isoleucine ratio greater than that of the bound fraction, which consists largely of slower epimerizing interior isoleucine. (iii) After hydrolysis, free isoleucine epimerizes at the much slower, free amino acid rate. Consequently, as the protein hydrolyzes to free amino acids, the overall rate of epimerization will decrease, and the slope of the second linear segment of the kinetic curve, which is approximately parallel to the rate curve of free isoleucine, will be governed largely by the rate of epimerization of free isoleucine.

The alloisoleucine/isoleucine ratios of the free fractions of heated dipeptides and proteins provide additional evidence for this interpretation. With the exception of two polypeptides (eledoisin and melittin), the ratio in the free fraction of heated polypeptide and proteins (and fossil proteins) is greater than that of the bound fraction: for di- and tripeptides and two polypeptides, this relation is reversed (Table 1). In the case of proteins, only a small portion of the total bound isoleucine will be in the preferentially epimerizing terminal position; overall, therefore, the ratio in the total bound fraction (terminal and interior) will be relatively low. Because the free isoleucine of these samples is derived from preferential hydrolysis of the terminal, highly epimerized amino acid, the ratio in the free fraction will exceed that in the bound fraction. However, in the case of dipeptides, or any polypeptides having isoleucine rapidly hydrolyzed to the terminal position, the bound isoleucine occurs only in terminal positions and the ratio in the bound fraction will therefore be relatively high. The ratio in free amino acids derived from the dipeptides will be less than that in the bound fraction because the first additions to the free amino acid fraction will be from dipeptides with initially low ratios of alloisoleucine to isoleucine, and these additions will subsequently epimerize very slowly compared to the epimerization rate of the remaining terminally bound isoleucine.

In conclusion, epimerization-racemization of amino acids is not only time- and temperature-dependent, but, as our study demonstrates, the rate of epimerization of isoleucine is also dependent on the position of isoleucine in the peptide chain and on the strength of the isoleucine peptide bonds. Because the position of isoleucine changes from internal to terminal to free during protein hydrolysis, and because K_{epim} of isoleucine is different for each position, the rate of epimerization changes during the course of the reaction; the gradual buildup of slowly epimerizing free isoleucine results in a decrease in the apparent first-order rate constant. Furthermore, inasmuch as the amino acid sequence of calcified protein is unique for each species, the shape of the isoleucine epimerization curves for fossils will be species-dependent; variable rates of isoleucine epimerization have already been demonstrated for different species of foraminifera and mollusk shells (*9*). In order to use kinetics of amino acid epimerization-racemization for dating purposes, it is necessary, therefore, to establish independently the kinetics for each matrix or species of interest; kinetics obtained for one species may not be applicable to other species.

NIVAT KRIAUSAKUL
RICHARD M. MITTERER
Programs in Geosciences,
University of Texas at Dallas,
Richardson 75080

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Inland Ice Sheet Thinning Due to Holocene Warmth

Abstract. *The climatic warming of 10,000 years ago is now affecting the central portions of ice sheets, causing ice-flow acceleration. This process explains the present-day thinning of the ice sheet in West Antarctica. Former ice sheets must have also responded to climatic warming with a delay of thousands of years. This lag in response is important in the climatic interpretation of glacial deposits and of changes in ice volume obtained from deep-sea cores.*

The response of large ice sheets to climatic change is important to understanding the dynamics of the present-day ice sheets as well as to understanding the volumetric changes of ice during glaciations. A number of mechanisms have been proposed to account for ice sheet changes (*1*), but one of the simplest has escaped close attention in the literature.

The temperature of an ice sheet is generally somewhat less than freezing for most of the thickness. A climatic change in temperature at the surface is slowly propagated into the ice mass with the ice motion and by conduction. Because the creep of ice is temperature-sensitive, a climatic warming must cause an ice-flow acceleration some time later than the climatic change.

It is possible to calculate the lag time from climatic warming to ice acceleration and the amount of acceleration. I have done this for the present-day West Antarctic ice sheet, and the slow thinning of the central portion (*2*) can be explained in this way as a result of the Holocene warmth. The mechanism is also applicable to the former Laurentide and Scandinavian ice sheets, and the rapid expansions of those ice sheets, especially at the end of the glaciation, could have been responses to climatic warming.

The change in the heat content of a particle of ice in an ice sheet is described by

$$C_{\mathrm{v}} \frac{d\theta}{dt} = \vec{\nabla} \cdot K \vec{\nabla} \theta + \text{heat} \qquad (1)$$

where θ represents temperature, t is time, K is the conductivity, C_{v} is the heat capacity, and $\vec{\nabla}$ is the gradient operator. Heat is released as a result of deformation of the ice as it flows. In the central portion of an ice sheet, heat conduction is almost entirely in the vertical direction, z, and horizontal advection and variations in conductivity and capacity are not very important. Applying these simplifications, Eq. 1 becomes

$$C_{\mathrm{v}} \frac{\partial \theta}{\partial t} = K \frac{\partial^2 \theta}{\partial z^2} - C_{\mathrm{v}} \frac{\partial \theta}{\partial z} w + \text{heat}$$

The vertical velocity of a particle in the ice sheet, $|w|$, is about 0.2 m year^{-1} at the top surface of a typical ice sheet and decreases to near zero at the bed.

Let the steady-state temperature before a climatic change be described by θ_0 and the temperature after a climatic change by $\theta = \theta_0 + \theta_1$. Thus, θ_1 represents the climatic perturbation and $\partial\theta_0/\partial t = 0$. The steady-state heat flow is governed by

$$0 = K\frac{\partial^2\theta_0}{\partial z^2} - C_v\frac{\partial\theta_0}{\partial z}w + \text{heat} \qquad (2)$$

and nonsteady heat flow by

$$C_v\frac{\partial\theta_1}{\partial t} = K\frac{\partial^2\theta_0}{\partial z^2} + K\frac{\partial^2\theta_1}{\partial z^2} - C_v\frac{\partial\theta_0}{\partial z}w - C_v\frac{\partial\theta_1}{\partial z}w + \text{heat} \qquad (3)$$

Changes in heat production associated with the increased velocity after the warming are second order to this calculation and need not be included to describe the first effects on ice flow. Such feedback effects would enhance somewhat the ice thinning result obtained below.

Subtracting Eq. 2 from Eq. 3 provides a description of the temperature perturbation (*3*):

$$\frac{\partial\theta_1}{\partial t} = \frac{K}{C_v}\frac{\partial^2\theta_1}{\partial z^2} - \frac{\partial\theta_1}{\partial z}w \qquad (4)$$

Equation 4 has been solved numerically, and the temperature perturbation due to a warming 10,000 years ago is illustrated in Fig. 1.

A value for the warming at the top surface about 10,000 years ago can be obtained from the change of 7 per mil in the stable oxygen isotopic ratio ($\delta^{18}O$) of ice deposited before and after that time (*4*). Aldaz and Deutsch (*5*) established with data from the South Pole that, on the short term, a change in $\delta^{18}O$ of 1.4 per mil is associated with an air temperature change of 1°C; from this, and the present-day geographic distribution of $\delta^{18}O$ and temperature, a top surface warming of about 5°C in Antarctica is inferred (*6*, *7*). There is a problem with using short-term variations to estimate long-term climatic changes in this way. However, few workers would question the sense of the temperature change some 10,000 years ago, and 5°C is a suitable round-figure value for this change. From Fig. 1, this causes a net warming of about 1°C at a depth of 2000 m, after 10,000 years.

This warming within the ice causes more rapid ice deformation. The temperature sensitivity of ice in creep is described by an activation energy which has been determined from laboratory experiments to be in the range of 50 to 200 kJ/mole (*8*, *9*). A favored value is 70 kJ/mole (*9*). Differentiating the Arrhenius relation (*8*), these activation energies result in a temperature sensitivity of ice creep of 9 to 33 percent per degree Celsius, with about 10 percent being preferred. The central part of the West Antarctic ice sheet, where the temperature perturbation calculation applies, is therefore expected to be flowing 10 to 30 percent faster than it was 10,000 years ago. A more exact method of calculation, based on an integration of the relative changes in ice velocity through the ice thickness, gives about the same result.

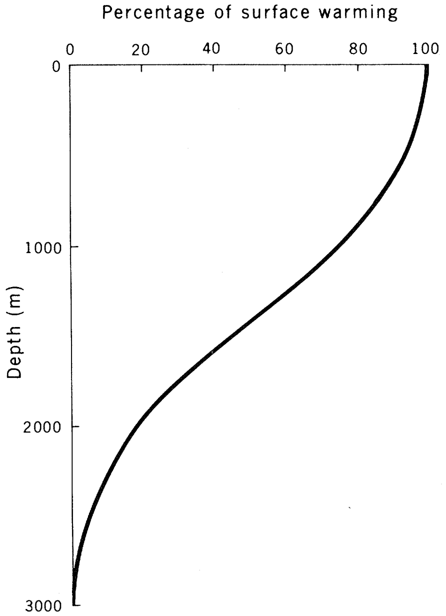

Fig. 1. Calculated temperature perturbation in central West Antarctica, 10,000 years after a surface temperature change (*12*).

A comparison of the ice outflow rate in central West Antarctica with present-day snow accumulation rates shows that the ice velocity is about 20 percent greater than the velocity needed for steady state and the ice sheet must be thinning (*2*). In earlier publications (*2*) I have argued that the most probable explanation for this imbalance is reduced net snow accumulation and that values some thousands of years ago must have been larger than those measured for the period 1964 through 1974. I argued against an ice outflow acceleration because I was unable to devise a satisfactory mechanism for uniform acceleration. The theory presented here provides such a mechanism, and it predicts the appropriate amount of excessive ice flow. Reduced net snow accumulation is a possible interpretation for part of the imbalance; however, the warming effect described here is sufficient, and I consider it the best explanation for the thinning in central West Antarctica.

Figure 2 demonstrates the time progression of warming. The warming at depth depends on the time and amount of surface warming and not critically on the suddenness of surface warming. The warming is taken as having started 10,000 years ago, but the date is also not critical. At about 15,000 years after the surface warming, the effect at 2000 m is about twice that after 10,000 years, and, within the uncertainties of the amount of warming and the activation energy, a warming at that time is also consistent with the measured thinning.

This theory applies to those parts of ice sheets where the motion is caused primarily by internal deformation, and it describes only the effect of surface temperature changes. Changes in net snow accumulation are not treated here because data are lacking on even the sense of possible changes. The effects of sea-level changes or changes in the controls on bottom sliding are not addressed here.

This theory is expected to apply to the central portions of all ice sheets. There are no data with which to test the application of the theory to East Antarctica. The lag time there is very much longer than for West Antarctica because of the small accumulation rate. Data from Greenland show thickening in the central area (*10*) which, if correct, would suggest that the thinning due to warming is more than compensated by, perhaps, increased Holocene snow accumulation in Greenland.

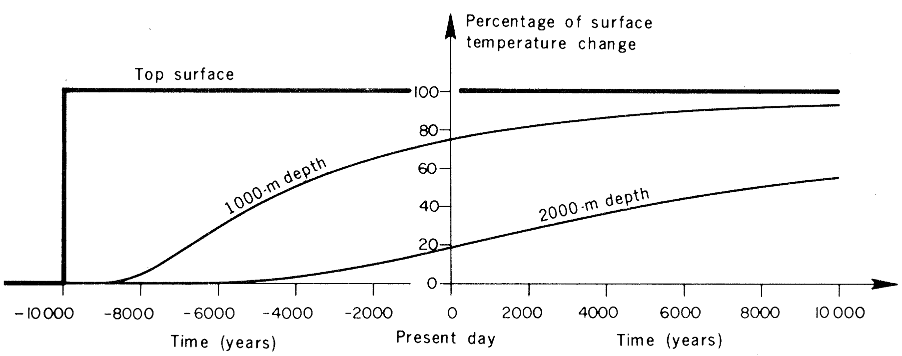

Fig. 2. Time progression of deep temperature change. The calculations apply to central West Antarctica. The time needed for surface temperature changes to affect deep ice is longer for thick ice sheets and for ice sheets with smaller snow accumulation rates, and shorter for thin ice sheets and for ice sheets with larger snow accumulation rates.

The theory is important to interpretations of ice-marginal changes. As developed above, the theory does not directly describe the reaction of the outer portions of ice sheets because the flow there is dominated by bottom sliding. The ice thickness in these outer portions is controlled, in large part, by the supply of ice from the interior. Increased ice export from the central areas, as a delayed response to climatic warming, must be accommodated by ice thickening and an advance of the ice sheet margin. Because of central ice sheet warming, ice sheets are expected to advance some thousands of years after the warming. A marginal advance or at least a thickening of the marginal areas of West Antarctica is therefore expected in the future. The rather rapid final advance of the Laurentide and Scandinavian ice sheets (*11*) may have been in response to such a warming and not to a cooling, as has sometimes been inferred.

These considerations are important to the interpretation, in terms of climate, of changes in continental ice volumes obtained from studies on ocean bottom cores. A general and simple climatic warming would immediately affect ice volume by increasing net ablation and runoff from the ablation zones. This would be followed, some thousands of years later, by an ice advance and by an increase in the area of ablation zones due to the delayed warming effect on the central ice sheet. The most dramatic decrease in the continental ice volumes may be expected after the climatic warmth penetrates into the central ice sheet and the ice sheet margin subsequently advances.

I. M. WHILLANS
Department of Geology and Mineralogy
and *Institute of Polar Studies,*
Ohio State University,
Columbus 43210

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Oceanic Residence Times of Dissolved Beryllium and Aluminum Deduced from Cosmogenic Tracers ^{10}Be and ^{26}Al

Abstract. *The residence times of the soluble fractions of beryllium and aluminum in seawater are estimated to be 1500 years or more. These residence times are estimated from a comparison of the annual deposition rates of cosmogenic beryllium-10 and aluminum-26 with the concentrations of beryllium-10 and aluminum-26 in seawater estimated from the specific activities of these radionuclides in an authigenic mineral assembly such as a manganese nodule. These residence times are greater by an order of magnitude than the mean residence times of beryllium and aluminum estimated from the geochemical balance.*

The relative reactivities of elements in the marine hydrosphere can be determined from a knowledge of the average time an element spends in the oceans (*1*). Barth (*2*) and Goldberg and Arrhenius (*3*) have defined the mean residence time T of an element as

$$T = A/Q \qquad (1)$$

where A is the total quantity of the element in the sea and Q is its rate of introduction or removal; in the steady state, these two rates become equal and either can be used (*4*). As a first approximation, Goldberg and Arrhenius considered a single cycle of introduction and deposition, and estimated the residence times of 15 major and minor elements. The results obtained were found to vary between 2.6×10^8 years for the most soluble element, Na, and between 100 and 160 years for the most quickly precipitating elements such as Al, Fe, and Ti. Using the same method, Merrill *et al.* (*5*) estimated the residence time of Be to be 150 years (*6*).

Arnold (*7*) has examined the usefulness of more complex models, in particular, one that consists of three independent cycles: a cycle for the soluble fraction (including exchangeable sorbed ions), an inshore particulate cycle, and a pelagic particulate cycle. He concluded that the bulk of each of the three elements, Al, Fe, and Ti, pass through the ocean in particulate form, so that their residence times are largely controlled by the particulate cycles. Assuming a very short residence time for the nearshore particulates, Arnold deduced that the residence time of the pelagic clay particles may be much more than a hundred years and therefore comparable to the estimated general mixing time for the oceans (which is on the order of 10^3 years). This residence time may therefore represent a geophysical phenomenon, the mixing of the oceans, through which the residence times for nearly all elements in particulate form should be about the same (*8*).

The true reactivity for each element should therefore be reflected in the residence time of the soluble fraction. Since the particulate cycles dominate over the cycle for the soluble fraction for Al, Fe, and Ti, however, it has been very difficult to estimate the residence time of the soluble fraction from classical considerations of the geochemical balance of each element. We propose here the use of the naturally occurring radioactive tracers ^{10}Be and ^{26}Al for this estimate. These nuclides are produced by the bombardment of atmospheric constituents by cosmic rays. Their half-lives [1.5×10^6 years for ^{10}Be and 0.716×10^6 years for ^{26}Al (*9*)] are long enough so that the radioactive decay is negligible in comparison with the residence times in the marine hydrosphere.

We consider an average 1-cm^2 column in the ocean. We use Eq. 1, but here A is the total quantity of ^{10}Be (or ^{26}Al) in the column and Q is the annual deposition rate of ^{10}Be (or ^{26}Al) per square centime-

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