Baseline acidity of ancient precipitation from the South Pole

Cover: South Pole Station, January 1982. Location of geographic South Pole is marked by tripod-based tower in the left center foreground. Living facilities are contained in the geodesic dome (center) and the clean air facility is the dome-topped structure (right center).
Baseline acidity of ancient precipitation from the South Pole

J.H. Cragin, M.B. Giovinetto and A.J. Gow
Measurements of meltwater pH from annual layers of South Pole firn and ice samples ranging in age from 40 to 2000 years B.P. show that precipitation at this remote site has a higher natural acidity than that expected from atmospheric equilibrium with CO₂. The average pH of deaerated (CO₂-free) samples was 5.64 ± 0.08, while air-equilibrated samples averaged 5.37 ± 0.08, a pH that is about a factor of two more acidic than the expected background pH of 5.65. The observed "excess" acidity can be accounted for by natural SO₄²⁻ and NO₃⁻ levels in the samples probably originating from non-anthropogenic H₂SO₄ and HNO₃. Because of the presence of these naturally occurring acids in South Pole precipitation, a pH of 5.4 is considered a more representative baseline reference pH for acid precipitation studies.
PREFACE

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BASELINE ACIDITY OF ANCIENT PRECIPITATION FROM THE SOUTH POLE

J.H. Cragin, M.B. Giovinetto and A.J. Gow

INTRODUCTION

Most studies of acid precipitation have used relatively recent rain or snow samples from either populated (Cogbill and Likens 1974, Galloway et al. 1976, Wolff et al. 1977, Brezonik et al. 1980, Lewis and Grant 1980) or remote (Weiss et al. 1977, Sequeira 1981, Galloway et al. 1982, Jickells et al. 1982, Koerner and Fisher 1982, Pszenny et al. 1982, Keene et al. 1983) locations. While remote precipitation is generally less acidic than that from industrialized areas, even samples from remote locations are often more acidic than the pH 5.65 expected from dissolution of atmospheric CO$_2$. (See Appendix A for derivation of the effect of CO$_2$ on the acidity of pure, i.e., distilled, water.) A major concern is whether this excess acidity is of natural or anthropogenic origin. Acid rain on Bermuda has been ascribed to long-range atmospheric transport of sulfates and nitrates from North America (Jickells et al. 1982). Galloway et al. (1982) recently measured the pH of precipitation from five remote areas of the world and attributed much of the acidity at these locations to long-range transport. The well-known arctic haze over Alaska is believed to be caused by northward transport of pollutants from Eurasia and North America to the Arctic during winter (Rahn 1981). Because of potential long-range transport, the possibility always exists that present-day precipitation, however remote its location, will contain anthropogenic H$_2$SO$_4$ or HNO$_3$.

One way to eliminate the anthropogenic component is to use samples of polar snow and ice that were deposited before the industrial revolution and are now preserved chronologically in permanent ice sheets. Impurities are incorporated into the snow by rainout, washout and dry fallout, and polar snow and ice samples have been used extensively to provide natural background concentrations and enrichments of many pollutants, especially metals (Cragin et al. 1975, Herron et al. 1977, Boutron and Lorius 1979, Weiss et al. 1979, Boutron 1980, Boutron 1982). The only pH measurements reported for pre-1800 liquid samples are those of Koerner and Fisher (1982), who found a mean Holocene (200-5500 years B.P.) pH of 5.48 in cores from the Agassiz Ice Cap, Elsmere Island, Canada. However, no attempt was made to eliminate or control CO$_2$-induced acidity which could introduce variability in the background pH results (Koerner and Fisher 1982). Titration of acidity in ancient (30,000 years B.P.) ice core samples from Dome C, Antarctica (74°39'S, 124°10'E) gave an average H$^+$ concentration of 2.44 μEq/L (Delmas et al. 1980), which is equivalent to a pH of 5.61. In similar titrations of seven deeper (800 to 900 m) samples from the Dome C ice core, Delmas et al. (1980) obtained an average acidity of 1.07 ± 0.52 μEq H$^+$/L, corresponding to a pH of 5.97. These older samples, though, correspond to Wisconsin age ice when the acid-neutralizing terrestrial dust input to ice sheets was considerably higher than during the last 10,000 years (Cragin et
Table 1. Values for pH and corresponding acidities for firn and ice core samples from the South Pole, Antarctica.

<table>
<thead>
<tr>
<th>Sample depth (m)</th>
<th>Age in years before 1982 (est. error ± 5%)</th>
<th>N; atmosphere pH after 15 min.</th>
<th>pH after 30 min.</th>
<th>[H+] (μEq/L)</th>
<th>Air pH</th>
<th>[H+] (μEq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.72-7.92</td>
<td>40</td>
<td>5.62</td>
<td>-</td>
<td>2.40</td>
<td>5.37</td>
<td>4.27</td>
</tr>
<tr>
<td>14.63-14.82</td>
<td>90</td>
<td>5.61</td>
<td>-</td>
<td>2.45</td>
<td>5.34</td>
<td>4.57</td>
</tr>
<tr>
<td>20.00-20.15</td>
<td>130</td>
<td>5.57</td>
<td>-</td>
<td>2.69</td>
<td>5.42</td>
<td>3.80</td>
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<tr>
<td>39.72-39.84</td>
<td>270</td>
<td>5.72</td>
<td>-</td>
<td>1.91</td>
<td>5.37</td>
<td>4.27</td>
</tr>
<tr>
<td>59.00-59.13</td>
<td>440</td>
<td>5.73</td>
<td>-</td>
<td>1.86</td>
<td>5.48</td>
<td>3.31</td>
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<tr>
<td>79.05-79.15</td>
<td>640</td>
<td>5.69</td>
<td>-</td>
<td>2.04</td>
<td>5.42</td>
<td>3.80</td>
</tr>
<tr>
<td>101.26-101.39</td>
<td>860</td>
<td>5.51</td>
<td>-</td>
<td>3.09</td>
<td>5.33</td>
<td>4.68</td>
</tr>
<tr>
<td>120.54-120.65</td>
<td>1070</td>
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<td>-</td>
<td>2.09</td>
<td>5.38</td>
<td>4.17</td>
</tr>
<tr>
<td>141.00-141.15</td>
<td>1300</td>
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<td>5.79</td>
<td>1.62</td>
<td>5.40</td>
<td>3.98</td>
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<tr>
<td>160.00-160.12</td>
<td>1530</td>
<td>5.90</td>
<td>-</td>
<td>1.26</td>
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<td>4.17</td>
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<td>179.12-179.27</td>
<td>1750</td>
<td>5.47</td>
<td>-</td>
<td>3.39</td>
<td>5.24</td>
<td>5.75</td>
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<td>200.39-200.53</td>
<td>2000</td>
<td>5.64</td>
<td>5.62</td>
<td>2.40</td>
<td>5.32</td>
<td>4.79</td>
</tr>
</tbody>
</table>

Average and standard deviation*  

<table>
<thead>
<tr>
<th>Sample depth (m)</th>
<th>Age in years before 1982 (est. error ± 5%)</th>
<th>N; atmosphere pH after 15 min.</th>
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</tr>
</thead>
</table>

Average and standard deviation*  

*Standard deviations shown mainly represent variability between sample concentrations rather than analytical precision.

al. 1977, Briat et al. 1982). Here we present values of pH from both air-saturated and CO₂-free South Pole ice core samples spanning the last 2000 years (Table 1).

EXPERIMENTAL METHODS

A 200-m-long, 10-cm-diameter ice core was recovered from the Amundsen-Scott South Pole Station (Fig. 1) during the 1981-82 austral summer using an electromechanical drill (Rand 1976, Kuivinen et al. 1982). The core was dated stratigraphically (Fig. 2) along its entire length (Kuivinen et al. 1982, Gow et al., in prep.) by continuous counting of coarse-grained depth hoar layers that are known to occur on an annually repeating basis (Giovinetto 1960, Gow 1965). With this technique, age errors increase with depth because of missed years ascribable to hiatuses in accumulation. However, the error is estimated not to exceed 100 years for the deepest and oldest (approximately 2000 years B.P.) portion of the core.

The core was transported frozen to the U.S. for subsequent analysis at CRREL. For the chemical measurements reported here, we used 10- to 20-cm-long half-core segments, each representing exactly one year's accumulation to eliminate chemical variability due to seasonal concentration differences (Langway et al. 1975). The first three samples from depths of 7.72-7.92 m, 14.63-14.82 m and 20.00-20.15 m are of snow deposited since the onset of the industrial revolution. Older samples were selected at 20-m intervals.

All subsequent laboratory work including sample cleaning, melting, deaeration and analysis was performed in a Class 100 clean room. Utensils and labware (Teflon, polyethylene) used to clean the core or contain sample meltwater were cleaned by rinsing first with distilled-deionized water, then by rinsing with electronic grade acetone and finally by leaching for 3 days with 18 megohm Milli-Q deionized water. Surface contaminants were removed from sections of firn core samples* by mechanically scraping off the outer 1.0 cm with a stainless steel chisel. This process was conducted within a Class 100 laminar-flow clean air station in a coldroom using extreme care to allow cleaned areas of the core to contact only cleaned Teflon (FEP) or polyethylene (LPE). Deeper core samples (depth range 120-200 m) consisting of imper-
Figure 1. Core drilling site, located approximately 800 m from South Pole Station geodesic dome. The drill tower and electromechanical drill can be seen emerging from the roof of the wind-shelter tent. Scientist in foreground is carrying the inner drill barrel from which an ice core, approximately 1-m long, will be extracted.

Figure 2. Scientist logging a core section for length and stratigraphic features.
meable glacial ice were cleaned in a Class 100 clean room by repeated washings with 18 megohm Milli-Q deionized water as described elsewhere (Langway et al. 1974, Cragin et al. 1975, Herron et al. 1977). Immediately after cleaning, these samples of firn or ice were placed in individual wide-mouth polyethylene (LPE) bottles and allowed to melt. After each melted sample had reached room temperature (25 ± 1°C), it was deaerated by bubbling filtered (0.4 μm) purified nitrogen gas through it for 15 minutes to remove CO₂ and eliminate pH variability caused by differing amounts of H₂CO₃. Additional deaeration (Table 1, fourth column) produced no significant pH change, indicating that 15 minutes was sufficient. The sample pH was then measured under a nitrogen atmosphere in a specially constructed plexiglass chamber (Fig. 3). Samples were then allowed to equilibrate overnight in the dark with air and measurements were again made to determine the pH of CO₂-saturated samples.

All pH measurements were made with an Orion model 81-03 combination Ross electrode. This electrode differs from ordinary combination pH electrodes in that the reference half cell potential is controlled by reversible redox equilibria rather than by the conventional calomel or Ag/AgCl. Compared to a conventional combination pH electrode, the Ross electrode responded more rapidly and showed negligible drift even in low ionic strength solutions of South Pole meltwater. The precision and accuracy of these measurements is estimated to be ± 0.05 pH unit.

RESULTS AND DISCUSSION

The values for pH and corresponding calculated acidities presented in Table 1 are for 12 annual increments of South Pole core covering approximately the last two millennia. Important features of these data include the uniformity of pH values and the absence of any appreciable trend in pH over the core profile. The lack of an observed increase in acidity (decrease in pH) is probably due to the age of the samples; the most recent sample fell as snow 40 years ago, before “tall stacks” of the 1950s exacerbated the SO₂ transport problem.* Furthermore, since acid pollutants are generated mainly in the Northern Hemisphere, they may not reach the Antarctic Ice Sheet in measurable amounts because of poor interhemispheric mixing and because of washout and dry deposition during extended transport to Antarctica. This is supported by the absence of an increase of sulfate

*Snow layers younger than 1940 (above 7.7 m) were not sampled because of possible local contamination from South Pole Station, constructed and occupied since 1957. Future studies of pH in more recently deposited snow layers will include measurements on pit samples collected 10 to 20 km upwind of South Pole Station.
ion, a major component of acid precipitation, in cores covering the last 100 years from Dome C, Antarctica (Delmas et al. 1980, Delmas and Burton 1980). Our pH values thus provide a baseline or reference pH against which present-day precipitation can be compared.

Another important aspect of the data is the actual magnitude of the pH values themselves. For the air-equilibrated samples, the average pH is 5.37 ± 0.08—about twice as acidic as the 5.65 pH expected for “pure” rainwater in equilibrium with atmospheric CO₂. The average pH of deaerated samples is 5.64 ± 0.08. The difference of 0.27 pH units between aerated and deaerated samples is about what would be expected from dissolution of atmospheric CO₂; air-saturated water contains 2.2 × 10⁻¹₄ Eq H⁺/L from H₂CO₃ dissociation, which would lower a 5.65 pH sample by 0.28 pH units. Converting the above aerated and deaerated pH values to H⁺ concentrations (Table 1, fifth and seventh columns) shows that half of the acidity is caused by CO₂ dissolution and half by other naturally occurring acids. Preliminary ion chromatographic measurements of SO₄²⁻ and NO₃⁻ concentrations in eight samples gave concentrations of 1.0-2.1 μEq SO₄²⁻/L and 1.5-2.2 μEq NO₃⁻/L. Based on Na⁺ concentrations (0.57-1.4 μEq/L) measured in four samples, the sea salt contribution to SO₄²⁻ is calculated not to exceed 10% of the total SO₄²⁻ present in the samples. The average sum of SO₄²⁻ and NO₃⁻ concentrations, 3.3 μEq/L, is more than enough to balance the average 2.3 μEq/L of H⁺ (pH 5.64) in the deaerated samples. Thus, on a molar equivalent basis the pH of deaerated samples can easily be accounted for by the SO₄²⁻ and NO₃⁻ concentrations if these ions originate from H₂SO₄ and HNO₃. Some acidity may also be contributed by weak organic acids (acetic, formic), but we have no experimental evidence to support this.

Electrolytic conductivities of the deaerated samples ranged from 1.0 to 1.7 μmho/cm and correlated well (r = 0.87, p = 0.01) with values calculated from the observed pH's and ion concentrations. Most of the background H₂SO₄ present in the ancient precipitation samples reaches the South Pole through advection as well as subsidence from the upper troposphere and lower stratosphere, which facilitate direct contribution from the “Junge layer,” a good source of H⁺ that is replenished by violent and nonviolent volcanic eruptions (Berresheim and Jaeschke 1983).

Alkaline minerals contained in airborne particulate matter can neutralize acidity in precipitation, resulting in lower background acidity (higher pH). Greater dust content may be the reason for higher pH values found in ancient ice samples from Baffin Island by Koerner and Fisher (1982). But the concentration of terrestrial dust at the South Pole is very low (less than 0.25 μEq Ca + Mg) (Boutron 1982) and most of the Ca and Mg present probably originates from sea salt rather than from acid-neutralizing minerals. Thus, the acidity of South Pole samples is a good representation of background levels without undue influence from wind-transported dust. Samples from less remote locations on the globe, with local or regional dust sources, would be expected to have higher pH values for similar acid inputs.

**CONCLUSION**

Our results, showing South Pole ice deposits to be a factor of two or more acidic than the presumed pH of 5.65, confirm the postulation of Charlson and Rodhe (1982) that the natural acidity of pristine precipitation is indeed greater than that expected from H₂CO₃ equilibrium alone. Thus, in assessing anthropogenic contributions to present-day precipitation, a pH of 5.4 is probably more representative of natural background conditions than the generally accepted value of 5.65.

**LITERATURE CITED**


Gow, A.J. (in prep.) Physical and structural properties of a 2000-year-old ice core from the South Pole.


Langway, C.C., Jr., J.H. Cragin, G. Klouda and M.M. Herron (1975) Seasonal variation of chemical constituents in annual layers of Greenland deep ice deposits. USA Cold Regions Research and Engineering Laboratory, Research Report 347. ADA 021319.


APPENDIX A: EFFECT OF CO$_2$ ON ACIDITY OF PURE WATER

Water is a very weak electrolyte and undergoes self-ionization to produce hydrogen and hydroxyl ions according to the equation

$$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \quad K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}.$$ (1)

Mass balance considerations indicate that ionization produces equal numbers of H$^+$ and OH$^-$ ions, and thus pure water is neither acidic nor basic. At 25°C, only 0.00000018% of the water molecules are ionized, resulting in $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-14}$ mol/L, which is equivalent to a pH of 7.00. The degree of ionization increases with temperature so that a neutral solution has a pH of 6.5 ($[\text{H}^+] = 3.16 \times 10^{-7}$ mol/L) at 100°C and a pH of 7.4 ($[\text{H}^+] = 3.98 \times 10^{-8}$ mol/L) at 0°C. Our concern here is with solutions at 25°C and subsequent discussion will be restricted to this temperature.

In actual practice, however, pure water in contact with atmospheric air does not have a pH of 7 because of dissolution of CO$_2$, an acidic gas. Carbon dioxide forms carbonic acid, which dissociates to form hydrogen and bicarbonate ions. The equilibria can be shown as

$$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$$ (2)

$$[\text{H}^+] = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.31 \times 10^{-7}$$ (3)

Subsequently, bicarbonate ion can dissociate to produce carbonate and additional hydrogen ions:

$$[\text{HCO}_3^-] = [\text{H}^+] + [\text{CO}_3^{2-}] \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 5.6 \times 10^{-11}$$ (4)

The first equilibrium constant $K_1$ shows that only about 6% ($4.31 \times 10^{-7}$) of the H$_2$CO$_3$ (actually CO$_2$ + H$_2$O) dissociates to form H$^+$ and HCO$_3^-$ ions. The second equilibrium constant $K_2$ shows that of the 6% HCO$_3^-$, only about 0.00075% ($5.6 \times 10^{-11}$), dissociates to form CO$_3^{2-}$ and additional H$^+$ ions in neutral solution. However, the solution is not neutral because of H$^+$ ions from the first dissociation; the presence of these ions suppresses the second ionization (H$^+$ drives the equilibrium in eq 4 to the left). The net result is that the contribution of H$^+$ from the second dissociation is very small and can be neglected.

Using the first dissociation, eq 3, we can calculate the H$^+$ concentration and hence pH of a solution of known CO$_2$ content. Air-saturated water contains $1.35 \times 10^{-7}$ mol/L CO$_2$ at 25°C (Kolthoff et al. 1969). Thus, if we let $x = [\text{H}^+] = [\text{HCO}_3^-]$ then $[\text{H}_2\text{CO}_3] = (1.35 \times 10^{-7}) - x$. Substituting into eq 3

$$\frac{x^2}{(1.35 \times 10^{-7}) - x} = K_1 = 4.31 \times 10^{-7}$$

and the quadratic solution yields

$$[\text{H}^+] = 2.2 \times 10^{-8} \text{ mol/L}$$

which corresponds to a pH of 5.65.
A facsimile catalog card in Library of Congress MARC format is reproduced below.

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Bibliography: p. 5.