

Bomb-test ^{36}Cl measurements in Vostok snow (Antarctica) and the use of ^{36}Cl as a dating tool for deep ice cores

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ABSTRACT

A large pulse of atmospheric ^{36}Cl generated by a limited number of nuclear tests peaked in the late 1950s to early 1960s. The corresponding enhanced ^{36}Cl deposition is seen in various glaciological archives in the Northern Hemisphere. The profile of the bomb spike recorded in firn layers at Vostok Station, central East Antarctica, has been measured by employing accelerator mass spectrometry (AMS). The records obtained from two well-dated data sets collected in snow pits in 1997 and 1998 show a broad ^{36}Cl peak, beginning as early as the 1940s and reaching its maximum in the 1960s. The signal is followed by a long-lasting tail up to the surface. This pattern is totally unexpected. We show that the results, unlike the Greenland data, can be explained by a mobility of HCl in the Antarctic firn. This experiment demonstrates the instability of gaseous Cl^- deposits, a phenomenon which has important implications for the use of natural cosmogenic ^{36}Cl radionuclides as a reliable dating tool for deep ice cores from low-accumulation areas. However, during glacial times, under favourable atmospheric chemistry conditions this dating method may still be applicable. Snow metamorphism and ventilation are assumed to be the two main physical processes responsible for the observed patterns.

1. Introduction

The long-lived radionuclide ^{36}Cl (half-life 301 000 yr) is naturally produced in the atmosphere by cosmic ray spallation of argon gas molecules at a rate of the order of $15\text{--}20\text{ atoms m}^{-2}\text{ s}^{-1}$ (Lal and Peters, 1967; Masarik and Beer, 1999). Once in the atmosphere, ^{36}Cl atoms are transported to the ground in two different ways. On the one hand, ^{36}Cl atoms become attached to aerosol and follow these particles in stratospheric/tropospheric air exchange processes and their deposition pathways. On the other hand, gaseous transport is also of importance: ^{36}Cl atoms are transported as HCl molecules by atmospheric circulation and are dry and/or wet deposited on the ground.

Between 1952 and 1964, thermonuclear weapons tests at oceanic sites resulted in a large pulse of ^{36}Cl , with peak concentrations in precipitation about two to three orders of magnitude higher than natural levels (Bentley et al., 1982; Synal et al.,

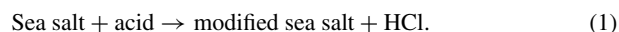
1990). In this case, ^{36}Cl was produced by neutron activation of ^{35}Cl coming from seawater NaCl.

Since ^{36}Cl and ^{10}Be are produced by similar nuclear reactions in the atmosphere but differ by their half-lives, the $^{10}\text{Be}/^{36}\text{Cl}$ ratio has the potential to be an ideal dating tool for old polar ice cores (Yiou et al., 1997; Baumgartner et al., 1998). The ratio is independent of production changes and increases exponentially with an apparent half-life of 376 000 yr. However, first measurements revealed large unexpected fluctuations of the $^{10}\text{Be}/^{36}\text{Cl}$ ratio of up to a factor of 4 for modern samples (Suter et al., 1987; Elmore et al., 1987) making any dating attempt obsolete. We suspect that the reason for this failure may be found in the incorporation mechanisms of HCl in polar ice: recent measurements carried out in the Antarctic revealed strong post-deposition effects of this gas in central polar snow (De Angelis and Legrand, 1995; Legrand et al., 1996; Wagnon et al., 1999).

Let us first examine the global atmospheric cycle of stable chloride. Most of this species is present in the atmosphere in the form of sea salt (Cicerone, 1981; Erickson and Duce, 1988; Graedel and Keene, 1996). The release of gaseous HCl from sea-salt aerosol is a common phenomenon over the ocean due

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to the strong interaction of sea-salt aerosol with atmospheric acid species (H_2SO_4 and HNO_3 in particular) (Chameides and Stelson, 1992; McInnes et al., 1994; O'Dowd et al., 1997) according to reaction (1):



The finding that reactive chlorine can also be produced in significant amounts by heterogeneous reactions of nitrogen gases on sea-salt particles is more recent (Vogt et al., 1996). In the Antarctic, Cl is assumed to be mainly deposited in snow as NaCl. However, it has been demonstrated that sea-salt aerosol is partly modified due to interactions, as at other latitudes, with acids during transport (Legrand and Delmas, 1988) according to reaction (1). The gaseous HCl formed is then transported in the atmosphere and incorporated separately from NaCl in the snow. The deposition of particulate NaCl is a simple process in comparison to the transfer of gaseous HCl to the snow, which appears to be more complex.

With the exception of air, which is entrapped and incorporated in the ice at the firn/transition, atmospheric impurities recorded in ice are collected at cloud level. Once deposited, snow crystals undergo intense changes which modify their physical aspect and in several cases their impurity content. Water vapour and some trace species are redistributed. For instance, it has been observed and modelled that the concentrations of *in situ* produced ^{14}C in Vostok and Taylor Dome firn layers are much lower than theoretically expected due to grain metamorphism (Lal et al., 2001). These processes are poorly documented (Gow, 1969; Alley and Bentley, 1988; Arnaud et al., 2000). Deposited snow and firn have to be considered as unstable materials in permanent evolution, in particular in their uppermost layers. In the snowpack, as temperature gradients progressively decrease and tortuosity becomes more important, the changes tend to reduce (Arnaud et al., 2000). Below a depth of about 10 m transformations can still occur until the pores close (i.e. until the final transformation of firn into ice) in closed system conditions. The exchanges with the free atmosphere cease (Arnaud et al., 2000).

This study concerns the first upper 4.5 m, where snow metamorphism occurs and exchanges with the free atmosphere are easy and considerable.

The recent glaciochemical studies which revealed post-depositional processes affecting Cl^- concentration in Central Antarctic firn (De Angelis and Legrand, 1995; Wagnon et al., 1999) did not precisely elucidate the nature of the interactions prevailing between acid trace gases and the polar ice. Furthermore, much attention is currently being paid to the interaction between gaseous HCl and ice in the atmosphere due to the involvement of ice surfaces and gaseous Cl species in heterogeneous atmospheric chemistry processes (e.g. stratospheric ozone destruction Molina and Molina, 1987). In spite of numerous laboratory studies concerning these issues, the interaction between ice and gaseous HCl is not fully understood and the exact location

of HCl in the ice matrix is uncertain. In our study, the thermonuclear ^{36}Cl spike of the 1950s has been used for investigating the mobility of Cl^- in the Vostok snow.

Vostok is an Antarctic site where a 420 kyr palaeoclimatic record has been obtained over the last two decades (Petit et al., 1999). The interpretation of the chemical records demands a solid understanding of the physical and chemical processes governing the incorporation of atmospheric species in the ice. Data reported in this study shed a new light on the physicochemical phenomena occurring in the polar firn and at the surface of the ice. They are also of interest to confirm the use of cosmogenic ^{36}Cl as a reliable dating tool in deep ice core studies.

2. Experimental methods

2.1. Field sampling

Due to the extremely low accumulation rate of snow at Vostok (East Antarctica, 78.9°S , 103.0°E , elevation 3450 m, mean accumulation rate $2.1 \text{ g cm}^{-2} \text{ yr}^{-1}$ Ekaykin et al., 2002), the last decades can be sampled at a reasonable depth by digging a snow pit. Two sets of samples were collected in January 1997 and January 1998 (25 and 45 individual samples respectively) along the walls of snow pits of some metres depth with the aid of clean stainless steel tools. The 1997 and 1998 sampling sites were dug about 3 km apart. Each sample was 0.1 m thick, which corresponds approximately to an annual to biennial sampling rate, depending on depth. After collection, the snow samples were placed in sealed polyethylene plastic bags and transported in a solid state to Europe for radioactivity analysis.

2.2. Dating

Due to the lack of seasonal variations of any chemical or physical parameters in Vostok snow, year-by-year dating of the snow layers is impossible at this location. Only specific reference horizons (radioactive events and volcanic signals) can be used. In our study, the chronology of snow layers was established with the aid of artificial radionuclide ^{137}Cs deposition patterns according to the method commonly used by glaciologists in both polar regions (Petit et al., 1982). Deposition patterns of radioactive species are well documented in Antarctica. They generally show a well-marked steep increase in January 1965 (Croaz, 1969) corresponding to the invasion of high southern latitudes by radioactive debris transported via the stratosphere from Northern Hemisphere nuclear bomb test series starting in October 1962 in Siberia and Nevada. Thereafter high radioactivity levels are still observed for a few years in Antarctic snow. Background values are estimated to be reached again in the 1980s, well after the final French and Chinese atmospheric tests.

Concentrations of ^{137}Cs determined at the Laboratoire de Glaciologie et Geophysique de l'Environnement (LGGE) are

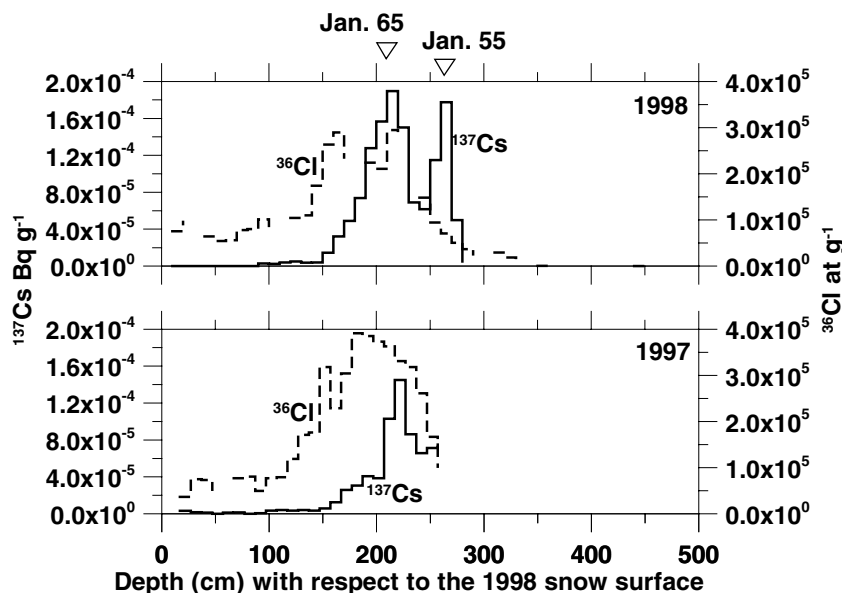


Fig. 1. ^{137}Cs (left scale) and ^{36}Cl (right scale) fallout at Vostok as a function of depth (1997 and 1998 snow pits). The depth of the 1997 samples has been shifted by -7 cm to take into account the 1-yr time lag between the two sampling dates.

shown in Fig. 1. The data are similar to the ones found at Amundsen–Scott Station (South Pole) where the easy identification of annual layers made it possible to date precisely the timing of radioactive fallout for the Antarctic (Lambert et al., 1977). In our study, ^{137}Cs concentration patterns indicate that January 1965 is situated at 220 cm depth in both snow pits and January 1955 at 260 cm in the 1998 snow pit (the 1997 record was too short to reach down to 1955). The agreement between the two samplings is excellent, if we take into account the annual accumulation rate (about 10 cm snow), the thickness of one sample (10 cm) and the marked spatial variability of snow deposition (Ekaykin et al., 2002). Background level is reached again at about 130 cm.

2.3. ^{36}Cl detection method

Accelerator mass spectrometry (AMS) is used to detect ^{36}Cl atoms in the ice samples. The measurements have been performed at the PSI/ETH AMS facility (Synal et al., 1997). The sample sets from the two different snow pits have been analysed in independent measurement runs in 1998 and in 1999.

2.3.1. Sample preparation. ^{36}Cl was extracted from ice samples of typically 1 kg. After melting the ice, the solution was acidified with molar HNO_3 (0.3 ml per litre of sample water) and subsequently filtered with a Millipore filter ($<0.45 \mu\text{m}$) to remove particles. Then 3.8 mg of chlorine carrier was added and the volume of the sample solution was filtered and rinsed through ion exchange columns. The sample was eluted with the aid of 100 ml of molar HNO_3 and AgCl precipitated by adding AgNO_3 to the solution. After keeping the sample in the dark for 1–2 h, AgCl was separated with a centrifuge. The AgCl was again dissolved with NH_4OH and saturated $\text{Ba}(\text{NO}_3)_2$ solution

was added. After keeping the solution in the dark for another 12 h, sulfur was removed in the form of BaSO_4 with a centrifuge. To reprecipitate AgCl , the solution was acidified and the precipitate was separated with a centrifuge, washed with deionized H_2O and dried at 70°C for about 10 h. This material was pressed into a tantalum target holder that could be introduced into the ion source of the AMS facility.

2.3.2. Measurement procedure. Typically, 5–10 μA of negative ions (^{36}Cl) are extracted from the ion source and injected into the EN tandem accelerator running at a terminal voltage of 6 MV. A total beam energy of 48 MeV was achieved by using the 7^+ charge state. This is sufficient to apply particle identification techniques and suppress ^{36}Cl from its isobar ^{36}S by four to five orders of magnitude. Typically, the background of ^{36}S ions in the final detector was 10^{-11} relative to the stable ^{35}Cl ions measured at the Faraday cup in the focal plane of the mass-analysing magnet at the high-energy end of the accelerator. Thus, a detection limit ($^{36}\text{Cl}/\text{Cl}$) of 10^{-15} or less was reached. The blank samples prepared in the same way as the ice samples gave isotopic ratios of typically $2\text{--}3 \times 10^{-15}$. The measured isotopic $^{36}\text{Cl}/\text{Cl}$ ratios of the samples were between 1×10^{-13} and 5×10^{-12} . Measurement uncertainties are primarily due to counting statistics and therefore depend on the measured isotopic ratio. The median of the overall relative uncertainty was 5% for the measurements of the 1997 samples and 2.2% for the results obtained from the samples taken in 1998.

3. Results and discussion

The two ^{36}Cl concentration profiles obtained in the upper firn layers at Vostok are reported in Fig. 1. Both records, for 1997 and 1998 samplings, look rather similar. To match samples of

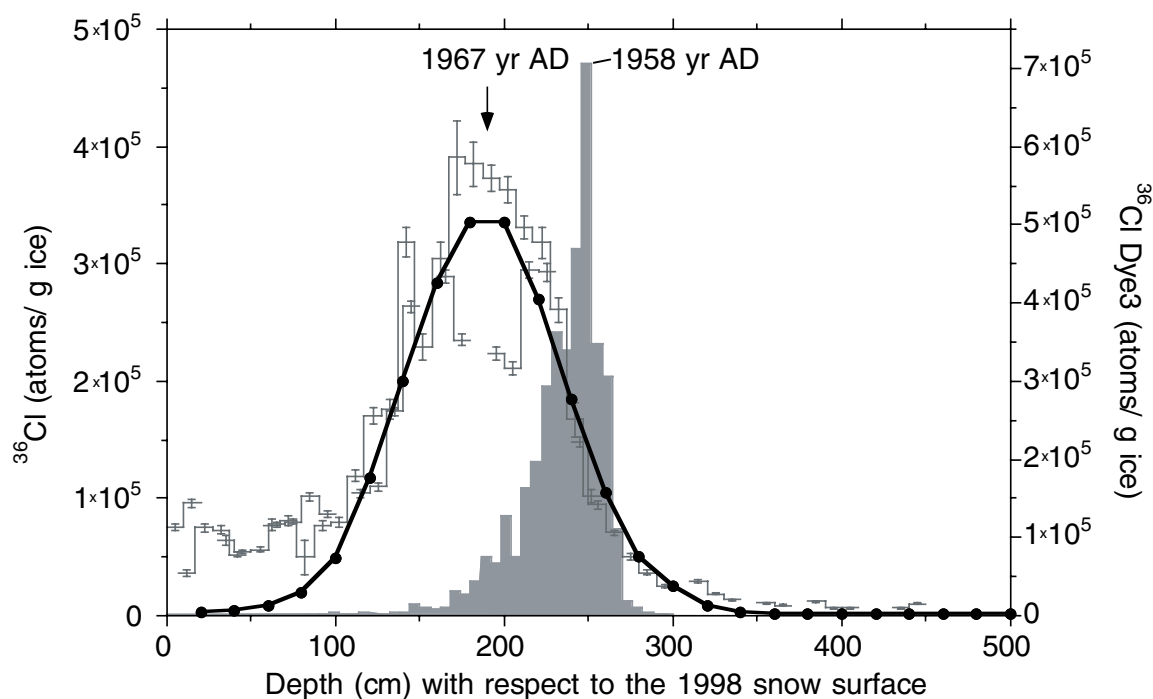


Fig 2. Comparison of modelled ^{36}Cl (thick black curve) and measured ^{36}Cl concentration at Vostok (1997 and 1998 step plots, as in Fig. 1). Undisturbed ^{36}Cl deposition at Dye3 (Greenland) is also reported (grey area). The diffusive mixing causes the peak to broaden and a lower than expected advective transport causes the peak to be shifted towards younger ages.

the same deposition time, the depth scale of the 1998 record was shifted by 7 cm in order to compensate for the snow accumulated between the two sampling periods. During the peak of the ^{36}Cl fallout at 150–200 cm depth, however, the differences between the two records are significant. Whereas the 1998 record reveals a much greater scatter of the ^{36}Cl concentration data, the 1997 maximum is about 20% higher than the 1998 one. This cannot be explained by experimental uncertainties. It is more likely that differences in sample handling and HCl adsorption instability were the cause of this discrepancy. The pre-bomb period is reached by the 1998 sampling only. High ^{36}Cl values cease at a depth of about 130 cm. Starting from the bottom, the very beginning of the increase may be located at about 280 cm in the 1998 profile (i.e. about AD 1954). An unusual radioactivity level is already observed from 370 cm (i.e. about AD 1940). Surprisingly, the ^{36}Cl concentration in most recent snow layers (6×10^4 ^{36}Cl atoms g^{-1}) is still more than one order of magnitude higher than the natural background level. Maximum ^{36}Cl values are observed in the form of a broad peak between 230 and 130 cm, i.e. from about 1958 to 1975.

This pattern is rather unexpected since the formation of ^{36}Cl , which involves seawater activation, was restricted to a limited number of nuclear tests carried out mainly from 1952 to 1958 on small islands and barges (Elmore et al., 1982; Bentley et al., 1982; Synal et al., 1990). Predicted fallout of thermonuclear ^{36}Cl in the Northern Hemisphere, as modelled by Bentley et al.

(1982) and Synal et al. (1990), reach their climax in the years 1956–1960. At Dye3, Greenland, in agreement with model predictions, ^{36}Cl deposition peaks from 1955 to 1960 (Elmore et al., 1982; Suter et al., 1987; Synal et al., 1990). The Vostok ^{36}Cl deposition pattern was expected to be similar. Measurements of the ^{36}Cl bomb fallout at higher accumulation sites in Antarctica such as Berkner Island result in a very similar fallout pattern as observed at Dye3 Greenland (Synal, private communication). This is clearly not the case at Vostok (see Fig. 2). A broadening of the ^{36}Cl peak is observable, in particular towards more recent years. Vostok's shallowest snow layers do not return to the pre-bomb ^{36}Cl level, contrary to Greenland, where this had already occurred by the mid-1980s (Fig. 2). Why are the Dye3 and Vostok ^{36}Cl deposition patterns so different?

These discrepancies must be discussed in terms of post-depositional phenomena recently pointed out for gaseous Cl^- species in upper firn layers (Legrand et al., 1996; Wagnon et al., 1999). Ice is formed by the densification of dry snow and firn (consolidated snow).

Metamorphism is a well-known process which leads to serious rearrangements and physical transformations of the deposited snow. Due to seasonal temperature changes affecting the upper firn layers, internal evaporation–condensation cycles and surface diffusion processes take place (Arnaud et al., 2000). It can be assumed that, during these transformations, gaseous species initially present in snowflakes are released to the interstitial air.

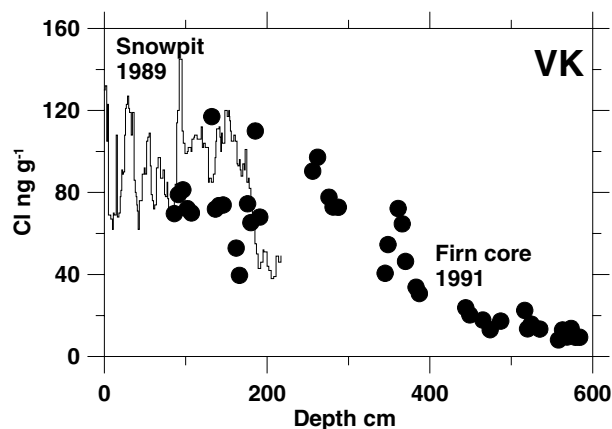


Fig 3. Chloride records in Vostok snow (0–6 m). Data are from Feniet (1990) and Wagnon et al. (1999).

Some of them can be redeposited by co-condensation with water vapour or partly remain in the gaseous phase which is mixed convectively by surface wind stress. As mentioned earlier, chloride is deposited both in the form of NaCl (aerosol) and HCl (gas). ^{36}Cl is assumed to be essentially deposited as HCl. Several Cl profiles have been obtained in Vostok snow layers. Two of these, collected in the field during the summers of 1989/90 and 1990/91, are reported in Fig. 3. The data of Wagnon et al. (1999) were obtained from a snow core transported in plastic bags and subsampled in the laboratory. The upper 2.5 m were sampled in Accuvettes[®] each 1 to 3 cm and transported in sealed individual plastic bags (Feniet, 1990), as was in the case for our 1997 and 1998 samples. Sampling methods may cause marked differences between the results due to possible physical modifications of the snow samples during storage. The data indicate that the Cl/Na ratio is markedly higher than 1.8 (the marine reference value) in upper Vostok snow. This shows that the content of HCl is relatively high in comparison to the content of NaCl. The ratio tends to be closer to or even lower than 1.8 at depth, indicating that some HCl is progressively lost (Wagnon et al., 1999).

A simple model calculation shows that diffusion can explain the main structure of the ^{36}Cl deposition at Vostok. For this calculation we assumed that the ^{36}Cl deposition at Vostok was proportional to the deposition at Dye3 (see Elmore et al., 1982). We normalized the Dye3-based input to obtain an agreement between modelled and measured peak intensity for the Vostok ice core. Subsequent downward transport due to snowfall and the broadening of the peak was modelled by including advective transport and diffusive mixing within the firn layer.

Figure 2 shows the result of a model calculation assuming a diffusive exchange of approximately $0.0025 \text{ m}^2 \text{ yr}^{-1}$. To obtain similar timing of modelled and measured ^{36}Cl peaks we had to assume an advective transport of 5 cm yr^{-1} that is lower than one would expect from the mean accumulation rate (6 cm of

firm per year). This indicates an upward transport of ^{36}Cl relative to the firn matrix. With these parameters the ^{36}Cl bomb peak can be reproduced very well. However, it is not possible to explain the relatively high ^{36}Cl below and above the ^{36}Cl bomb peak. Compared with the measured ^{36}Cl concentration the modelled ^{36}Cl is approximately five times too low for the deepest part of the snow pit and approximately a factor of 20 too low for recent snow. This difference cannot be explained by a simple diffusion process. It rather indicates that a fraction of the ^{36}Cl in the firn is more mobile than expected. In addition, the high ^{36}Cl concentration for recent snow points to an even higher ^{36}Cl mobility in the uppermost part of the firn and to a redeposition of ^{36}Cl formerly expelled from the firn. The snow layers concerned in our study are those where post-depositional phenomena are most active. Our measurements show that upper firn layers are contaminated by artificial ^{36}Cl most likely expelled from deeper layers during snow metamorphism. This indicates that HCl can be redeposited after being released to the interstitial air and that gaseous transport mainly occurs upwards. This transport is responsible for the release of gases (HCl in our case) to the free atmosphere. H^{36}Cl moving to the surface is in thermodynamic equilibrium with the chloride present in the ice phase of the shallowest snow layers. In addition to these processes in natural conditions, there is probably a loss of HCl during sample storage, when, due to temperature perturbations, sublimation processes occur and new “pseudosolubility” equilibria are established. In this case, released HCl is lost and not measured after melting the sample for analysis. We will call this process, responsible for the presence of HCl in the solid phase, “pseudosolubility”: it can be true solubility, adsorption or co-condensation.

It can be imagined also that outgassing ^{36}Cl could be redeposited with snowfall which could explain the rather stable high ^{36}Cl values for recent firn.

This isotope study documents several interesting aspects of the behavior of Cl in upper Vostok firn:

- (1) HCl in the interstitial gaseous phase and HCl located in or on the solid are in isotopic equilibrium, as indicated by the contamination of most shallow layers by artificial ^{36}Cl contained in the air exhaled from deeper layers. This air does not just pass through the pores, it exchanges isotopically with the deposited HCl. This indicates that a dynamic process occurs in this medium, obeying a pseudo Henry law. This process, which most probably depends on temperature, regulates the amount of HCl entrapped in the ice during snow metamorphic processes.

- (2) Cl is mobile in the form of HCl, but not mobile when linked to Na, since salts do not suffer post-deposition phenomena. This observation can be explained by the different locations of salts and acids in the ice: the former inside the ice crystals, the latter at grain boundaries (Wolff et al., 1988). Moreover, Thibert and Dominé (1997) have shown that the diffusion process of HCl from the surface into solid

ice is an extremely slow process. We have, therefore, good reason to assume that NaCl aerosol scavenged by snow is not concerned with the isotopic processes involved in this study.

Our finding has serious consequences for the use of ^{36}Cl as a dating tool: as the record of HCl in shallow snow layers is unstable and may depend on various post-deposition physical and chemical processes affecting this gas, ^{36}Cl data are probably unreliable in central Antarctic regions where ice accumulation is low, just where this radioisotope would be very helpful for dating deep ice cores covering several ice ages. However, environmental conditions could have been different in the past and more favourable to the stability of the Cl deposits.

Glaciochemical studies of deep Antarctic ice cores show that the Cl/Na ratio has varied markedly according to climate (Legrand et al., 1988; Röthlisberger et al., 2002, 2003). This indicates that HCl may not be always present in the ice and that the processes described above were therefore less effective for some periods. Particularly during ice age conditions, when the acidity of ice was very low, this artefact may be negligible and ^{36}Cl records could be more reliable than in interglacial ice. Thus, by selecting appropriate samples there is a good chance to apply the $^{10}\text{Be}/^{36}\text{Cl}$ dating technique. This remains to be investigated. Finally, ^{36}Cl could be used as a tracer to assess the contribution of HCl (which is enriched in ^{36}Cl) degassing from central Antarctic firn on the Cl budget in Antarctic snow. This could be done by measuring the ^{36}Cl content of surface snow in various regions of the continent.

4. Conclusions

The bomb-produced atmospheric ^{36}Cl spike of the early 1960s has been clearly identified in Vostok snow, but its record is strongly modified when compared with Greenland data and model predictions. The deposition pattern is consistent with a significant migration of gaseous HCl in the snowpack. In addition, our data give a new insight into the post-deposition phenomena that affect Cl concentration in central Antarctica. The contamination of upper snow layers is a strong indication that there is a thermodynamic equilibrium between gaseous phase HCl and solid phase HCl. More work has to be done regarding the validity of ^{36}Cl records in glacial and interglacial ice at Antarctic sites with extremely low accumulation.

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