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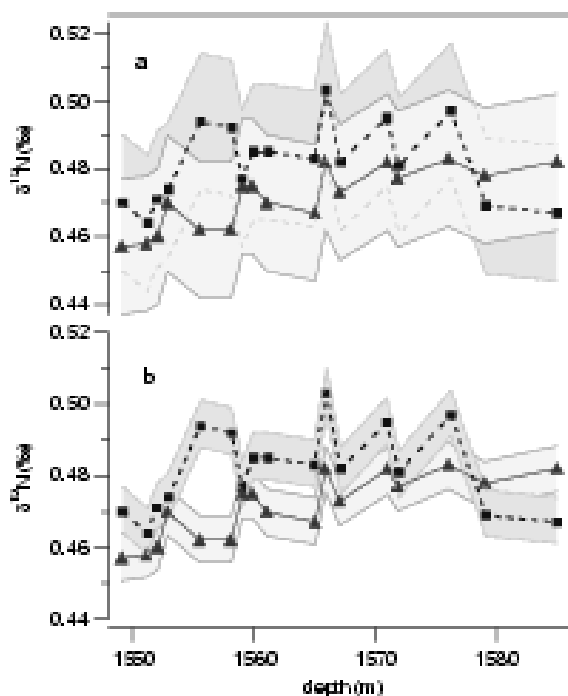
**IMPACT OF REFRIGERATION TEMPERATURE HISTORY ON
 $\delta^{15}\text{N}$ OF AIR BUBBLES TRAPPED IN POLAR ICE SAMPLES**

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Impact of refrigeration temperature history on isotopic composition of nitrogen of air bubbles trapped in polar ice samples

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Abstract

Air bubbles preserved in polar ice cores are unique archives of past atmospheric composition. Ice samples must be stored and handled cautiously between ice coring and analysis in order to minimize the possible adverse effects of gas loss due to temperature and pressure fluctuations. In this study we have quantified the impact of a large temperature increase on the preservation of the nitrogen isotopic composition, using an inadvertent warming of ice core samples during shipment. The results show that even if ice samples lost half of their gas content, the average isotopic ratio of nitrogen remains unaffected. This confirms that gas loss is not a simple mass-dependent process. However, our results also indicate that obtaining the best precision on the nitrogen isotopic measurements requires a rigorous control of storage temperature for the ice samples.

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1. Introduction

Air enclosed in ice core bubbles provides our primary source of information about past atmospheres. The nitrogen isotopic ratio $^{29}\text{N}_2/^{28}\text{N}_2$ in the atmosphere is constant over the time scales covered by ice cores. Its measurement in air bubbles permits an estimate of the temperature shifts associated with abrupt climate changes because of thermal isotopic fractionation occurring in response to temperature gradients in the snow layers on top of polar ice sheets (Caillon et al., 2001a; Caillon et al., 2001b; Lang et al., 1999; Leuenberger et al., 1999; Severinghaus et al., 1998; Severinghaus and Brook, 1999). The mixing ratios of molecular nitrogen and oxygen in ice samples appear to be influenced by partial gas loss through fractures developing in the ice as the core relaxes after recovery from the ice sheet (Sowers et al., 1997; Uchida et al., 1994). Therefore, the fossil air is usually extracted from samples located in the most central portion of the ice core. To prevent further fractionation and gas loss, ice cores are handled, shipped and stored at refrigeration temperatures below -15°C .

Here we have conducted $^{29}\text{N}_2/^{28}\text{N}_2$ ratio measurements in gas from two series of 17 ice samples from the Vostok ice core (core 5G drilled between 1990 and 1998 in central Eastern Antarctica, $78^\circ28'\text{S}$, $106^\circ48'\text{E}$) at depths between 1545 and 1587 m. The two series were taken from adjacent locations in the core (10 cm apart, i.e. the sample length) and therefore had identical refrigeration histories, except for the last transport step from France to the USA in 1999. The first series (hereinafter set 1) underwent a breakdown in the refrigeration chain during the shipment from LGGE ice storage (Grenoble, France) to the Scripps Institution of Oceanography (SIO in San Diego, USA). The temperature recorded at the upper surface of the shipment box rose progressively from -20°C to $+2^\circ\text{C}$ over the course of 5 days (Figure 1). Note that most of the ice itself did not melt but its temperature was probably close to 0°C . The

second series (hereinafter set 2) was also sent to SIO and remained below -15°C (Figure 1); it is therefore considered as the reference series.

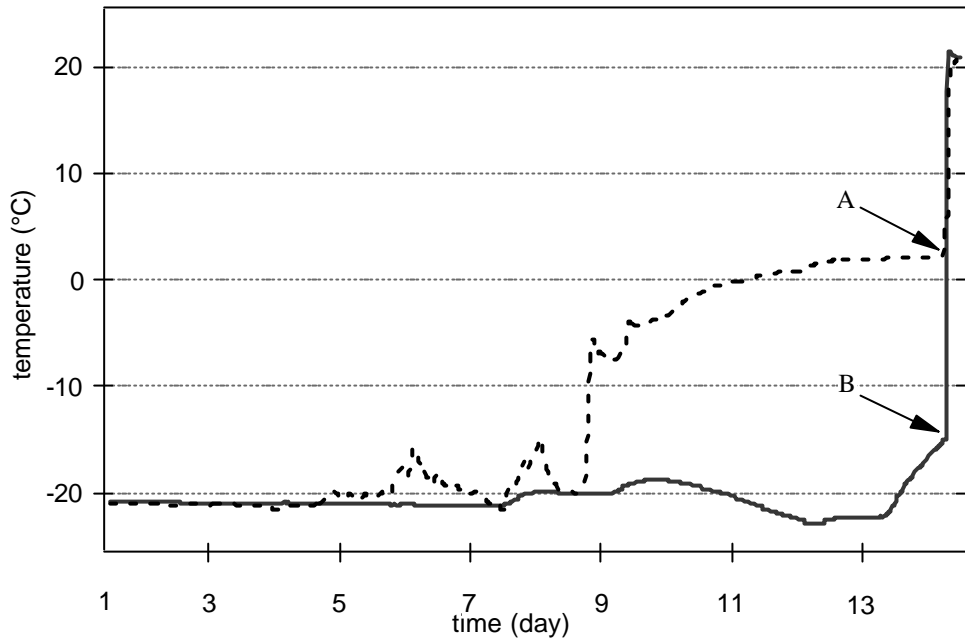


Figure 1: Temperatures ($^{\circ}\text{C}$) recorded at 24-minute time steps by automatic thermometers located in the upper surface of the insulated box containing the ice samples, for set 1 (dashed line) and set 2 (solid line). A and B show the time when the temperature recorders were removed from the boxes.

2. Results and discussion

The gas contained in the 17 ice samples from sets 1 and 2 was extracted with a melt-refreeze method (Severinghaus and Brook, 1999; Sowers et al., 1989) and the $\delta^{15}\text{N}$, which is defined as

$$\delta^{15}\text{N} = \left(\frac{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{sample}}}{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{atmosphere}}} - 1 \right) \times 1000,$$

was measured in triplicate on a Finnigan mat 252 mass-spectrometer at SIO (Caillon et al., 2001b). To quantify gas loss, the relative total air content of each sample is estimated using the ratio between the gas pressure after extraction and the initial ice sample mass. The air contents obtained for set 2 are almost constant across the series, with a standard deviation of $0.005 \text{ cm}^3/\text{g}$. This is expected according to absolute measurements of the total air content previously performed in the same depth range of the Vostok ice (Martinerie et al., 1994). Compared to set 2 values, all samples from set 1 reveal lower values, with a loss of 10% to 60% of the trapped gas (Figure 2). Gas loss through ice near the melting temperature most probably occur along microcracks and by liquid-state diffusion at grain boundaries where liquid films develop preferentially. Therefore the flux of nitrogen isotopes should be proportional to their respective concentration gradient between trapped bubbles and the surrounding atmosphere, times their respective diffusion coefficient in water, following the Fick's first law. The light isotope being more mobile and diffusing faster than the heavy isotope, it is therefore expected that the $\delta^{15}\text{N}$ of samples from set 1 should be enriched compared to set 2.

The $\delta^{15}\text{N}$ measurements on sets 1 and 2 are displayed on figure 2. Results from set 1 indeed show a slight enrichment compared to set 2. But the maximum difference between the two curves is only about 0.025‰. Considering the analytical reproducibility (standard deviation of each measurement series 0.0065‰), the systematic deviation between the two series of 17 measurements (mean difference 0.013‰, maximum difference 0.025‰) is statistically significant at a 99% confidence level (student T test). Although different degrees of gas loss are observed in set 1 (7 points with air loss lower than 15% and 10 points with air loss larger than 25%) probably due to the location of the samples in the shipment box, it is not possible to relate the amplitude of the $\delta^{15}\text{N}$ difference between the two sets to the amplitude of the gas loss. A shift of 0.025‰ represents a very small artefact compared to the usual range

of nitrogen isotope variability measured in ice cores. Changes in gravitational settling or thermal diffusion of gas isotopes with climate changes often correspond to signals of about one order of magnitude larger than the shift observed in our circumstantial experiment. It is thus noteworthy to say that the isotopic composition of nitrogen in ice cores appears to be a fairly robust signal, surviving a breakdown in the refrigeration chain and associated gas loss.

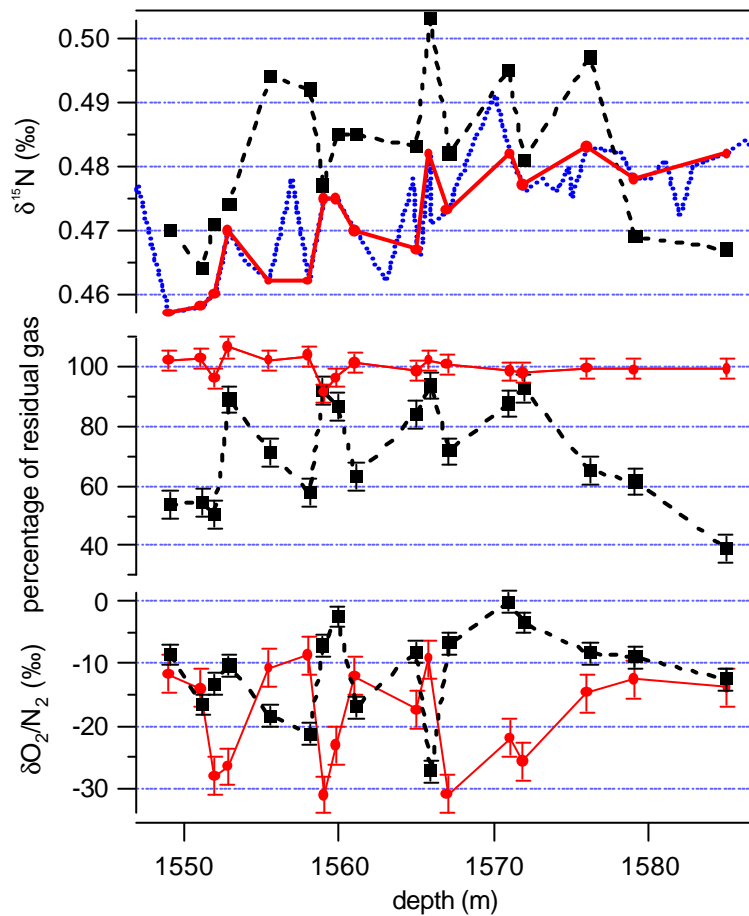


Figure 2: $\delta\text{O}_2/\text{N}_2$ (bottom), total air content (middle, relative to the mean value of set 2) and $\delta^{15}\text{N}$ measurements (top) as a function of depth along the Vostok ice core. For set 1 (dashed line) and set 2 (solely depths next to set 1, solid line); other data (dotted line). For each set the $\delta^{15}\text{N}$ measurement precision is $\pm 0.0065\text{‰}$. The air content measurements are uncalibrated, and thus should be interpreted in a relative sense only.

The O_2/N_2 ratio had been also measured on each samples for the two sets. Previous studies showed that this elemental ratio is influenced by partial gas loss through small fractures in the ice during and after coring, through a process which fractionates elements according to their molecular diameter (Bender et al., 1995; Craig et al., 1988; Sowers et al., 1989). The consequence of this gas loss is that N_2 (bigger molecule) is enriched relative to O_2 (smaller molecule) (Bender et al., 1995; Craig et al., 1988). When comparing the $\delta O_2/N_2$ profile (figure 2) of each set from our experiment, it appears that the sense of the variation in elemental ratio is reversed, that is to say, ice samples from set 1 are enriched in O_2 compared to samples from set 2. This feature suggests that a property other than molecular diameter alone influences gas loss-induced fractionation. Comparing $\delta O_2/N_2$ and $\delta^{15}N$ (figure 2), there is no statistically significant relationship between these two proxies. This confirms previous results obtained by Bender and colleagues in 1995 indicating that whatever the process fractionating O_2 and N_2 in ice cores samples, the isotopic composition of the enclosed gas remains nearly or completely unchanged.

Some of the earlier works focusing on large $\delta^{15}N$ spikes during large abrupt temperature changes in Greenland (typically 0.15 to 0.17‰) were conducted with a lower analytical precision, 0.02‰ (Lang et al., 1999; Severinghaus et al., 1998). Considering a 0.02‰ precision envelope (figure 3), the results from our two datasets would be indistinguishable. We can therefore speculate that if the two ice series had shown such large signals as seen in Greenland ice, the amplitude of the isotopic signal would have been preserved. Set 2 shows only a small but significant step-like decrease, around 1567 m, (amplitude of the signal: 0.0170 ± 0.0065 ‰) which is not preserved in set 1 (the standard deviation of the difference between the mean values above and below 1566 m is lower than 0.002‰). This isotopic anomaly is interpreted as the signature of a temperature increase in Antarctica 108 000 years ago (Caillon et al., 2001b), which corresponds to a warming signal

in the isotopic composition of ice (Petit et al., 1999). At this level of precision, the difference between the two sets (figure 3) is significant and points out that the best possible temperature preservation of ice samples is required for high precision isotopic measurements.

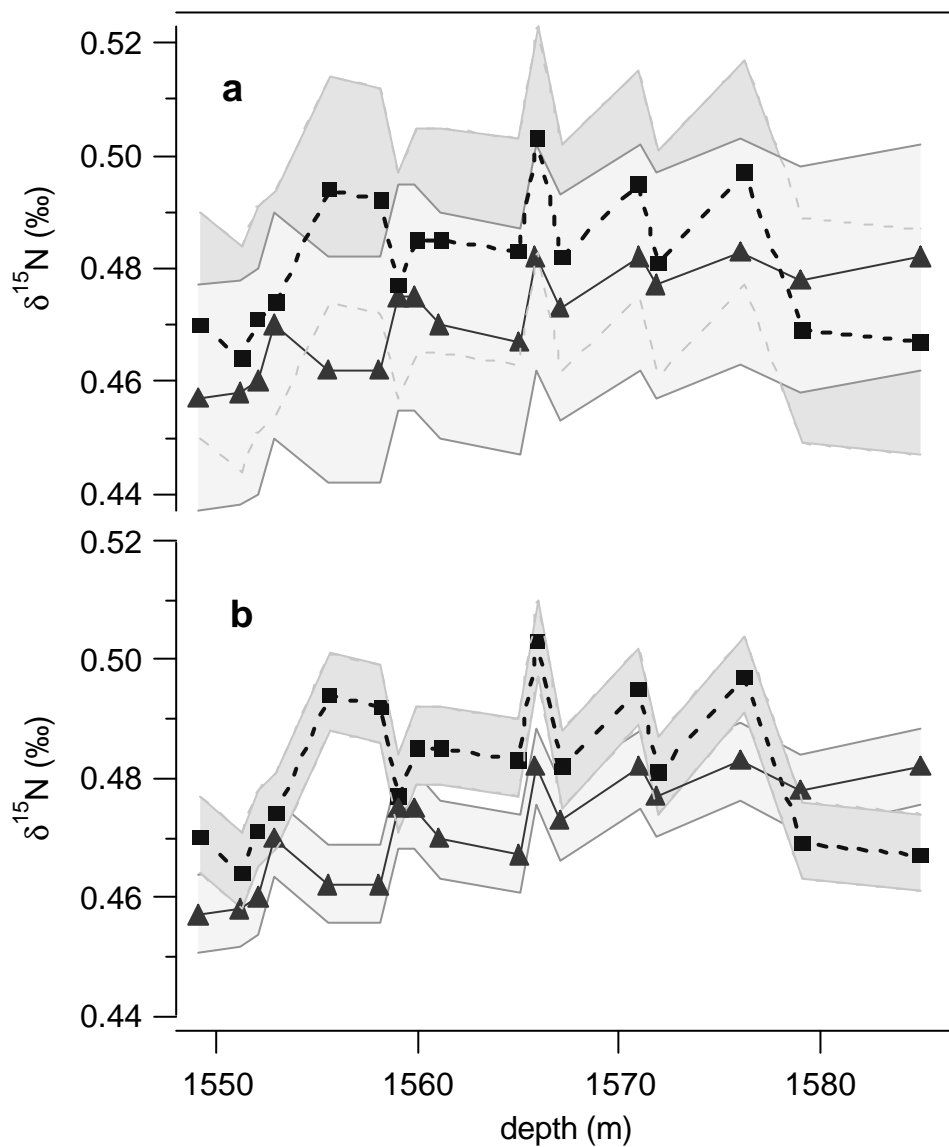


Figure 3: Same as figure 2 (top) but with envelope contours corresponding to an analytical precision of 0.02‰ (a) and 0.0065‰ (b).

3. Conclusion

For the first time, we quantify in this study the impact of a large temperature increase during the handling of ice samples on the preservation of the nitrogen isotopic composition. Even if the bubbles have lost half of the total gas content, the isotopic signal appears to be nearly preserved compared to the analytical precision and the amplitude of climatic spikes obtained in the case of early studies (Lang et al., 1999; Leuenberger et al., 1999; Severinghaus et al., 1998). However, for the purpose of very precise analyses and given the improvement now obtained on the analytical precision for the nitrogen isotope measurements (Severinghaus and Brook, 1999; Caillon et al., 2001b), it is still important that the refrigeration temperature is maintained far away from the melting point.

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