Chemical and mineralogical effects of acid deposition on Shelburne Marble and Salem Limestone test samples placed at four NAPAP weather-monitoring sites

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Abstract

Marble and limestone briquettes were placed at National Acid Precipitation Assessment Program (NAPAP) test sites in North Carolina, Washington, D.C., New Jersey, and New York to determine mineralogical changes that might be attributed to acid deposition. Samples have been examined after exposures of 1 and 2 yr, and the most significant change is the development of a gypsum-rich "spot" on the sheltered side of the briquettes. X-ray and SEM analyses reveal that gypsum plus calcite is present within the "spot" area, but outside this area and on the upper surface of the briquettes, only calcite is detected. The gypsum varies from thinly bladed to nearly blocky crystals, and in some places it forms a dense mat on the underlying calcite. There is no apparent difference between the gypsum deposited on the limestone and that deposited on the marble. Rounded particles, morphologically similar to various C soots, were also observed, and it is suggested that these may catalyze the oxidation of SO_2 to H_2SO_4.

The atmospheric chemistry relating to acid deposition is presented and interpreted in terms of the gas concentrations and rain chemistry measured at the four sites. Statistical analysis of possible relationships between various ion concentrations from the sites reveals some significant correlations. Strong correlations are found between SO_4^{2-} and H^+, between NO_3^- and H^+, and between H^+ and $SO_4^{2-} + NO_3^-$. There are also high correlations between SO_4^{2-} and NO_3^- at three sites (Washington, D.C., North Carolina, and New Jersey). The high correlations suggest that the sulfate and nitrate ions (or their SO_2 and NO_x progenitors) are interdependent. The lack of correlation between SO_4^{2-} and NO_3^- at the rural New York site suggests independent sources of these ions. Analysis of the water chemistry of the four sites suggests that 24% to 37% of H ion is supplied by nitric acid, the rest by sulfuric acid.

A model, based on the sequence of salts observed to crystallize from a progressively more concentrated solution, is presented to explain the presence of the "spot" on the undersides of the briquettes. Two possible crystallization sequences are outlined: first for the system $CaCO_3$-$CaSO_4$-H_2O and second for the system $CaCO_3$-$CaSO_4$-$Ca(NO_3)_2$-H_2O. In the models, the $CaCO_3$-saturated solutions filling the pore space in the stone continuously precipitate calcite during the drying period after the rain event; gypsum is precipitated only after evaporation is nearly complete. As evaporation proceeds, the solution migrates by gravity to the lower surface of the briquette and the last residual liquid precipitates gypsum and produces the gypsum-rich "spot." No calcium nitrate tetrahydrate has been observed on any of the test stones, probably because this salt readily absorbs water from air to form a liquid when the relative humidity of the air is greater than 50% (at 25 °C).

It is proposed that the most significant stone damage is due to salt build up on and within the stone rather than due to stone removal through dissolution.

Introduction

In the past five or ten years a great deal of concern has arisen over the possible effects of air pollution and acid deposition on our important historic monuments, public buildings, and other cultural resources. Prominent examples of important cultural monuments that are threatened, presumably by air pollution and acid deposition, are the St. Paul's Cathedral in London, England, and the Lincoln Cathedral in Somerset, England (Pearce, 1985), many buildings and monuments in Venice, Italy (del Monte and Vittori, 1985), the Cologne Cathedral in Germany (Luckat, 1975), the Parthenon in Athens, Greece (Skoulikidis and Papakonstantinou-Ziotis, 1981), and the Reggio Emilia Cathedral in the Po Valley, Italy (del Monte

and Sabbioni, 1986). Numerous observers in Europe have commented that stone deterioration appears to have become much more pronounced since just prior to World War II; for example, Amoroso and Fassina (1983, p. 3–6) noted that substantial damage has been observed on the facade of the St. Mark's Basilica in Venice since the beginning of large-scale industrialization in 1930. However, quantitative data are lacking at the present time to confirm the various observations that suggest that stone deterioration has accelerated in the past few decades.

The building stones that appear to be particularly affected by polluted environments are limestone, marble, and calcareous sandstone. The former two rock types are composed mostly of calcite ($CaCO_3$) and/or dolomite [$CaMg(CO_3)_2$]—minerals that readily dissolve in acid solutions. The urban atmosphere contains four common inorganic acids, carbonic, sulfurous, sulfuric, and nitric, as well as oxidants and catalysts, and all may play an important role in the deterioration of carbonate building stone. Although measurable effects, generally expressed by dissolution, can be observed in a period of just a few years when carbonate-rich stone is exposed to an uncontaminated atmosphere, the effects seem to be much more pronounced when exposure is to a polluted atmosphere.

To gain a better understanding of the nature of acid deposition on carbonate stone, the National Park Service, under the auspices of the United States National Acid Precipitation Assessment Program (NAPAP, Task Group VII: Effects on Materials and Cultural Resources), established five sites for a 10-yr period of measuring the effects of acid deposition on limestone and marble samples. These sites are located in Research Triangle Park, North Carolina; Washington, D.C.; Chester, New Jersey; Newcomb, New York; and Steubenville, Ohio. The sites in North Carolina, New Jersey, and New York are located in rural areas, whereas the sites in Washington, D.C., and Steubenville, Ohio, are located near the center of an urban area. The stone samples in the three rural areas are positioned 1 to 2 m above the ground; those in the two cities are positioned on the roofs of two-story buildings, 7 to 9 m above the city street. A full description of these sites, including their geographic setting, longitude, latitude, elevation above sea level, mode of operation, and the types of environmental monitoring employed at them, is given by Flinn et al. (1985), Sherwood and Doe (1984), and Reddy et al. (1986).

In the following we will give the gas concentrations and rain chemistry measured at four of the NAPAP monitoring sites, describe the mineralogical and chemical changes noted in the marble and limestone test briquettes exposed for 1- and 2-yr periods at four of the sites, and propose models for salt crystallization within the test stones in context with the measured gas and rain chemistry. The chemical species that are deposited upon and react with the test samples employed in this study are formed through many complex atmospheric processes. Since the nature of the stone deterioration is directly related to the types and amounts of chemicals formed by these pro-
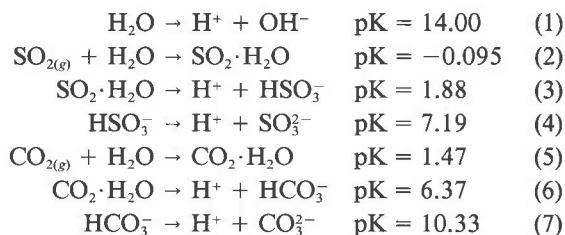
cesses, it is pertinent to first review the chemistry of acid deposition.

ATMOSPHERE CHEMISTRY AND ACID DEPOSITION

The most important acids to consider in regard to stone damage are (1) $CO_2 \cdot H_2O$ (carbonic acid) formed when atmospheric CO_2 dissolves in water, (2) $SO_2 \cdot H_2O$ (sulfurous acid) formed when atmospheric SO_2 dissolves in water, (3) H_2SO_4 (sulfuric acid) formed by the oxidation of sulfurous acid and SO_2, and (4) HNO_3 (nitric acid) formed by the oxidation of nitrogen oxides. The contribution of nitric acid to stone weathering is not clear, but it appears to take on some importance in polluted areas where there are significant NO and NO_2 emissions. Even if the ambient levels of SO_2, NO, and NO_2 are high, sulfuric and nitric acid production in significant quantity may occur only if suitable oxidants and catalysts are present.

The system CO_2-SO_2-H_2O

The presence of dissolved SO_2 and CO_2 in rainwater contributes to its acidity. Because SO_2 is much more soluble than CO_2 in aqueous solutions and because $SO_2 \cdot H_2O$ is a stronger acid than $CO_2 \cdot H_2O$, it will be useful to first consider the effect, in conjunction with that of ambient CO_2, of atmospheric SO_2 at various concentrations on the acidity of rainwater and thus on the dissolution of limestone and marble. In this aqueous chemical system (SO_2-CO_2-H_2O), the pertinent chemical reactions and equilibrium constants are

$$H_2O \rightarrow H^+ + OH^- \qquad pK = 14.00 \qquad (1)$$
$$SO_{2(g)} + H_2O \rightarrow SO_2 \cdot H_2O \qquad pK = -0.095 \qquad (2)$$
$$SO_2 \cdot H_2O \rightarrow H^+ + HSO_3^- \qquad pK = 1.88 \qquad (3)$$
$$HSO_3^- \rightarrow H^+ + SO_3^{2-} \qquad pK = 7.19 \qquad (4)$$
$$CO_{2(g)} + H_2O \rightarrow CO_2 \cdot H_2O \qquad pK = 1.47 \qquad (5)$$
$$CO_2 \cdot H_2O \rightarrow H^+ + HCO_3^- \qquad pK = 6.37 \qquad (6)$$
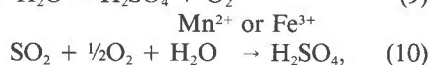$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \qquad pK = 10.33 \qquad (7)$$

where pK's are the aqueous-phase equilibrium constants (Jacob and Hoffman, 1983; Maahs, 1982). Using these equilibrium constants, concentrations were calculated for the important aqueous species (Table 1) found in pure water that is in equilibrium with CO_2 gas present in the lower atmosphere at a concentration of 342 ppmv (Watson, 1985, vol. I, p. 107) and with SO_2 gas at concentrations of (1) zero, (2) 0.3 ppbv (clean rural air), (3) 3 ppbv (clean city air and slightly polluted rural air), (4) 30 ppbv (polluted city air), and (5) 1600 ppbv (extreme pollution). For such dilute solutions, the activity coefficients were assumed to be unity. As can be seen from the values given in Table 1, the effect of CO_2 gas at a concentration of 342 ppmv on the acidity of the solution is insignificant relative to the effect of SO_2 until the SO_2 concentration in the atmosphere drops to 0.3 ppbv. At this concentration the contribution of SO_2 to acidity is equal to that of the atmospheric CO_2 (compare columns 1, 2, and 3 of Table

1). If the concentration of SO_2 is zero, the pH of the rain is fixed at 5.66 by the CO_2 gas. In a moderately polluted city where the atmosphere contains 30 ppbv SO_2 and 342 ppmv CO_2, the pH of the rain would be 4.66. At this pH, dissolution of limestone or marble would significantly increase over that observed in the pure CO_2-H_2O system where the pH = 5.66.

Oxidation of SO_2 and NO to form sulfuric and nitric acid

H_2SO_4. Gas or aqueous phase oxidation of SO_2 is accomplished through many diverse and complex chemical reactions. Three of the quantitatively more important oxidation reactions that occur in aqueous solutions or within thin liquid films on surfaces and that lead to the formation of sulfuric acid are (intermediate steps, some hypothetical, where present are omitted)
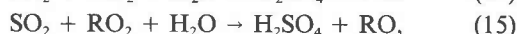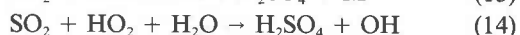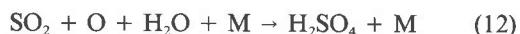
$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \tag{8}$$
$$SO_2 + O_3 + H_2O \rightarrow H_2SO_4 + O_2 \tag{9}$$
$$SO_2 + \tfrac{1}{2}O_2 + H_2O \xrightarrow{Mn^{2+} \text{ or } Fe^{3+}} H_2SO_4, \tag{10}$$

where Mn^{2+} and Fe^{3+} are oxidation catalysts (Brosset, 1986; Ibusuki and Barnes, 1984; Hoffmann and Jacob, 1984).

Another important reaction that is thought to occur in both the gas and aqueous phase in the presence of NO_2 (sometimes with the presence of suitable catalysts) is

$$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO \tag{11}$$

(Finlayson-Pitts and Pitts, 1986; Gertler et al., 1984; Johansson et al., 1986; Schryer et al., 1983; Brodzinsky et al., 1980; Rogowski et al., 1982). At low concentrations of reactants, however, Reaction 11 was found to proceed very slowly if at all (Harrison and Pio, 1983; Cofer et al., 1984). Other gas-phase SO_2 oxidation processes that may be quantitatively important under certain conditions are suggested as follows (Liberti, 1986; Brosset, 1986):

$$SO_2 + O + H_2O + M \rightarrow H_2SO_4 + M \tag{12}$$
$$SO_2 + 2OH + M \rightarrow H_2SO_4 + M \tag{13}$$
$$SO_2 + HO_2 + H_2O \rightarrow H_2SO_4 + OH \tag{14}$$
$$SO_2 + RO_2 + H_2O \rightarrow H_2SO_4 + RO, \tag{15}$$

where O, OH, and HO_2 are high-energy free radicals, M is a secondary collision partner (such as molecular nitrogen) required to carry away the energy released in the combination reaction, and RO_2 stands for organic peroxy radicals such as CH_3O_2.

Two examples of important free radical-forming reactions are

$$O_3 + h\nu \rightarrow O + O_2 \tag{16}$$
$$O + H_2O \rightarrow 2OH, \tag{17}$$
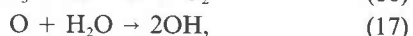
where $h\nu$ designates a particular energy range of electromagnetic radiation. Hewitt and Harrison (1985) considered that the OH radical plays a dominant role in the photochemistry of the troposphere and could be important in some SO_2 oxidation reactions such as (13) above.

TABLE 1. Equilibrium concentrations of the important aqueous species

	(1)	(2)	(3)	(4)	(5)	(6)
CO_2(gas) (ppmv)	0	342	342	342	342	342
SO_2(gas) (ppbv)	0.3	0	0.3	3	30	1600
$[SO_2 \cdot H_2O]$	9.43	0	9.43	8.43	7.43	5.71
$[HSO_3^-]$	5.65	0	5.80	5.15	4.65	3.79
$[SO_3^{2-}]$	7.18	0	7.48	7.18	7.18	7.18
$[CO_2 \cdot H_2O]$	0	4.94	4.94	4.94	4.94	4.94
$[HCO_3^-]$	0	5.65	5.80	6.15	6.65	7.51
$[CO_3^{2-}]$	0	10.32	10.62	11.32	12.32	14.04
pH	5.66	5.66	5.51	5.16	4.66	3.80

Note: Species present in pure water that is in equilibrium with CO_2 and SO_2 gas at selected atmospheric concentrations. Gas concentrations are given in parts per million or billion by volume (ppmv, ppbv). Aqueous species are given as $-\log$ concentration (pC) and are calculated from the equilibrium constants given in Reactions (1–7). The activity coefficients are assumed to equal unity.
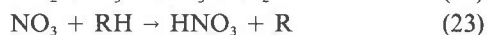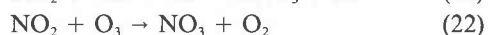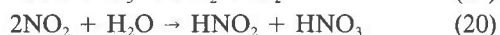
These same authors find that the tropospheric daytime mean concentrations of OH are 0.02 to 0.2 pptv. However, atmospheric SO_2 concentrations greatly exceed these values; thus, OH would be quickly depleted, unless it is continuously generated, through reactions such as (17).

Direct oxidation of SO_2 by O_2 is very slow, both in the aqueous and gas phase, relative to oxidation by O_3 and H_2O_2 (Brosset, 1986, p. 184). However, Mn^{2+}, Fe^{3+}, and combustion-produced soot (carbonaceous matter) have been found to be efficient catalysts for promoting the oxidation of SO_2 by O_2, especially in the presence of water; for example,

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \xrightarrow{C} H_2SO_4, \tag{18}$$

where C is the carbonaceous catalyst (Brodzinsky et al., 1980; Harrison and Pio, 1983). Reaction 18 may be of importance in regard to carbonate dissolution within city environments that are polluted with soot from oil-fired power plants, diesel engines, etc. (del Monte and Vittori, 1985; Camuffo et al., 1984; Camuffo, 1986).

HNO_3. Important oxidation-reduction reactions of nitrogen oxides, five of which lead to the formation of nitric acid, are

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{19}$$
$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{20}$$
$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{21}$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{22}$$
$$NO_3 + RH \rightarrow HNO_3 + R \tag{23}$$
$$NO_3 + RCHO \rightarrow HNO_3 + RCO \tag{24}$$
$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \tag{25}$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3, \tag{26}$$

where RH and RCHO refer to organic alkanes and aldehydes, respectively (Liberti, 1986; Lenner, 1987; Finlayson-Pitts and Pitts, 1986; Singh, 1987).

In the lower altitudes of the troposphere, atomic oxygen forms from the photoreduction of NO_2 (Watson, 1985, vol. 1, p. 27), that is,

$$NO_2 + h\nu \rightarrow NO + O. \tag{27}$$
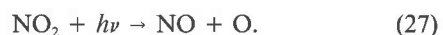
Thus, during daylight hours, NO_2 is converted to NO, releasing an oxygen radical that combines with O_2 to form O_3,

$$O + O_2 + M \rightarrow O_3 + M \qquad (28)$$
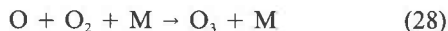
where the secondary collision partner M is N_2 or O_2 (Chameides and Davis, 1986). High ozone concentrations are particularly noted during the afternoons of the summer months. At night, O_3 is consumed by reaction with NO to form NO_2 (Reaction 19).

With regard to the production or destruction of ozone by the daytime and nighttime reactions with nitrogen oxides, there will be no net change in ozone concentration unless other reactions occur that add or remove critical chemical species to or from the system. Reactive organic compounds, such as aldehydes, alkenes, and aromatics, are very effective in oxidizing NO to NO_2, circumventing the destruction of ozone by Reaction 19 (Chock and Heuss, 1987). However, if nitrogen oxides are removed from the atmospheric system through the formation of HNO_3 (Reactions 19–26) more rapidly than they are produced, the formation of ozone would be suppressed.

Important acid-producing oxidants

H_2O_2. Hydrogen peroxide rapidly oxidizes SO_2 to H_2SO_4 in aqueous solution (Reaction 8), and the reaction is relatively independent of pH (Finlayson-Pitts and Pitts, 1986, p. 685–687). A mitigating factor in the importance of H_2O_2 as an oxidant is its low concentration in the lower atmosphere. McElroy (1986) found in a study of cloud water that the available H_2O_2 was rapidly depleted by the excess SO_2; thus only a small fraction of the total SO_2 was oxidized. Jacob et al. (1987) came to the same conclusion in their study of fog conditions in the San Joaquin Valley, California.

The sources of hydrogen peroxide in the atmosphere are not well known, but it is shown experimentally that H_2O_2 is generated during incomplete combustion in a propane flame (Benner et al., 1985). A possible direct field observation of combustion-produced H_2O_2 was made by Kok et al. (1978) who observed an increase in ambient H_2O_2 in the atmosphere downwind from a local grass fire.

Graedel et al. (1976) found that the atmosphere at a polluted site in Los Angeles, California, contained 1 ppbv H_2O_2. Analysis of 387 sequential rain and snow samples by Lee et al. (1986), collected during the period from October 1983 to June 1985 at the Brookhaven National laboratory, Long Island, New York, gives an average H_2O_2 content of $7\mu M$ (7 micromoles per liter of H_2O). Some of these samples, however, had H_2O_2 concentrations as high as $120\mu M$. H_2O_2 concentrations measured in rainwater collected in Tokyo, Japan, from October 1981 to September 1982 showed an average of $8.3\mu M$, with a high value of $33\mu M$ in the summer and a low value of $1\mu M$ to $2\mu M$ in the autumn (Yoshizumi et al., 1984). Measurements of H_2O_2 vapor in the lower troposphere of the eastern United States gave a range of 0.2 to 4.1 ppbv (Heikes et al., 1987).

O_3. Atmospheric ozone is formed by reaction of atomic and molecular oxygen (Reaction 28). At high altitudes, above approximately 20 km, production of atomic oxygen results almost exclusively from photodissociation of molecular O_2 by short-wavelength ultraviolet radiation:

$$O_2 + h\nu \rightarrow O + O. \qquad (29)$$

In the lower altitudes of the troposphere, an important source of atomic oxygen is from the photodissociation of nitrogen dioxide (Reaction 27).

Although O_3 is not directly produced by anthropogenic emissions, the presence of NO, NO_2, O, and various nonmethane organic compounds tends to enhance the production of O_3 (Chameides and Davis, 1986, p. 245). At pH values less than 4, ozone is a much less effective oxidant of SO_2 than H_2O_2, but at pH values of 4.5 to 6.0, O_3 and H_2O_2 produce similar oxidation rates (Finlayson-Pitts and Pitts, 1986, p. 692).

Ozone concentrations from various localities are summarized by Altshuller (1986) and Finlayson-Pitts and Pitts (1986, p. 962). O_3 concentrations typically show significant seasonal and diurnal variations. For example, seasonal variations in O_3 levels measured in the Ohio River Valley show 9 ppbv in the early winter morning and 80 ppbv in the early summer afternoon (Shaw and Paur, 1983). In east-central England, remote from any local pollution sources, O_3 levels measured 36 ppbv in May and 15 ppbv in November (Martin and Barber, 1984). Diurnal variation of O_3 concentrations was demonstrated with measurements made in the atmosphere over southern California in June 1974, during a period of severe smog characterized by high oxidant and nitric acid levels (McRae and Russell, 1984). At 0600 hours, the O_3 concentration was 20 ppbv, at 1200 hours it was 220 ppbv, and the concentration peaked at 330 ppbv at about 1420 hours.

Sources and concentrations of NO, NO_2, and SO_2

NO and NO_2. In remote areas, such as the sparsely populated areas of the United States or in the Pacific Ocean, tropospheric nitrogen oxides are dominated by natural rather than anthropogenic sources, such as generation of NO by lightning and the direct release of NO and NO_2 from soils and marine waters. Anthropogenic sources of NO and NO_2 can be attributed mostly to the burning of fossil fuels and particularly to vehicular emissions in large urban areas. The NO and NO_2 concentrations may reach 500 ppbv in urban centers whereas this value drops to as low as 1 ppbv in atmospheres over remote regions (Finlayson-Pitts and Pitts, 1986, p. 37). A generally declining production of NO and NO_2 from industrial combustion in recent years has been more than offset by a large increase in production of these gases from electric utilities, motor vehicles, and the use of pipelines to transport natural gas. It is estimated that 9 billion kilograms of nitrogen oxides were emitted from anthropogenic sources in the United States in 1950, but by 1980, the annual emission of these oxides reached 20 billion

kilograms (NAPAP, 1985, p. 30, Fig. B-5). Atmospheric concentrations of NO and NO_2 measured in various parts of the world are summarized by Altshuller (1986) and Finlayson-Pitts and Pitts (1986, p. 571–575).

SO_2. At present, electrical utilities are the main source of SO_2, emitting about 64 percent of the national total; nonutility combustion furnishes about 15% (NAPAP, 1985, p. 20–29). Varhelyi (1985) estimated that in 1979 the North American emissions of SO_2 came from the following sources: 11.64 billion kilograms from the burning of coal and coke and 3.7 billion kilograms from the combustion of motor fuel and fuel oil. Annual emissions of SO_2 in the United States increased from about 9 billion kilograms in 1900 to a high of about 27 billion kilograms in 1970; however, between 1970 and 1984 these emissions declined to about 23 billion kilograms per year.

Atmospheric concentrations of sulfur dioxide measured in various parts of the world are given by Finlayson-Pitts and Pitts (1986, p. 38). Analysis of long-term trends of sulfur dioxide levels in London and New York City show that they have dropped from a maximum of 130 and 230 ppbv, respectively, in the 1960s to 15 and 35 ppbv, respectively, in the 1980s (Brimblecombe, 1986, p. 128, Fig. 7.2).

ATMOSPHERIC GAS AND RAIN CHEMISTRY AT NAPAP TEST SITES

Environmental parameters measured at the NAPAP sites include atmospheric gas concentrations, rain amount and chemistry, particle concentration and chemistry, relative humidity, temperature, and wind speed and direction. This data is available in SAROAD format in the computerized files maintained by the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (see Flinn et al., 1985, p. 154).

Gas concentrations

The average daily concentrations at the Washington, D.C., site for O_3, SO_2, NO, and NO_2 over the period from January 1, 1984, through December 31, 1986, are plotted in Figure 1. A seasonal variation of the O_3, SO_2, and NO gases is noted at all four sites and is particularly well defined at the Washington, D.C., site (Fig. 1). Marked ozone maxima appear in early summer (May–June) with the minima appearing in early winter (November–December)—with the exception that these highs and lows appear about a month earlier at the New York site. The highs and lows for the SO_2 and NO concentrations occur at approximately the same time as the lows and highs occur, respectively, for ozone. Such a reciprocal relationship could occur if, during the period when ozone levels are elevated in the spring or early summer, O_3 reacts with NO and SO_2 to form NO_2 and H_2SO_4, respectively (Reactions 19 and 9). The NO_2 levels at the Washington, D.C., and North Carolina sites do not show the distinct maxima and minima of the other three gases; the concentrations remain high throughout the year. Maxima and minima in the NO_2 concentrations do appear, however,
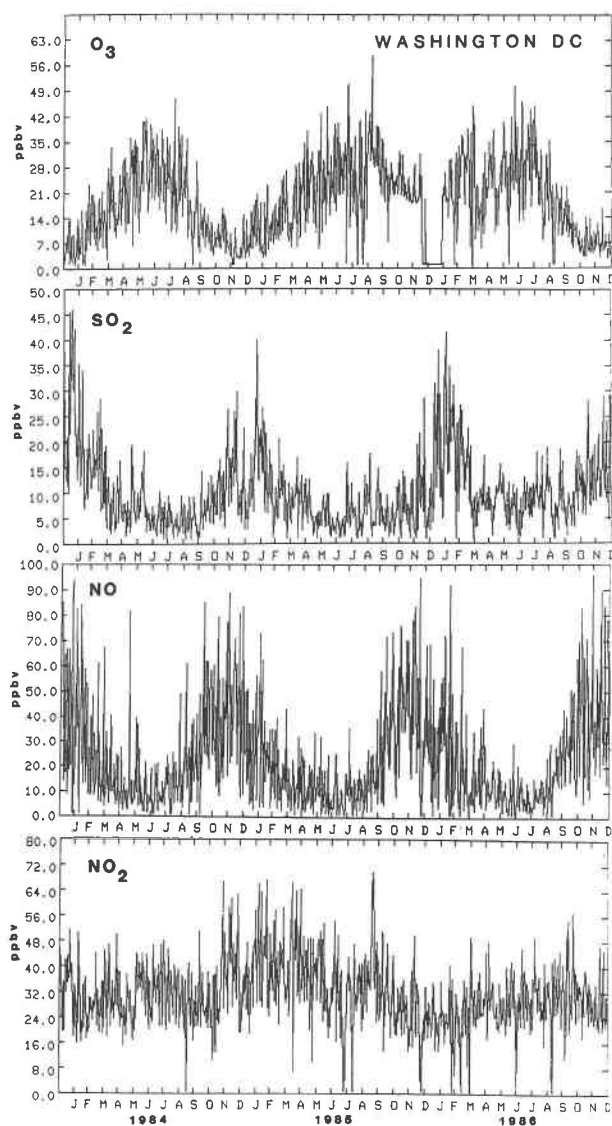

Fig. 1. Average daily concentrations (in ppbv) of O_3, SO_2, NO, and NO_2 gases at the Washington, D.C., site for the period January 1, 1984, through December 31, 1986.

at the New Jersey site. The average, minimum, maximum and range of O_3, SO_2, NO, and NO_2 gas concentrations at the four sites for the period January 1985 through December 1986 are given in Table 2 (also, see Flinn et al., 1985, p. 154). It is noted that the most polluted site with regard to SO_2, NO, and NO_2 is Washington, D.C., whereas the least polluted site with respect to these gases is the New York site. At the North Carolina and Washington, D.C., sites, it is noted that during the winter months the NO concentrations become greater than the NO_2 concentrations. At the two other sites, NO is usually less than NO_2 throughout the year. The particularly high values of NO relative to those of NO_2 observed during the winter months at the Washington, D.C., site may be due to the dominance of Reactions 11, 20, 21, 22, and

TABLE 2. Atmospheric gas concentrations at the four NAPAP monitoring sites

	SO_2 (ppbv)	NO_2 (ppbv)	NO (ppbv)	O_3 (ppbv)	R.H. (%)
	Research Triangle Park, North Carolina				
Average*	3	14	7	25	59.2
Range**	0–12	8–20	1–18	8–44	37.2–77.7
Min.–Max.†	0–78	0–78	0–100	0–100	10.6–107.0
	Washington, D.C.				
Average*	10	31	20	19	65.7
Range**	4–22	22–43	7–87	2–34	51.9–77.3
Min.–Max.†	0–91	0–100	0–100	0–99	17.0–100.0
	Chester, New Jersey				
Average*	6	14	9	32	70.9‡
Range**	2–13	9–22	3–20	13–48	61.2–84.3‡
Min.–Max.†	1–87	1–98	0–99	1–114	22.2–101.4‡
	Newcomb, New York				
Average*	2	2	1	30	71.6§
Range**	1–5	0–7	0–2	21–39	43.9–90.1§
Min.–Max.†	0–29	0–27	0–62	0–99	12.0–100.0§

* Average value for the period 1/85 to 12/86.
** Range of monthly averages for the period 1/85 to 12/86.
† Minimum and maximum values for the period 1/85 to 12/86.
‡ For the period 8/84 to 12/86.
§ For the period 1/86 to 12/86.

27 over Reaction 19. The gas concentrations found at Newcomb, New York, are significantly different from those of the other three sites; ozone remains relatively high throughout the winter months, perhaps partly because there is little SO_2 (1 to 5 ppbv), NO (0 to 2 ppbv), or NO_2 (0 to 7 ppbv) to enter into reactions that destroy O_3 (reactions 9, 19, and 22).

Rain chemistry

The volume-weighted average Ca^{2+}, NO_3^-, SO_4^{2-}, and H^+ ion concentrations in rain collected at the four sites are given in Table 3. The chemical composition was obtained on rain collected in Aerochem Metrics "wet-bucket" collectors and as runoff from slabs and blanks. The wet-bucket collectors are open only when rain is falling, and thus the rain composition is not affected to any great extent by dry deposition. (Dry deposition includes all gases that are adsorbed and/or absorbed and all particles that are deposited on the stone or blank surfaces—the surface itself may be wet or dry; the term "dry deposition" refers only to the mechanism of transport to the surface.) The rain runoff was collected from slabs of marble and limestone and from the polypropylene bases (blanks) of the empty experimental racks (Reddy, 1987; Reddy et al., 1986; See and Reddy, 1987). The ion concentrations from the blank reflect both wet deposition and the dry deposition contribution to the polypropylene surface; there is no contribution from dissolution. The ion concentrations from the slabs reflect both wet and dry deposition and dissolution of the stone (chemical compositions of the stones, Table 4, show that they are composed of about 99% $CaCO_3$). The differences between the volume-weighted averages for Ca^{2+}, SO_4^{2-}, and NO_3^- ion concentrations in the marble or limestone runoff and the ion concentrations in the blank runoff (marble or limestone

TABLE 3. Average rain runoff and wet bucket chemistry at four NAPAP monitoring sites

	Ca^{2+} (μeq/L)	NO_3^- (μeq/L)	SO_4^{2-} (μeq/L)	H^+ (μeq/L)	pH
	Research Triangle Park, North Carolina (1985, JD 100–297)*				
Blank	16.0	21.8	45.6	28.2	4.55
Wet bucket*	2.7	20.1	43.8	42.7	4.37
Marble	380.8	30.3	83.9	0.2	6.80
Marble − blank	364.8	8.5	38.3		
Marble − wet bucket	378.0	10.2	40.2		
Limestone	434.2	44.0	137.5	0.2	6.65
Limestone − blank	418.3	22.3	91.9		
Limestone − wet bucket	431.5	23.9	93.8		
	Washington, D.C. (1985, JD 133–301)*				
Blank	108.5	45.1	82.1	3.4	5.47
Wet bucket*	18.3	33.8	86.0	72.4	4.14
Marble	663.6	58.4	163.5	0.1	7.07
Marble − blank	555.0	13.2	81.4		
Marble − wet bucket	645.3	24.6	77.5		
Limestone	1049.5	105.9	311.3	0.1	7.30
Limestone − blank	941.0	60.7	229.2		
Limestone − wet bucket	1031.2	72.1	225.3		
	Chester, New Jersey (1985, JD 91–298)*				
Blank	8.7	50.8	100.1	72.4	4.14
Wet bucket*	5.3	28.3	56.1	57.5	4.24
Marble	472.4	48.3	115.9	0.1	7.20
Marble − blank	463.7	−2.6	15.8		
Marble − wet bucket	467.1	20.0	59.8		
Limestone	652.2	73.2	192.8	0.1	7.32
Limestone − blank	643.5	22.3	92.7		
Limestone − wet bucket	646.9	45.0	136.7		
	Newcomb, New York (1985, JD 93–310)*				
Blank	73.2	38.0	62.8	7.6	5.12
Wet bucket*	5.9	24.1	43.5	47.9	4.32
Marble	492.1	45.9	80.0	0.1	7.07
Marble − blank	419.0	7.9	17.1		
Marble − wet bucket	486.2	21.8	36.6		
Limestone	657.9	65.4	120.9	0	7.35
Limestone − blank	584.7	27.4	58.1		
Limestone − wet bucket	652.0	41.4	77.5		

Note: The complete chemical analyses are not given in Table 3. In addition to Ca^{2+}, NO_3^-, SO_4^{2-}, and H^+, they include Mg^{2+}, Na^+, K^+, Cl^-, NH_4^+, and PO_4^{3-} (wet bucket), and total alkalinity, Mg^{2+}, Na^+, K^+, and Cl^- (rain runoff). Note that the rain runoff was not collected during the winter months; thus these averages are biased toward summer conditions.
* Averages are for the period in 1985 given in Julian Days (JD) except for the wet-bucket averages, which are for the period June 1984 through July 1985. Values are weighted for the volume of rain collected for each measurement period. Data are available in SAROAD format and are maintained by the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

− blank) represent the contribution from stone dissolution plus the difference between the amount of dry deposition on the stone and on the blank. The differences between the stone runoff and wet-bucket ion concentrations (marble or limestone − wet bucket) reflect the contribution of dry deposition onto the continuously exposed stone plus the contribution (mostly Ca^{2+}) from stone dissolution. The ratio of SO_4^{2-} from dry deposition plus dissolution (marble or limestone − wet bucket) to SO_4^{2-} from wet deposition (wet bucket) ranges from 0.84 to 1.1 for marble and from 1.8 to 2.6 for limestone. For NO_3^-, the ratio of dry deposition plus dissolution to wet deposition ranges from 0.51 to 0.90 for marble and from 1.2 to 2.1 for limestone (Table 3). Thus, in the marble, 33% to 48% of the nitrate and 46% to 52% of the sulfate is

TABLE 4. Chemical analyses of unexposed Salem Limestone and Shelburne Marble

	Salem Limestone (sample AU3)	Shelburne Marble (sample H1-3)
SiO_2	0.44	0.4
Al_2O_3	0.19	0.20
Fe_2O_3	0.10	<0.05
FeO	0.02	—
MgO	0.44	0.52
CaO	56.2	55.5
Na_2O	0.06	<0.1
K_2O	0.22	0.09
H_2O^+	0.17	—
H_2O^-	<0.01	—
TiO_2	0.01	0.02
P_2O_5	0.01	<0.03
MnO	<0.01	<0.01
CO_2	43.2	—
LOI	—	43.2
Total	101.06	99.93
S	70	—
Ba	24	22
Sr	240	302
Zr	20	51
Mn	150	234
Zn	7	648

Note: Conventional rapid-rock and XRF analyses; analysts—H. Smith, J. Lindsay, and P. Hearne, USGS. Oxide values in weight percent; trace elements in parts per million by weight.

TABLE 5. Coefficients of correlation (r) between selected ion pairs

	1 ($N = 14$)	2 ($N = 13$)	3 ($N = 13$)	4 ($N = 14$)
H^+ vs. SO_4^{2-}	0.902*	0.928*	0.932*	0.823*
H^+ vs. NO_3^-	0.865*	0.853*	0.867*	0.523
H^+ vs. $SO_4^{2-} + NO_3^-$	0.896*	0.920*	0.934*	0.890*
H^+ vs. Ca^{2+}	0.386	0.359	0.658	0.579
H^+ vs. NH_4^+	0.625	0.755	0.814*	0.685
SO_4^{2-} vs. NO_3^-	0.962*	0.928*	0.888*	0.219
SO_4^{2-} vs. Ca^{2+}	0.636	0.570	0.769	0.524
SO_4^{2-} vs. NH_4^+	0.741	0.822*	0.928*	0.832*
NO_3^- vs. Ca^{2+}	0.697	0.602	0.908*	0.758*
NO_3^- vs. NH_4^+	0.777*	0.898*	0.937*	0.517
Na^+ vs. Cl^-	0.849*	0.788*	0.976*	0.882*

Note: Based on average monthly concentrations in the wet-bucket collectors for the period June 1984 to July 1985. Columns are (1) Research Triangle Park, North Carolina; (2) Washington, D.C.; (3) Chester, New Jersey; (4) Newcomb, New York. N = no. of monthly measurements.
* Coefficients of correlation statistically significant ($P < 0.001$). Little or no correlation was observed between Na^+ or Cl^- and H^+, SO_4^{2-}, NO_3^-, Ca^{2+}, and NH_4^+.

produced by dry deposition; in the limestone, 54% to 68% of the nitrate and 64% to 72% of the sulfate is due to dry deposition (neglecting a small amount of NO_3^- and SO_4^{2-} possibly contributed by dissolution of the stone or from previously deposited salts).

In regard to dry deposition of SO_2, the uptake of this gas by limestone has been measured experimentally by exposing an oolitic limestone to SO_2 under different conditions of humidity (Spedding, 1969). The experiments show that there is a strong correlation between SO_2 uptake and relative humidity; at an atmospheric concentration of 128 ppbv SO_2 and relative humidities of 11% and 81%, the SO_2 uptake on the surface was found to be 0.069 and 0.28 $\mu g/cm^2$, respectively. The greater pore surface area (and concomitant water retention) would explain why the limestone receives more solid deposition than the marble.

A statistical analysis of possible relationships between various ion concentrations measured in the monthly wet-bucket samples uncovers some very significant correlations. Correlation analysis indicates a strong positive correlation between SO_4^{2-} and H^+ and between NO_3^- and H^+. Coefficients of correlation for these and additional selected ion pairs are given in Table 5 (a number of similar statistical relationships were noted by Bowersox and de Pena, 1980, in their study of rain chemistry in Pennsylvania; see also Pratt and Krupa, 1985). Very high correlations, statistically significant at the $P < 0.001$ level, appear between many of these pairs. Of particular interest are the very high r values found for the (SO_4^{2-}, NO_3^-) pairs at three of the four sites. Similar high correlations appear between SO_4^{2-} and NO_3^- in the limestone runoff

at the Washington, D.C., site. These high correlations suggest that the sulfate and nitrate ions (or their SO_2 and NO_x progenitors) are for some reason interdependent. Perhaps one would not expect such a high correlation between SO_4^{2-} and NO_3^- in large urban areas such as Washington, D.C., because it is likely that there would be many different and independent sources of S and N. There is a very low correlation ($r = 0.219$) between SO_4^{2-} and NO_3^- at the New York site, suggesting that the two ions are statistically independent of one another. A precipitation model for the New York site is proposed that assumes (1) the sulfate, in the form of sulfuric acid, is produced by oxidation of SO_2 that originated in the midwestern United States and (2) the nitrate, in the form of nitric acid, is produced by oxidation of nitrogen oxides derived from local sources; the local and foreign sources producing independently varying amounts of S and N compounds.

Chemical analyses of rain water collected in the wet-bucket collectors show that there is an approximately stoichiometric relationship between the H^+ and the other quantitatively important ions, that is,

$$[H^+] = 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+] - 2[Ca^{2+}]. \quad (30)$$

Thus, a certain portion of the H^+ ions in the rain water were neutralized by atmospheric NH_3 to form NH_4^+ and by calcium carbonate–containing dusts to form $Ca^{2+} + HCO_3^-$. If NH_4^+ and Ca^{2+} ions were furnished by salts such as $CaCl_2$, NH_4NO_3, etc., relation 30 would not hold. On the basis of relation 30 and the high correlation noted between H^+ and ($SO_4^{2-} + NO_3^-$) at all four sites (Table 5), it is assumed that almost all of the H^+ concentration, prior to partial neutralization by NH_3 and $CaCO_3$, is furnished by the ionization of sulfuric and nitric acid. If there is a one-to-one correspondence between SO_4^{2-} and H_2SO_4 and between NO_3^- and HNO_3, then the contribution to the rainwater acidity by these two acids can be calculated as shown in Table 6. These calculations indi-

TABLE 6. The maximum contribution of NO_3^- to the acidity of rain and rain runoff

	NO_3^- (μeq/L)	SO_4^{2-} + NO_3^- (μeq/L)	H^+ (%) as NHO_3	H^+ (μeq/L)	H^+ (%) neutralized by NH_3, CaO_3
Blank	Research Triangle Park, North Carolina				
Blank	21.8	67.4	32.3		
Wet bucket	20.1	63.9	31.5	42.7	33.2
Marble	30.3	114.2	26.5		
Limestone	44.0	181.6	24.3		
	Washington, D.C.				
Blank	45.1	127.3	35.5		
Wet bucket	33.8	119.8	26.6	72.4	39.5
Marble	58.4	221.9	26.3		
Limestone	105.9	417.2	25.4		
	Chester, New Jersey				
Blank	50.8	151.0	33.7		
Wet bucket	28.3	84.4	33.5	60.3	28.6
Marble	48.3	164.2	29.4		
Limestone	73.2	266.1	27.5		
	Newcomb, New York				
Blank	38.0	100.9	37.7		
Wet bucket	24.1	67.5	35.6	47.9	29.1
Marble	45.9	125.9	36.4		
Limestone	65.4	186.3	35.1		

Note: Assuming a one-to-one correlation of these ions with the formation of NHO_3 and H_2SO_4.

cate that a maximum of 24% to 37% of the H^+ ion in the rain at the four NAPAP monitoring sites is related to the formation of HNO_3. Amoroso and Fassina (1983, p. 78) stated that nitrate ion accounts for about 30% to 40% of the acidity measured in rainfall in the eastern part of the United States. In their review of dry deposition of N-containing species, McRae and Russell (1984, p. 188) stated, "NO_x emissions and their photochemical oxidation products are significant sources of acidic compounds in the atmosphere."

MINERALOGICAL CHARACTERIZATION OF EXPOSED MARBLE AND LIMESTONE BRIQUETTES

For this and other NAPAP consortium studies, blocks of Salem Limestone and Shelburne Marble were obtained from quarries in Bloomington, Indiana, and Danby, Vermont, respectively. The selection and procurement of these stones has been described by Ross and Knab (1984) and Ross (1985), and the unexposed marble has been characterized by McGee (1987). The marble and limestone blocks were cut into slabs measuring 5.1 × 30.5 × 61.0 cm in size and into briquettes measuring approximately 5.1 × 7.5 × 8.5 cm in size and then were placed into the test racks at five NAPAP weather monitoring sites (samples from the Steubenville site have not yet been examined). The slabs have been used in the rain-runoff studies of Reddy and coworkers (previously described) and the briquettes have been used for multiple studies (Sherwood and Doe, 1984) including those described here. The briquettes are fully exposed to the atmosphere and rest on two 1-cm diameter polypropylene rods, the only

places where the samples touch the holder. At each site, two adjacent south-facing sample racks each hold an array of 72 briquettes at an angle of 30° to the horizontal. These same racks also hold the 30.5 × 61.0 cm slabs. For our mineralogical studies the samples were removed at 1-yr intervals. Samples were placed at four of the sites (North Carolina, Washington, D.C., New Jersey, and New York) during the summer of 1984 and at the fifth site (Ohio) during the summer of 1986.

The limestone and marble briquettes exposed for one- and two-year periods were examined by light and electron optical techniques, by X-ray powder-diffraction analysis, and by energy-dispersive X-ray chemical analysis. The upper (boldly exposed) surfaces of both the limestone and marble samples show a "frosting" of very fine white powder on some of the calcite grains and a minor accumulation of black particles that resemble C soot. The fine white particles, not seen on the unexposed stone, may be calcite reprecipitated as the stone dries out from the previous rainfall. The lower (sheltered) surfaces of the briquettes show a more dramatic change; after at least 1 yr of exposure, all briquettes show a darkened, roughly circular, "spot" on the bottom surface (Fig. 2). The color of the limestone in the area outside of the "spot" is light beige; the stone within the "spot" is darker and takes on an orange tinge. The color of the marble is white, except within the "spot," the color is gray-white. For briquettes from the same site, the intensity of the color within the "spot" was greater in the stone exposed for 2 yr than in the stone exposed for only 1 yr. There was, however, a significant difference in the intensity of color within the "spot" area of briquettes from different sites but having the same exposure period. The "spot" on the limestone briquette exposed for 2 yr at the Washington, D.C., site is the most intense in color, that on the marble exposed for 1 yr at Newcomb, New York, is the least intense in color. Within the "spot" on the limestone samples, the crystallites and fossil fragments appear to be fused together by a clear coating; also the pore spaces between fossil fragments appear to be partially to completely filled (Fig. 3a). The overall appearance within the "spot" area is of recrystallized or precipitated material. Small, 10- to 35-μm diameter, black specks are sparsely scattered on the upper surfaces of the briquette. On the lower surfaces of the briquettes, however, these black particles are concentrated around the outer edges of the "spot" (Fig. 3b). To date we have been unable to identify the black specks using either X-ray powder diffraction or scanning electron microscopy. During attempts to identify these black particles by using the SEM, we found a few rounded particles with unusual surfaces. The rounded particles have spongy or glassy appearing textures, and some are almost completely covered by gypsum crystals. Energy-dispersive analyses of these particles show that they vary in composition but commonly contain Si, Ti, and Al in addition to Ca and S. The particles (Fig. 4a) are morphologically and compositionally similar to particles from auto emissions and to soots; for example, see the pho-
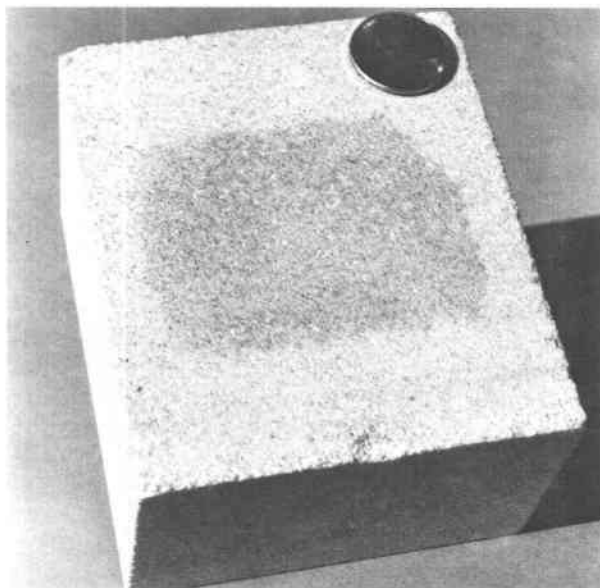
Fig. 2. Photograph of the bottom surface of a Salem Limestone briquette exposed for two years at the Research Triangle Park, North Carolina, site. The "spot" appears as the darkened area.

tomicrographs of McCrone and Delly (1973, Figs. 552, 556, 558, 570). Particles like these could be readily incorporated with the growing gypsum crystals and so probably contribute to the blackened appearance of the alteration crust that often forms on older limestone or marble buildings. It has been suggested by del Monte and Vittori (1985) that carbonaceous particles, owing to their compositions and large surface areas, may act as catalysts for the oxidation of SO_2 to sulfuric acid. In this regard, Camuffo (1986, p. 215) has presented a photograph that shows gypsum crystals that have nucleated on carbonaceous particles identical in morphology to those seen in our studies.

X-ray diffraction analysis of powdered material scraped from within the "spot" area was accomplished using a SCINTAG automated diffractometer system. With this system, we estimate that gypsum can be detected in sample powders containing somewhat less than 1 wt% of this mineral. This analysis reveals that gypsum and calcite are present in 8 out of 9 samples examined (Table 7); only in the limestone sample exposed for 1 yr in North Carolina did gypsum not appear in the X-ray pattern. Gypsum was not detected in the X-ray patterns of powders scraped from areas on the upper surface and from areas outside the "spot" on the lower surface. Trace amounts

Fig. 3. Light optical photomicrographs of Salem Limestone sample IL5-06 exposed for 2 yr at the Washington, D.C., site: (a) clear coating within the "spot" (right side of photograph) and (b) concentration of black particles around the outer edge of the "spot."
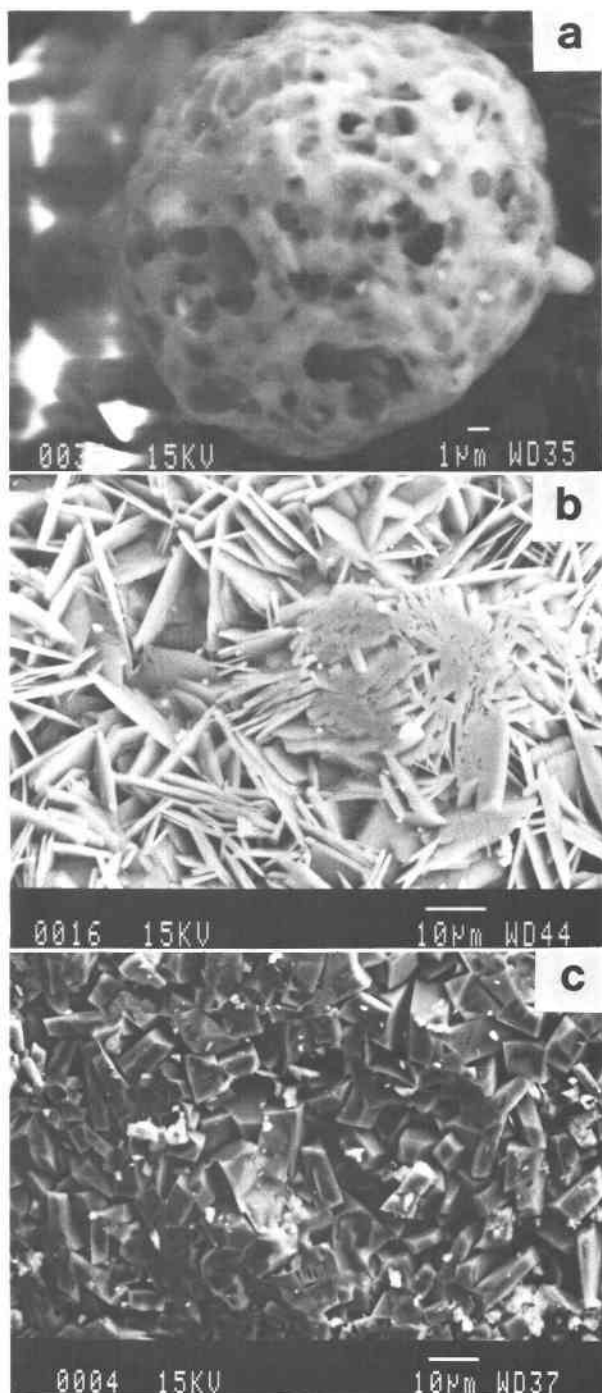
of mica and quartz were detected in two marble samples; both minerals have also been identified as present in small quantities in the unexposed stone (McGee, 1987).

Individual mineral grains were identified with the scanning electron microscope from their crystal habit and from compositional information obtained with an energy-dispersive analyzer. Quantitative electron-microprobe analysis has not yet been made because the necessary sample preparation would destroy many features of interest. SEM examination of limestone and marble samples exposed for 2 yr at the North Carolina and Washington, D.C., sites reveals that the abundance and habit of the gypsum crystals change from the center to the edges of the "spot." The gypsum crystals formed within the "spot" appear as thin, well-defined blades, as blocky-shaped crystals, or as thin plates that partially or completely coat the underlying calcite matrix (Fig. 4b). Near the center of the "spot," the bladed gypsum crystals are abundant, but in some areas the gypsum forms a thick mat of blocky, rectangular crystals (Fig. 4c). Near the edges of the "spot," the gypsum crystals are much less abundant and smaller than those seen in the central area. The appearance of the gypsum crystals is similar in both the limestone and the marble samples except that the crystals form a much thicker layer on the limestone samples.

With regard to previous NAPAP consortium studies on materials effects, Mossotti et al. (1986, 1987) showed that sulfate ion occurs within the stained area appearing on the underside of the limestone test briquettes that were exposed for 1 yr at the North Carolina, Washington, D.C., and New Jersey sites. The sulfate ion was identified by means of narrow-band X-ray photo-electron spectroscopy (XPS). X-ray powder-diffraction analysis and scanning electron microscopy further identified the source of the sulfate as gypsum. XPS spectra also showed that the calcite grains within the test stones and unexposed control stones contained very thin films of sulfate, only a few monolayers thick. Also, these XPS spectra were not quite identical to those obtained from the well-crystallized gypsum formed within the stained area of the briquettes. The shift of the spectra from the predicted position is perhaps due to strain within the monolayers, which were thought by Mossotti et al. (1987) to be some form of calcium sulfate. Mossotti et al. also reported submonolayers of N_2 on calcite surfaces; the N_2 is suggested to be due to air exposure. They found no evidence for the presence of nitrate ion in their samples.

Kingston and Rowan (1987) have also detected, with near-infrared spectral reflectance techniques, gypsum within the "spot" of the marble and limestone briquettes. They estimated, based on laboratory calibration, the following amounts of gypsum (in mg/cm²) within the "spot" after 2 yr of exposure: North Carolina, 0.28 (marble) and 0.99 (limestone); Washington, D.C., 0.93 (marble) and 1.70 (limestone); New Jersey, <0.11 (marble) and 1.51 (limestone); and New York, 0.35 (marble) and 0.05 (limestone). The amount of gypsum occurring in the limestone briquettes (except for the New York site) was found to be

Fig. 4. Scanning electron micrographs of Salem Limestone sample IL5-06 and Shelburne Marble sample N15-14 exposed for 2 yr at the Washington, D.C., site: (a) rounded particle, probably from auto emissions, found within the "spot" of the marble briquette, (b) thin-bladed crystals of gypsum coating calcite within the "spot" of the limestone briquette, (c) mat of thick blocky gypsum crystals within the "spot" of the marble briquette.

TABLE 7. Summary of mineral phases identified by X-ray powder diffraction

Sample	Exposure	Locality	Phases
		Salem Limestone within the "spot"	
HL5-02	1 year	Research Triangle Park, North Carolina	calcite (~100%)
HL5-14	1 year	Washington, D.C.	calcite + gypsum (~1%)
HL5-06	1 year	Chester, New Jersey	calcite + gypsum (~1%)
IL5-02	2 year	Newcomb, New York	calcite + gypsum (~1%)
IL5-06	2 year	Washington, D.C.	calcite + gypsum (>5%)
		Shelburne Marble within the "spot"	
G36-18	1 year	Washington, D.C.	calcite + gypsum (<1%)
G36-16	1 year	Chester, New Jersey	calcite + gypsum (~1%)
E26-19	2 year	Research Triangle Park, North Carolina	calcite + gypsum + mica (<1%)
N15-14	2 year	Washington, D.C.	calcite + gypsum + quartz + mica (~1%)

significantly greater in stones exposed for 2 yr than in those exposed for only 1 yr.

SALT CRYSTALLIZATION IN EXPOSED MARBLE AND LIMESTONE BRIQUETTES

In light of our findings and those of Mossotti et al. (1986, 1987) and Kingston and Rowan (1987), we here propose chemical models for the crystallization of various salts on the surface of or within marble and limestone in context with the atmospheric chemistry discussed above.

### The system $CaO-CO_2-H_2O-NO_2$

Johansson et al. (1986) subjected limestone, marble, and travertine samples that were isolated in closed chambers maintained at constant relative humidity to various partial pressures of SO_2 and NO_2 gas. These equilibration experiments were of 6 weeks' duration. Most significant to our present study are three of their experiments that involved the introduction of known quantities of gas into the reaction chamber maintained at 90% relative humidity: (1) SO_2 gas at a concentration of 1600 ppbv, (2) SO_2 and NO_2 gas at concentrations of 1600 ppbv and 3100 ppbv, respectively, and (3) NO_2 gas at a concentration of 3100 ppbv. After exposure to only SO_2, it was found that all samples contained incrustations of calcium sulfite hemihydrate, suggesting the solid–gas-phase reaction

$$CaCO_3 + SO_2 + \frac{1}{2}H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O + CO_2. \quad (31)$$
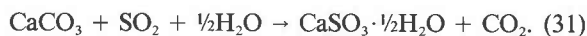
The standard free-energy change (ΔG^0) for (31) is -12.029 kcal; thus, this reaction should proceed strongly to the right, equilibrating when p_{CO_2} equals 174 atm. Of the three samples studied, the limestone contained the most calcium sulfite; in addition, it contained a very small amount of gypsum. After exposure to both SO_2 and NO_2, all three carbonate samples were found to contain large quantities of gypsum; however, no sulfite could be detected. The samples subjected to exposure to only NO_2 showed no evidence of crystalline corrosion products. If sulfuric acid formed in the experiment that utilized both SO_2 and NO_2 gases, the overall reaction may have proceeded in three steps (Liberti, 1986):

$$SO_2 + NO_2 \rightarrow SO_3 + NO \quad (32)$$
$$SO_3 + H_2O \rightarrow SO_3H_2O \quad (33)$$
$$SO_3H_2O \rightarrow H_2SO_4, \quad (34)$$
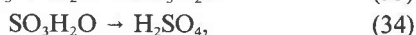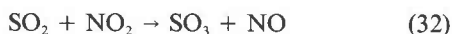
followed by reaction of calcite with sulfuric acid and water to form gypsum,

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2. \quad (35)$$
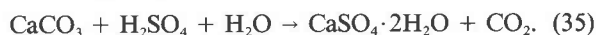
In experiments in which $CaSO_3 \cdot \frac{1}{2}H_2O$ had previously formed, the sulfite oxidized to gypsum when the samples were subjected to exposure to NO_2 at a concentration of 3000 ppbv.

The experiments of others noted in the discussion of Reaction 11 show that, at suitable gas concentrations, NO_2 in the presence of water vapor can promote the formation of sulfuric acid from SO_2. However, the studies of Harrison and Pio (1983) and Cofer et al. (1984) cast some doubt on whether these sulfuric acid–producing reactions can proceed at measurable rates at the much lower gas concentrations (15–200 ppbv SO_2 and 15–500 ppbv NO_2) found in many cities. The experiments of Harrison and Pio and of Cofer et al., however, did not duplicate the conditions of the experiments of Johansson and co-workers, particularly in regard to the presence of a calcium carbonate reaction surface.

The evidence presented in the preceding sections would suggest that nitrogen dioxide might be an important factor in the dissolution of carbonate stone in city environments. However, present information would suggest that the oxidation of dry-deposited SO_2 by O_3 on the wetted stone surfaces and pore spaces (Reaction 9) is the most important factor in sulfuric acid production (M. L. Wesely, Argonne National Laboratory, pers. comm.). To test these speculations, the experiments of Johansson et al. (1986) should be repeated using gas concentrations corresponding to those found in urban areas. Since no calcium sulfite was detected in our experimental briquettes, it would appear that all the SO_2 had been oxidized to sulfuric acid prior to reaction with the calcium carbonate stone, or if calcium sulfite did form, it was quickly and completely converted to gypsum.

Models for salt deposition within the briquettes

The models proposed here for the development of the gypsum-rich "spot" on the underside of the marble and limestone briquettes are similar to the model proposed for the origin of evaporite salt deposits in Death Valley, California (Hunt, 1960)—a model that is based on the
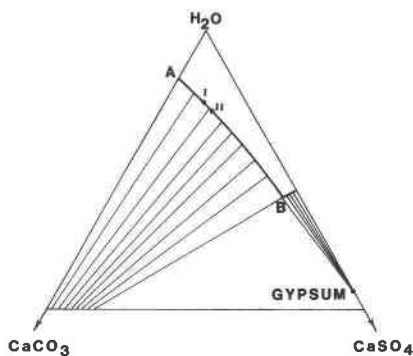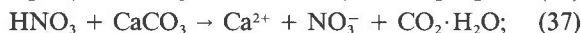
Fig. 5. Crystallization sequence of calcite and gypsum in the ternary system $CaCO_3$-$CaSO_4$-H_2O. Compositions are not plotted to scale. Case I (marble) and Case II (limestone) are for solutions saturated with respect to calcite; SO_4^{2-} concentrations are from Table 3 (Washington, D.C., site).

sequence of salts observed to crystallize from a progressively more concentrated solution.

The marble and limestone briquettes have a total volume of 324.8 cm³ and an average H_2O assessable porosity of 0.277 and 17.45%, respectively (porosity measurements made by G. R. Olhoeft, U.S. Geological Survey). These porosities correspond to an H_2O assessable volume of 0.90 mL for the marble briquettes and 56.7 mL for the limestone briquettes. Our models assume that (1) the SO_4^{2-} and NO_3^- ions reported in the runoff from the marble and limestone slabs (Table 6) form by the reaction of sulfuric and nitric acid with marble and limestone, namely,

$$H_2SO_4 + CaCO_3 \rightarrow Ca^{2+} + SO_4^{2-} + CO_2 \cdot H_2O \quad (36)$$
$$HNO_3 + CaCO_3 \rightarrow Ca^{2+} + NO_3^- + CO_2 \cdot H_2O; \quad (37)$$

(2) the H_2SO_4 and HNO_3 not carried to the stone by the rainwater is formed within the stone by oxidation of the solid-deposited SO_2, NO, and NO_2; (3) the briquette pore space is filled with rainwater at the termination of each rain event; (4) the volume of water on the surface and enclosed within the pore space of the stone becomes saturated with respect to calcite at the end of the rain event; (5) the volume of water slowly evaporates between rain events with the last water disappearing as a small volume or drop on the underside of the briquette; and (6) during evaporation, heterogeneous equilibrium is maintained as the dissolved salts in solution precipitate on the surface or within the pore surface of the stone.

The solubilities, in pure water at 25 °C, of salts pertinent to these models are as follows: (1) calcite ($CaCO_3$), 0.040 g/L (calculated for p_{CO_2} = 342 ppmv), (2) gypsum ($CaSO_4 \cdot 2H_2O$), 2.41 g/L (measured, Weast, 1984), and (3) calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], 2660 g/L (measured, Weast, 1984). In proposing these models, we have ignored the role of the other ions found in the runoff experiments, that is, Mg^{2+}, Na^+, K^+, NH_4^+, and Cl^-. Compared to Ca^{2+}, SO_4^{2-}, NO_3^-, and H^+, these ions are in much lower concentration in the runoff solutions and will
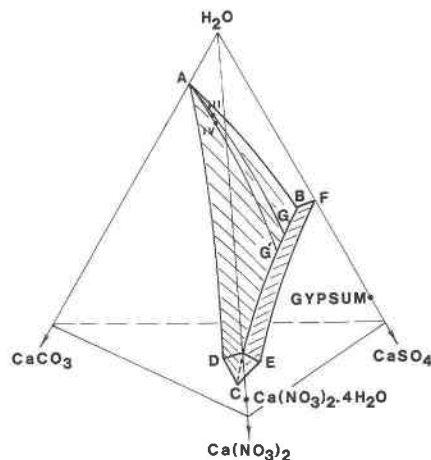

Fig. 6. Crystallization sequence of calcite, gypsum, and $Ca(NO_3)_2 \cdot 4H_2O$ in the quarternary system $CaCO_3$-$CaSO_4$-$Ca(NO_3)_2$-H_2O. Compositions are not plotted to scale. Case III (marble) and Case IV (limestone) are for solutions saturated with respect to calcite; SO_4^{2-} and NO_3^- concentrations are from Table 3 (Washington, D.C., site).

generally play a minor role in the phase equilibria discussed below.

Model system $CaCO_3$-$CaSO_4$-H_2O. After cessation of a rain event at the Washington, D.C., site, the volumes of water filling the pore space within the marble (case I) and limestone briquettes (case II) will have average SO_4^{2-} ion concentrations of 163.5 and 311.3 μeq/L, respectively (Table 3). These initial concentrations are depicted as points I (marble) and II (limestone) in Figure 5, which shows the ternary system $CaCO_3$-$CaSO_4$-H_2O. As evaporation proceeds, the saturated solutions will start to precipitate calcite, and the solutions will change composition as described by the calcite solubility curve A–B. When point B is reached, the solutions will become saturated with respect to gypsum as well as calcite. Upon further evaporation, calcite and gypsum will coprecipitate until the solutions, now of fixed composition B, disappear.

Model system $CaCO_3$-$CaSO_4$-$Ca(NO_3)_2$-H_2O. The crystallization sequence shown in Figure 6, depicting the quarternary system $CaCO_3$-$CaSO_4$-$Ca(NO_3)_2$-H_2O, applies when the $Ca(NO_3)_2$ component is added to the above described ternary model. On completion of a rain event at the Washington, D.C., site, the solution in the marble (case III) is assumed to have average SO_4^{2-} and NO_3^- concentrations of 163.5 and 58.4 μeq/L, respectively; the limestone (case IV), is assumed to have SO_4^{2-} and NO_3^- concentrations of 311.3 and 105.9 μeq/L, respectively (Table 3). The initial evaporation starts at points III and IV (Fig. 6), and as calcite crystallizes, the compositions of the two solutions change as described by the curves A–G and A–G′ lying on the calcite solubility surface A–B–C–D. At points G and G′, which also lie on the curve B–C at the intersection of the calcite and gypsum solubility surfaces, A–B–C–D and B–C–E–F, respectively,

TABLE 8.   Precipitation model in the system $CaCO_3$-$CaSO_4$-$Ca(NO_3)_2$-H_2O

	Case III (marble)	Case IV (limestone)
Volume of solution (mL) at first appearance of calcite	0.900	56.7
Volume of solution (mL) at first appearance of gypsum	0.0053	0.631
Amount of calcite (mg) precipitated along curve A–G or A–G′	0.0358	2.243
Volume of solution (μL) at first appearance of $Ca(NO_3)_2 \cdot 4H_2O$	0.0023	0.266
Amount of calcite (mg) precipitated along curve G–C or G′–C	0.0002	0.025
Amount of gypsum (mg) precipitated along curve G–C or G′–C	0.0127	1.519
Total calcite (mg) precipitated on complete evaporation	0.0360	2.268
Total gypsum (mg) precipitated on complete evaporation	0.0127	1.520
Total $Ca(NO_3)_2 \cdot 4H_2O$ (mg) precipitated on complete evaporation	0.0062	0.709

Note: For marble and limestone briquettes exposed at Washington, D.C., monitoring site (see Fig. 6).

gypsum begins to crystallize with calcite. On continued evaporation, the two solutions now change composition along curve segments G–C and G′–C as they coprecipitate calcite and gypsum. When the solution compositions reach point C, a third solid phase, $Ca(NO_3)_2 \cdot 4H_2O$ (nitrocalcite), begins to crystallize along with calcite and gypsum. Here the compositions of the solutions remain fixed until evaporation ceases. The calculated volume changes of the evaporating solutions and the amount of salts precipitated in the briquettes at various stages in the evaporation sequence for this quarternary model are given in Table 8. For the purpose of constructing this model, and the ternary model described above, the activity coefficients of the ions and the activity of water are assumed to be unity, and complexing is assumed not to occur.

In these models, it is noted that the $CaCO_3$-saturated solutions continuously precipitate calcite, whereas gypsum is precipitated only after evaporation is nearly complete (Table 8). Also, as evaporation proceeds, the solution migrates by gravity to the lower surface of the briquette, and it is here that the last residual liquid precipitates gypsum and produces the gypsum-rich "spot" described above. Note that the last 0.005 mL of solution precipitates gypsum in the marble, but the last 0.6 mL precipitates gypsum in the limestone (Table 8). With each rain event, some gypsum will be deposited and some of the previously crystallized salts will be washed away. However, incomplete washing of the underside of the stone will permit the slow build up of gypsum over time. The reprecipitation of calcite within the pore space also occurs and with time may tend to reduce the pore volume and perhaps cause the limestone to be less susceptible to acid dissolution. After complete evaporation, even at very low humidities, there will be a very thin layer of absorbed solution on the surface of the mineral grains. The monolayers of sulfate found by Mossotti et al. (1986, 1987) may represent the "residual" of this adsorbed solution, most of the volatile water being removed in the vacuum chamber.

No nitrocalcite has yet been observed on any of our test stones. Its nonappearance is probably due to the fact that this salt is deliquescent and readily absorbs water from air to form a liquid when the relative humidity of the air is greater than that of a solution saturated with respect to $Ca(NO_3)_2$. This value is 50.0% R.H. (relative humidity) at 25 °C according to Amoroso and Fassina (1983, p. 42). For example, at a relative humidity of 65.7% (the average for Washington, D.C., in 1985–1986, Table 2) any crystals of $Ca(NO_3)_2 \cdot 4H_2O$ that are present in the stone will absorb water until a solution is formed that has a vapor pressure matching that of the outside air. It is suggested that the very soluble calcium nitrate may seldom precipitate in the humid atmospheres of the eastern United States; the ions will generally remain dissolved in the absorbed water on the stone surface and within the pore space. Salts such as $CaCl_2 \cdot 6H_2O$ (antarcticite) and $MgCl_2 \cdot 6H_2O$ (bischofite), having equilibrium relative humidities of 29% and 33% (Amoroso and Fassina, 1983, p. 42), respectively, should also not crystallize in humid climates. However, salts such as KNO_3, $MgSO_4$, Na_2SO_4, KCl, $(NH_4)_2SO_4$, NH_4Cl, NaCl, and $NaNO_3$, having deliquescence points of 92, 91, 86, 85, 80, 77, 76, and 74% R.H., respectively (Amoroso and Fassina, 1983, p. 117), could commonly precipitate in humid atmospheres if the concentration of these salts within the stone is high enough to saturate the residual liquid. As yet, we have not detected any of these salts within our test stones.

It is useful to compare the precipitation models described above to those proposed by Lewin (1982); see also Amoroso and Fassima (1983, p. 28–43). Lewin's "efflorescence," or surface-crystallization model applies when the pore space connecting to a stone surface is continually filled with a solution saturated with respect to one or more salts. As evaporation occurs from the surface, salts will deposit at or very close to this surface and will appear as an efflorescence (Amoroso and Fassina, 1983, p. 29, Fig. 21). For surface crystallization to continue, the pore space must be continually replenished with saturated solution as evaporation proceeds. The "spot" or "efflorescence" observed on the underside of the test limestone and marble briquettes is an example of surface or near-surface crystallization of gypsum and calcite. Gravity ensures that the pore space near the lower surface of the briquettes will remain filled with solution as evaporation proceeds.

Lewin's second model, the "subflorescence" or subsurface crystallization model, applies when there is liquid-free pore space lying between the stone surface and the volume of saturated solution situated within the stone (Amoroso and Fassina, 1983, p. 32, Fig. 25). If this liq-

uid-free pore space can conduct water vapor from the saturated solution to the stone surface, salts will crystallize inside the stone in the region where evaporation takes place. This "subflorescence" model is represented in our study by the continuous precipitation of calcite from the volume of saturated calcium carbonate solution included within the briquette as it shrinks away from the top and side surfaces. Initially calcite will precipitate on these surfaces, but as the pore fluid recedes away from these surfaces, calcite will form internally to the stone at the solution-vapor interface. Through most of the evaporation process the solution is undersaturated with respect to gypsum; thus, this mineral precipitates only when the last residual solution is about to disappear from the underside of the briquettes. Here, surface or near-surface crystallization of gypsum occurs.

DISCUSSION

Stone deterioration appears in a variety of forms and is caused not only by the effects of atmospheric pollution, but by natural geochemical and physical processes—slow dissolution by rain water, salt deposition and recrystallization, freeze-thawing cycles, spalling, etc. In order to evaluate man's contribution to stone damage, it thus is necessary to distinguish the anthropogenic effects from those caused by these natural processes. Several current studies (NAPAP, 1987) are attempting to evaluate the anthropogenic effects through careful monitoring of stone damage at the five experimental sties where atmospheric conditions are also measured. For example, important stone-weathering studies have been undertaken by Reddy (1987) and Reddy and Youngdahl (1987). They find that the stone recession caused by slow dissolution of $CaCO_3$ from the limestone and marble surfaces is directly proportional to (1) the amount of rainfall and (2) the H^+ loading onto the stone surface. Youngdahl (1987) found, through weight-loss measurements of the test stones, that the marble loss at the North Carolina, Washington, D.C., New Jersey, and New York sites averaged 0.33 g per year per briquette for both the first and second year of exposure, whereas the respective limestone loss per briquette averaged 1.59 g the first year and 0.57 g for the second year.

Previous studies have suggested that stone damage is more severe in urban areas than in rural areas, the former being considered the more polluted. For example, Honeyborne and Price (1977) conducted exposure experiments with a fine-grained oolitic limestone at a rural and an urban site in Great Britain. Their first set of experiments (1955–1965) gave a stone loss of 0.31 wt% per year for central London and 0.12 wt% for rural Garston; the second set of experiments (1957–1965) using a better-quality stone gave losses of 0.23 and 0.10 wt%, respectively, for London and Garston. Other studies of this type have been reviewed by Jaynes and Cooke (1987). The first exposure study to come to our attention where stone damage was correlated with concurrent atmospheric

monitoring is that of Jaynes and Cooke (1987). They placed samples of two types of oolitic limestone at 25 sties in southeast England, including greater London and outer rural areas. A major conclusion derived from this two-year study was that the stone weight loss was significantly higher in central London than in the provincial centers, and both were higher than in rural areas. Jaynes and Cooke (1987, p. 1621) stated that "while these results are not always unequivocal they do support the notion that weathering is accelerated as a consequence of atmospheric pollution in urban areas." For definitive results, the study of Jaynes and Cooke should be continued for several more years.

A relationship between stone recession and apparent air pollution has also been demonstrated through retrospective studies of weathering of marble tombstones. Husar et al. (1985), in a study of tombstones in the northeastern United States, reported a linear relationship between stone erosion rates and estimated SO_2 concentrations; the highest values were found in the city centers. Feddema and Meierding (1987) examined marble tombstone erosion in the greater Philadelphia area. They found that the surface recession rates of tombstones located in the center of the city are an order of magnitude greater than the recession rates of tombstones located within rural areas located 20 km away. They also stated that SO_2 gas appears to be the most damaging pollutant, as indicated by the presence of gypsum within the tombstones located in the urban areas. Thus, evidence has accumulated to show that limestone and marble are much more affected by urban pollution than by the pollution found in rural areas. Therefore, in regard to acid precipitation damage throughout the United States, the effects of atmospheric pollution should not be entirely attributed to the large midwestern coal-fired power plants—local sources contribute significantly to stone damage.

As shown in Tables 3 and 6, the average concentration of nitrate and sulfate ions in the wet-bucket rain water is 46% of the average concentration of these ions in the marble and limestone runoff. This implies that dry deposition upon the stone is the more important factor with regard to stone damage. Thus, the differences in ambient concentrations of gases at the various sites (Table 2) might be more significant than the differences in the wet-bucket chemistry.

Much emphasis is placed on stone-recession measurements as a surrogate for stone damage. However, the most significant damage may not be due to the removal, over a period of many years, of a few millimeters of calcium carbonate from the vertical surface of limestone building blocks, but rather the destruction of stone through the precipitation and recrystallization of salts. The visual and economic effects of salt damage are amply documented in the references given in the first paragraph of this paper that describe the nature of acid precipitation damage on historic buildings and monuments of Europe.

Gypsum, the most common salt affecting building stone,

generally forms by reaction of $CaCO_3$ and atmospherically derived H_2SO_4. However, several other kinds of salts, plus gypsum, may form under special conditions through the hydraulic action of ground water or sea water underlying building foundations; stone decay in Venice is greatly promoted by sea water rising into the lower levels of buildings. A good example of damage caused by gypsum is found in many of the marble balusters forming the balustrade around the patio and along the west side of the Pan American Union Building located in Washington, D.C. (Bruce R. Doe, U.S. Geological Survey, pers. comm.). The black areas in the photograph (Fig. 7) of one of these balusters are composed of a mixture of gypsum, calcium carbonate, and carbonaceous material, the latter giving the black color to the stone. In the upper part of the baluster the outer soot-rich scale has spalled off exposing a thick gypsum-rich underlayer (white areas, Fig. 7). These gypsum and soot-rich layers not only give the building a very ugly appearance, but being thick and soft, are subject to intense spalling and hence stone loss.

Salt build up appears to occur in special places in a building. For example, gypsum forms within the balusters of the Pan American Union Building but not within the marble railing which are supported on top of the balusters. The model presented previously for gypsum precipitation and build up within the marble and limestone briquettes may be used to postulate a mechanism of gypsum deposition within these balusters. Consider the whole balustrade structure, including the massive railings, to be saturated with rainwater at the end of a rain event. As evaporation proceeds, the dissolved salts in the rainwater will become more concentrated, and the water will move via the pore spaces and along the stone surfaces to the lower parts of the structure. If final evaporation occurs within the baluster, most salts will be deposited there. Also, since the balusters are partly protected from washing by the railing above, the gypsum deposit can build up with each rain event. An understanding of the damage that is caused by salt build up within calcium carbonate stone is not new; many centuries ago, architects learned to design sills, cornices, etc. with "drips" to carry off the rain water so that the dissolved salts would not end up crystallizing within the stone.

Much needs to be done in order to correlate and interpret the many laboratory studies that have been made on mechanisms and rates of formation of acids that can attack stone. Many of these experiments employed gas concentrations, pH values, catalysts, etc., that do not closely correspond to conditions found in most urban environments (for example, see Amoroso and Fassina, 1983, p. 205). It is not at all clear which chemical reactions are the most important in acid production in urban versus rural environments and why there is apparently more stone damage within the cities and less in the countryside. For a more complete understanding of the effects on stone weathering by the chemically complex atmosphere, more complete and precise measurements of gas, free radical,

Fig. 7. Photograph of salt damage to one of the marble balusters in the balustrade of the patio and west side of the Pan American Union Building, Washington, D.C. The black area is an outer layer composed mostly of gypsum mixed with soot. The white area is composed mostly of gypsum.

and solute concentrations in a variety of urban and rural environments are needed. With good environmental data, chamber experiments can be designed that more closely duplicate real conditions.

Important questions should be answered by subsequent acid deposition research. Would acid production and stone damage in the urban environment be significantly reduced by reducing sulfur dioxide emissions if the concentration of other polluting gases, oxidants, and catalysts remained the same or increased? Would a significant decrease in the atmospheric concentrations of SO_2 raise the ozone concentrations (see Reaction 9), with a concomitant increase in forest damage? Would it be more cost effective to reduce the concentration of some of the other pollutants instead of SO_2?

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