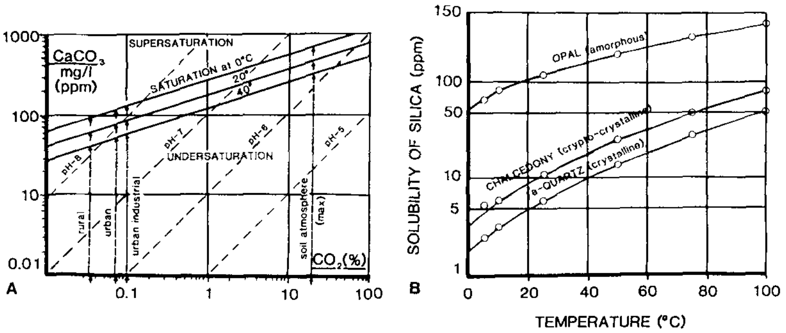


Figure 5A. Solubility of calcite as a function of temperature, the CO_2 content, and pH. **B.** Solubility of silica as amorphous opal, crypto-crystalline chalcedony, and crystalline quartz at near pH = 7; solubility accelerates above pH = 9.

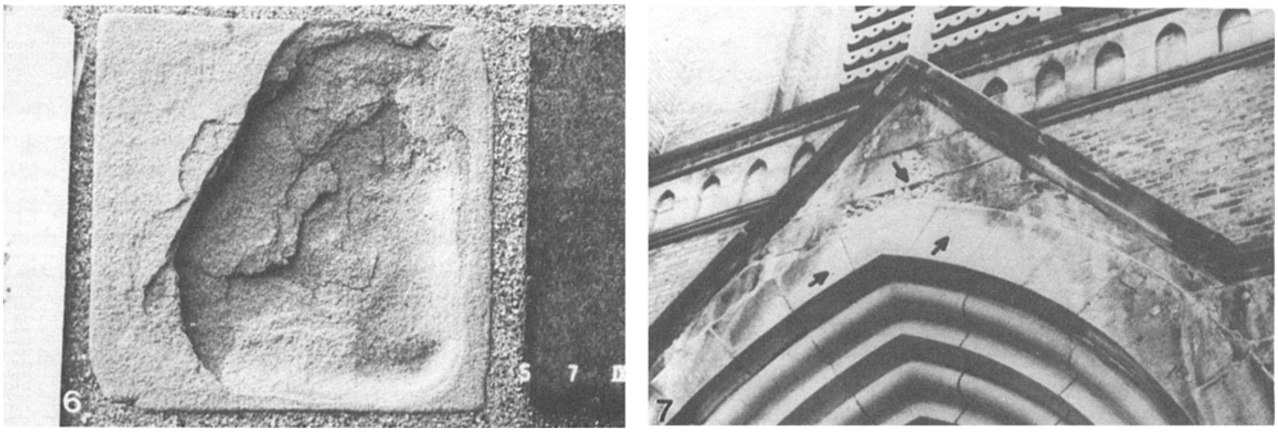


Figure 6. Weathering of sandstone by scaling. Migration of grain cement from inside to the surface, migration also from mortar joint. Specimen is 10 cm long. National Bureau of Standards Stone Test Wall.

Figure 7. Honeycombs and efflorescence of de-icing salts developed in fine-grained quartz sandstone. South entrance to Sacred Heart Church, Notre Dame, Indiana.

and basalts is chiefly derived from black micas, hornblende, and some other minerals; iron may also be found finely distributed as grain coatings and grain cement. The thickness of the brown weathered rim depends on the length of exposure to a given amount of annual precipitation, the permeability of the stone, and the degree of iron bond in the crystal lattice. A cornerstone of gray Ohio sandstone in the Stone Test Wall of the National Bureau of Standards was physically damaged during the transport of the wall from downtown Washington, D.C., to its new location in rural Gaithersburg, Maryland, but now, after 30 y of exposure, it displays a narrow brown rim 2–2.5 mm wide. A similar Ohio sandstone could develop a 3.5-mm-wide brown rim after more than 60 y of exposure in downtown Cleveland, Ohio. Granites and basalts with very litle permeability may show a penetration of about 1 mm in 40,000 y, according to Černohouc and Šolc (1966) and Fritz and Ragland (1980).

Salt Action

Great destructive effect is attributed to salt action. The visual evidence of salt corrosion or salt fretting occurs along the upper fringe of the capillary water transport (Arnold 1981). The sources of the salts may be different; most comes from de-icing roads with NaCl, sulfates and chlorides of Na and Mg from groundwater rising through masonry from salts entrapped in the masonry, salts from ocean spray, and desert dust. The effectiveness of salt action depends on the kinds of salts present, on the size and shape of the capillary system, on the moisture content, and on the exposure to solar radiation. The west entrance to St. Marc's in Venice gives a good example of the influence of solar exposure; the salt line runs parallel with the stairway down into the interior of the church, higher on the northwest side exposed to intense afternoon sun than on the southwest side with no after-

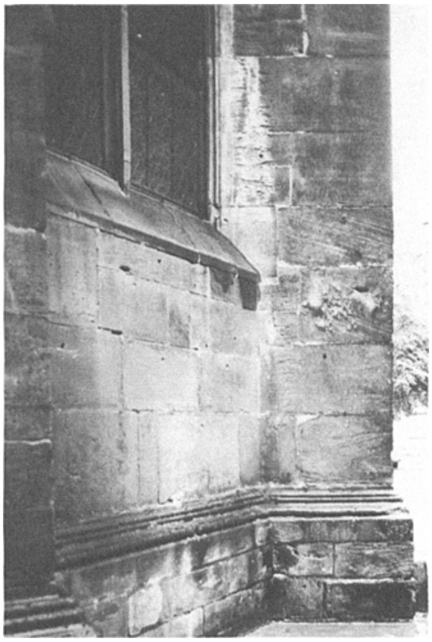


Figure 8. Honeycombs developed beneath secondary crust of calcite on calcite-free red Buntsandstein, Cathedral of Freiburg, West Germany.

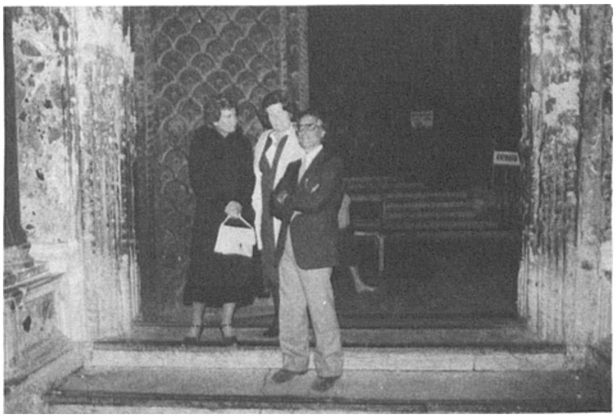


Figure 9. Line of salt fretting to both sides of west entrance to St. Marc's Cathedral, Venice. Saltwater from the lagoon rises higher where the sun hits, left, than on the righthand side.

noon sun (Fig. 9). The corroded upper margin caused by salt fretting involves a variety of potential salt actions, such as crystallization pressures (Winkler and Singer 1972), hydration pressure (Winkler and Wilhelm 1970), hygroscopic water retention (Vos and Tammes 1969), expansion and contraction of salts caused shearing on a rock surface by changes of the temperature, and relative humidity (Puehringer 1983).

Table 1. Crystallization pressures of a few common salts.

		Crystallization pressure (atm)			
		C/C = 2		C/C = 10	
Salt	Chemical formula	0°C	50°C	0°C	50°C
Bischofite	$McCl_2 \cdot 6H_2$	119	142	397	470
Epsomite	$McSO_4 \cdot 7H_2O$	102	125	350	415
Gypsum	$CaSO_4 \cdot 2H_2O$	282	334	938	1110
Halite	NaCl	554	654	1945	2190
Hexahydrite	$MgSO_4 \cdot 6H_2O$	118	141	395	469
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	72	83	234	277
Natron	$Na_2CO_3 \cdot 10H_2O$	78	92	259	308
Thenardite	Na_2SO_4	292	345	970	1150

Table 2. Hydration pressures of gypsum and epsomite (atm).

Rel. hum.	Temperature (C)			
%	0°	20°	40°	60°
$CaSO_4 \cdot$	$\frac{1}{2}H_2O$ to	$CaSO_4 \cdot$	$2H_2O$	(plaster of Paris to gypsum)
100	2190	1755	1350	926
90	2000	1571	1158	724
80	1820	1372	941	511
70	1600	1145	702	254
60	1375	884	422	0
50	1072	575	88	0
$MgSO_4 \cdot$	$6H_2O$ to	$MgSO_4 \cdot$	$7H_2O$	(hexahydrite to epsomite)
100	146	117	96	92
90	132	103	77	69
80	115	87	59	39
70	97	68	40	5
60	76	45	17	0
50	50	19	0	0
40	20	0	0	0

Calculated crystallization pressures give an indication of the great potential pressures that may develop during crystallization in narrow closed channels. Table 1 presents some data at various degrees of supersaturation as the function of developing pressures and the temperature. Under favorable conditions some salts may crystallize or recrystallize to different hydrates, which occupy a larger space, being less dense, and exert additional pressure, the hydration pressure. Table 2 gives the hydration pressure for plaster of Paris to gypsum, and for hexahydrite to epsomite, both common in masonry. The crystallization pressure depends on the temperature and the degree of super-

Figure 10. Ballustrade of fossiliferous Indiana limestone showing strong corrosion in upper portion by combination of salt fretting by de-icing salt and acid rain attack. Hygroscopic retention leaves the wetline permanently visible. South entrance to Main Building, University of Notre Dame, Indiana.

Figure 12. Slab of fine-grained Italian White marble, weathered and warped after exposure of about 100 y to 2000 mm precipitation and high relative humidity of New Orleans, Louisiana.

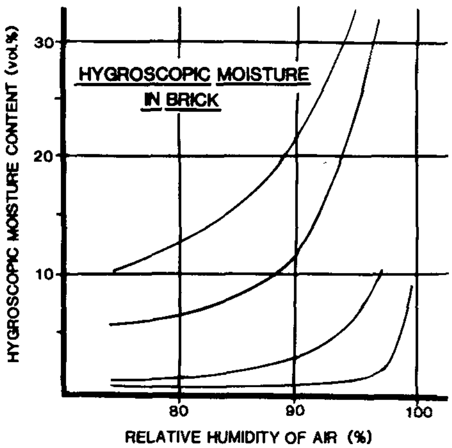


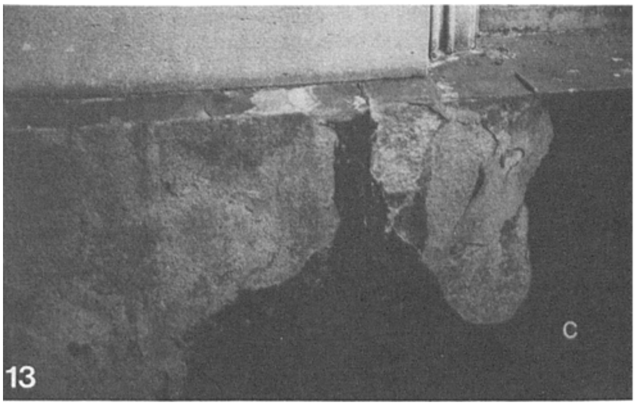
Figure 11. Hygroscopic moisture retention in brick masonry depending on salt content and relative humidity. After Vos and Tammes (1969).

saturation of the solution, C/C_s, whereas the hydration pressure depends on the ambient temperature and the relative humidity.

Some salts attract moisture through hygroscopicity without hydrating. Halite as de-icing salt can retain considerable quantities of moisture when entrapped in stone, leaving the areas of salt concentrations moist throughout the entire year. Figure 10 shows a balustrade of Indiana limestone composed of even-sized smal fossil shell fragments; it is visibly corroding above the wetline; the result is a combination of salt fretting and dissolution by acid rain. The degree of hygroscopic attraction by halite was quantified by Vos and Tammes (1969) on brick masonry (Fig. 11). The vertical distribution of rising damp and soluble salts on buildings was well analyzed by Arnold (1982).

Decay of Marble

Rapid disintegration of some fine-grained marbles of the Carrara type, known as Italian White Marble, has often puzzled the architect. The process is commonly associated with warping if the slabs are thin. High precipitation and relative humidity in the Gulf Coast area permit the rapid introduction of moisture into the marble slabs, as initial cracks tend to develop along the grain boundaries and propagate inward, a phenomenon known as *corrosion cracking* in metals and plastics (Whalley and others 1982). Bowing of marble slabs and internal disintegration are believed to be caused by a combination of stress relief of locked-in stresses from the geological past loading history of the stone and expansion-contraction cycles of moisture



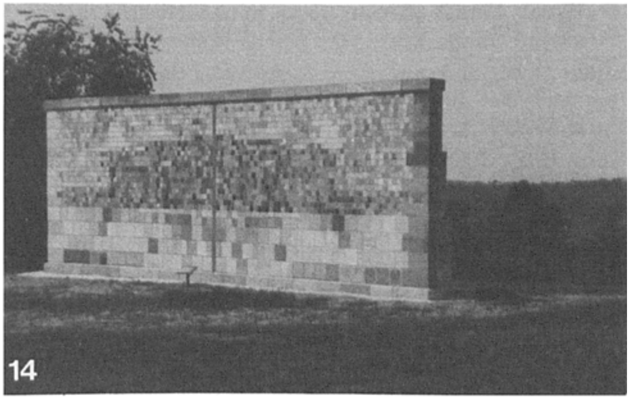


Figure 13. Spalling of thin slabs of granite in several layers. Base of Tweed Courthouse, Lower Manhattan, New York.
Figure 14. National Bureau of Standards Exposure Stone Test Wall. Front view, south side. Wall is built of over 2000 test specimens, 11.5 m long and 3.6 m high. National Bureau of Standards, Gaithersburg, Maryland.

entrapped in the narrow capillary system, leading to warping and cracking, followed by volume expansion (Fig. 12) (Winkler 1982).

Spalling of Granite

Tentlike spalling of thin, even slabs of granite at the base of buildings near the ground level is common in urban areas. The phenomenon is similar to the natural process at the outcrop, a combination of stress relief formed many kilometers beneath the earth's surface but now exposed, and expansion-contraction of entrapped moisture and salt action of de-icing salts from streets and sidewalks. Figure 13 shows spalling of exposed fine-grained Massachusetts granite along the base of the old Tweed Courthouse, peeling in several even layers superimposed on top of each other. The blistering is probably enhanced by the process used to polish granite surfaces in the mill, which added stresses to the already locked-in natural stress. Thin surface spalls are common on granite surfaces in natural outcrops, mostly near the ground surface.

Stone Test Wall

In 1948 the National Bureau of Standards in Washington, D.C., erected a stone test wall 11.5 m long and 3.6 m high (Fig. 14), composed of 2352 pieces of stone blocks from various commercial quarries in the United States and from many parts of Europe (Kessler and Anderson 1951). I studied the state of preservation after 30 y of exposure of the wall to the urban atmosphere of Washington, D.C. The wall was built to measure weathering rates in a given time and climate. Only very few stone types permitted the measurement of surface reduction rates: blocks of Indiana limestone top the wall as coping stones with full exposure to the top, north, and south sides. A strong relief has developed between the shell fragments of densely crystalline calcite and the loose fibrous calcite matrix. Fossil limestone labeled Austrian Marble (Adneth-type limestone, Salzburg) developed a similar relief between unweathered shells and a fine-grained matrix. Some sandstones show roughening and limited sanding along lines of weakness, such as bedding planes. Most small specimens measure only 10 cm square and are a few cm thick. Some sandstones show spalling of thin surface crusts which are the result of outward migration of grain cement and of both lime and silica from mortar between the blocks, leading to inside crumbling and surface hardening (Fig. 6). The National Bureau of Standards Stone Test Wall is thus of only very limited value in the study of weathering rates. Similarly, any future stone test wall will allow us to study weathering rates only in a given climatic environment for a given time.

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