

The Ice Speaks—Scientists Use Ion Chromatography to Listen

Locked beneath hundreds of meters of ice, secrets about the Earth's past lie waiting to be discovered. Scientists armed with ice core samples and powerful instrumentation are now helping to uncover new information about prehistoric climate, precipitation, and geologic events.

For some geologists and chemists, the Earth's most valuable resource is ice. Ice cores archive whatever was in the atmosphere at the time snow fell. In areas that have remained cold enough, these clues are stored as a frozen record of the Earth's history. To unlock them, scientists travel to remote, elevated, and frozen locations, drilling to bedrock in some cases. They evaluate the concentration and size distribution of insoluble dust in the ice cores. Stable isotopic ratios can be extrapolated to the air temperatures when the ice was formed. Dust concentrations indicate precipitation in the region. And the analysis of Cl^- , SO_4^{2-} , and

NO_3^- , as well as Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , and F^- , provide clues about volcanic activity, desertification, the oxidation of fossil fuels, and other major geologic events.

Byrd Polar Research Center

Lonnie G. Thompson, Professor of Geological Sciences at Byrd Polar Research Center (BPRC), Ohio State University, is a leader in ice research. He recently retrieved samples from the Puruogangri ice cap in the center of Tibet on his 37th expedition, where his team worked from September 10 to November 5, 2000. The ice is brought back frozen to BPRC and stored between -30°C

and -40°C until it is analyzed in a Class 100 clean room. Much of the labwork is done by geochemist Tracy Mashiotto, who performs ion analysis on a daily basis. "We have two DX-500 systems, one set up for cations and the other for anions," said Mashiotto, who has been with the ice core group since August 2000. These instruments use the IonPac AS12A and CS12A (4 x 250 mm) columns. In addition to the Dionex ion chromatographs, the ice core group uses laser ablation systems, ICP-MS, SEM, and other methods to characterize particles from the cores. Beta radioactivity measurements that detect documented thermonuclear tests provide information about geologic timelines around the world.



Lonnie Thompson examines stratigraphy of freshly drilled ice core in drilling dome at field site, Dasuopu Ice Cap, Himalayas.



Solar-powered ice core drilling on Nevado Huascarán, Peru. This is the highest tropical mountain in the world.

Highlights of Thompson's previous ice core work include:

- Expeditions to four ice caps in Tibet, where his team recovered the highest ice cores ever drilled—from 7200 meters at the top of the Himalayas—in 1997.
- Drilling six cores to bedrock in the icefields of Kilimanjaro in January and February of 2000.
- Recovering cores from Huascarán, Quelccaya, and Sajama in the tropical Andes of Peru, as well as from Franz Josef Land in the Russian Arctic, and successful expeditions to Greenland and Antarctica.

"Our next drilling site is Bona-Churchill in the Wrangell Mountains of Alaska," Thompson said. He chooses only sites at high elevation where melting does not occur. Drilling can last months. "Our research has

resulted in over 165 publications in the last 20 years, 12 published in *Science* and *Nature*." He is involved with climate reconstruction work in areas away from ice caps as well. "In the tropics we work on reconstruction of climate variations associated with El Niño and monsoon variability." One of the most important practical applications of his group's work is that past changes in deserts, winds, precipitation, temperature, etc. have helped environmental scientists put the 20th century into long term perspective, he said.

European Work

Other labs working with ice cores include two European teams that presented ice core results at the International Ion Chromatography Symposium (IICS 2000). Emiliano Castellano, of the Department of Public Health and Environmental Analytical Chemistry, University of Florence, Italy, presented research of ice core samples covering the last 30,000 years. In Castellano's work, the liquid sample is continuously delivered by a snow melter and injected in a preconcentration column by a peristaltic pump at 1 mL/min. Reproducibility was found to be better than 2% for sulfate and 4% for chloride and nitrate, with detection limits about 0.5 µg/L for each analyte. Such techniques were able to give a signal mainly related to H⁺ content, his group reported. "The simultaneous determination of Cl⁻, NO₃⁻, and SO₄²⁻ allows the determination of the main counter ion of H⁺. This is particularly important in investigations of volcanic activity using the spikes in sulfate profiles." Castellano's group analyzed ice from



Sample preparation in the cold storage lab (20 °F) at Byrd Polar Research Center, Ohio State University.

Antarctica using Dionex IonPac AS4A and AS17 columns.

Another group, led by Tamara Huber of the Department of Chemistry and Biochemistry, University of Bern, Switzerland, also discussed time- and labor-saving IC techniques for analysis of ice cores from the Swiss Alps. Their chromatography is done with an IonPac AS17 column on a DX-320 ion chromatograph. The sample preparation involves continuously melting ice cores and separating the meltwater in an inner and outer fraction. The inner, uncontaminated sample is analyzed continuously for concentrations of various anions (fluoride, acetate, formate, methanesulfonate, chloride, nitrate, sulfate, and oxalate) and cations (sodium, ammonium, potassium, magnesium, and calcium). To do this, two sets of two parallel

concentrator columns are used—one for anions and one for cations. While concentrating the sample on one set of columns, the sample collected on the other set is eluted to the corresponding ion chromatograph.

The most common way of analyzing ice cores is to cut the cores into segments, melt them, and analyze each segment separately. But geologic chemists are continuously looking for procedures that are less time-consuming and have a lower risk of contamination.

According to the Data

One of the most interesting findings from this work is information on the "Dansgaard-Oeschger", or D-O, warming events that punctuate ice ages. Comparing ice core data from Greenland with Byrd data from Antarctica, it becomes clear that two rapid warming events of 15 °C occurred in Greenland a millennium after less dramatic increases in Antarctica. This has led to much speculation and new work on the climatic relationship between the Northern and Southern hemispheres. It was previously thought that ice ages were brought on by changes in incoming solar radiation in the Northern Hemisphere but now that theory is called into question. One thing is for sure: more ice core expeditions and analysis of samples is needed to piece together the puzzle of ice ages and other prehistoric climatic and geologic events.



Class 100 clean room with Dionex DX-500 ion chromatographs at Byrd Polar Research Center, Ohio State University.



Deep freeze core storage facility (-30 to -40 °C) at Byrd Polar Research Center, Ohio State University.