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7. Contribution No. 430, from Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600025, India.

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Acid Precipitation in the Northeastern United States: *p*H and Acidity

Abstract. *Detailed chemical analyses reveal that acid precipitation* ($pH < 5.6$) *in the northeastern United States is caused by the strong mineral acids sulfuric and nitric. There is a large array of other proton sources in precipitation, weak acids and Brønsted acids; however, although these other acids contribute to the total acidity of precipitation, they have a minimal influence on the free acidity (ambient* pH*) of acid precipitation.*

Precipitation in northeastern United States has a mean *p*H of about 4 (*1, 2*). Atmospheric CO_2 in equilibrium with precipitation would not be expected to produce a *p*H less than 5.6. Thus it has been hypothesized that SO_2 and NO_x (NO and NO_2) from the combustion of fossil fuels are precursors of strong acids in precipitation (*1–4*). This phenomenon of high acidity is not unique to the United States; large areas of Scandinavia downwind of dense industrial complexes receive precipitation with a *p*H of 4 or lower (*3, 4*).

Elucidation of the acid precipitation ($pH < 5.6$) phenomenon depends upon the answer to the following question: What chemical compounds found in precipitation cause acidity, and to what degree? This question is best answered by complete chemical analysis of the precipitation. Analysis of over 1500 precipitation samples in northern New Hampshire showed that the ambient *p*H of precipitation was caused by the strong acids H_2SO_4 and HNO_3 (*1, 2*). This finding was also the conclusion of workers in Scandinavia (*4*). Frohliger and Kane (*5*), however, concluded that acid precipitation was caused by unidentified weak acids. This conclusion was based solely on the determination of *p*H and total acidity in 26 precipitation samples collected during one winter in Pittsburgh, Pennsylvania. The specific deficiencies in their approach have been dealt with elsewhere (*6*). We present here results of an investigation on the relative effect of strong acids (for example, H_2SO_4 and HNO_3), weak acids (for example, organic acids and H_2CO_3), Brønsted acids (for example, dissolved Al, dissolved Fe, and NH_4^+), and particulate matter on the free and total acidity of precipitation as determined by titration, chemical analysis, and equilibrium calculations.

Precipitation samples (rain or snow only, no dry deposition) were collected in thoroughly rinsed, acid-washed containers, plastic for inorganic analysis and glass for organic analysis. Samples were stored at 4°C until analyzed, usually less than 1 week for the inorganic constituents. Organic acids were analyzed immediately after individual storms. There was no significant change in the inorganic composition of these precipitation samples when stored at 4°C if the *p*H of the sample was < 5 (*7*).

Analyses for Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, Fe^{3+}, and Mn^{2+} were carried out on an atomic absorption spectrophotometer (Perkin-Elmer model 403) equipped with a graphite furnace (Perkin-Elmer HGA 2100). Standard procedures adapted for use with a Technicon Autoanalyzer were used for the analysis of NH_4^+, NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl^-, and H_4SiO_4 (*7*). We determined organic acids (C_1 to C_{10} volatile carboxylic acids) by using column and gas chromatography (*8*) and mass spectrometry (*9*). Ambient *p*H determination and titrations to *p*H 9.0 were carried out with a *p*H meter (Sargent-Welch PBL), equipped with a combination electrode. The measurement of *p*H with this system was accurate to ± 0.03 *p*H unit, which introduces a 6 to 7 percent error in the calculation of the $[H^+]$. Therefore, at *p*H 4.00 $[H^+]$ would be 100 ± 7 μeq/liter.

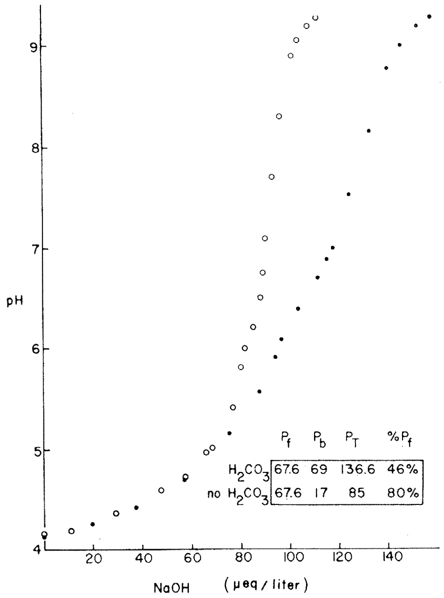

Fig. 1. The effect of H_2CO_3 on the free, bound, and total acidity of precipitation. The open circles represent an aliquot from a sample from which the H_2CO_3 has been removed by N_2 purging. The closed circles represent an aliquot of the same sample with the H_2CO_3 present. The symbols P_f, P_b, and P_T represent, respectively, the concentration of free protons, bound protons, and total protons (in microequivalents per liter); P_b is determined by difference, $P_T - P_f$. The symbol $\%P_f$ represents the percentage of the total protons that are free.

For all precipitation samples that we have collected in the rural northeastern United States the *p*H has been < 5. Since H_2CO_3 does not contribute to the free acidity below *p*H 5 (*10*), we excluded this acid by flushing the samples with N_2 so as not to mask other possible contributors (*11*). The actual effect of H_2CO_3 on the free and total acidity is demonstrated by the following experiment (Fig. 1). Two aliquots of the sample were titrated identically. In one (open circles in Fig. 1), all of the H_2CO_3 was removed by the bubbling of N_2 through the sample prior to titration. During the titration of this sample, a N_2 atmosphere was maintained over the surface. Thus the influence of H_2CO_3 was eliminated, and the effect on the free acidity could be determined. In the second (closed circles in Fig. 1), no N_2 was used; that is, the titration was done under a normal laboratory atmosphere.

Two conclusions can be drawn from this experiment. (i) Carbonic acid has no influence on the measured *p*H of this precipitation sample and indeed has no effect on the measured *p*H of any aqueous sample with a $pH < 5$ that is in equilibrium with the atmosphere (*10*). (ii) Although it has no effect on the free acidity, H_2CO_3 has a potentially large effect on the total acidity when titrated to *p*H > 5 because of the increasing solubility of CO_2 as the *p*H increases. The solubility of CO_2 at $pH < 5$ is 20 μeq/liter and at *p*H 9 is 5000 μeq/liter (*10*). If H_2CO_3 were removed, such titrations would reflect exchange rates of CO_2 between the atmosphere and the water sample as influenced by stirring and other operations, and would be totally misleading with respect to the proton chemistry of the initial sample.

In an aqueous medium, such as precipitation, protons may exist in two states, free and bound, and together they constitute the total acidity. Free protons constitute the measurable pH as determined with an electrode. Bound protons have no influence on the pH and can be determined only by the addition of a strong base (for example, NaOH) to the aqueous system (titration). Thus a precipitation sample that has 100 μeq/liter of free protons (measured pH of 4.0) and a total acidity of 150 μeq/liter would have 50 μeq/liter of bound protons.

For a strong acid, such as HNO_3, there are no molecules of undissociated acid in an aqueous solution. Thus no sources of bound protons exist, and the total acidity of an HNO_3 solution is equal to the measured, free acidity. For a weak acid, such as H_2CO_3, a partial and pH-dependent dissociation occurs. Therefore, there is a contribution to both the free acidity and the bound acidity of the solution at $pH > 5$, but at $pH < 5$ the only contribution is to the total acidity and there is no contribution to the free acidity.

Another source of protons is the Brønsted acids. Although these acids certainly contribute to the total acidity in a titration to pH 9, they do not contribute to the free acidity below pH 5 at the concentrations typical in precipitation (*10*).

Free acidity (pH) and total acidity were determined for precipitation samples from Ithaca, New York (a semiurban community), Hubbard Brook Experimental Forest, New Hampshire (a forested area in the White Mountains), and Paul Smith, New York (a forested area in the Adirondack Mountains) (*12*). Over 200 wet samples were collected from February to September 1975. Precipitation from the two rural areas was consistently between pH 3.5 and 4.5; the free acidity was 80 to 100 percent of the total acidity, indicating low quantities of weak and Brønsted acids. Samples from Ithaca had the same range of pH, but the free acidities were only 50 to 80 percent of the total acidity, indicating a greater abundance of weak and Brønsted acids. These data indicate that low pH occurs in both semiurban and rural areas throughout the northeastern United States. Semiurban areas apparently have additional amounts of weak and Brønsted acids in their atmospheres that contribute to the total acidity but do not contribute significantly to the pH. To test this hypothesis, analyses of weak and Brønsted acids were conducted to determine if these acids were contributing to the pH or just to the total acidity. If the latter is the case, then acid precipitation is a dilute solution of strong acids.

Table 1. Sources of acidity in acid precipitation collected in Ithaca, New York, on 11 July 1975.

Component	Concentration in precipitation* (mg/liter)	Contribution to: Free acidity at pH 3.84 (μeq/liter)	Contribution to: Total acidity in a titration to pH 9.0 (μeq/liter)
H_2CO_3	0.62	0	20†
Clay	5	0	5
NH_4^+	0.53	0	29
Dissolved Al	0.050	0	5
Dissolved Fe	0.040	0	2
Dissolved Mn	0.005	0	0.1
Total organic acids	0.43	2	5.7
HNO_3	2.80	40	40
H_2SO_4	5.60	102	103
Total		144	210

*See (*15*). †See (*16*).

We determined organic acids in 20 precipitation samples representing 15 storm events in two locations—Ithaca and Hubbard Brook. Of the 20 samples, 8 showed no detectable acids (< 1 μeq/liter), whereas 12 had trace amounts. We identified acetic, butyric, formic, lactic, succinic, glycolic, propionic, and isocitric acids; the sum of the concentrations ranged from 1.1 to 15.6 μeq/liter. Since all of these are weak acids (with pK values of about 4, where pK is the negative logarithm of the equilibrium constant), the total contribution to the free acidity of a sample at an ambient pH of 4.0 would be from 0 to 10 percent. No organic acids were detected in dry deposition samples, thus suggesting that organic acid deposition is an aqueous phenomenon.

In a titration to pH 9 the following reaction will occur above pH 8 (*10*):

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

Approximately 30 to 50 percent of the NH_4^+ will be converted to NH_3 by pH 9. Therefore, at an original concentration in the sample of 30 μeq of NH_4^+ per liter (*13*), there will be a contribution of 10 to 30 μeq/liter to the total acidity. However, since NH_4^+ does not begin to release protons until above pH 8, NH_4^+ will have no effect on the free acidity (Table 1).

The concentration of dissolved Al in our precipitation samples varied from 1 to 4 μmole/liter (*13*). In a titration between pH 4 to 9, Al can "consume" about three times its molar concentrations of OH^- (*10*). At pH 4 it exists primarily as Al^{3+}, and at pH 9 it exists as the soluble $Al(OH)_3$ complex. Therefore, if the initial concentration were 2 μmole/liter, then the potential contribution to the total acidity would be 6 μeq/liter. As in the case of NH_4^+, although dissolved Al exerts an influence on the total acidity, there is no influence on the free acidity at pH 4 (Table 1).

The aqueous chemistry of dissolved Fe in a titration is similar to that of dissolved Al with the exception that Fe will "consume" two equivalent amounts of OH^- because at pH 4 it exists as the $Fe(OH)^{2+}$ complex, and at pH 9 it is present as the solid $Fe(OH)_3$. If the concentration of Fe were about 1 μmole/liter in the precipitation (*13*), the possible contribution to the total acidity would be 2 μeq/liter (*10*) (Table 1).

The concentrations of dissolved Mn and dissolved silica are so low (0.1 and 0.4 μeq/liter, respectively) (*13*) that they contribute a negligible amount to the total acidity and make no contribution to the free acidity (Table 1).

If the particulate matter in precipitation is entirely montmorillonite [the exchange capacity of montmorillonite is 10^5 μeq per 100 g (*14*)], the expected contribution to the total acidity from 10 mg per liter of particulates (Table 1) in a precipitation sample would be 10 μeq/liter (*13*). There would be no contribution to the free acidity (*14*).

From the analysis of all proton sources in precipitation (strong, weak, and Brønsted acids) we conclude that the primary sources of H^+ that cause acid precipitation in widespread areas of the northeastern United States are the strong mineral acids H_2SO_4 and HNO_3 (Table 1). All other acids, with the exception of a small and irregular contribution from organic acids, contribute only to the total acidity (Table 1). When one is concerned with the sources of acidity in aqueous solutions, measurements of only pH and total acidity are obviously not adequate (6). Detailed chemical analyses of all components that could contribute to either the pH or the total acidity also must be carried out.

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9. Mass spectrometric confirmation of organic acids was achieved with the use of a gas chromatograph–mass spectrometer interface.
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11. A three-port, round-bottom flask was used for the titrations. One port held the *p*H electrode, one held an aerator through which N_2 flowed, and the other was left open for the addition of titrant (NaOH). At all times a positive pressure of N_2 was maintained in the flask to exclude H_2CO_3 from the sample.
12. The precipitation samples from the Adirondack Mountains were collected and analyzed by C. Schofield, Natural Resources Department, Cornell University.
13. The values for the concentrations of Al^{3+}, Fe^{3+}, Mn^{2+}, H_4SiO_4, particulates, and NH_4^+ were selected from an Ithaca storm that had concentrations representing the yearly mean of composition for Ithaca precipitation. The rural precipitation samples (Hubbard Brook and Adirondack Mountains) had substantially lower concentrations.
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15. The chemical composition (concentrations given here are in microequivalents per liter), including *p*H, of this storm falls well within the range of that of storms in the Ithaca area (*1*, *2*). The inorganic composition is as follows: *p*H, 3.84; Ca^{2+}, 13.0; Mg^{2+}, 3.0; Na^+, 1.2; K^+, 0.26; NH_4^+, 29.4; NO_3^-, 45.2; SO_4^{2-}, 116.7; Cl^-, 19.2; PO_4^{3-}, 0.25; H_4SiO_4, 1.6; Al^{3+}, 3.8; Fe^{3+}, 0.72; and Mn^{2+}, 0.19. The following organic acids were present: formic, 0.4; acetic, 2.1; propionic, 1.0; butyric, 0.6; and glycolic, 1.6. These organic acids were determined by gas chromatography (*8*) and confirmed by mass spectrometry (*9*). Their total concentration in the sample is 5.7 μeq/liter. Their contribution to the *p*H of the sample is 2 μeq/liter, since they are only partially dissociated at this *p*H. The total concentration of cations is 196.1 μeq/liter. The total concentration of anions is 183.4 μeq/liter. The difference between the two is ~ 6 percent, which would be the equivalent of 0.03 *p*H unit. The contribution to the free acidity of NO_3^- and SO_4^{2-} is determined by a stoichiometric formation process in which a sea salt anionic component is subtracted from the total anions (*2*).
16. In our titration, H_2CO_3 was removed from the system by N_2 purging. If the H_2CO_3 had not been removed and the sample was then isolated from the atmosphere, only the H_2CO_3 initially in the sample (0.62 mg/liter) would be titrated, resulting in a contribution of 20 μeq/liter to the total acidity. If the system were at equilibrium with the atmosphere, there could have been a contribution of 5000 μeq/liter to the total acidity and no contribution to the free acidity in a titration from *p*H 4 to 9.
17. We thank D. Kuehl, Environmental Protection Agency National Water Quality Laboratory, Duluth, Minn., for his assistance in confirming the organic acids by mass spectrometry. We thank Drs. N. M. Johnson and J. J. Morgan for critical comments. This report is a contribution to the Hubbard Brook Ecosystem Study. Financial support was provided by the National Oceanic and Atmospheric Administration and by the National Science Foundation. The Hubbard Brook Experimental Forest is operated by the U.S. Department of Agriculture Forest Service, Upper Darby, Pa.

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Spherules on Shatter Cone Surfaces from the Vredefort Structure, South Africa

Abstract. *Spherical particles of silicate composition occur on the surface of some shatter cones from the collar rocks around the Vredefort structure, South Africa. They are best developed on shatter cones from a shale horizon but are also found on more arenaceous rocks and banded ironstones. They have not been found on shatter cones from the purer quartzites.*

Glassy and metallic spherules have been reported in lunar fines and impactite glasses from terrestrial craters by many workers and may be genetically related to meteor impact (*1*). I report here, to my knowledge for the first time, the presence of spherical and other structures on the surfaces of shatter cones. The shatter cones were collected from rocks of the Witwatersrand sediments which form the collar around the Vredefort structure and from Transvaal sediments in the rim syncline around the structure (*2*). The spheres are best developed on shatter cones in the Kimberley shales; they also occur in shatter cones from banded ironstones and argillaceous sandstones but appear to be absent or very poorly developed on quartzite specimens. They were discovered during a study of shatter cone surfaces with a scanning electron microscope (SEM).

The spheres range in diameter from 0.1 to 10 μm but are generally less than 5 μm. On the shale host rock they tend to be perfectly spherical (Fig. 1a) or to form parts of spheres. Cooling cracks can sometimes be seen on the surfaces (Fig. 1b), and small parasite spheres grow off them. The spheres tend to nestle in grooves or holes lower than the general surface where clusters of them can sometimes be seen (Fig. 1c), but they also occur on ridges (Fig. 1d). On shatter cones from other rock types the spheres have a more irregular lumpy form (Fig. 1e), which deteriorates to a rounded aggregate of particles in the purer quartzites (Fig. 1f). Doublets (Fig. 1g), hemispheres, and cup-shaped particles (Fig. 1h) are also found. When rotated into suitable orientations, the spheres are seen to be welded to the shatter cone surface (for example, Fig. 1e) and often have minute fragments adhering to them. Preliminary analyses of the spherules with an energy-dispersive x-ray analysis system attached to the SEM show that they have an elemental composition similar to that of the host rocks (*3*).

The presence of the spherules clearly indicates that extremely rapid melting

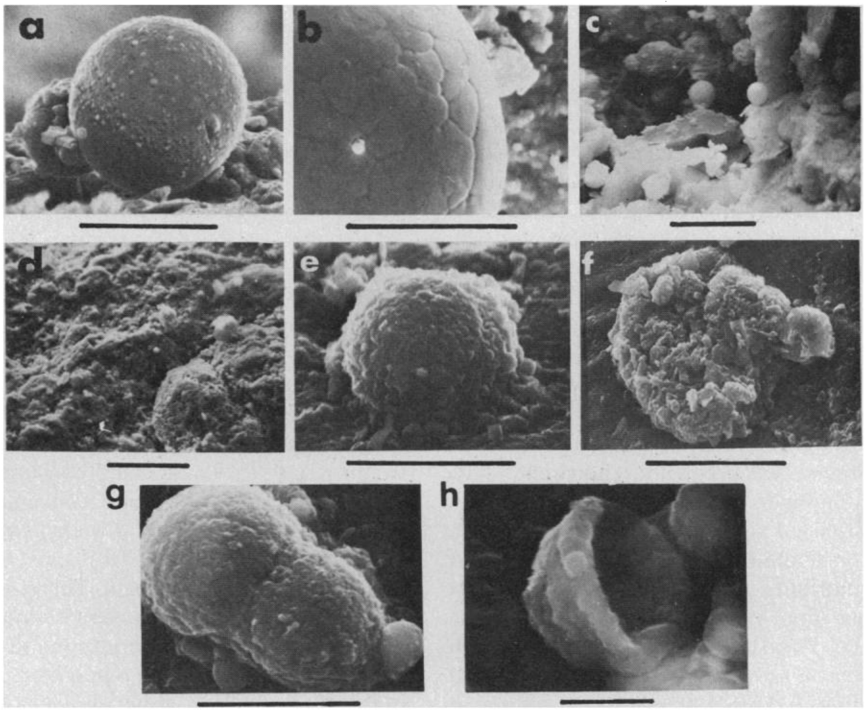

Fig. 1. Scanning electron micrographs of spherules and other structures on shatter cone surfaces: (a through c) on shale host rock, Kimberley-Elsburg Series; (d and h) on banded ironstone, Hospital Hill Series; (e and g) sandstone, Timeball Series, Transvaal system; (f) quartzite, Kimberley-Elsburg Series. Scale bars: for (a, b, e, g, and h), 2 μm; for (c and f), 5 μm; and for (d), 10 μm.