Ледники и ледниковые покровы

УДК 551.324.82

The integrity of the ice record of greenhouse gases with a special focus on atmospheric CO_2

© 2012 г. Dominique Raynaud

Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS/UJF Saint-Martin-d'Hères, France

raynaud@lgge.obs.ujf-grenoble.fr

Принята к печати 30 января 2012 г.

Антарктида, диоксид углерода, ледниковая скважина, ледяной керн, метан, станция Восток.
Antarctica, carbon dioxide, glacier borehole, ice core, methane, Vostok station.

Over the last 25 years, the ice core record has provided a unique and precious archive of past changes in three important greenhouse gases: carbon dioxide CO_2, methane CH_4 and nitrous oxide N_2O. Recovering the Vostok ice core has played a major role, being the first ice record showing the variations of CO_2 and CH_4 during a full glacial-interglacial cycle, and a few years later being extended to three more cycles. This information, by revealing the tight coupling between climate and carbon cycle during the last glacial-interglacial cycles, has become a benchmark against which climate and carbon cycle models can be tested. The purpose of the present work is to discuss the degree of integrity of the ice core record of greenhouse gases and to assess to which degree it provides an accurate reconstruction of the past atmospheric changes. The various processes potentially affecting the integrity of the record are discussed. They include the interactions of trace gases with precipitation or firn grains, the effect of summer-melting at the surface of the ice sheet, the diffusion and the gravitational setting of gases in the open spaces of the firn, the physical, chemical and biological interactions between the air trapped and the ice matrix, the role of the transformation of air bubbles into air hydrates with depth in the ice column. Providing to select an appropriate sampling site, to take specific precautions during storage and transportation of the ice cores, and to select ice of good quality, the ice core record of initial atmospheric gases is hardly affected by the processes listed above. Such conclusion is strongly supported by the remarkable agreement of global signals like CO_2 or CH_4 measured in different cores taken at different locations. Finally, I bring back here the history of how the ice core record of atmospheric CO_2 has been obtained, from the pioneering times to today, and summarize the main conclusions reached in terms of climate – carbon cycle interactions.

1. Introduction

Concerning the present and future evolution of the climate, the lesson of past changes, from the multi-decadal to the orbital time scales, can be essential. Indeed, we need to disentangle in the current changes of the climate, the part due to «natural» forcing from the one due to anthropogenic activities. Also, by recording accurately the past we get precious information related to the mechanisms of our climate machine. This information is needed for improving the hierarchy of climatic models used at the international level to simulate the future climate. It is not by chance that the huge assessment effort made by the International Panel for Climatic Change (IPCC) henceforth devotes a full chapter to paleoclimatology [19].

Paleo-archives are found in various environments: marine sediments, corals, lake sediments, soils, trees, fossils of fauna and vegetation, carbonate concretions and ice cores. All have kept climatic imprints of the past. In this rich context of indicators, providing past climatic information from the different oceanic basins and continents both in the Northern and in Southern hemispheres we may question the interest to look at ice cores situated in the very remote Polar Regions. In fact, the possibility to observe the evolution of climatic or atmospheric properties, like temperature or dust, with good resolution, even year by year over the last 10000 years in some Greenland sites, is unequalled and climatic changes are expected to be amplified at high latitudes. Also, the archives preserved in Antarctic or Greenland ice provide a wealth of other information (Fig. 1) due to the ability of the ice to trap the past atmosphere and to its very high-purity level allowing to keep traces of tiny fallouts from continental, oceanic, volcanic, extra-terrestrial, or anthropogenic origin. Unique, is the capacity of the ice to continuously sample over time a parcel of atmospheric air. This occurs during the transformation of the snow accumulat-

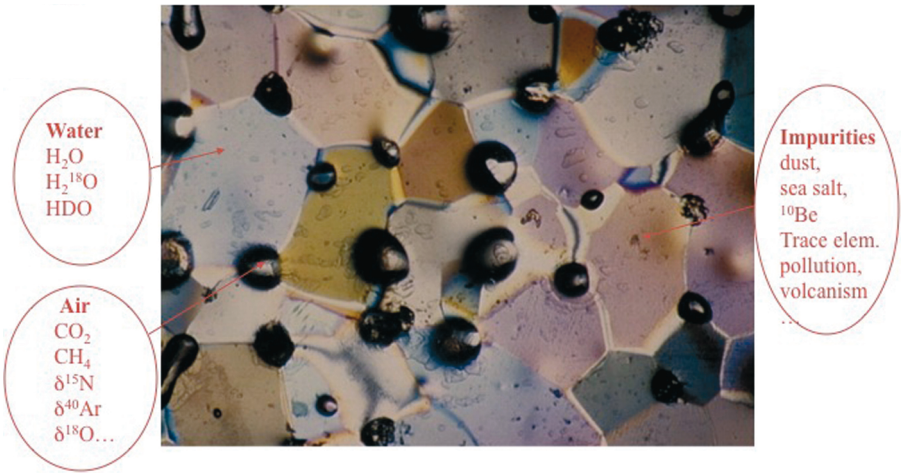

Fig. 1. The wealth of information provided by ice cores about the evolution of the Earth's atmosphere and climate. The snow falling down at the surface of the ice sheet washes out the atmosphere and samples dust and aerosols. The isotopic composition (D/H or $^{18}O/^{16}O$) of the snow H_2O molecules reflects the temperature of the snow formation and then provides precious indications about the past evolution of the climate at the surface of the ice sheets. The analyses of the air entrapped as bubbles in ice have led over the last 40 years to a set of discoveries. Part of the information is of regional or hemispheric scale, some like CO_2, or CH_4 are even of global significance.
The figure shows a picture of a thin layer of ice under polarized light. The ice crystals appear with different colours, depending on their orientations and the black spots are air bubbles. The bubbles at trapping time occupy roughly 10% of the total volume
Рис. 1. Богатство информации об эволюции земной атмосферы и климата, получаемое из ледяных кернов. Снег, выпадающий на поверхность ледникового щита, вымывает из атмосферы и включает в себя пыль и аэрозоли. Изотопное содержание (D/H или $^{18}O/^{16}O$) молекул воды в снеге отражает температуру воздуха в момент формирования снежных кристаллов и таким образом даёт драгоценную информацию о прошлой эволюции климата на поверхности ледниковых покровов. Анализ включённого в пузырьки воздуха приносит всё новые открытия на протяжении уже 40 лет. Часть информации отражает масштаб регионов или отдельного полушария, но сведения о CO_2 или CH_4 имеют глобальное значение.
Рисунок показывает тонкий шлиф льда в поляризованном свете. Кристаллы льда имеют различные радужные цвета в зависимости от ориентации их оптических осей, а чёрные точки представляют собой пузырьки воздуха. Захваченные пузырьки занимают около 10% общего объёма льда

ed at the surface of the ice sheet into airtight bubbly ice, usually in the first 100 meters or so below the surface. Thus, the ice records of trapped air are unique and precious archives of our atmosphere. Nevertheless, because of the important implications of the paleo-record of greenhouse gases in terms of climate sensitivity to their changes and of understanding their cycles in the absence of anthropogenic perturbation or under different climatic conditions, it is essential to understand how close is the composition of the air extracted from the ice in the laboratory to the atmospheric composition prevailing at the time the air is trapped in ice.

In 1993, Raynaud et al. [30] discussed the reliability of the ice record of greenhouse gases. Since then, more ice core data have been obtained and more process studies have been carried out. The aim of this paper is to provide an updated and wider assessment of the various processes, which can alter the initial atmospheric composition, and to address the uncertainties limiting the climatic interpretation of the ice core record of greenhouse gases. I also will summarize some of the main lessons we got in terms of climate and carbon cycle from looking at the past record of CO_2.

2. Processes involved in the trapping of air by ice and sources of uncertainties in reconstructing the original atmospheric signal

As illustrated in Fig. 2, various physical, chemical and biological processes can take place during air trapping in the snow and firn layers and later, in situ in ice. How far can they deviate the gas composition of the air enclosed in ice from its initial atmospheric composition? How accurately can we reconstruct the changes in atmospheric CO_2 and other greenhouse trace gases from their ice core records?

2.1. ***Snow and its transformation into ice.*** Freshly fallen snow at the surface of the ice sheet can incorporate a small amount of air enriched in CO_2 content [38]. If the air has been enclosed in the snowflakes as micro-bubbles, most of them should be lost during recristallization in the upper layers near the surface [32]. Also, ice formed at or near the surface of the ice sheet by refreezing of summer melting layers may enclose air whose initial atmospheric composition has been changed due to the different solubility coefficients of its various gaseous components (especially for the most soluble components like CO_2 and N_2O, which become enriched) or due to fractionation processes occurring during refreezing. After deposition, the snow grains

are progressively overlaid by new precipitations and the polar ice results from the densification of the snow deposited at the surface. The transformation of snow into ice (this stage is called firn, Fig. 3), which generally occurs in the first 50 to 120 meters, takes from decades to millennia, depending on temperature and accumulation rate. During the first stage of densification, rearrangement of the snow grains occurs until the closest dense packing stage is reached at relative densities of about 0.55–0.6, which corresponds to the snow-firn transition; the pores between the grains are still communicating with the atmosphere and convection can takes place under the influence of the wind. Then plastic deformation becomes the dominant process and the pores progressively become isolated from the atmosphere. The end product of this huge – probably the worldwide largest – natural sintering experiment is ice, an airtight material, which encloses air bubbles.

As illustrated in Fig. 3, the air is well mixed by convection in the upper layers, close to the surface. Below, the air column, still communicating with the surface layers, is in pure diffusive equilibrium and submitted to gravitational settling, the heavier gas molecules being preferentially enriched toward the base of the firn [13, 32]. As a consequence the air, at the time to be trapped as bubbles at the base of the firn column, has a composition that departs slightly from the atmosphere prevailing at the surface, but the gravitational effect is generally small (of the order of 1% of the initial atmospheric concentration) compared to the variations observed in the ice record, and can be corrected for with confidence. Note also that air composition, at the time to be trapped in ice, is smoothed because of the diffusion and due to the fact that the ice samples analysed for air measurements correspond to the trapping of a large number of air bubbles (up to several thousands) that closed off at the base of the firn at different times [36, 40]. This smoothing effect removes high frequency variations from the record.

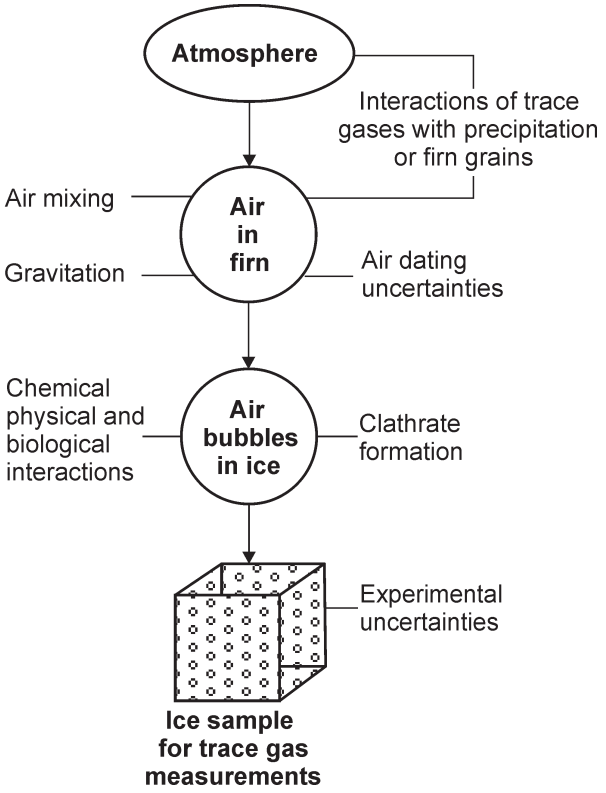

Fig. 2. Diagram illustrating the physical and chemical processes involved in the trapping of air by the ice. Adapted from [30]
Рис. 2. Диаграмма, иллюстрирующая физические и химические процессы, происходящие в захваченном льдом воздухе. Адаптировано по [30]

Also, physic-chemical processes, like physisorption or chemisorption, may take place between the gas phase

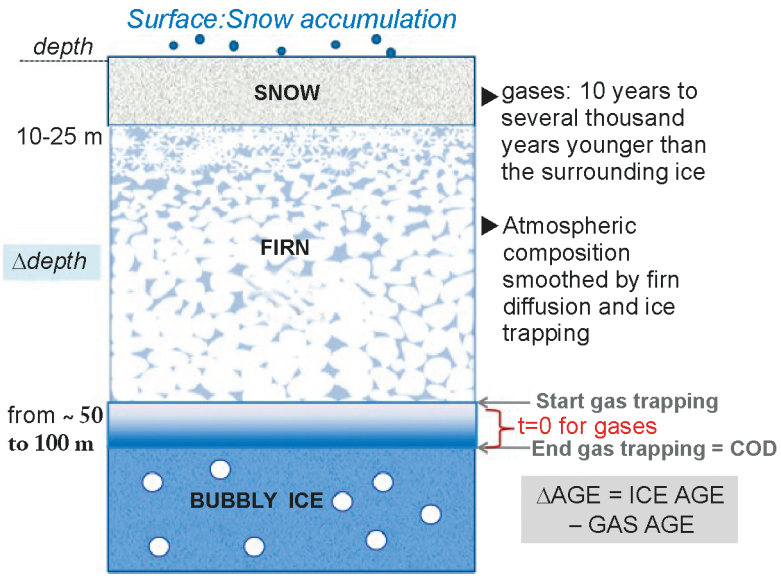

Fig. 3. Transformation of snow into bubbly ice. By courtesy of D. Buiron
Рис. 3. Превращение снега в пузырчатый лёд. По представлению D. Buiron

and the surface of the snow or firn grains. In principle, the adsorption of trace gases like CO_2 or CH_4 on the surface of snow or firn grains should be weak. On the other hand, liquid-like layers may occur on ice well below the bulk melting point and be enriched in soluble trace-gases like CO_2 and N_2O. If such processes affect significantly the air composition in the firn, we should observe a deviation between the contemporaneous air measured directly in the atmosphere and measured in the air entrapped in the ice. This is not the case (see section 3).

So, we can with confidence and in the limit of the experimental uncertainties (1 to 5 ppmv, see section 2.3) consider that the concentrations in greenhouse trace gases (like CO_2, CH_4, N_2O) of the air at the base of the firn, just before its enclosure in ice, is in pure diffusive and gravitational equilibrium with the atmosphere at the surface of the ice sheet, and then accurately records smoothed changes in their atmospheric composition.

2.2. ***Processes involved below the firn-ice transition.*** After the close-off of the bubbles, the ice is buried, and follows the flow-lines. The size of the bubbles progressively decreases and the air pressure inside them proportionally increases. Several hundred meters below the surface, the increasing load pressure leads to the formation of air clathrates: the bubbles progressively disappear and the gas molecules become encaged inside the ice molecular structure.

Chemical, physical and biological interactions. Chemical and physical interactions may occur and possibly affect the integrity of the ice core air record. For instance, CO_2 diffusion in ice, after the air was trapped in bubbles, may alter the original atmospheric signal. CO_2 diffusion coefficient is too small in ice to be accurately measured in the laboratory, but the smoothing of CO_2 spikes, associated with refrozen summer melting layers in ice cores, can be calculated from molecular volume – diffusion model [26]. Thus, measuring the gradual decrease of CO_2 concentrations away from the melt layer at Siple Dome (Antarctica), provides a way to estimate CO_2 diffusion rates in ice or their upper limit and shows no evidence that the diffusion in ice will smooth the CO_2 record significantly more than the smoothing in the firn [4]. However, more investigation about the different way CO_2 can diffuse in ice is needed.

CO_2 can also be slowly produced in situ in the ice after bubble close-off by carbonate-acid reaction or oxidation of organic material, when the ice contains enough impurities (carbonate dust particles or organic material). CO_2 measurements performed on the gas extracted from Greenland ice can show CO_2 peaks, which are not observed in Antarctica on ice samples with the same gas age, and which cannot be explained in terms of atmospheric composition change; these «CO_2 deviations» of no palaeo-atmospheric significance observed in Greenland ice are attributed to the high level of impurities in Greenland ice versus Antarctic ice [5, 15, 34, 41]. This makes the Greenland ice not suitable to get a reliable and accurate atmospheric CO_2 record. On the other hand, due to the very high-purity level of the Antarctic ice, such CO_2 enrichment of the gas extracted from the ice versus the atmospheric composition is on the whole negligible, and all the available CO_2 records are, in fact, provided by Antarctic ice cores.

We note that impurities can also affect the ice core record of N_2O (see [37] and references herein) but not the one of CH_4. In the case of N_2O, artefacts found are likely produced by bacteria or chemical reactions in the ice [35, 39].

Zone of transformation of bubbles into gas hydrates. A major concern for the people measuring trace gases, especially CO_2, in deep ice cores is linked with the zone of the clathrate or air hydrate formation. Non-fractured ice is a basic prerequisite for preserving the integrity of the ice core record of gases. The clathrate formation zone, which generally extends between about 500 and 1700 m depending on the temperature and accumulation rate of the site, is a brittle ice zone. Special precautions are required for coring non-fractured ice there, which may be a challenge. Furthermore, special care should be taken to avoid post-coring processes. The recovered ice should relax on the coring site, often during a full year, before to be transported from the field to the laboratories. Providing such precautions, reliable records of air content and greenhouse trace gases can be obtained. Furthermore, recent high resolution CO_2 measurements performed on Antarctic ice sampled from the bubble-clathrate transition zone and just below reveal, at the centimetre scale, a large and unexpected scatter of the data, up to 25 ppmv, around the mean atmospheric composition [24]. This scatter must be due to the processes involved in the transformation of bubbles to clathrates and Lüthi et al. [24] proposed a hypothetical explanation involving episodically increasing clathrate formation followed by diffusion processes from bubbles to clathrates. It is important to note that the mean atmospheric CO_2 composition is not affected if CO_2 values are averaged over a sufficiently long depth scale (> 10 cm in the case of ice core from the European Project for Ice Coring in Antarctica (EPICA) at Dronning Maud Land (DML).

2.3. ***Experimental uncertainties.*** As illustrated through Fig. 2, the final step of the path leading from the atmosphere to the measured composition of the air trapped in ice is the sampling stage, which includes recovering and storing the ice core, cutting the sample for air analysis and measuring the trace gases. All these operations generate experimental uncertainties, which can be in specific cases well assessed, as analytical accuracy, but not always. That is why often the scientists working on ice core records are replicating measurements, which in principle should lead to the same result. Replicates of measurements for CO_2 are overall between 1 and 5 ppmv. The width of the replicate estimate (1 to 5 ppmv) reflects mainly the improvement of the sampling and analytical techniques with time. We should also note that very accurate measurements are necessary when our aim is to match the instrumental record over decades, but we

don't need, on the whole, such high accuracy when investigating the long-term glacial-interglacial changes.

3. Integrity of the ice core record of greenhouse gases

In summary of section 2, the degree of integrity of the ice core record of greenhouse gases is determined by the various processes, which can alter the initial atmospheric composition, but is also limited by the experimental uncertainties.

The choice of the sampling site is essential. It is primordial to avoid ice formation sites where summer melting can occur, especially when investigating the most soluble components like CO_2 and N_2O. In the case of CO_2, due to its very high-purity level, the Antarctic ice must be preferentially chosen since the Greenland ice is not suitable because in situ production of CO_2 by carbonate dust decomposition or oxidation of organic material. We note that the N_2O record can also be affected by impurities incorporated in the ice.

The integrity of the ice core record of greenhouse gases depends on the quality of the ice, which can be fractured especially when drilling through the brittle zone. In the same zone, some fractionation may also occur during the transformation of bubbles to clathrate, which can affect the gas composition at the centimetre scale.

So, providing that (i) we use appropriate analytical methods (for instance CO_2 measurements require that the gas will be extracted from the ice by using a dry extraction method, as discussed in section 4), (ii) we select appropriate sampling sites, and (iii) we carefully select ice samples, the ice core measurements can provide, within the experimental uncertainties listed in 2.3, an accurate and faithful record of the smoothed changes in atmospheric greenhouse trace gases during the past. The smoothing effect, which depends on the site conditions (temperature, accumulation), removes high frequency variations from the record.

When focussing on CO_2, we can say that, under the conditions stated above, the CO_2 measured in the ice is not a proxy but a true measurement performed on a parcel of air, which has been sampled during the past and preserved for long periods (as long as several hundred of thousands of years) in an ultra-clean container, the ice.

There are two ways to check the overall integrity of the ice core record of atmospheric CO_2 and more generally greenhouse trace-gases.

The first one is to measure air in recently formed ice, which overlaps in age with a record of air whose composition has been directly measured in the atmosphere (instrumental records). This is possible for CO_2 since 1958, the year the measurement of the first records of global significance started at the Mauna Loa Observatory and South Pole Station. This also requires getting an Antarctic ice record whose entrapped air extends into recent decades, as it has been achieved at two sites, Siple Station and Law Dome [16, 27]. Since 1958, the averaged increase rate of atmospheric CO_2 has been about 1.5 ppmv/year. To match such instrumental record we need accurate CO_2 measurements in ice (say about $\pm$1 to 2 ppmv) and accurate dating of the enclosed air. It is also essential that the measurements of trace gases are made on the same scale as the atmospheric measurements. Furthermore, because the ice record of CO_2 is smoothed due to the diffusion through the firn and the air trapping processes (see 2.1), we should select sampling sites whose temperature and snow accumulation conditions allow a minimal smoothing effect, i.e. measured CO_2 concentrations averaged over a small number of years (possibly less than 10). To my knowledge, the most extensive and accurate study has been obtained by Etheridge et al., who analysed the air extracted from three ice cores taken at Law Dome, Antarctica [16]. The Law Dome sites provide CO_2 concentrations averaged over about 12 years (D. Etheridge, personal communication) and covering the 1959–1978 period; the reproducibility of CO_2 values measured on the same annual ice layer is better than 1.2 ppmv (1s). Atmospheric CO_2 concentrations are nearly identical at Law Dome and South Pole and the two records should overlap closely (allowing for the smoothing of rapid variations such as seasonality), unless there are errors in the dating of the air entrapped in the Law Dome ice. The results show that the CO_2 Law Dome record overlaps tightly, within the measurement uncertainty, for up to 20 years with the atmospheric South Pole record.

Since then, those results have been reproduced and extended to CH_4 and N_2O [25]. These evidences convincingly confirm the integrity of the ice core record of atmospheric CO_2 and other greenhouse trace gases, at least for the recent time.

A second way to check the integrity of the ice core record of greenhouse trace-gases, especially over the long periods of the past, is to assess the degree of agreement between records from various ice cores obtained from different types of contemporaneous ice (for instance with and without air hydrates, at sites with different temperature and snow accumulation rate conditions, with different crystal sizes and fabrics) and also to measure again the same ice core record after a while to check its stability with time [8, 25].

4. The ice core record of greenhouse gases: climate and carbon cycle

84 years after Arrhenius prediction that the Ice Age cooling results from a decrease of about 40% of the capacity of CO_2 to absorb the heat from the ground [6], air bubbles of Antarctic ice revealed that the atmospheric concentrations in CO_2 indeed did increase by about 40% between the LGM (Last Glacial Maximum) and the Holocene [9, 14]. In fact, several attempts were made previously during the 1960's and 1970's in order to get a reliable atmospheric CO_2 record from the gas extracted from the ice, but the results showed a large and discouraging scatter to the point that we even thought at this time that the hope to get a record of the past atmospheric composition in CO_2 by analyzing the air trapped in ice was uncertain, not to say completely illusory. But a major analytical step regarding the integrity of the ice core record

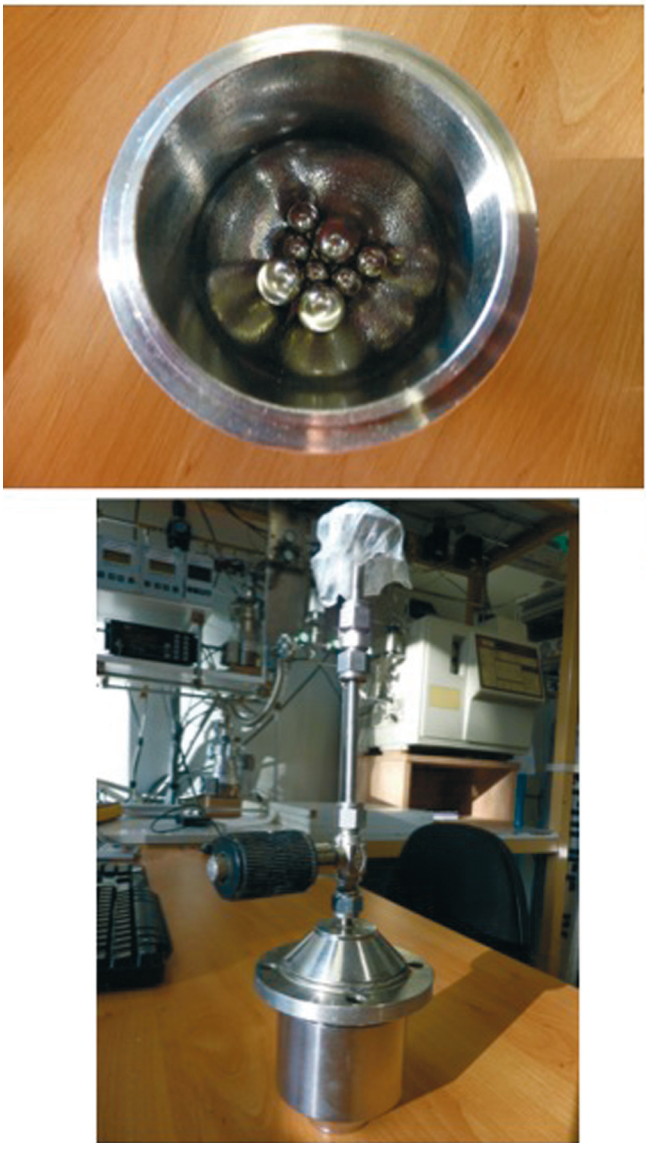

Fig. 4. Dry extraction method used for CO_2 measurements. The picture shows a closed stainless container with metallic balls inside, used at LGGE for pulverising ice samples under vacuum and extracting the gas for CO_2 measurements

Рис. 4. Метод сухого экстрагирования, использованный для измерений CO_2. Фотографии показывают закрытый стальной контейнер с металлическими шариками внутри, использованный в Лаборатории Гренобльского университета для превращения в порошок ледяных образцов в условиях вакуума и экстрагирования газа для измерения CO_2

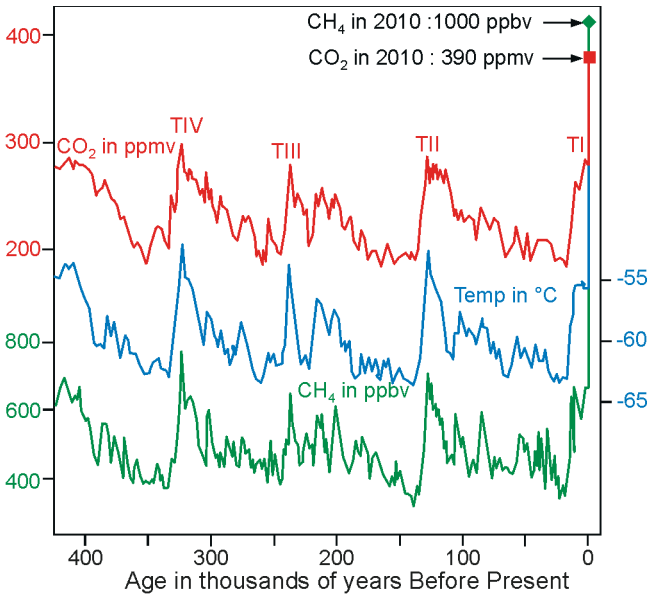

Fig. 5. The middle curve indicates the variation in isotopic temperature at Vostok throughout the last 420,000 years. These variations are obtained from ice deuterium measurements along the core. The upper and lower curves represent concentrations of CO_2 and CH_4 over the same period, indicating on the right the recent spike of these two greenhouse gases. TI to TIV indicates the four glacial-interglacial transitions. After [29]

Рис. 5. Средняя кривая показывает изменения «изотопной температуры» в районе станции Восток на протяжении 420 тыс. лет. Она получена по измерениям содержания дейтерия по всей колонке льда. Верхняя и нижняя кривые отражают содержание CO_2 и CH_4 за это время и показывают прошлые и современный пики концентрации обоих парниковых газов. Символы от TI до TIV указывают на четыре переходных периода от ледниковья к межледниковью. По [29]

of CO_2 was reached, when Delmas et al. [14] proposed in 1980 to shift from a wet to a dry extraction method by crushing the ice samples (Fig. 4), instead to melt them, under vacuum, in order to avoid the apparent but, at this time, not well understood enrichment of CO_2 hitherto observed in the extracted air from the ice.

After the pioneering results published in 1980 and showing a marked depletion in CO_2 concentrations during the Last Glacial Maximum compared to the Holocene period, the question was to know how well the observed correlation between CO_2 and climate during the LGM and Holocene periods was also valid during a full glacial-interglacial cycle. The magnificent effort made by the Soviet drillers at Vostok permitted to obtain and publish in 1987 a first and memorable CO_2 record of the last climatic cycle [7]. Its comparison with the deuterium isotope temperature [21] highlighted the marked similarity and the high correlation between their temporal variations, which confirms the link between CO_2 and climate as predicted by Arrhenius and suggested the potential climatic role of CO_2 during the late Pleistocene in amplifying the relatively weak orbital forcing [18]. That was only the start of the cornucopia of Vostok ice core results. In 1990, the first CH_4 record over a complete climatic cycle was obtained [12] and the extended record of CO_2 and CH_4 to four glacial-interglacial cycles back to 430,000 years BP was published in 1999 [29]. The four climatic cycles long record at Vostok, rapidly became an iconic figure in palaeo-climatology [2] (Fig. 5). It also generated exciting works dealing with physical prop-

Vostok and EDC ice cores. Time resolution of CO_2 and CH_4 records

Vostok CO_2 (the last 420 kyrs BP)

The mean time resolution is about 1200 years [28, 29]. It can go up to 6,000 years in the fractured zones and in the bottom part of the record. Three of the four different Glacial–Interglacial transitions – TII, TIII and TIV (see Fig. 5) – have been studied with relatively high resolution (respectively: 600, 750, 1050 years). Unfortunately, the temporal resolution of TI (Last Glacial Maximum to Holocene) is significantly lower (1800 years), because this transition is situated in the fractured brittle zone.

EDC CO_2 (extending the Vostok record to 800 kyrs BP)

The mean time resolution down to 650 kyrs BP is 730 years [33] and 570 years from 650 to 800 kyrs BP [23].

Vostok CH_4 (the last 420 kyrs BP)

The mean resolution for CH_4 is about 950 years. It ranges between a few tens of years to 4,500 years [29].

EDC CH_4 (the last 800 kyrs BP)

The average time resolution over the full length of the 800 kyr record is about 380 years [22]. It depends on the period considered and increase on the whole with the age from an average of 210 years between 0 to 215 kyr BP to reach a mean temporal resolution of 550 years between 665 to 800 kyrs BP.

erties of ice and ice-sheet modelling (e.g. [3]). Since then the Vostok ice record of greenhouse gases has been extended to the last 800 kyr for CO_2 [23, 33], CH_4 [22] and N_2O [31], by measuring the EPICA Dome C (EDC) ice.

The lesson from the ice core record of greenhouse gases. Finally, based on the long Vostok and EDC ice core records I would like to highlight here some crucial information we got in terms of understanding the climate-carbon cycle coupling during the past, and about the future CO_2-Climate behaviour.

– The present-day atmospheric concentration in CO_2 and CH_4 are likely unprecedented during the last 800,000 years.

– The close correlation between greenhouse gases and climate over glacial-interglacial cycles attests to the tight coupling between climate and carbon cycle during the late Pleistocene.

– Orbitally-driven insolation changes are pacemakers of the glacial-interglacial cycles, and radiative forcing of greenhouse gases (3 W/m^2) together with extent and decay of the northern ice sheets (3 W/m^2) are key drivers of glacial-interglacial cycles.

– The delay of a few centuries of the CO_2 increase compared to the Antarctic warming and observed at the onset of major climatic transitions (e.g. [1, 11, 17, 28]) can suggest, that climate changes in the South alter the carbon cycle, and highlight the role of the Southern Ocean in the global cycle. However, it is necessary to decrease the dating uncertainties due to the estimate of the difference in age between the gas trapped in ice and the ice itself (because the ice isotopic signature is the proxy used for deducing Antarctic temperature).

– Changes in climate and CO_2 reconstructed from ice cores offer a benchmark against which climate and carbon cycle models can be tested.

Conclusion

Following the first 1980's reports of CO_2 measurements in Antarctic ice [23, 24] suggesting CO_2 in the glacial atmosphere substantially lower than during the Holocene period, two eminent geochemists of the ocean wrote: «The hottest topic for those interested in the Earth's carbon cycle is the change in atmospheric CO_2 content between glacial and interglacial time» [10]. Since then numerous studies, disregarded or misinterpreted by some [20], have been performed to assess the degree of integrity of the Antarctic ice core record of atmospheric CO_2 and validate the glacial-interglacial changes of CO_2 documented over several glacial-interglacial cycles and for crucial time intervals with high temporal resolution. If the two fundamental questions asked by Broecker and Peng: «What causes the glacial-interglacial CO_2 changes? What is their role in glacial cycles?» are still under discussion, nevertheless fundamental progresses have been made.

Aknowledgements. I dedicate this work to my Russian and French colleagues, who have been involved in the Vostok venture. Without them, it will be no such paper.

A special thank is addressed to Vladimir Kotlyakov for his continuous support of the collaboration between

Russian and French glaciologists and to my colleague and friend Vladimir Lipenkov for sharing with me for a long time a branch of great scientific excitements.

I would like to thank David Etheridge for discussions about how the ice core record of trace gases overlap the atmospheric instrumental record and Bernhard Stauffer for discussions concerning physical and chemical interactions between gases and ice.

Литература

1. *Вакуленко Н.В., Котляков В.М., Монин А.С., Сонечкин Д.М.* Доказательство упреждения изменений концентрации парниковых газов вариациями температуры в данных станции Восток // ДАН. 2004. Т. 396. № 5. С. 686–690.
2. *Котляков В.М.* Избранные сочинения: Кн. 1. Гляциология Антарктиды. М.: Наука, 2000. 423 с.
3. *Липенков В.Я., Барков Н.И., Саламатин А.Н.* История климата и оледенения Антарктиды по результатам изучения ледяного керна со станции Восток // Проблемы Арктики и Антарктики. 2000. Вып. 72. С. 197–236.
4. *Ahn J., Headly M., Wahlen M., Brook E.J., Mayewski P.A., Taylor K.C.* CO_2 diffusion in polar ice: observations from naturally formed CO_2 spikes in the Siple Dome (Antarctica) ice core // Journ. of Glaciology. 2008. V. 54 P. 685–695.
5. *Anklin M., Barnola J.-M., Schwander J., Stauffer B., Raynaud D.* Processes affecting the CO_2 concentrations measured in Greenland ice // Tellus. 1995. V. 47B. P. 461–470.
6. *Arrhenius S.* On the influence of carbonic acid in the air upon the temperature of the ground // The London, Edinburgh, and Dublin Philosophical Magazine. 1896. V. 41. P. 237–275.
7. *Barnola J.-M., Raynaud D., Korotkevich Y.S., Lorius C.* Vostok ice core provides 160,000-year record of atmospheric CO_2 // Nature. 1987. V. 329. P. 408–414.
8. *Barnola J.-M., Pimienta P., Raynaud D., Korotkevitch Y.S.* CO_2 climate relationship as deduced from the Vostok ice core: a re-examination based on new measurements and on a re-evaluation of the air dating // Tellus. 1991. V. 43B. P. 83–91.
9. *Berner W., Oeschger H., Stauffer B.* Information on the CO_2 cycle from ice core studies // Radiocarbon. 1980. V. 22. P. 227–235.
10. *Broecker W.S., Peng T.-H.* Glacial to interglacial changes in the operation of the global carbon cycle // Radiocarbon. 1986. V. 28. P. 309–327.
11. *Caillon N., Severinghaus J.P., Jouzel J., Barnola J.-M., Kang J., Lipenkov V.Y.* Timing of atmospheric CO_2 and Antarctic temperature changes across Termination III // Science. 2003. V. 299. P. 1728–1731.
12. *Chappellaz J., Barnola J.-M., Raynaud D., Korotkevich Y.S., Lorius C.* Ice-core record of atmospheric methane over the past 160,000 years // Nature. 1990. V. 345. P. 127–131.
13. *Craig H., Horibe Y., Sowers T.* Gravitational separation of gases and isotopes in polar ice caps // Science. 1988. V. 242. P. 1675–1678.
14. *Delmas R.J., Ascencio J.M., Legrand M.* Polar ice evidence that atmospheric CO_2 20 000 BP was 50% of the present // Nature. 1980. V. 284. P. 155–157.
15. *Delmas R.J.* A natural artefact in Greenland ice-core CO_2 measurements // Tellus. 1993. V. 45B. P. 391–396.
16. *Etheridge D.M., Steele L.P., Langenfields R.L., Francey R.J., Barnola J.-M., Morgan V.I.* Natural and anthropogenic changes in atmospheric CO_2 over the last 1000 years from air in Antarctic ice and firn // Journ. of Geophys. Research. 1996. V. 101. P. 4115–4128.
17. *Fischer H., Wahlen M., Smith J., Mastroianni D., Deck B.* Ice core records of atmospheric CO_2 around the last three glacial terminations // Science. 1999. V. 283. P. 1712–1714.
18. *Genthon C., Barnola J.-M., Raynaud D., Lorius C., Jouzel J., Barkov N. I., Korotkevitch Y.S., Kotlyakov V.M.* Vostok ice core: climatic response to CO_2 and orbital forcing changes over the last climatic cycle // Nature. 1987. V. 329. P. 414–418.
19. IPCC: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment report of the Intergovernmental Panel on Climate Change / Eds. S. Solomon et al. Cambridge, 2007. 996 p.
20. *Jaworowski Z., Segalstad T.V., Ono N.* Do glaciers tell a true atmospheric CO_2 story? // Science of the Total Environment. 1992. V. 114. P. 227–284.
21. *Jouzel J., Lorius C., Petit J.R., Genthon C., Barkov N.I., Kotlyakov V.M., Petrov V.M.* Vostok ice core: a continuous isotope temperature record over the last climatic cycle (160,000 years) // Nature. 1987. V. 329. P. 403–408.
22. *Loulergue L., Schilt A., Spahni R., Masson-Delmotte V., Blunier T., Lemieux B., Barnola J.-M., Raynaud D., Stocker T.F., Chappellaz J.* Orbital and millennial-scale features of atmospheric CH_4 over the past 800,000 years // Nature. 2008. V. 453. P. 383–386.
23. *Lüthi D., Le Floch M., Bereiter B., Blunier T., Barnola J.-M., Siegenthaler U., Raynaud D., Jouzel J., Fischer H., Kawamura K., Stocker T.F.* High-resolution carbon dioxide concentration record 650,000–800,000 years before present // Nature. 2008. V. 453. P. 379–382.
24. *Lüthi D., Bereiter B., Stauffer B., Winkler R., Schwander J., Kindler P., Leuenberger M., Kipstuhl S., Capron E., Landais A., Fischer H., Stocker T.F.* CO_2 and O_2/N_2 variations in and just below the bubble-clathrate transformation zone of Antarctic ice cores // Earth and Planetary Science Letters. 2010. V. 297. P. 226–233.
25. *MacFarling Meure C., Etheridge D., Trudinger C., Steele P., Langenfelds R., van Ommen T., Smith A., Elkins J.* Law Dome CO_2, CH_4 and N_2O ice records extended to 2000 years BP // Geophys. Research Letters. 2006. V. 33. doi:10.1029/2006GL026152, 10.1029/2006GL026152
26. *Neftel A., Oeschger H., Schwander J., Stauffer B.* Carbon Dioxide concentration in bubbles of natural cold ice // Journ. of Physical Chemistry. 1983. V. 87. P. 4116–4120.
27. *Neftel A., Moor E., Oeschger H., Stauffer B.* Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries // Nature. 1985. V. 315. P. 45–47.
28. *Pépin L., Raynaud D., Barnola J.-M., Loutre M.F.* Hemispheric roles of climate forcings during glacial-interglacial transitions, as deduced from the Vostok record and LLN-2D model experiments // Journ. of Geophys. Research. 2001. V. 106. № 31. P. 885–831, 892.
29. *Petit J.R., Jouzel J., Raynaud D., Barkov N.I., Barnola J.-M., Basile I., Bender M., Chappellaz J., Davis M., Delaygue G., Delmotte M., Kotlyakov V.M., Legrand M., Lipenkov V.Y., Lorius C., Pépin L., Ritz C., Saltzman E., Stievenard M.* Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica // Nature. 1999. V. 399. P. 429–436.

30. *Raynaud D., Jouzel J., Barnola J.-M., Chappellaz J., Delmas R.J., Lorius C.* The ice record of greenhouse gases // Science. 1993. V. 259. P. 926–933.
31. *Schilt A., Baumgartner M., Blunier T., Schwander J., Spahni R., Fischer H., Stocker T.F.* Glacial-interglacial and millennial-scale variations in the atmospheric nitrous oxide concentration during the last 800,000 years // Quaternary Science Reviews. 2010. V. 29. P. 182–192.
32. *Schwander J.* The transformation of snow to ice and the occlusion of gases // The Environmental Record in Glaciers and Ice Sheets / Eds. Oeschger H., Langway Jr. C.C. New York: John Wiley, 1989. P. 53–67.
33. *Siegenthaler U., Stocker T.F., Monnin E., Lüthi D., Schwander J., Stauffer B., Raynaud D., Barnola J.-M., Fischer H., Masson-Delmotte V., Jouzel J.* Stable carbon cycle – climate relationship during the Late Pleistocene // Science. 2005. V. 310. P. 1313–1317.
34. *Smith H.J., Wahlen M., Mastroianni D.* The CO_2 concentration of air trapped in Greenland Ice Sheet Project 2 ice formed during periods of rapid climate change // Journ. of Geophys. Research. 1997. V. 102. № 26. P. 577–526, 582.
35. *Sowers T.* The N_2O record spanning the penultimate deglaciation from the Vostok ice core // Journ. of Geophys. Research. 2001. V. 106. P. 31903–31914.
36. *Spahni R., Schwander J., Flückiger J.B.S., Chappellaz J., Raynaud D.* The attenuation of fast atmospheric CH_4 variations recorded in polar ice cores // Geophys. Research Letters. 2003. V. 30. P. 1571. doi:1510.1029/2003GL017093.
37. *Spahni R., Chappellaz J., Stocker T.F., Loulergue L., Hausammann G., Kawamura K., Flûckiger J., Schwander J., Raynaud D., Masson-Delmotte V., Jouzel J.* Atmospheric methane and nitrous oxide of the Late Pleistocene from Antarctic ice cores // Science. 2005. V. 310. P. 1317–1321.
38. *Stauffer B., Berner W., Oeschger H., Schwander J.* Atmospheric CO_2 history from ice core studies // Zeitschrift für Gletscherkunde und Glazialgeologie. 1981. Bd. 17. S. 1–15.
39. *Stauffer B., Monnin E., Nakazava T., Aoki S.* Discussion of the reliability of CO_2, CH_4 and N_2O records from polar ice cores // Mem. National Institute Polar Research. 2003. Spec. Issue 57. P. 139–152.
40. *Trudinger C.M., Enting I.G., Etheridge D.M., Francey R.J., Levchenko V.A., Steele L.P., Raynaud D., Arnaud L.* Modelling air movement and bubble trapping in firn // Journ. of Geophys. Research. 1997. V. 102. P. 6747–6763.
41. *Tschumi J., Stauffer B.* Reconstructing past atmospheric CO_2 concentration based on ice-core analyses: open questions due to in situ production of CO_2 in the ice // Journ. of Glaciology. 2000. V. 46. P. 45–53.

Достоверность сведений, извлекаемых из кернов льда, о содержании парниковых газов, особенно атмосферного CO_2

Образование льда на полярных ледниках сопровождается захватом пузырьков воздуха, которые в зависимости от условий льдообразования изолируются от атмосферы на глубине 50–120 м от поверхности ледника. Долговременные ряды содержания атмосферных газов (несколько сотен тысяч лет) могут быть получены на основании исследования ледяных кернов, содержащих информацию о газовом составе атмосферы. Анализируя состав экстрагированного из ледяных кернов атмосферного воздуха, можно получить, например, временные ряды концентрации диоксида углерода и метана, охватывающие период времени, в течение которого происходило накопление изученной ледниковой толщи. Изменения концентрации этих парниковых газов, влияющих на радиационный и тепловой режим Земли, рассматривают, наряду с колебаниями уровня моря (объёма континентального льда), в качестве основных индикаторов глобальных изменений на нашей планете. Теоретические и экспериментальные исследования последних лет позволили значительно расширить возможности использования результатов газовых анализов ледяных кернов для изучения прошлых изменений климата и окружающей среды.

Наиболее значительным событием в области палеоклиматологии за последние полвека стало экспериментальное доказательство существования тесной связи между вариациями температуры и концентрации CO_2 и CH_4 на протяжении последних 160 тыс. лет (от предшествующего ледникового максимума до голоцена) по данным ледяного керна с российской антарктической станции Восток. Получение более глубокого керна на станции Восток и осуществление проекта глубокого бурения EPICA на Куполе С (Антарктида) позволили подтвердить и задокументировать взаимосвязь между климатом, парниковым эффектом и углеродным циклом на протяжении соответственно 420 000 и 800 000 лет.

В какой степени результаты газовых анализов извлечённого изо льда воздуха отражают газовый и изотопный состав древней атмосферы Земли? Исследования показали, что на различных стадиях образования и метаморфизма льда, а также во время экстракции воздуха из ледяных образцов происходят процессы, которые могут изменять первоначальный газовый и изотопный состав захватываемого льдом атмосферного воздуха. Такими процессами служат: физическая и химическая адсорбция газов на поверхности ледяных зёрен фирна; летнее таяние и повторное замерзание талой воды на поверхности ледника; диффузия и гравитационное разделение газов в пределах фирновой толщи; диффузионное фракционирование газов в зоне закрытия фирновых пор; диффузия газовых молекул во льду после изоляции пузырьков воздуха от атмосферы; образование CO_2 *in-situ* в результате окисления содержащейся во льду карбонатной пыли; трансформация воздушных пузырьков в газовые гидраты на боль-

ших глубинах в теле ледника и связанный с ней процесс диффузионного обмена между газовыми и гидратными включениями, приводящий к мелкомасштабным вариациям (искажениям) газового состава содержащегося во льду воздуха.

Тщательный анализ всех имеющихся в настоящее время данных показывает, что соблюдение определённых требований, относящихся к выбору пункта бурения льда, технике отбора образцов, условиям их хранения и транспортировки, а также к методу экстракции воздуха изо льда, может обеспечить получение достоверных данных об эволюции газового состава атмосферы по результатам газовых анализов заключённого в ледяной породе воздуха. Например, повышенное содержание кислотных и карбонатных осадков в отдельных интервалах гренландских кернов делает их непригодными для измерений содержания CO_2. Вместе с тем антарктические керны, практически лишённые карбонатных примесей, – идеальный источник информации об изменении концентрации этого парникового газа в атмосфере Земли в прошлом. В целом, можно утверждать, что ледниковые покровы Антарктиды и Гренландии – это наиболее надёжные природные архивы атмосферных газов. Такой вывод подтверждается превосходным совпадением экспериментальных рядов CO_2, полученных по кернам из разных районов Антарктиды, а также совпадением рядов CH_4, измеренных по антарктическим и гренландским кернам. Веским доказательством надёжности данных по кернам служит также их замечательная согласованность – в интервале перекрытия – с инструментальными данными мониторинга газового состава атмосферы, который начал проводиться со второй половины прошлого века.

Некоторые процессы, изменяющие состав и общее количество воздуха, захватываемого ледниковым льдом, формируют в экспериментальных рядах газовых характеристик ледяных кернов сигналы, которые несут полезную палеоклиматическую информацию. Например, на глубине изоляции пор фирна от атмосферы наблюдается диффузионный отток газов из уже замкнутых и подвергшихся сжатию воздушных пузырьков в сторону открытых пор. Этот процесс приводит к обеднению захваченного льдом воздуха газами, которые легче диффундируют во льду, и отклонению в нём отношений O_2/N_2, Ne/N_2 и Ar/N_2 от значений, характерных для атмосферного воздуха. Показано, что вариации O_2/N_2 и общего количества воздуха во льду связаны цепочкой физических и структурных процессов с изменяющимися структурными характеристиками поверхностного слоя снега, которые, в свою очередь, формируются под воздействием солнечной радиации. Обнаружение во льду индикаторов местной инсоляции открыло путь к абсолютному (орбитальному) датированию льда. Проведённые исследования показали, что путём совмещения экспериментальных рядов $\delta(O_2/N_2)$ и общего газового содержания льда с соответствующими кривыми местной инсоляции, рассчитанными по астрономическим формулам, можно получить хроностратиграфические шкалы ледяных кернов, по точности значительно превосходящие общепринятые датировки льда, основанные на модельных расчётах. Прогресс в области датирования льда, в свою очередь, ведёт к более точным оценкам фазовых соотношений между вариациями основных климатообразующих факторов и характеристик климата в ходе глобальных изменений на нашей планете, т.е. к углублению нашего понимания причинно-следственных связей и механизмов этих изменений.

В статье также обсуждаются проблемы, связанные с использованием общего газового содержания льда как палеобарометра – индикатора изменений высоты (мощности) ледникового покрова, а также эффекта термодиффузии (термического фракционирования) газов в фирне для получения информации о скорости и амплитуде так называемых «быстрых» климатических изменений в прошлом.