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Long-term record of H_2O_2 in polar ice cores

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ABSTRACT

At Dye 3 and Camp Century, Greenland, and at Byrd Station, West-Antarctica, ice cores were drilled to bedrock. They offer an archive of solid precipitation over the last 50,000 to 100,000 years. H_2O_2 has been found to be one of the dominant trace components in the ice. We present a survey of the H_2O_2 levels in the three deep cores. In the Greenland ice cores the H_2O_2 level decreases with increasing depth and is extremely low during the last glaciation. In the Byrd core an H_2O_2 concentration spike is observed in the time period 6000 to 12,000 years before present. Possible explanations for the decreasing trend with age and depth and the drop during the Ice Age are discussed.

1. Introduction

Polar ice sheets represent an archive of the precipitation of the past several 10,000 years. The concentrations of trace substances in the precipitation are related to the corresponding concentration of these substances in the atmosphere (Junge, 1977). Therefore the variations of trace substances recorded in polar ice cores reflect variations of the atmospheric concentrations in the past. Improvements in analytical techniques during the last years have made it possible to measure various trace species in low concentration ranges. Extensive studies to determine the levels and variations of the principal inorganic ions have been done by several laboratories (see e.g. Legrand and Delmas, 1984; Herron, 1982; Hammer, 1980). Recently we found that H_2O_2 is one of the dominant trace components in polar ice cores (Neftel et al., 1984). These first measurements pointed toward the following behviour of the H_2O_2 concentration in polar ice cores:

Strong seasonal variations with high values in summer and low values in winter.
Low H_2O_2 concentration in ice from the last glaciation.
Generally lower values in ice cores from the southern hemisphere than in cores from the northern hemisphere.

We report here H_2O_2 measurements from the three ice cores which were drilled to bedrock to date, the Camp Century and Dye 3 core from Greenland and the Byrd core from West-Antarctica. The new data allow a better characterization of the long-term course in the three cores.

2. Experimental set-up

H_2O_2 is measured through the chemiluminescence radiation emitted during its reaction with bis(2,4,6-trichlorophenyl)oxalate (TCPO) (Klockow and Jacob, 1986). Perylene is used as a fluorescent agent. The reaction between the aqueous sample solution and the TCPO reagent (acetone to water ratio 3:1) takes place in a mixing chamber placed in front of a photomultiplier. The measuring system is drawn in Fig. 1. To determine the H_2O_2 concentration in the ice, the samples have to be melted. The samples are adjusted to a pH of 8 with a borate buffer solution, because the reaction rate of H_2O_2 with TCPO strongly depends on the pH of the

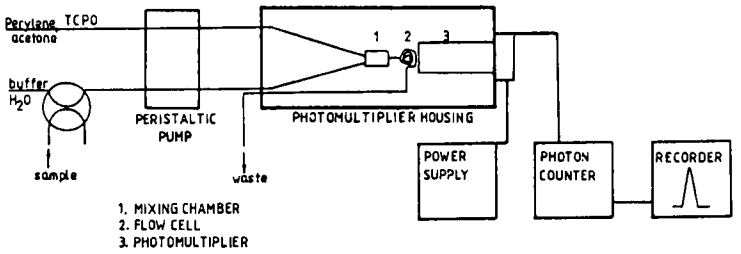

Fig. 1. The analytical system.

solution. Once the ice samples have been melted, chemical reactions can alter the H_2O_2 concentration, especially through catalytic destruction on the surface of the beakers in which the ice was melted. We used polyethylene beakers in our studies. We traced routinely the H_2O_2 level after the melting over time periods of several hours and observed decay rates of 1–10% per hour. No significant decrease was observed within 10 minutes following the melting process. All reported concentrations were therefore measured within 10 minutes after melting. The detection limit is 0.3 ppb (by weight), the accuracy of the measurements is 0.2 ppb or 4% for H_2O_2 concentrations above 5 ppb. The system was calibrated by measuring a stepwise diluted H_2O_2-stock solution (10^{-2} molar). The concentration of this stock solution was determined by titration with a standard $KMnO_4$ solution.

3. Sample preparation and selection of samples

The Camp Century core was drilled in the year 1966, the Byrd core in 1967–1968, both by the US Cold Region Research and Engineering Laboratory (CRREL) (Ueda and Garfield, 1968). The Dye 3 deep core was drilled in 1979–1981 within the frame of the US-Danish-Swiss Greenland Ice Sheet Program (GISP) (Langway et al., 1985).

Table 1 gives an overview of the characteristics of the three drill locations. To counterbalance the hydrostatic pressure of the ice sheet, the drillholes had to be filled with a mixture of kerosene and trichlorethylene or tetrachlorethylene, commonly referred to as drill fluid. Cores from the depth interval 400 to 1000 meters below surface (m.b.s.) are generally brittle due to the pressure relaxation when they are brought to the surface. Samples from this depth interval often have internal cracks, filled with drill fluid. As far as possible, we avoided to use sample material with visible internal fractures.

In preparing the Camp Century and Byrd core samples, 1.5 cm of ice have been removed from each surface in order to obtain unaffected ice. In the case of the Dye 3 samples 1 cm has been removed. The final sample sizes varied between 3 and 10g. The samples were cut with a bandsaw in a cold room (−20°C), and the sawdust was removed with a teflon brush. The samples were then melted in polyethylene beakers in a waterbath kept at approximately 40°C. After

Table 1

Station	Geographical location	Drill operation	Elevation (meters above sea level)	Accumulation (meter water equivalent)	Mean termperature °C
Camp Century	77°N 61°W	1966	1885	0.32	−24.0
Dye 3	65°N 43°W	1979–1981	2480	0.5	−19.6
Byrd	80°S 110°W	1967–1968	1530	0.16	−28.0

melting, a 1 ml fraction was adjusted with borate buffer to a pH of 8 and injected into the measuring system.

In this work, we address the question of the course of the mean H_2O_2 values. The samples have been selected to gain an overview of the course of the H_2O_2 concentration as a function of depth. Previous measurements (Neftel et al., 1984), showed a seasonal variation in phase with the oxygen isotope ratio variation ($\delta^{18}O$). The oxygen isotope ratio indicates the temperature of the precipitating cloud, and the yearly mean values are well correlated with the yearly mean temperature (Dansgaard et al., 1973). The seasonal variations of the $\delta^{18}O$ are smoothed out during the firnification process due to recrystallization at locations with yearly snow accumulation rates below 0.2 meter water equivalent (Johnsen, 1977; Whillans, 1985). There is good evidence that the H_2O_2 concentration does behave in a similar way. The seasonal structures, such as the $\delta^{18}O$ variation, are preserved in the two Greenland ice cores back to the transition into the Last glacial age starting 10,000 years before present (Hammer et al., 1975). Above 1700 m.b.s., sample series of the Dye 3 core have been selected, so that each series covered at least two seasonal cycles in order to get an appropriate estimate of the yearly mean values. Below this depth the seasonal variation could not be resolved anymore because of the thinning of the annual layers due to the ice-flow. One sample already contains more than one year, and the measured concentrations represent yearly mean values. From the Camp Century core, unfortunately, only short core segments were on stock, without any information about the seasonality.

In the Byrd core, the seasonal variations are already smoothed out during the firnification process due to the low accumulation rate of only 0.16 m water equivalent. For each depth, 2–4 samples have been measured. Because the seasonal variations are levelled out in this core, the mean value for each depth can be regarded as representative of the mean H_2O_2 concentration in the ice.

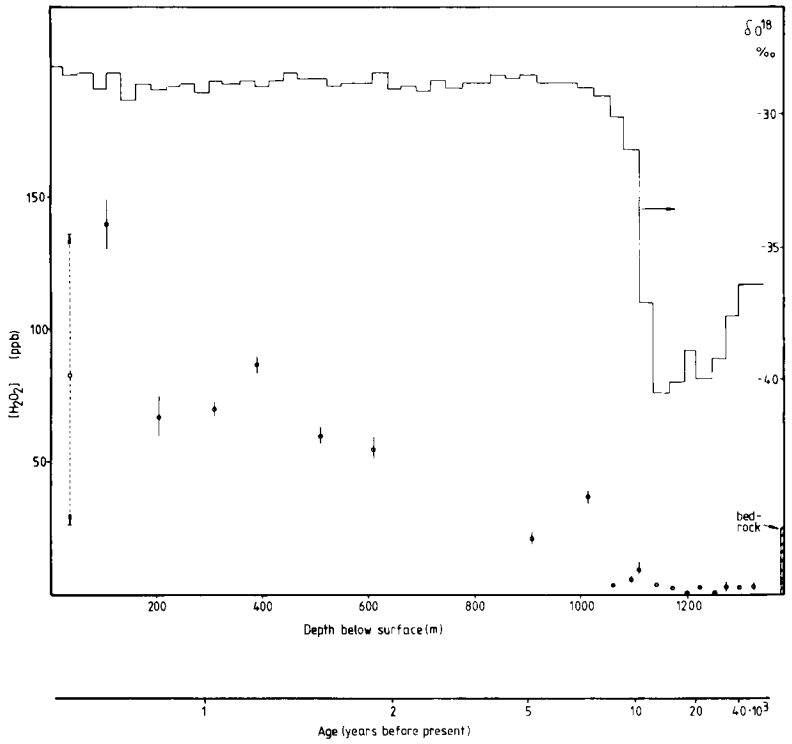

Fig. 2. H_2O_2 record in the Camp Century core with a schematic $\delta^{18}O$ curve.

4. Results

Fig. 2–4 show the measured H_2O_2 concentrations of the three ice cores as a function of the depth below surface. The dots represent mean values of the individual series. The dotted lines indicate the range between the summer maxima and the winter minima, where seasonal variations could be defined. When no seasonal fluctuation could be seen, the measured concentration with its error limits is indicated by a solid bar. Additionally, schematic $\delta^{18}O$ curves are shown for the Camp Century and Byrd cores in order to visualize the transition of the current interglacial (Holocene) into the Last glacial age (Johnson et al., 1977). For the Dye 3 core, only a part of the $\delta^{18}O$ record has already been published (Dansgaard et al., 1985). The Holocene/Last glacial age transition is a time marker, which allows a synchronization of the core dating. The dating of the younger part is much better than that of the older part. For this part the depth/age relations published so far vary greatly (Johnson et al., 1972; Thompson, 1977; Dansgaard et al., 1985). The age scale in the figures is drawn with dotted lines, where large discrepancies exist in the literature.

The general features of the measured data are:

(a) Greenland ice cores:
Moderately decreasing levels during the Holocene to 30% of the recent value just before the transition into the Last glacial age.
Sharp drop to values near or at the detection limit of 0.3 ppb in the transition zone between Holocene and Last glacial age.

(b) Byrd core:
Elevated values during the time period of the deglaciation (6000–12,000 years B.P.).
Lowest values in ice from the last glaciation.

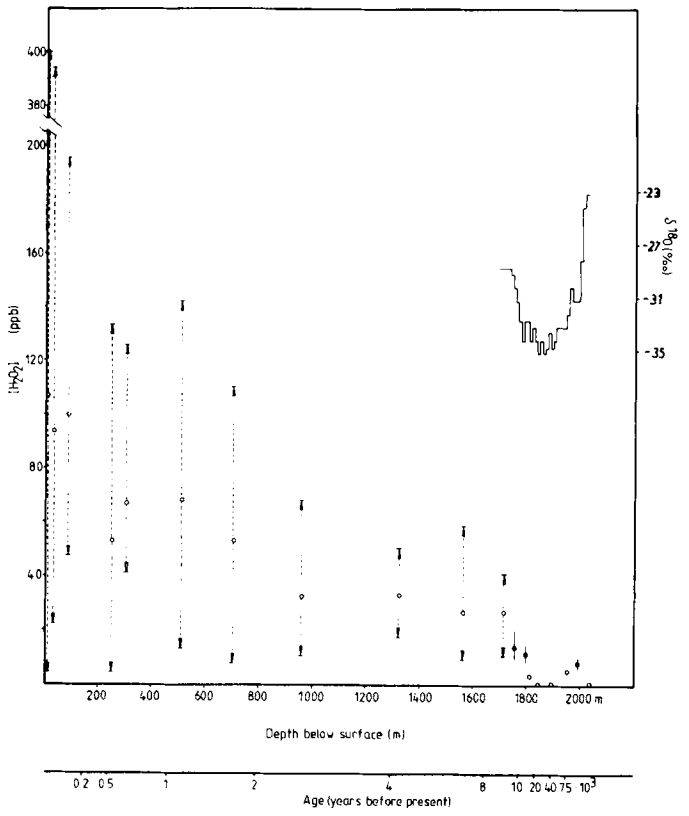

Fig. 3. H_2O_2 record in the Dye 3 core. The dotted vertical bars indicate the range between the summer maxima and the winter minima. The schematic $\delta^{18}O$ curve is shown for the lowest 300 m of the core.

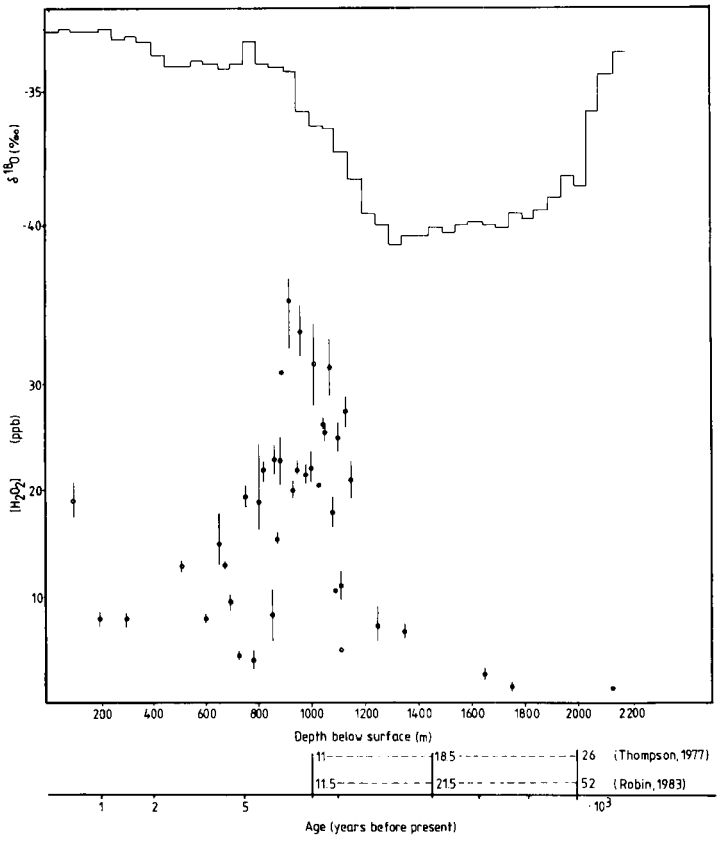

Fig. 4. H_2O_2 record in the Byrd core with a schematic $\delta^{18}O$ curve.

In the Dye 3 core an abrupt change in the total acidity and $\delta^{18}O$ ratio at 1786 m.b.s. marked the end of the last glaciation. Below 1850 meters, several sharp transitions have been recorded, where all parameters measured switched from "cold" to "warm" conditions and vice-versa (Stauffer et al., 1984). For one of these transitions, at 1897 m.b.s., we measured the H_2O_2 concentration. No similar changes were observed, the measured values are very low for the "warm" and the "cold" side of the transition.

5. Discussion

The main production of H_2O_2 in remote locations is the recombination of two HO_2 radicals, the main loss pathways are washout and photolysis. HO_2 radicals are produced in the oxidation cycles of hydrocarbons which are initiated by the reaction of OH radicals with CO, CH_4, H_2, O_3 or organic compounds. Major input to the OH radical concentration occurs via the reaction scheme

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \rightarrow OH + OH$$

The atmospheric H_2O_2 concentration depends therefore on the ozone concentration, the intensity and spectral distribution of light, the amount of water vapour, and the concentrations of the most important OH reaction partners. Additionally the amount of NO, NO_2 and SO_2 plays an important role in the distribution of the odd hydrogen compounds (H, OH, HO_2, H_2O_2). High levels of NO_2 and SO_2 suppress the H_2O_2 concentration (Kelly et al., 1985; Fishman et al., 1979).

The ratio of the atmospheric H_2O_2 concentration to the concentration in the

precipitation depends primarily on the precipitation mechanism, i.e. whether the precipitation is formed via the liquid phase or via the gas phase. In the liquid phase the ratio is given by the inverse Henry coefficient (Kelly et al., 1985). If the model of a co-condensation is assumed for the scavenging in the gas phase, the ratio c_{air}/c_{ice} is given by the water vapour concentration. The concentration in the solid precipitation depends therefore on the atmospheric concentration and the amount of scavenged liquid droplets, thus the degree of riming. This degree of riming depends primarily on the cloud temperature during the precipitation event. The best temperature indicator available for the long-term trend is the $\delta^{18}O$ ratio, which is in all three cores essentially constant during the Holocene and decreases to lower values in the Last glacial age part of the cores. We conclude therefore that the scavenging of H_2O_2 from the atmosphere remained constant during the Holocene regarding the long-term mean values. The changed global temperature and the precipitation pattern in the Last glacial age compared to the Holocene most probably also changed the scavenging behaviour.

Trace compounds in the ice, such as microparticles, acidity, the chemical compounds Cl^-, NO_3^-, SO_4^{2-}, the ^{10}Be content and the composition of the gas occluded in the bubbles are conservative in the way as their concentrations do not change during the thousands of years since they have been trapped in the ice, not taking smoothing processes due to diffusion into consideration. Systematic analysis of the course of the mentioned species in the three ice cores show essentially constant values during the Holocene, disregarding the anthropogenically caused increase of many trace species since industrialization. Systematic shifts have been recorded at the transition into the Last glacial age time period (Thompson, 1977; Cragin et al., 1977; Hammer et al., 1985; Herron and Langway, 1985; Beer et al., 1985; Johnson et al., 1972; Dansgaard et al., 1985). Smaller deviations from the Holocene mean values are of short duration (1 to a few 100 years) and can be partially associated with smaller climatic perturbations such as the Little Ice Age or volcanic eruptions (Hammer et al., 1980).

None of the mentioned records shows a systematic variation similar to the H_2O_2 record measured in the three cores. It seems that the H_2O_2 in the ice cannot be regarded as a conservative tracer. Of course this renders more difficult any interpretation of the H_2O_2 concentration in the ice in terms of atmospheric H_2O_2 concentration. If H_2O_2 would be a conservative tracer, either the scavenging and/or the atmospheric concentration must have changed.

5.1. The H_2O_2 record in the Greenland ice cores

Some sort of a disintegration of H_2O_2 in the ice seems to be the most plausible explanation for the observed decreasing trend in the Greenland ice cores during the Holocene time period.

The decomposition of H_2O_2 is exothermic.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad \Delta H = 202 \cdot 10^3 \text{ J/mol}$$

In the liquid phase a lot of homogeneous and heterogeneous catalysts are known, which accelerate the above mentioned reaction (Schumb et al., 1955). From the former Fe(III) is the most efficient and it is found typically in the low ppb range in polar ice cores (Herron et al., 1977; Boutron and Martin, 1980). But nothing is known about this reaction in the ice matrix. Even if we translate kinetic data from the liquid phase, in order to estimate the halflife, it is obvious that this process is too slow to explain the decreasing trend of the H_2O_2 level of the past 3000 years.

The disintegration of H_2O_2 on the surface of insoluble micro-particles in the ice is another possibility. Thompson (1977) has made studies of the number, morphology and chemical composition on samples along the Camp Century and Byrd ice cores. Hammer et al. (1985) measured directly in the field the integral microparticle concentration continuously on the Dye 3 core. All these measurements show elevated microparticle concentrations in ice from the Last glacial age, in the Greenland ice cores by a factor of 10 or more, and in the Byrd core by a factor of roughly 5. In the Holocene part of the Camp Century core, Thompson counted between 12,000 and 120,000 particles with diameters greater than $0.65 * 10^{-6}$ meters per g of ice. Hammer (1977) found similar concentrations in the Dye 3 core.

Microparticles induce dislocations in the ice structure along which the diffusion may be enhanced, and the H_2O_2 molecules could migrate preferentially to such particles. It is therefore

possible that each H_2O_2 molecule encounters within reasonable time (1 ~ 100 years) an insoluble particle and decays with a certain probability. This probability depends on the chemical composition and the surface characteristics of the microparticles. If the described way of decay is important, the measured H_2O_2 concentration in the ice cores will be anticorrelated to the dust concentration. The dust profile from the Dye 3 core, (Hammer et al., 1985) show the lowest dust concentration in the depth interval 800 m.b.s. to 1600 m.b.s. The H_2O_2 concentrations stay on a constant level between 1000 and 1700 m.b.s. But the disintegration rate should be proportional to the amount of particles, the decreasing trend should be smaller between 1000 m.b.s. and the transition into the Last glacial age instead of being a constant value. The number of particles alone may not be a good parameter to quantify the H_2O_2 disintegration.

In both Greenland ice cores, the very low H_2O_2 concentrations measured in the Last glacial age ice coincide with roughly an order of magnitude higher dust concentrations. The interference between the H_2O_2 level and the dust level must be regarded as a working hypothesis and has to be examined in more details for further studies. It is an open question whether elevated atmospheric dust level enhances the destruction of H_2O_2 already during the snow formation in the cloud.

The turning point from a decreasing level into a constant level at 100 m.b.s. in the Dye 3 core coincides with the disappearance of the bubbles (Shoji and Langway, 1985). This suggests a decay of the H_2O_2 in the bubbles, thus in the gas phase. Even if this is thermodynamically possible, we do not know any reaction mechanism for such a decay. As long as the cores were not brought to the surface, a photolytical decay is excluded. After core recovery a photolytical decay is theoretically possible, but cannot explain the decreasing trend observed in the Greenland cores.

The Last glacial age ice in the Greenland cores, thus the lowest 10% of the cores, are characterized by several fast changes from ice with typical interglacial characteristics to ice with glacial characteristics. It is remarkable that the H_2O_2 concentration does not follow the sharp changes between "warm" and "cold" stages. We exclude therefore the possibility that the "warmer" part is an ice layer formed in the Holocene and folded into older ice. This is also supported by the higher dust level found in the "warmer" part, compared to the Holocene level.

5.2. The Byrd H_2O_2 record

The analyses made so far on the Byrd core are less systematic than for the Greenland ice cores. The dust measurements by Thompson (1977) show an increase by a factor of ca 5 going from Holocene ice to Last glacial age ice, thus roughly half the increase recorded in the Greenland ice cores. Contrary to Greenland, Thompson also measured a qualititative shift in the Byrd core, with a higher contribution of particles of volcanic origin in the Last glacial age ice. None of the variations of the particles examined by Thompson, as particle numbers, morphology or elemental composition, shows a pattern similar to the H_2O_2 pattern. Apparently the H_2O_2 variations in the Byrd core cannot be explained with the measured dust variations.

The core quality is poor between 400 and 900 m.b.s. Some of the measured samples were visually contaminated with drill fluid. We did not observe an influence of drill fluid on the measured H_2O_2 concentration. No correlation could be seen between the measured H_2O_2 concentration and the visual degree of fracturation of the piece from which the sample was taken. In view of the long storage time (the Byrd core was drilled in the years 1967–1968), it seems uncertain whether the measured concentrations correspond to the original concentration in the ice. It is important to determine the H_2O_2 concentration in another ice core from Westantarctica to confirm or disconfirm the elvated H_2O_2 level during the deglaciation period. As for the Greenland ice cores, the H_2O_2 concentrations from the Last glacial age period are lower than the Holocene values. The ratio of the youngest Holocene level (0 to 1000 years B.P.) to the Last glacial age level (20,000 years B.P.) is higher in the Greenland ice cores (>100) than in the Byrd core (~ 10). The same holds qualitatively for the dust concentrations (Camp Century: ~ 10, Byrd: ~ 5).

The course of the H_2O_2 level has no correspondence in any of the other records of this core measured to date. In view of a possible disintegration of the H_2O_2 molecules in the ice, which

cannot be fundamentally different in the three ice cores, the recorded peak in the Byrd core could well be originally even more pronounced.

Because of the lack of experimental data for the odd hydrogen compounds in remote areas of high latitude, it is uncertain how well the atmospheric chemistry models describe the actual chemical cycles at high latitudes. The applicability of such models to describe the past 10,000 years is even less possible. Nevertheless, the information which can be extracted from the ice cores give certain limitations. We restrict the discussion to the Holocene, the current interglacial.

The $\delta^{18}O$ records tell that neither the temperature nor the accumulation have drastically changed (Robin, 1983).

The atmospheric load with the fully oxidized nitrogen and sulphur species in high latitude did not change on the long-term scale, except for the systematic increase due to anthropogenic activities in the last 200 years.

The only moderate changes in the dust records point toward stable long-range transport conditions, except for a few distinct events (e.g. the visible dust layer at 751.51 m in the Dye 3 core). The analysis of the gas enclosed in the bubbles has shown a constant value for CO_2 and for CH_4 during the Holocene (Neftel et al., 1982; Craig and Chou, 1982). CO_2 is representative for the carbon-cycle, while CH_4 can be regarded as representative for the hydrocarbons.

Recalculation of the intensity of the solar light in the summer seasons by means of the Milankovitch theory by Blatter et al. (1984) shows positive deviation in summer up to 6% for the high latitudes and up to 3% for the southern high latitudes during the last 20,000 years. The highest intensities in these latitudes occurred 10,000 years ago.

Nothing is known about the development of the ozone concentration over the last 10,000 years, one of the key parameters for the atmospheric production of H_2O_2.

It seems therefore that the measured H_2O_2 concentrations found in the three ice cores are determined by both, the local atmospheric concentration and the disintegration after deposition.

6. Conclusions

The measured H_2O_2 long-term trend in the three ice cores shows a different behaviour than all other trace species measured to date. In the Greenland ice cores the H_2O_2 decreases moderately during the Holocene, whereas in the Byrd core elevated values by a factor of four have been measured in the depth interval corresponding to the deglaciation period 6000–12,000 years B.P. At this stage of the investigation no mechanisms are evident which could produce the higher level in the Byrd core.

The decreasing values in the first 1000 m of the two Greenland ice cores support the possibility of a disintegration of H_2O_2 in the ice, most probably by a catalytic destruction on the surface of microparticles.

In all three cores the lowest H_2O_2 levels have been measured in ice from the Last glacial age ice with clearly elevated dust levels. This also favours a disintegration by the above mentioned mechanism.

In view of the impossibility of disentangling, the different mechanisms which determine the H_2O_2 level recorded in the deep ice cores, we cannot give an interpretation in terms of long-term variation of the atmospheric H_2O_2 concentration.

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