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Abstract. The CO_2 content of air occluded in Greenland Ice Sheet Project 2 (GISP2) ice formed over two separate intervals of rapidly changing climate, centered at approximately 46 and 63 kyr B.P., is as much as 90 ppm more during warm periods (interstadials) than during cold periods (stadials). These CO_2 variations are superimposed on changes in annual layer thickness and $\delta^{18}O$ of the ice and do not show the 200- to 700-year offsets which would be expected for concurrent variations in the atmosphere and the ice. The CO_2 concentrations during the stadials are similar to the atmospheric values recorded by Antarctic ice of the same age, so processes occurring in the ice after bubble enclosure must be enriching the air trapped in GISP2 ice formed during the interstadials. This conclusion is supported by Ca content and electrical conductivity measurements of the ice, which show that adequate carbonate is present to produce these enrichments and that CO_2 content is high only when the electrical conductivity (a proxy for H^+ concentration) is high. High-resolution mapping of one 4-cm section of ice shows a 200-ppm increase in the CO_2 content of the trapped air, from approximately 275 to 475 ppm. Analyses of the total inorganic carbon of ice from both the LGM and Holocene show that most of the Ca in the ice is from $CaCO_3$ and that the $\delta^{13}CO_2$ approaches that of soil and marine carbonates. These results show that the CO_2 record preserved in ice can be altered by in situ decarbonation reactions and that only ice containing either abundant carbonate or essentially no carbonate contains a reliable record of paleoatmospheric CO_2.

1. Introduction

The CO_2 content of the atmosphere is a quantity of great interest since CO_2 is the most important trace greenhouse gas and since changes of atmospheric CO_2 concentrations, over periods up to as much as 100,000 years, are believed primarily to reflect changes in oceanic and biospheric carbon cycling. One way better to understand the role of atmospheric CO_2 in present and future climates is to study how CO_2 has varied in the past, especially in relation to variations in other physical, chemical and isotopic tracers of climate change. A method which has been widely used to reconstruct paleoatmospheric compositions over the past 250,000 years is the analysis of air contained in polar ice. This air, trapped as bubbles during the course of ice production, has been generally considered an accurate record of the composition of the atmosphere. Therefore it is possible in principal to determine how the CO_2 content of ancient atmosphere has changed by the analysis of air from polar ice cores. The accuracy of this CO_2 record, however, depends on whether the air remained unaltered by

chemical reactions over the course of its entrapment. We have measured the CO_2 content of air occluded in Greenland Ice Sheet Project 2 (GISP2), Greenland, ice formed during periods of rapid climate change in order to determine whether or not CO_2 varies and, if it does, to identify the cause(s) of these variations.

The process of polar ice formation begins with the deposition of snow. As snow accumulates, the underlying layers begin to compact and recrystallize into a porous structure called firn. Atmospheric air ventilates the firn as long as it remains porous, so the firn is continually flushed with air younger than the snow from which it formed. Air is trapped as bubbles in the ice when the firn recrystallizes completely enough to seal the voids which the atmosphere has ventilated up to that time. The process of air enclosure does not preserve air of a single, unique age because bubble formation occurs gradually, over a range of depths, while air continues to mix throughout the remaining, still porous sections of firn. Therefore ice traps a time-integrated sample of the atmosphere, whose average age (younger than the surrounding ice) depends on temperature and accumulation rate [Schwander, 1989]. At the site of the GISP2 core, during the intervals studied in this work, the temperature and accumulation rate varied in a manner such that trapped air should have an average age from 220 to 700 years less than

that of the surrounding ice [*Wahlen et al.*, 1991; *Sowers et al.*, 1992; *Meese et al.*, 1994].

A series of extremely rapid climate fluctuations, referred to as Dansgaard-Oeschger events or interstadials (warm periods between periods of cold) and each typically lasting from several hundred to several thousand years, are recorded in Arctic ice formed between approximately 110 and 14 ka [*Johnsen et al.*, 1992; *Dansgaard et al.*, 1993; *Taylor et al.*, 1993]. During these fluctuations, climate in Greenland seems to have shifted back and forth between cold and warm states in times often as short as decades, as recorded by structural, chemical and isotopic changes in the ice. We have measured the CO_2 content of air extracted from GISP2 ice for five of these rapid transitions across two stadials. The CO_2 results are compared to the annual layer thickness, $\delta^{18}O$, electrical conductivity and the Ca concentration of the ice in order to determine the relative timing of any changes in these quantities. Total inorganic carbon (TIC) and its $\delta^{13}CO_2$ were also measured for ice from both the last glacial maximum (LGM) and the Holocene in order to better assess the possibility that carbonate chemistry might be responsible for elevated CO_2 concentrations in some ice, by postdepositional decarbonation reactions when there is sufficient acidity present [*Neftel et al.*, 1982, 1988]. Finally, a high-resolution series of the CO_2 content of a piece of ice formed at the end of one interstadial was made in order to document the fine scale structure of a dramatic increase in CO_2 concentration.

2. Materials and Methods

The interstadial samples analyzed in this work were taken at 0.5- to 1-m intervals from two sections of GISP2 ice, with depths between 2355 and 2390 m and between 2580 and 2605 m, corresponding to ages of roughly 45 to 47 ka and 62 to 64 ka, respectively [*Meese et al.*, 1994]. The younger section spans the cold interval (stadial) between the interstadials IS13 and IS14 while the older section spans the stadial between IS20 and IS21 [*Dansgaard et al.*, 1993]. Additionally, a short interval of ice from the end of IS21 [*Dansgaard et al.*, 1993], from a depth between 2599.09 and 2599.16 m, was analyzed in 1-cm increments after an unusually high CO_2 concentration was measured at 2599.09 m. Only ice which appeared optically clear (no fracturing, no dust layers) was used. All samples were carefully trimmed in order to reduce the possibility of atmospheric contamination from ice near the outer surfaces of the core. All cutting and loading were done in a walk-in freezer at $-27°C$. The ice was stored in a commercial freezer at $-18°C$.

Our analytical apparatus contains three basic components: a dry extraction crusher, a cryogenic trap for condensation of the entire air sample and a high-resolution tunable infrared (IR) diode laser spectrometer. The dry extraction technique used to measure CO_2 concentration, in which three sample/standard pairs are extracted sequentially and run at the same pressure [*Wahlen et al.*, 1991], has a precision of ±3 ppm. Three pieces of ice, taken from depths differing by no more than 1 cm in order to minimize any compositional differences, were analyzed for each data point, resulting in an average external precision of ±7 ppm. The internal standard after each sample is loaded over the previously crushed ice, after the ice has been pumped for 15 minutes, in order to reproduce the conditions under which the samples are collected. Three standards with precisely known CO_2 concentrations of approximately 163, 330 and 430 ppm are used. The CO_2 concentration measurements are made first on the three samples and then on the three standards. Four measurements are made for each CO_2 concentration determination.

Total inorganic carbon and $\delta^{13}CO_2$ were measured for ice from the LGM and the Holocene. Glacial ice samples were from GISP2 ice of 1865- to 1865.12-m depth, while Holocene samples were taken from GISP2 ice of 567.0- to 567.3-m depth. Total inorganic carbon was measured on pieces of uncrushed ice by melting under vacuum and acidifying the water with an excess of phosphoric acid. The resulting CO_2 (i.e., CO_2 from bubbles plus that formed from the acidification of any carbonate and bicarbonate in the ice) was separated cryogenically and its standard volume calculated by expanding it into a known volume and determining the pressure with a transducer, after which it was collected in a cold finger at liquid nitrogen temperature. The $\delta^{13}CO_2$ was analyzed on a VG Prism II Series dual inlet mass spectrometer.

3. Results

The concentration of CO_2 in occluded air across the two stadials shows clear minima in each case (Figures 1 and 2). The older stadial (2605- to 2575-m depth) is preceded by a noisy interval with CO_2 concentrations of 260-295 ppm. The scatter of the CO_2 data is consistent with that observed for other Greenland ice [*Wahlen et al.*, 1991; *Anklin*, 1994; *Smith et al.*, 1997]. The CO_2 concentration begins to decrease at a depth near 2593 m, remains between roughly 230 and 250 ppm for the 7 m (800 years) from 2592- to 2585-m depth and then rises rapidly to 284 ppm at a depth of 2584 m. The 55-ppm increase at the end of the cold period occurs within approximately 200 years, i.e., at a rate of 27 ppm per hundred years. For comparison, the average rate of atmospheric CO_2 increase during the last deglaciation was 1.2 ppm per hundred years and 0.9 ppm per hundred years during the penultimate deglaciation [*Barnola et al.*, 1987; *Neftel et al.*, 1988; *Stauffelbach et al.*, 1991]. The difference between the highest and lowest CO_2 concentrations measured in this section is 64 ppm. The increase in atmospheric CO_2 during the last deglaciation was approximately 80 ppm (from 195 to 275 ppm); the increase during the penultimate deglaciation was approximately 105 ppm (from 190 to 295 ppm). Therefore the changes in CO_2 concentrations of the air trapped in GISP2 ice formed across this stadial are similar in magnitude to, but much more rapid than, the changes observed during major deglaciations.

The younger stadial (2390- to 2350-m depth) shows a similar pattern. The CO_2 concentration decreases from an erratic maximum during the warm interval, with values as high as 278 ppm at 2384 m, to between roughly 180 and 220 ppm in the depth range of 2378 to 2360 m. CO_2 remains low for the 1100 years from 2378 to 2364 m, with the exception of two points at 2363 and 2374 m (discussed below), and rises rapidly from 187 ppm at 2360 to 223 ppm at 2359 m and to 269 ppm at 2358 m. The highest value is 285 ppm at 2355 m. The maximum rate of increase is 80 ppm per hundred years, occurring in the 102-year interval between the depths of 2360 and 2358 m. An additional transition from cold to warm
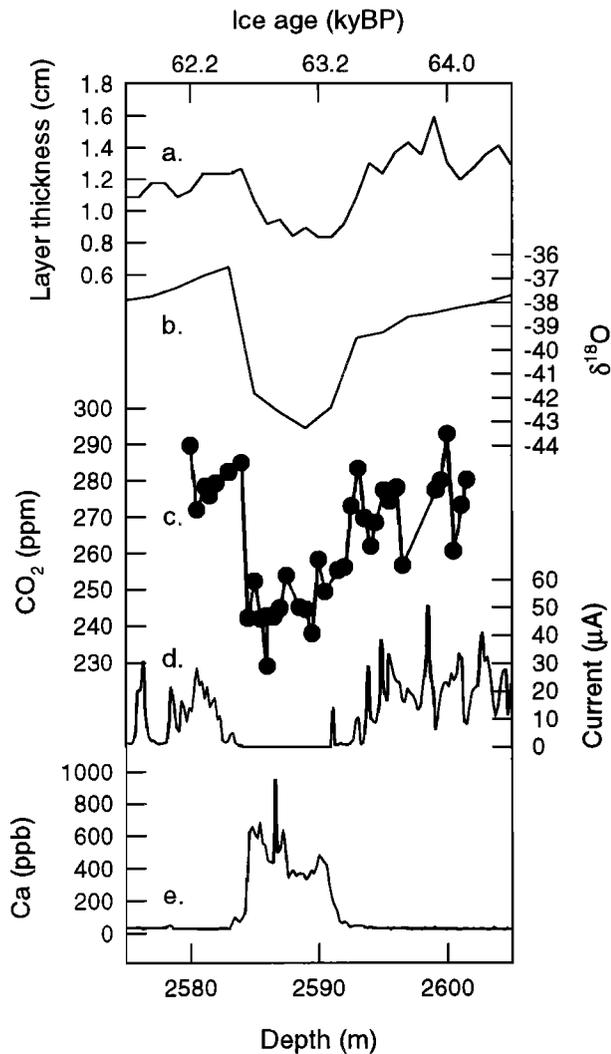
Figure 1. Data from GISP2 ice between 2580- and 2605-m depths. (a) Annual layer thickness of the ice [*Meese et al.*, 1994]. (b) The $\delta^{18}O$ of the ice [*Grootes et al.*, 1993]. (c) CO₂ concentrations (this paper). (d) ECM values are averages over 20 cm of measurements taken at 1 mm intervals [*Taylor et al.*, 1993]. (e) Ca concentrations in the ice [*Mayewski et al.*, 1994]; the low Ca content of ice from warm intervals is typically between 20 and 60 ppb.
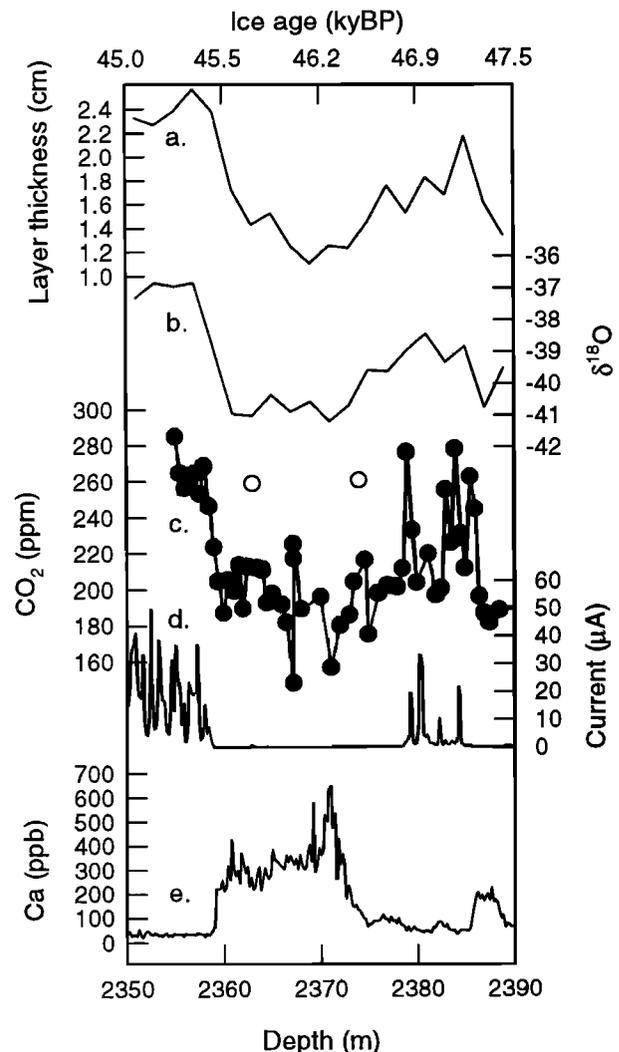
Figure 1), also had an unusually high CO₂ content of 349 ppm.

4. Discussion

Figures 1 and 2 show how the CO₂ concentration changes with respect to the annual layer thickness and the $\delta^{18}O$ of the ice, versus depth. Accumulation rate (and thus annual layer thickness) and the $\delta^{18}O$ of ice primarily reflect the delivery of precipitation and the temperature at which the snow formed, making them good indicators of climate on a regional scale or larger. A number of important observations can be made about these plots. First, the CO₂ variations are superimposed on those of annual layer thickness and $\delta^{18}O$ of the ice: the 5- to 6-m shift toward older ice that would be expected for concurrent changes in the atmosphere and ice is entirely absent. Second, the 50- to 100-ppm CO₂ differences between stadials and interstadials occur over periods of only 100 to

conditions at the beginning of IS21 is also recorded in this section. Like the others, it also displays a large and rapid increase in CO₂ concentration, from 187 to 263 ppm in 115 years.

The most extreme example of CO₂ enrichment in these samples can be seen in the depth interval between 2599.16 and 2599.09 m, where the concentration of CO₂ rises by 200 ppm in only 4 cm (Figure 3). This short interval of ice from the end of IS21 [*Dansgaard et al.*, 1993] was analyzed in 1-cm increments after an unusually high CO₂ concentration was measured at 2599.09 m. The CO₂ concentration of the section increased from a constant value of approximately 275 to 475 ppm over the 4 cm (corresponding to approximately 3 years) between 2599.12 and 2599.09 m (Figure 3). This is the largest variation which we observed in any of the ice and the highest CO₂ content, although another sample from a region of high electrical conductivity, at 2583-m depth (not shown in


Figure 2. Data from GISP2 ice between 2355- and 2390-m depth. (a) Annual layer thickness of the ice. (b) The $\delta^{18}O$ of the ice. (c) CO₂ concentrations (this paper). The open circles are for samples from depths which have narrow ECM maxima not visible on the smoothed electrical conductivity curve. (c) ECM values (averaged over 20-cm intervals). (e) Ca concentrations in the ice. References are as in Figure 1.
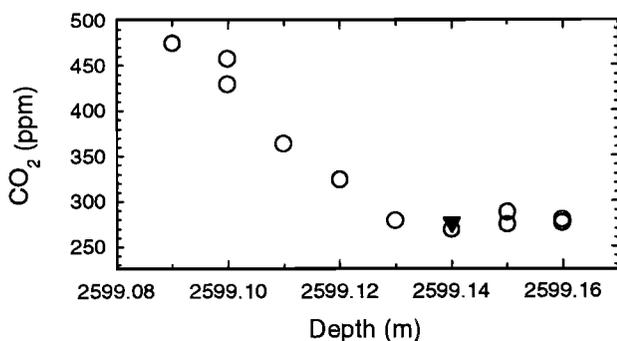
Figure 3. CO_2 concentrations from GISP2 ice between 2599.09- and 2599.16-m depth. The inverted triangle is for ice warmed to approximately 0°C for 1 hour (no melting observed), in order to test whether such warming could cause measurable CO_2 contamination.

200 years, a surprisingly short time for the atmosphere to have changed so dramatically. Third, the minimum values of the CO_2 concentrations are similar to the atmospheric values deduced from measurements of Vostok ice [*Barnola et al.*, 1987, 1991]. These facts strongly argue against the possibility that these CO_2 variations are atmospheric in origin and show that the high CO_2 concentrations are increases above atmospheric values which must have resulted from chemical reactions in the ice. Furthermore, the observed gradients show that diffusion has not affected the shapes or positions of the signals. Therefore these reactions must have happened after the bubbles were sealed, since CO_2-producing reactions occurring in the firn would either display a shift toward deeper ice (if they were preserved) or not be recorded at all because of atmospheric ventilation of the firn.

The reaction most likely to have produced these CO_2 increases is decarbonation of $CaCO_3$ by

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

[*Neftel et al.*, 1988; *Delmas*, 1993; *Anklin et al.*, 1995]. This process depends on the availability of sufficient carbonate (including bicarbonate) and acidity to enrich the occluded air by the amounts observed. The acidity of ice is reflected by its electrical conductivity [*Hammer*, 1980; *Taylor et al.*, 1992]. The electrical conductivity of ice is high during warm, wet periods due to the presence of strong acids in the snow and low during cold, dry periods because any acids are neutralized by the high concentrations of alkaline dust that occur during those periods [*Taylor et al.*, 1993]. It is unclear how much of the reaction between $CaCO_3$ and H^+ occurs during transport of the precipitation and how much occurs in the firn, but the important point here is that when there is abundant carbonate, the acidity of the ice is low because the strong acids have already been neutralized. Figures 1 and 2 show the Ca concentrations and the electrical conductivity of the ice. Elevated CO_2 concentrations only occur during the warm periods when electrical conductivity measurement (ECM) values are also high, exactly what would be expected if CO_2 production occurred from the decarbonation of $CaCO_3$. Although decarbonation cannot occur without adequate acidity, the component which limits the magnitude of CO_2 production by this reaction in GISP2 ice is $CaCO_3$, not H^+ [*Anklin et al.*, 1995].

For the mechanism discussed above to be viable, sufficient carbonate must exist in the ice to enrich CO_2 by 50-100 ppm. Evidence that this is possible is provided by our measurements of TIC and $\delta^{13}CO_2$ on GISP2 ice from both glacial and interglacial periods. The TIC of ice includes trapped CO_2 as well as carbonate dispersed throughout the ice. Since the carbonate content of ice cannot be measured directly, because to do so the ice must be melted and melting would result in the destruction of carbonate by reaction with H^+ in aqueous solution, the carbonate content must be estimated indirectly. We have done this for ice from the LGM and the Holocene by subtracting the amount of CO_2 expected from occluded air (assuming 10% air by volume in the ice and atmospheric CO_2 concentrations of 200 and 280 ppm for the LGM and Holocene, respectively) from the amount of CO_2 extracted after melting and acidifying the ice. The difference is the CO_2 equivalent of the carbonate. The LGM samples from 1865- to 1865.12-m depth (~17 kyr B.P.) have TIC contents of 4.1 and 5.5 nmol per gram of ice and corresponding $\delta^{13}CO_2$ values of −4.45and −3.70‰, while Holocene samples from 567.0- to 567.3-m depth (~2500 years B.P.) have TIC contents of 1.4 and 1.5 nmol per gram of ice and $\delta^{13}CO_2$ values of −7.23 and −7.43‰, respectively. The LGM samples were taken from ice differing in depth by approximately 2 cm. They have clearly different CO_2 concentrations and $\delta^{13}C$ values, which we interpret as evidence of fine scale variability in GISP2 ice. The Holocene samples were prepared from equivalent depths so that they were as identical as practical, a fact reflected in the similarity of their CO_2 concentrations and $\delta^{13}CO_2$ values.

Indirect measurements of carbonate as described above are time consuming and inexact, and there is no existing database of such information, so it would be useful to be able to employ a proxy which has already been commonly measured in order to estimate the carbonate content of ice. The Ca content of the ice is a good candidate for this since the most likely source of carbonate is $CaCO_3$. The Holocene ice which we measured has a carbonate content of 0.18-0.23 nmol/g and a Ca content of approximately 0.14 nmol per gram of ice (5.6 ppb), while the LGM ice has a carbonate content of 3.2-4.6 nmol/g and a Ca content between 4 and 7.9 nmol per gram of ice (160-315 ppb). This shows that the $CaCO_3$ in the precipitation was only partially neutralized by strong acids during transport, a possibility recognized by *Delmas* [1993]. Given the uncertainty of the estimate of the amount of occluded air, the fact that the Ca and CO_3 contents of the ice are within 30% of each other shows that Ca is a good proxy for carbonate. These TIC results imply that the ice formed during interstadials (with Ca contents between 25 and 40 ppb) contains more than enough carbonate to account for the variability seen in CO_2 since every 10 ppb of Ca means 0.25 nmol/g carbonate or a 56-ppm enrichment of CO_2 in the occluded air if Ca equals $CaCO_3$ on a molar basis.

These results suggest that Antarctic ice is probably a more reliable source of information about paleoatmospheric CO_2 since its Ca content, and therefore presumably its carbonate content, is so low: *Legrand and Delmas* [1988] report average soluble Ca contents of only 0.03 ppb for the Holocene, 1.66 ppb for the LGM and 20 ppb for the LGM/Holocene transition. These results also have important implications for the study of the $\delta^{13}CO_2$ of air trapped in ice. For example, the greatest TIC burdens in GISP2 ice (i.e., the highest alkaline

dust concentrations) are found for the LGM, which is consistent with the idea that increased transport during cold, dry climatic periods helped produce the high dust contents [*Yung et al.*, 1996]. The $\delta^{13}CO_2$ of these samples approaches the $\delta^{13}C$ of soil carbonates [*Cerling and Quade*, 1993] and marine carbonates, the two most probable sources of the dust. Therefore the $\delta^{13}CO_2$ of occluded air is also likely to be higher than that of the atmosphere at the time of bubble formation if decarbonation has occurred in the ice.

In contrast to the enrichment discussed above, several samples from low ECM regimes had CO_2 concentrations from 15 to 40 ppm lower than that of the surrounding ice. One possible explanation for these low values is that CO_2 was consumed by the reaction

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-$$

occurring in the ice [*Neftel et al.*, 1982]. Therefore CO_2 depletion may also be possible under certain conditions, although this seems to be a less common occurrence in this ice. The exact mechanisms of CO_2 production or depletion are still not known, however, and the absence of this knowledge remains the largest gap in our understanding of the CO_2 record of polar ice.

The results of this work indicate that measurements of the CO_2 concentration of air trapped in ice may reflect atmospheric values only when there is either no (or very little) carbonate or a high concentration of carbonate present in the ice. We therefore propose that ice can be divided into three categories for the purpose of evaluating the CO_2 record which it contains: low carbonate, high carbonate and intermediate carbonate. When there is only enough $CaCO_3$ in the precipitation to supply less than approximately 5 ppb of Ca ("low carbonate"), essentially all of the $CaCO_3$ reacts with H^+ before ice formation and the CO_2 content of the trapped air reflects ambient atmospheric values at the time of bubble formation. Antarctic ice, for example, should contain a more accurate record of atmospheric CO_2 than ice from Greenland since its carbonate content is so much lower [*Legrand and Delmas*, 1988]. When there is abundant $CaCO_3$ in the precipitation ("high carbonate"), e.g. enough to supply approximately 70 ppb or more of Ca, there is apparently sufficient carbonate to neutralize the available H^+ without the formation of CO_2 and the trapped air should record the CO_2 content of the ambient atmosphere. This case is complicated, however, by the possibility that these alkaline conditions might allow CO_2 uptake by the reaction of CO_2, H_2O and CO_3^{2-} to form bicarbonate, HCO_3^-. When there are "intermediate carbonate" concentrations in the precipitation, enough to supply between approximately 5 and 70 ppb Ca, significant amounts of CO_2 can be generated in the ice, by the reaction of H^+ and $CaCO_3$, thereby obscuring the atmospheric record. Therefore the record of "atmospheric" CO_2 concentrations in polar ice must be reconsidered in the light of carbonate chemistry if it is to be understood correctly.

5. Summary and Conclusions

Measurements of the CO_2 content of air trapped in GISP2 ice formed approximately 46 and 63 kyr B.P. have shown that large, rapid variations exist during the transitions between stadials and interstadials. The concentration of CO_2 in occluded air varies from atmospheric values during cold periods to as much as 200 ppm higher during warm periods.

These variations do not display the 5- to 6-m shifts from signatures of climate change contained within the ice itself that would be expected for concurrent atmospheric changes. Measurements of TIC in glacial and interglacial ice show that it is approximately equal to Ca on a molar basis and that most of the carbonate is from $CaCO_3$. Furthermore, the pattern of CO_2 enrichment above ambient atmospheric levels matches the H^+ content of the ice as shown by ECM, implying that acidification of carbonate from $CaCO_3$ is the source of excess CO_2. Some important questions which still must be answered before the CO_2 record of polar ice can be correctly interpreted include how much carbonate is available for reaction and what mechanisms are involved in CO_2 production (or depletion) in the ice.

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