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J H. Cragin
U.S. Army Cold Regions Research and Engineering Laboratory

M B. Giovinetto
University of Calgary

A J. Gow
U.S. Army Cold Regions Research and Engineering Laboratory

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J.H. Cragin

U.S. Army Cold Regions Research and Engineering Laboratory

M.B. Giovinetto

University of Calgary, Alberta

A.J. Gow

U.S. Army Cold Regions Research and Engineering Laboratory

Abstract. 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 CO_2. The average pH of deaerated (CO_2-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 SO_4^{2-} and NO_3^- levels in the samples originating from non-anthropogenic H_2SO_4 and HNO_3. 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.

Introduction

Most studies of acid precipitation have used relatively recent rain or snow samples from either populated areas [Cogbill and Likens, 1974; Galloway et al., 1976; Wolff et al., 1977; Brezonik et al., 1980; Lewis and Grant, 1980] or remote locations [Weiss et al., 19778 Sequeira, 1981; Galloway et al., 1982; Jickells et al., 1982; Koerner and Fisher, 1982; Pszenny et al., 1982; Keene et al., 1983]. 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. (A derivation of the effect of CO_2 on the acidity of pure, i.e., distilled, water can be found in Cragin et al. [1984].) 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 north-ward 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_2SO_4 or HNO_3.

One way to eliminate the anthropogenic component is to use samples of polar snow and ice which 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. 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]. Although ice core acidity has been estimated indirectly by surface conductivity methods [Hammer 1980; Hammer et al. 1980], the only measurements of pH on liquid samples reported for pre-1800 ice 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, Ellesmere Island, Canada. However, as they state, 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]. Titrations 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 correspond to Wisconsin age ice deposited when the acid-neutralizing terrestrial dust input to ice sheets was considerably higher than during the last 10,000 years [Cragin et al., 1977; Briat et al., 1982]. Here we present values of pH from both air-saturated and CO_2-free South Pole ice core samples spanning the last 2000 years.

Experimental

A 200-m-long, 10-cm-diameter ice core was recovered from the Amundsen-Scott South Pole Station during the 1981-82 austral summer using an electromechanical drill [Rand, 1976; Kuivinen et al., 1982]. The core was "dated"

stratigraphically along its entire length [Kuivinen et al., 1982] 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 attributable 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 the U.S. Army Cold Regions Research and Engineering Laboratory (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. Snow layers deposited since 1940 (above 7.7 m) were not sampled because of possible local contamination from the South Pole Station, constructed and occupied since 1957. 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 0.5–1.0 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 impermeable glacial ice were cleaned in a Class 100 clean room by repeated washings with 18 megohm Milli-Q® deionized water as de-

scribed 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. Several samples were initially melted under a nitrogen atmosphere but pH values were similar to those obtained by nitrogen deaeration only, indicating that melting under nitrogen was not necessary. 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 CO_2 and eliminate pH variability caused by differing amounts of H_2CO_3. Additional deaeration (Table 1, column four) 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 Plexiglas chamber. Samples were then allowed to equilibrate with air overnight in the dark for several days and measurements were again made to determine the pH of air-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

Table 1. Values for pH and corresponding acidities for firn and ice core samples
from the South Pole, Antarctica

Sample depth (m)	Age in years before 1982 (est. error ± 5%)	N₂ atmosphere			Air	
		pH after 15 min.	pH after 30 min.	[H⁺] (μM/L)	pH	[H⁺] (μM/L)
7.72– 7.92	40	5.62	—	2.40	5.37	4.27
14.63– 14.82	90	5.61	—	2.45	5.34	4.57
20.00– 20.15	130	5.57	—	2.69	5.42	3.80
39.72– 39.84	270	5.72	—	1.91	5.37	4.27
59.00– 59.13	440	5.73	—	1.86	5.48	3.31
79.05– 79.15	640	5.69	—	2.04	5.42	3.80
101.26–101.39	860	5.51	—	3.09	5.33	4.68
120.54–120.65	1070	5.68	—	2.09	5.38	4.17
141.00–141.15	1300	5.83	5.79	1.62	5.40	3.98
160.00–160.12	1530	5.90	—	1.26	5.38	4.17
179.12–179.27	1750	5.47	—	3.39	5.24	5.75
200.39–200.53	2000	5.64	5.62	2.40	5.32	4.79
Mean and std. deviation*		5.64 ± 0.08			2.27 ± 0.60	5.37 ± 0.08	4.30 ± 0.62

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

years ago, before "tall stacks" of the 1950s exacerbated the SO_2 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 ion, a major component of acid precipitation, in cores covering the last 100 years from Dome C, Antarctica [Delmas et al., 1980; Delmas and Boutron, 1980]. These South Pole 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 CO_2. 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 CO_2; air-saturated water contains 2.2×10^{-6} M H^+/L from H_2CO_3 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, columns five and seven) shows that half of the acidity is caused by CO_2 dissolution and half by other naturally occurring acids. Preliminary ion chromatographic measurements of SO_4^{2-} and NO_3^- concentrations in eight samples gave concentrations of 1.0–2.1 μEq SO_4^{2-}/L and 1.5–2.2 μEq NO_3^-/L. Based on Na^+ concentrations (0.57–1.4 μEq/L) measured in four samples, the sea salt contribution to SO_4^{2-} is calculated not to exceed 10% of the total SO_4^{2-} present in the samples. The average sum of SO_4^{2-} and NO_3^- 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 SO_4^{2-} and NO_3^- concentrations if these ions originate from H_2SO_4 and HNO_3. 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 0.10 to 0.17 mS/m and correlated well ($r = 0.87$, $p = 0.01$ for 6 d.f.) with values calculated from the observed pH's and ion concentrations. Most of the background H_2SO_4 present in the ancient precipitation samples reaches the South Pole through advection as well as subsidence from the upper troposphere and possibly the lower stratosphere, which facilitates a direct contribution from the "Junge layer," a good source of H^+ that is replenished by eruptive and nonviolent volcanic activity [Berresheim and Jaeshke, 1983]. However, Legrand and Delmas [1986] found no evidence for a stratospheric input of nitrate in Antarctic snow and concluded that this ion originates from lightning at midlatitudes. It must then presumably be transported tropospherically to the Antarctic. Tropospheric transport paths are also believed to exist for continental aerosols [Polian et al., 1986] and sea salt [Bodhaine et al., 1986]. Sulfate, most of which is non-marine at the South Pole, can be transported through both tropospheric and stratospheric pathways, although tropospheric

transport may dominate for our samples since we specifically avoided selecting ice deposited during or shortly after known volcanic events. Furthermore, aerosol concentration measurements of Tomoyukuto et al. [1986] suggest that stratosphere to troposphere particle transport over Antarctica is less important than horizontal tropospheric transport of particles to the Antarctic.

On polar ice sheets snow is transformed into ice by compaction of the permeable firn that composes the upper 115 m at the South Pole. However, there is no evidence to indicate any significant change in the acidity of the snow caused by post-depositional diffusion of air through the permeable firn. Observations in support of this include the very sharp nature of changes in the chemical composition [Boutron, 1982] of firn from the South Pole and Dome C, Antarctica. Broader peaks would have been expected if post-depositional diffusion of air through the firn was contributing significantly to the measured chemical concentrations.

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/L) [Boutron, 1982] and most of the Ca and Mg present probably originates from sea salt rather than from acid-neutralizing minerals. Although no single background pH may be applicable to all locations of the globe because of varying alkaline dust inputs [Galloway et al., 1982] the acidity of South Pole samples is a good representation of background levels without substantial 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 dust-free precipitation is indeed greater than that expected from carbonic acid equilibrium alone. Thus, in assessing anthropogenic contributions to present-day precipitation, the background reference pH should take into account the contribution of H^+ from not only H_2CO_3, but other naturally occurring acids as well.

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