nated to a surface Al, providing a mechanism for the interchange of O and O₆⁻. These results also provide evidence for incipient Al(OH)₃ formation on the surface. The ultimate structure of the heavily hydrated surface is clearly very complicated and may depend strongly on sample history. It is possible that the Al(OH)₃ species can be removed completely (perhaps starting near steps or other defects), leaving a less reactive surface that is completely O₃H-terminated, which is similar to the known surfaces of aluminum hydroxides. An idealized model for fully hydroxylated α-Al₂O₃(0001) (28) replaces each surface Al with three H atoms (Fig. 5A), yielding a coverage >15 OH per square nanometer. Room-temperature MD simulations of this model revealed a complex dynamic structure (Fig. 5B), with one out of every three OH groups, on average, lying parallel to the surface because of in-plane hydrogen bonding. Calculated O–H vibrational spectra (29) yielded two broad peaks at ~3470 and 3650 cm⁻¹, with the peak at ~3470 cm⁻¹ corresponding to in-plane OH groups. The peak at ~3650 cm⁻¹ is close to the single peak (3720 to 3733 cm⁻¹) that is observed in most measurements on hydroxylated α-Al₂O₃(0001) (29) and to the range that is generally assigned to bridging OH groups (2, 26). The peak at ~3470 cm⁻¹ is red-shifted by hydrogen bonding and is generally not seen in single-crystal experiments, perhaps because of selection rules or because it is too broad. Our finding of two peaks split by 200 cm⁻¹ contradicts all previous classifications of OH stretching. On the basis of these results, a consistent interpretation of a diverse set of experimental data on hydroxylated alumina surfaces begins to emerge.

References

7. The gradient-corrected exchange-correlation [Bernstein, Lee, Yang, and Perdew (BLYP)] functional used here is from A. D. Becke [Phys. Rev. A 38, 3098 (1988)] and C. Lee, W. Yang, and R. Parr [Phys. Rev. B 37, 785 (1988)]. Norm-conserving numerical pseudopotentials were generated for Al and O with the procedure of N. Trouiller and J. L. Martins [ibid. 43, 1993 (1991)], and a local analytic pseudopotential was derived for H. This is essentially a softened Coulomb potential with a core radius of 0.25 atomic units. Electron wave functions are expanded in a plane-wave basis set with an energy cutoff of 70 rydbergs (Ry). We used the Car-Parrinello Molecular Dynamics code in the parallelized 2.5 version (developed by J. Hutter and copyrighted by IBM, Armonk, NY). All calculations were performed on a 32-node IBM RS6000 SP at the IBM Watson Research Laboratory (Yorktown Heights, NY).
8. In the MD runs, a value of 400 au was used for the fictitious electron mass of the Car-Parrinello Lagrangian multipliers (40), and each hydrogen molecule was replaced by deuterium to improve the separation between electronic and ionic degrees of freedom. The time step in the Verlet algorithm for the integration of the equations of motions was ~0.1 fs.
9. The importance of chemical reaction dynamics in general has recently been highlighted in a special issue of Science (Reaction Dynamics, Science 279, 875–895 (1998).)
17. Earlier calculations used much smaller supercells than the present work. Such studies were therefore limited in their ability to provide accurate adsorbate structures and energies and to study the H₂O coverage dependence and phenomena such as collective effects and surface diffusion.
20. Lagrange multipliers were introduced to constrain the relevant H–O, distance, and the average constraint forces were determined from constant temperature simulations [S. Nosé, J. Chem. Phys. 81, 511 (1984); W. G. Hoover, Phys. Rev. A. 31, 1695 (1985)] of at least 0.2 ps.
23. The temperature was not controlled but was increased slowly from ~100 to ~350 K. The system was then allowed to evolve for a time interval of >1 ps. The average temperature was 250 K.
25. Vibrational frequencies were estimated from the power spectra of the (partial) velocity–velocity auto-correlation functions and were rescaled to account for the fictitious electronic mass and the different mass used for the proton.
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Past Temperatures Directly from the Greenland Ice Sheet

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A Monte Carlo inverse method has been used on the temperature profiles measured down through the Greenland Ice Core Project (GRIP) borehole, at the summit of the Greenland Ice Sheet, and the Dye 3 borehole 865 kilometers farther south. The result is a 50,000-year-long temperature history at GRIP and a 7000-year history at Dye 3. The Last Glacial Maximum, the Climatic Optimum, the Medieval Warmth, the Little Ice Age, and a warm period at 1930 A.D. are resolved from the GRIP reconstruction with the amplitudes ~23 kelvin, ~2.5 kelvin, ~1 kelvin, ~1 kelvin, and ~0.5 kelvin, respectively. The Dye 3 temperature is similar to the GRIP history but has an amplitude 1.5 times larger, indicating higher climatic variability there. The calculated terrestrial heat flow density from the GRIP inversion is 51.3 milliwatts per square meter.

Measured temperatures down through an ice sheet relate directly to past surface temperature changes. Here, we use the measurements from two deep boreholes on the Greenland Ice Sheet to reconstruct past temperatures. The GRIP ice core (72.6°N, 37.6°W) was successfully recovered in 1992 (1, 2), and the 3028.6-m-deep liquid-filled borehole with a diameter of 13 cm was left undisturbed. Temperatures were then measured down through the borehole in 1993, 1994, and 1995 (3, 4). We used the measurements from 1995 (Fig. 1) (4), because there was no remaining evidence of disturbances from the drilling and
the measurements were the most precise (±5 mK). Temperatures measured in a thermally equilibrated shallow borehole near the drill site are used for the top 40 m, because they are more reliable than the GRIP profile over this depth (5). The present mean annual surface temperature at the site is –31.7°C. The 2037-m-deep ice core from Dye 3 (65.2°N, 203°W) was recovered in 1981. We used temperature data from 1983 measurements with a precission of 30 mK (6, 7). The temperatures at the bedrock are –8.58°C at GRIP and –13.22°C at Dye 3. Calculations show that the basal temperatures have been well below the melting point throughout the past 100,000 years (8). Because there are still climate-induced temperature changes near the bedrock, we included 3 km of bedrock in the heat flow calculation.

Past surface temperature changes are indicated from the shape of the temperature profiles (Fig. 1). We used a coupled heat- and ice-flow model to extract the climatic information from the measured temperature profiles. The temperatures down through the ice depend on the geothermal heat flow density (heat flux), the ice-flow pattern, and the past surface temperatures and accumulation rates. The past surface temperatures and the geothermal heat flow density are unknowns, whereas the past accumulation rates and ice-flow pattern are assumed to be coupled to the temperature history through relations found from ice-core studies (9–11). The total ice thickness is assumed to vary 200 m as described in (9). The coupled heat- and ice-flow equation is (7, 9, 12)

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (K \nabla T) - \rho c \nu \cdot \nabla T + f$$

where $T(x,z,t)$ is temperature, $t$ is time, $z$ is depth, $x$ is horizontal distance along the flow line, $\rho(z)$ is ice density, $K(T,p)$ the thermal conductivity, $c(T)$ the specific heat capacity, and $f(z)$ is the heat production term. The ice velocities, $v(x,z,t)$, are calculated by an ice-flow model (9, 13). Model calculations to reproduce a present-day temperature profile through the ice sheet are started 450,000 years ago (ka) at GRIP (100 ka at Dye 3),

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Fig. 1. The GRIP and Dye 3 temperature profiles (blue trace in [A] and [C]) are compared to temperature profiles (red trace in [A] and [C]) calculated under the condition that the present surface temperatures and accumulation rates have been unchanged back in time. (A) The GRIP temperature profile measured in 1995. The cold temperatures from the Glacial Period (115 to 11 ka) are seen as cold temperatures between 1200- to 2000-m depth. (B) The top 1000 m of the GRIP temperature profiles are enlarged so the Climatic Optimum (CO, 8 to 5 ka), the Little Ice Age (LIA, 1550 to 1850 A.D.), and the warmth around 1930 A.D. are indicated at the depths around 600, 140, and 60 m, respectively. (C) The Dye 3 temperature profile measured in 1983. Note the different shape of the temperature profiles when compared to GRIP and the different depth locations of the climate events. (D) The top 1500 m of the Dye 3 temperature profiles are enlarged so the CO, the LIA, and the warmth around 1930 A.D. are indicated at the depths around 800, 200, and 70 m, respectively.

Fig. 2. (A through E) The probability distributions of the past surface temperatures at the Greenland Ice Sheet summit at selected times before present. They are constructed as histograms of the 2000 Monte Carlo sampled and accepted temperature histories (17). All temperature distributions are seen to have a zone with maximum values, the most likely values, which are assumed to be the reconstructed surface temperature at these times (18). (F) The probability distribution of the sampled geothermal heat flow densities. The most likely value is 51.3 mW/m².
more than twice the time scale for thermal equilibrium of the ice-bedrock, so the unknown initial conditions are forgotten when generating the most recent 50,000-year temperature history (7000 years for Dye 3).

We developed a Monte Carlo method to fit the data and infer past climate. The Monte Carlo method tests randomly selected combinations of surface temperature histories and geothermal heat flow densities by using them as input to the coupled heat- and ice-flow model and considering the resulting degrees of fit between the reproduced and measured temperature profiles (14–16). Our results for each site are based on tests of $3.3 \times 10^6$ combinations of temperature histories and heat flow densities, of which 2000 solutions have been selected (17). The 2000 temperature histories and heat flow densities are sampled with a frequency proportional to their likelihood (14, 15), and all accepted solutions fit the observations within their limits of uncertainty.

Histograms of the sampled geothermal heat flow densities and of the temperature histories at each time before present can be made (for example, Fig. 2). The distributions in general show that there is a most likely value, a maximum, at all times, which we refer to as the temperature history (18). The distribution of accepted geothermal heat flow densities (Fig. 2F) has a median of $51.3 \pm 0.2 \text{ mW/m}^2$, which is slightly higher than the heat flow density from Archean continental crust across the Baffin Bay in Canada. A few heat flow measurements have been made from the coast of Greenland (36 and 43 mW/m²), but these are not corrected for long-term climate variations and are minimum values (19). The homogeneous thermal structure of ice is an advantage when the heat flow density and the temperature history are to be reconstructed (20).

Histograms from the GRIP reconstruction (Fig. 3) show that temperatures at the Last Glacial Maximum (LGM) were $23 \pm 2 \text{ K}$ colder than at present (21). The temperatures at this time, 25 ka, reflect the cold temperatures seen on the measured temperature profile at a depth of 1200 to 2000 m. Alternative reconstructions of the ice thickness and accumulation rates all reproduce LGM temperatures within 2 K (9, 10, 22, 23). The cold Younger Dryas and the warm Bølling/Allerød periods (24) are not resolved in the inverse reconstruction. The temperature signals of these periods have been obliterated by thermal diffusion because of their short duration (25). After the termination of the glacial period, temperatures in our record increase steadily, reaching a period 2.5 K warmer than present during what is referred to as the Climatic Optimum (CO), at 8 to 5 ka. Following the CO, temperatures cool to a minimum of 0.5 K colder than the present at around 2 ka. The record implies that the medieval period around 1000 A.D. was 1 K warmer than present in Greenland. Two cold periods, at 1550 and 1850 A.D., are observed during the Little Ice Age (LIA) with temperatures 0.5 and 0.7 K below the present. After the LIA, temperatures reach a maximum around 1930 A.D.; temperatures have decreased during the last decades (26). The climate history for the most recent times is in agreement with direct measurements in the Arctic regions (27). The climate history for the last 500 years agrees with the general understanding of the climate in the Arctic region (28) and can be used to verify the temperature amplitudes. The results show that the temperatures in general have decreased since the CO and that no warming in Greenland is observed in the most recent decades.

As seen in Fig. 3, resolution decreases back...
in time (25, 29). For the GRIP reconstruction, an event with a duration of 50 years and an amplitude of 1 K can be resolved 150 years back in time with a measurement accuracy of 5 mK; an event with a similar amplitude but a duration of 1000 years can be detected back to 5 ka. An event that occurred 50 ka will now be observed in the temperature profile at the bedrock. Climate events for times older than 50,000 years before present (ky BP) are not well resolved (30). At Dye 3, the reconstructed climate history extends only to 7 ka, because the ice is 1000 m thinner than at the summit and surface accumulation rate is 50% higher. The LGM is not well resolved in the Dye 3 record, and consequently the geothermal heat flow density is not uniquely determined (31). On the other hand, the recent climate history has a higher resolution because of the increased accumulation (Fig. 4).

The Dye 3 record is nearly identical with the GRIP record back to 7 ka, but the amplitudes are 50% higher. Thus, the resolved climate changes have taken place on a regional scale; many are seen throughout the Northern Hemisphere (28, 32). GRIP is located 865 km north of Dye 3 and is 730 m higher in elevation. Surface temperatures at the summit are influenced by maritime air coming in from the North Atlantic and air masses arriving from over northeastern Canada (associated with the Baffin trough) (28, 32, 33). Temperatures at Dye 3 will be influenced to a greater degree by the North Atlantic maritime air masses. Dye 3 is located closer to the center of the highest atmospheric variability, which is associated with large interseasonal, interannual, and decadal temperature changes (32, 34). It is therefore believed that the observed difference in amplitudes between the two sites is a result of their different geographic location in relation to variability of atmospheric circulation, even on the time scale of a millennium.

References and Notes


2. W. Dansgaard et al., ibid., p. 218.


5. The deep borehole is located in a building, and the liquid surface in the borehole is found at a depth of 40 m. The temperatures measured in the top 40 m are very disturbed, so we used measurements from an air-filled shallow borehole (100 m) near the borehole.


9. Between 50 and 20 ka, the ice thickness was 50 m less than at present, even though the ice sheet covered a larger area. The maximum ice thickness of 3230 m is found at 10 ka, after which the ice thickness gradually has decreased to the present 3028.6 m. The depression and uplift of the bedrock influenced the elevation of the surface [(S. J. Johnsen, D. Dahl-Jensen, W. Dansgaard, N. S. Gundestrup, Tellus B 47, 624 (1995)].