Gas isotopes in ice reveal a vegetated central Greenland during ice sheet invasion

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[1] Environmental conditions prevailing during build-up of the Greenland Ice Sheet (GIS) are not yet established. Here we use results from gas isotopes from basal ice of the GRIP ice core to show that central Greenland was vegetated during invasion by the ice sheet. The $\delta^{13}C_{CH4}$ and $\delta^{18}O$ of O_2 values obtained were never encountered before in ice core studies. Such values are indeed the signature of a significant biological activity. **Citation:** Souchez, R., J. Jouzel, A. Landais, J. Chappellaz, R. Lorrain, and J.-L. Tison (2006), Gas isotopes in ice reveal a vegetated central Greenland during ice sheet invasion, *Geophys. Res. Lett.*, *33*, L24503, doi:10.1029/2006GL028424.

1. Introduction

[2] Many studies have already been conducted on the Greenland basal ice and especially at Summit to understand the conditions of formation of the Greenland Ice Sheet (GIS). In this paper, we first gather the available data concerning ice sheet inception and the preliminary information on the environment of ice sheet growth. Then, we present gas isotope data indicating significant biological activity at that time and providing the first comprehensive picture of the environment prevailing during GIS formation.

2. A Unique Record of Ice Sheet Build-Up

[3] Previous work on the basal part of the GRIP ice core has shown:

[4] (1) ice from near 3000m depth is from Marine Isotopic Stage 7 about 250 kyrs [*Landais et al.*, 2003] so that the Summit region of GIS was not deglaciated during the last interglacial (Eemian);

[5] (2) ice from 3022.5 to 3028.5m (the bottom), presently at $-9°C$, contains silt and is therefore called silty ice. In contrast with the nearby (28 km to the west) banded basal ice at GISP2 with a particle load of $0.3-0.65$ weight percent, GRIP silty ice is made of well sorted dispersed silty particles at a concentration level of $0.01-0.2$ weight percent with some occasional gravel, suggesting an eolian origin [*Souchez*, 1997];

[6] (3) the stable isotopic composition of the silty ice, both in δD_{ice} and $\delta^{18}O_{ice}$, reaches values never observed anywhere else in the whole core, isotopically richer than either Holocene or Eemian ice. It has been shown by computation that such heavy isotope values can only be obtained if one assumes that the lowest, bottom ice was formed at the ground surface in the absence of the ice sheet, as snowdrift when the area was not glaciated [*Souchez et al.*, 1994];

[7] (4) in the main part of the silty ice (above about 3028 m depth), there is evidence for sub-metric scale mixing between the ice deposited on the ground surface as snowdrift and the ice sheet during a growing phase, with a mixing ratio of the local component decreasing upwards in the silty ice sequence. This is supported by gas composition studies [*Souchez et al.*, 1995] with strong multiple correlations between much higher than atmospheric CO_2 or CH_4 concentrations, δ_{ice}-values (Figure 1), total gas content and DEP [*Tison et al.*, 1998];

[8] (5) fabric studies [*Tison et al.*, 1994] reveal a situation inherited from previous stress conditions when the ice divide was not at the site and Nd, Sr and Pb isotopic compositions of the mineral particles suggest that the growing ice sheet was coming from the eastern mountainous part of Greenland [*Weis et al.*, 1997; *Souchez*, 1997] and has subsequently developed an ice dome at Summit;

[9] (6) in contrast with the whole core, ammonium (NH_4^+) in the basal ice shows a strong positive correlation ($r^2 = 0.81$) with oxalate ($C_2O_4^=$) in the silty ice, reaching values as high as 22 μM [*Tison et al.*, 1998]. Ammonium oxalate is produced during uric acid breakdown and has been demonstrated as a fingerprint of ornithogenic soils [*Legrand et al.*, 1998].

[10] Based on the aforementioned results, GRIP silty ice appears to be a unique record of the build-up of the present-day ice sheet. The snowdrift mentioned above would not have persisted if not rapidly transformed into wind-drift ice under the overriding ice sheet. Some melting and refreezing has affected it, as indicated by the low gas content at the bottom (0.046 cm^3/g, about half of the usual values in the whole core), but no significant run-off has taken place since the water isotopes do not display a freezing slope in a $\delta D_{ice} - \delta^{18}O_{ice}$ diagram. The snowdrift was rapidly overridden. The contemporaneousness between the snowdrift with its remarkable properties and the invasion of central Greenland by the growing ice sheet can be safely assumed. This invasion dates back to the last build-up of GIS but dating this event is not yet achieved. GIS has survived at Summit the Eemian, the warmest interglacial in the European Arctic [*Kellogg*, 1980] and in the Antarctic [*EPICA community members*, 2004] in the last 750000 years. Radioisotopes created by cosmogenic processes were found in the GISP2 rock core [*Nishiizumi et*

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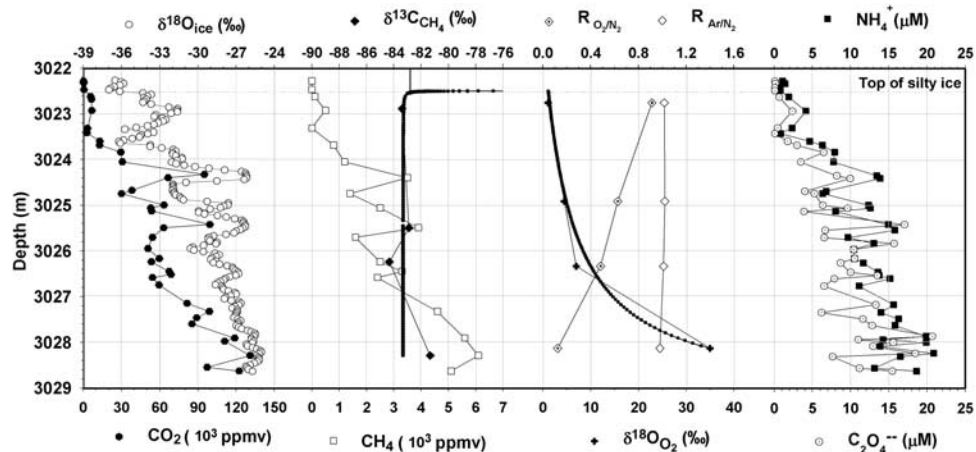
Figure 1. Chemical and isotopic distributions with depth in the basal ice of the GRIP core: new data ($\delta^{13}C_{CH4}$, $\delta^{18}O$ of O_2, $R_{O2/N2}$ and $R_{Ar/N2}$,) and previously published ones ($\delta^{18}O_{ice}$, CO_2, CH_4) giving the context. Also shown are the respective Keeling mixing plots for $\delta^{13}C_{CH4}$ (CH_4 6000 ppmV, $\delta^{13}C_{CH4}$ −83.33‰ for the base of the silty ice; CH_4 0.6 ppmV, $\delta^{13}C_{CH4}$ −49‰ for the top of the silty ice) and $\delta^{18}O$ of O_2 (O_2 3.5%, $\delta^{18}O$ of O_2 +35‰ for the base of the silty ice; O_2 21%, $\delta^{18}O$ of O_2 +1.5‰ for the top of the silty ice) - see text for details.

al., 1996] about 30 km from the GRIP site, but, unfortunately, this finding was not discussed in a full paper. A safe statement would be that the last build-up of GIS occurred sometime in the last million years.

[11] In view of the signature in the silty ice of a bird breeding ground producing ammonium oxalate, a study based on gas isotopes was conducted in this ice to better define the biological activity contemporary with ice sheet inception and development.

3. Gas Isotopes

[12] The research was concentrated on $\delta^{13}C_{CH4}$ and $\delta^{18}O$ of O_2. We took advantage of the high concentrations in CH_4 to perform an accurate determination of $\delta^{13}C_{CH4}$ (analytical precision of 0.5‰). The values obtained are in the range −81 to −84‰ (Figure 1). Such very light values are diagnostic of a bacterial CO_2 reduction process in marshy arctic soils submitted to seasonal melting [*Whiticar*, 1999]. Since atmospheric methane has a $\delta^{13}C_{CH4}$ value of −49‰, there is little doubt that the soil signature is overwhelming in the silty ice. The mass of CH_4 from the soil source is orders of magnitude larger than the mass of atmospheric CH_4 present in the ice, all along the silty ice section.

[13] Measurements of oxygen concentration and $\delta^{18}O$ of O_2 were performed on two different ice samples at each depth level. Since the results always fall within the uncertainty range of the method, only the mean values are shown in Figure 1.

[14] O_2 concentration is expressed as $R_{O2/N2}$ and we checked that N_2 was conservative by measuring $R_{Ar/N2}$ (Figure 1). The oxygen concentration decreases toward the bottom of the silty ice. At the very bottom, $R_{O2/N2}$ is 8 times smaller than in the atmosphere, confirming that a process consuming oxygen took place.

[15] The analytical uncertainty on $\delta^{18}O$ of O_2 is ∼0.1‰ for the upper samples and less than 0.7‰ for the lower samples. This variable uncertainty results mainly from the CO_2 (here much higher than atmospheric) isobaric influence on $\delta^{15}N$ which is used to correct $\delta^{18}O$ of O_2 for gravitational

enrichment as: $\delta^{18}O_{O2,corr} = \delta^{18}O − 2*\delta^{15}N$. Variations in the O_2/N_2 ratio do not influence the $\delta^{18}O$ of O_2 since, at each depth level, the N_2 amount of our standard gas is adjusted to have the same O_2/N_2 ratios in both the sample and the standard.

[16] The $\delta^{18}O$ of O_2 shows high values, up to 35‰ in the lowest part of the profile. Basal enrichment of $\delta^{18}O$ of O_2 is a significant feature of the silty ice; it was never higher than 1.5‰ in the records of the upper Quaternary [*Bender et al.*, 1994; *Petit et al.*, 1999] and this again suggests that some oxygen consumption mechanism occurred at the ground surface under the snowdrift before ice invasion. The 35‰ value is most probably related to a respiration process occurring in a semi-closed system. Indeed, dark respiration in soils or at the Earth's surface is associated with an oxygen isotopic discrimination $^{18}\varepsilon$ around 18‰ [*Angert and Luz*, 2001; *Guy et al.*, 1989]. It can be shown, by using a simple box model (see Appendix A), that $R_{O2/N2}$ decreases and $\delta^{18}O$ of O_2 increases with the development of respiration and that, if no exchange occurs with the layers above, $\delta^{18}O$ of O_2 would be 38‰ for the measured $R_{O2/N2}$ = 0.125 in the bottom ice (Rayleigh process). This value is decreasing if exchange increases. With this process, the observed value for $\delta^{18}O$ of O_2 of 35‰ can be easily explained. The semi-closed conditions required for the considerable lowering of the O_2 content as a consequence of consumption by biological respiration could have existed at the base since it is well known that impermeable ice layers are often present in the basal part of a snowdrift as a consequence of surface melting and refreezing at depth.

[17] Subsequent mixing of the basal part of the snow drift with the bottom ice of the growing ice sheet has resulted from the overriding process, as documented above. Although this process has been affected by the complex dynamical relationships occurring at the base of the ice sheet (see e.g. the wiggles of $\delta^{18}O_{ice}$ profile in Figure 1), a gradually decreasing contribution of the snowdrift signature is indicated from the bottom to the top of the silty ice. As shown before [*Souchez*, 1997], there is a general linear trend between mixing ratio and depth. This should also be reflected in the gas isotopic

compositions and is confirmed by the Keeling mixing plots which fit the observed data reasonably well (Figure 1).

[18] Measurements of δ^{40}Ar and δ^{15}N in the air trapped in the ice are traditionally used to indicate the degree of gravitational fractionation, directly proportional to the thickness of the diffusive zone and hence to the firn thickness. However, in view of the weak total gas content, the low oxygen concentration, the mixing that has occurred between the snowdrift and the overriding glacier ice, and the relative abundance of ammonium of biological origin which is known to influence the nitrogen isotopic composition, interpretation of δ^{40}Ar and δ^{15}N is not straightforward and this goal was not pursued.

[19] Finally, one could wonder if the biological processes evidenced above could not result from a post-mixing activity. Indeed, in GISP2, it was shown [*Tung et al.*, 2006, 2005] that gas properties in the basal ice partly resulted from the activity of Fe-reducing bacteria attached to Fe-rich smectites acting as microbial substrate. However at GRIP, the strong multiple correlations mentioned above combined with the weak clay content (and thus the paucity of Fe-rich smectites) do not support significant post-mixing activity of Fe-reducing bacteria within the basal ice.

4. Environmental Reconstruction

[20] On the basis of the new data described above, the environment of central Greenland contemporaneous with invasion by ice sheet growth can be reconstructed as follows. An undulating topography in crystalline rocks is sufficiently vegetated to account for a bird breeding ground producing ammonium oxalate. A marsh allowed anaerobic organic decomposition in the underlying soil and CH_4 production with its diagnostic δ^{13}C signature. The δ^{18}O of O_2 values show the importance of biological respiration at the soil surface in this type of environment. Moreover, highly weathered coniferous pollen grains are present within the well-sorted eolian silts (V. Maggi, personal communication, 1994), which suggest the presence of some prostrate conifers, although a long distance provenance cannot be entirely dismissed. A snowdrift can be present in this type of environment, incorporating by wind action fine silt from nearby patches of till and occasional gravel sliding on the snow.

5. Conclusion

[21] This study demonstrates the presence of a vegetated soil surface and strong biological activity during GIS inception and development. The ice sheet did not advance over a polar desert. This provides a constraint on climate and ice sheet models. As Greenland began to cool, as a result of extending snow and ice cover, a positive feedback loop occurred and this has allowed the full development of the ice sheet.

Appendix A: A Simple Box Model

[22] Box 1 is the lowest part of the snowdrift and the soil surface.

[23] Box 2 is the main and upper part of the snowdrift. There are no bacteria in box 2 which has an infinite volume,

because of free connection with the atmosphere, and the air has the normal atmospheric composition.

[24] Bacteria only respire in box 1.

[25] There is an ice layer between the two parts of the snowdrift limiting to some extent oxygen exchange between the two boxes.

[26] From these hypotheses, it is possible to write the following equations:

for oxygen of mass 32 in box 1,

$$\frac{d(O_{32})_{box\ 1}}{dt} = -R + \frac{E.S.\left((O_{32})_{box\ 2} - (O_{32})_{box\ 1}\right)}{V_1} \tag{A1}$$

where O_{32} and O_{34} are the oxygen concentrations, R is the oxygen consumed by *respiration* per unit time and per unit volume, E the *exchange* flux of oxygen molecules between the two boxes, S the surface between boxes 1 and 2, V_1 the volume of box 1 and t the time.

for oxygen of mass 34 in box 1,

$$\frac{d(O_{34})_{box\ 1}}{dt} = -R.\alpha.\frac{(O_{34})_{box\ 1}}{(O_{32})_{box\ 1}} + \frac{E.S.\left((O_{34})_{box\ 2} - (O_{34})_{box\ 1}\right)}{V_1} \tag{A2}$$

where α is the fractionation coefficient so that $\alpha = 1 - {}^{18}\varepsilon$.

[27] In box 2, the concentrations of O_{34} and O_{32} are considered constant.

[28] If E = 0, there is no exchange and a classical Rayleigh process occurs in box 1, increasing the value of δ^{18}O of O_2.

[29] If E is not 0, δ^{18}O of O_2 also increases in box 1, but less than in the classical Rayleigh process.

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