Formation of the Ice Core Isotopic Composition

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Abstract: Main processes of the ice core isotopic composition formation are overviewed. Theory of isotope-temperature relationship is discussed and confirmed by a number of experimental data. The factors related to wind-driven spatial snow redistribution and post-depositional isotopic changes that may alter or weaken this relationship, are also considered. For high-resolution isotopic time-series obtained at sites with low accumulation of snow, the signal-to-noise ratio is shown to be as low as 0.25, which means that noise accounts for about 80 % of the total variance. It is demonstrated that "classical isotopic method" (based on the present-day geographical isotope-temperature slope) underestimates the amplitude of past temperature changes in Antarctica. The most likely reason for the discrepancy is the change in the moisture source conditions. After correction for the latter, the paleo-temperature reconstructions produced by the isotopic method become consistent with those obtained from borehole temperature measurements. We show that in the case of the Vostok ice core, both approaches lead to the same temperature shift of 10ºC between LGM and the present time. The isotopic composition of the basal part of the Vostok ice core, comprising frozen subglacial Lake Vostok water, is also discussed.

Key words: Antarctica, Vostok station, ice core, isotopic composition, paleo-climate, Lake Vostok

1. Introduction and outline

Stable water isotopic composition (δD and $\delta^{18}O$) of ice cores is commonly known as one of the most valuable paleo-climate proxies for temperature conditions of the precipitation formation in the past [15]. The observed relationship between air temperature and isotopic content of the precipitation (both geographical and temporal) has been robustly confirmed experimentally and explained theoretically (see review in [20], for example). Isotopic data extracted from deep ice cores has allowed reconstructing paleo-temperature over about 120 ka in Greenland [60] and 800 ka in Antarctica [40].

On the other hand, the limitations of the isotopic paleo-thermometer method are also known [2, 33, 39, 46, 54], which makes the absolute values of isotope-temperature reconstructions somewhat uncertain.

In this work we overview the processes leading to the formation of the vertical profile of isotopic composition of an ice core, using the extensive data set obtained at the Russian Vostok Station, central Antarctica. At first, we present the theoretical background of the relationship between the stable water isotope content in precipitation and air temperature (Section 2). In Section 3 we consider the limitations of isotopic method due to the formation of non-climatic noise as a result of depositional and post-depositional processes in the upper snow thickness. In order to estimate the signal-to-noise ratio in vertical isotopic profiles, the data on local spatial isotopic distribution in the vicinity of Vostok Station are used. Temporal variability of isotopic content of the Vostok precipitation and snow thickness is then compared with the instrumental record of air temperature (Section 4) to derive the local isotope-temperature calibration coefficient needed for the deep ice core-based paleo-reconstructions. We also use the high-resolution isotopic profiles from deep snow pits to reconstruct Vostok temperature history over the past 200 years thus demonstrating the validity of the method within a shorter time scale. Finally, the isotopic record from the deep Vostok borehole is considered in Section 5. The paleotemperature reconstruction obtained with isotope approach is compared with that inferred from borehole temperature measurements. The most reliable estimate of the amplitude of the past temperature changes at Vostok, consistent with results of both methods, is presented. Section 6 of the paper deals with formation of the isotopic composition of the basal section of the Vostok ice core comprising frozen water of subglacial Lake Vostok.

2. Theory of isotope-temperature relationship. Modeling isotopic content of precipitation

In this section we discuss the theoretical background of the relationship between the stable water isotope content of precipitation and air temperature. The main principles of modeling the isotopic composition of liquid, mixed and solid precipitation are also given.

The relationship between isotopic composition of precipitation and temperature of its formation is based on the "isotopic depletion" of moisture in the precipitating air mass due to isotopic fractionation during phase transformation of water. Since saturation water vapor pressure is less for heavy water molecules ($HD^{16}O$ and $H_2{}^{18}O$) than for light molecules ($H_2{}^{16}O$), the

concentration of heavy isotopes in a liquid phase is higher than in a vapor phase equilibrated with this liquid. So, the isotopic content of water vapor of an air mass formed over the ocean is reduced compared to that of the ocean water. As the cooling of the air mass proceeds, the water vapor condenses and new portions of precipitation are enriched in heavy isotopes with respect to the vapor remaining in the air mass thus making the vapor more and more isotopically depleted (Fig. 1). Obviously, in the course of further cooling both vapor and condensate become isotopically lighter due to the washing out of heavy water molecules during precipitation formation.

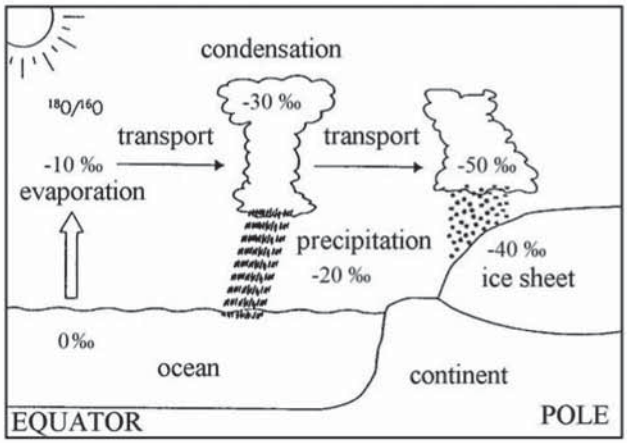

Figure 1. Natural water cycle and isotope fractionation of oxygen 18 (from [20])

Thus, the isotopic composition of precipitation is proportional to the ratio F of current amount of water in the air mass to its initial amount. In turn, F depends on the difference of condensation temperature at the current time and at the beginning of the distillation process. Isotopic composition of liquid precipitation (δ_p) can be sufficiently well predicted by a Rayleigh distillation approach which is based on the assumption that condensation takes place in the dynamic and isotopic equilibrium and that new portions of condensate are removed immediately from the air mass [15]:

$$\delta_p = \frac{\alpha}{\alpha_0} F^{\alpha_m - 1} - 1, \qquad (1)$$

where δ (δD or $\delta^{18}O$) is isotope composition expressed as ratio of heavy isotope concentration (mole fraction) in the sample (SA) to its concentration in standard water (ST), in per mil:

$$\delta = \frac{R_{SA} - R_{ST}}{R_{ST}} \times 1000 , \qquad (2)$$

where $R = \frac{\left[{}^2H\,{}^1H\,{}^{16}O\right]}{\left[{}^1H_2\,{}^{16}O\right]}$ for δD and $R = \frac{\left[{}^1H_2\,{}^{18}O\right]}{\left[{}^1H_2\,{}^{16}O\right]}$ for $\delta^{18}O$, and α is the fractionation coefficient at a certain moment of time, α_0 is the same coefficient in the beginning of the condensation process and α_m is the mean value of α from the beginning of the process to the current moment.

The equilibrium fractionation coefficient α (α_D for deuterium and α_{18} for oxygen 18) is by definition equal to ratio of heavy isotope concentration in liquid to its concentration in water vapor being in equilibrium with the liquid:

$$\alpha = \frac{R_{liquid}}{R_{vapor}} \text{ (always > 1)}, \qquad (3)$$

and can also be determined as ratio of saturation pressure of light molecules to that of heavy ones. In turn, the fractionation coefficients are temperature-dependent. The temperature functions of fractionation coefficients are discussed in [70].

Unlike the condensation in the atmosphere, the evaporation of water from the ocean takes place under non-equilibrium conditions characterized by under-saturated water vapor above the sea surface. As a consequence, a "kinetic isotopic effect" that occurs due to the slower diffusion of heavy molecules leads to larger effective fractionation coefficients as compared with those at equilibrium conditions. The first theoretical model satisfactorily describing the kinetic effect was developed by Merlivat and Jouzel (1979) [57]. According to the authors, the isotopic composition of water vapor forming over the sea surface, δ_{v0}, equals to:

$$\delta_{v0} = (1 + \delta_{oc}) \frac{1}{\alpha} \frac{1-k}{1-kh} - 1, \qquad (4)$$

where δ_{OC} is the isotopic composition of the ocean water, α is the equilibrium fractionation coefficient, h is the relative humidity of the air over the water surface and k is the coefficient that accounts for the molecular and turbulent diffusivity of water vapor. The latter coefficient differs by 12 % for D and ^{18}O, and is dependent on wind regime, though in some cases it can be took constant and equal to 0.006 (for oxygen 18) [36].

The equation (4) is based on the assumption that the air mass is formed in a closed system with no vapor being in the air before evaporation begins, which may be far from reality [11]. It was shown however that using this assumption for estimating the initial vapor isotopic composition leads to systematic differences compared to simulations conducted with three dimensional isotopic-atmospheric general circulation models (IGCM) [54]. The drawback was corrected in [70] by replacing k by $k^* = k + \Lambda(1-k)$, where Λ accounts for the involvement of outer water vapor into the area of air mass formation in addition to the water vapor formed by evaporation from ocean. Typical value of k^* is 0.022 (for oxygen 18), which means stronger apparent kinetic effect during the air mass formation.

One of the most suitable indexes of the kinetic effect intensity is "deuterium excess" which has been defined [15] as

$$dxs = \delta D - 8\delta^{18}O. \qquad (5)$$

Deuterium excess value in the air mass is proportional to the effective coefficient of isotopic fractionation during the air mass formation. Because *dxs* only slightly changes in the course of equilibrium condensation process it must bear quantitative information about the conditions in the moisture source [42].

The isotope model based on the above equations explains satisfactorily the global relationships between mean annual values of isotope composition of precipitation and air temperature [15]:

$$\delta^{18}O = 0.7T - 13.6, \quad (6a)$$

$$\delta D = 5.6T - 100, \quad (6b)$$

as well as between concentrations of δD and $\delta^{18}O$ in low and middle latitudes [9, 15]:

$$\delta D = 8\delta^{18}O - 10. \quad (7)$$

However, after performing the measurements of isotopic composition of snow samples collected along the inland Antarctic traverses [51] it became clear that the model does not work well for the snow falling in polar regions. Isotope models of Rayleigh type (for equilibrium conditions) gives too high values of *dxs* thus pointing to another unknown kinetic effect during the formation of solid precipitation. The issue was resolved in 1984 by Jouzel and Merlivat [41] who theoretically explained and empirically confirmed a kinetic effect during sublimation of water vapor on the surface of ice crystals in the air supersaturated with water vapor. According to their RMK model (Rayleigh Model taking into account Kinetic effect) the effective coefficient of fractionation in this case equals to: $\alpha_e = \alpha \times \alpha_k$, where α is the coefficient of fractionation for water vapor and ice in equilibrium, and α_k is the kinetic fractionation coefficient:

$$\alpha_k = \frac{S_i}{1 + \alpha(S_i - 1)D/D'} \text{ (always < 1)}, \quad (8)$$

where D and D' are the diffusion coefficients for light and heavy molecules, respectively, S_i is supersaturation of air with water vapor with respect to ice.

The uncertainty of the model prediction is mostly associated with value of S_i which is generally unknown. As an optimal solution of this problem the authors suggested to approximate S_i as a function of condensation temperature choosing the coefficient of the function by adjusting the model results to the observed distribution of isotope composition of snow, while keeping S_i values in reasonable limits [41].

Within temperature range from about -5 to about -20ºC all the three water phases coexist in clouds [68], which considerably complicates the isotopic processes during precipitation formation. This complexity is not taken into account in the RMK. This lack was filled up in so-called "mixed cloud isotope models" [5, 70].

The results obtained using a simple isotope model [70] are compared in Figure 2 with isotopic composition of surface snow samples collected along the traverse routes Dumont-d'Urville – Dome C [51], Mirny – Komsomolskaya [14, 20] and Patriot Hills – South Pole – Vostok [14]. Note that the model simulations refer to the condensation temperature (T_C), while experimental isotopic data are plotted against 10 m firn temperature (T_{10}) which is conventionally assumed [51] to correspond to the mean annual surface snow temperature (T_S) and near-surface (measured at 2 m height) air temperature (T_2), i.e., $T_{10} \approx T_S \approx T_2$. In this work we generally follow this assumption mainly due to the lack of the data, keeping in mind possible systematic offset between them [53]. For Vostok, the related uncertainty may be as large as 2.5ºC [50].

According to Robin [67], the condensation temperature in Antarctica corresponds to the temperature at the upper boundary of the inversion layer (T_i) within ± 4°C, i.e.:

$$T_C \approx T_i. \quad (9)$$

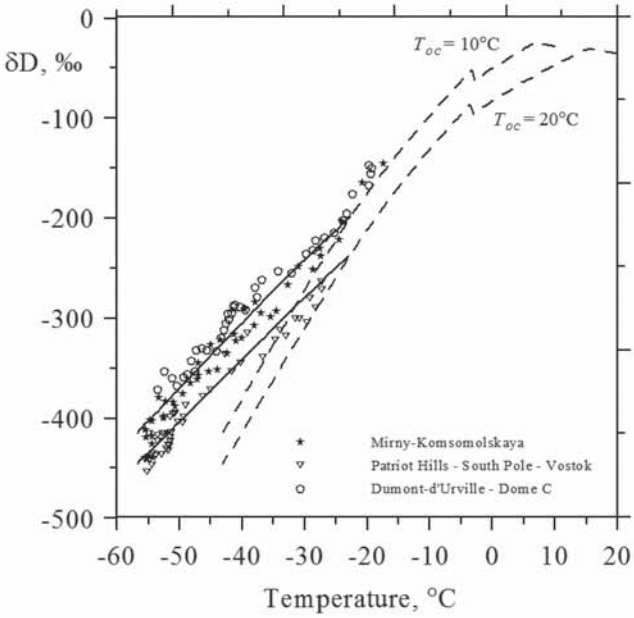

Figure 2. Isotope-temperature diagram for precipitation and deposited snow in Antarctica. Dashed lines are simple isotope model simulations ($\delta D/T_C$) [70] for two initial ocean surface temperatures (T_{OC}), 10 and 20ºC. Symbols represent isotopic values for the upper 1-2 m of Antarctic snow, collected along the three meridianal traverses (as indicated in the legend [14, 20, 51]) and plotted against 10-m firn temperature ($T_{10} \approx T_2$). Bold lines are $\delta D/T_2$ curves obtained from corresponding modeled $\delta D/T_C$ curves using a $\Delta T_C/\Delta T_2$ slope of 0.6.

In turn, temperature inversion intensity becomes weaker as one approaches the coast of Antarctica, which means the T_i–T_2 difference is not constant [8, 64] (see also Fig. 2). Geographical relationship between the near-surface and inversion air temperatures was obtained in [41] using the data from a number of Antarctic sites with T_2 ranging from -15 to -58°C:

$$T_i = C_i T_2 - 1.2, \quad (10)$$

where $C_i = 0.67$.

However, the condensation temperature in central Antarctica may differ from T_i. It has been shown [20] that weighted condensation temperature is considerably

lower than that on the upper boundary of the inversion layer, simply because the "clear-sky precipitation" (prevailing here) forms throughout the inversion layer. Our calculations (to be published elsewhere), confirmed by simple isotopic modeling [70], predict mean weighted condensation temperature for Vostok Station equal to -43ºC, which is 5ºC lower than temperature on the top of the inversion layer [20]. In the case of the coastal areas, inversion is weak and most of the precipitation is formed in lower clouds under temperature which is not necessarily equal to mean-annual air temperature in the inversion layer. According to our estimations (to be discussed elsewhere), the geographical near-surface/condensation air temperature slope for Antarctica is equal to 0.6.

In Fig. 2 the relationship between the isotopic composition (δD) of surface snow in Antarctica and the 10 m firn temperature ($T_{10} \approx T_2$) is also shown. Despite systematic difference in isotopic composition of snow in various sectors of Antarctica, the slope $\Delta\delta D/\Delta T_{10}$ in all cases is nearly the same and equals 6‰ °C^{-1}. Taking into account above established $\Delta T_C/\Delta T_2$ ratio (0.6), this value is consistent with the theoretical isotope-condensation temperature slope ($C_T = \Delta\delta D/\Delta T_C$) of 10‰ °C^{-1} produced by simple isotopic model (Fig. 2). If all model parameters except for the initial ocean surface temperature (T_{OC}) are kept constant, the difference in snow isotopic composition in different sectors of the Antarctic ice sheet implies variations of T_{OC} from about 10 to 20ºC.

The good coincidence between the experimental data and model predictions encouraged the use of the present-day geographical relationship between isotopic composition of surface snow in Antarctica and mean annual near-surface air temperature for paleo-temperature interpretation of the isotopic profiles from deep ice cores, which will be discussed in more details in Section 5.

In spite of firm physical basis of "simple" Rayleigh-type isotope models, it can be argued that they do not always adequately reproduce past changes in isotope composition of snow during such global climatic transitions as that from LGM to Holocene [39]. This is mainly due to the fact that simple models do not take into account changes in atmospheric trajectories (circulation), physical conditions in clouds etc. This is why, since the late 1980s, a number of attempts have been made to incorporate isotopic transformations in the course of the global water cycle into the General Circulation Models (GCM), as well as into hydrological models of intermediate complexity (see review in [54]). Though GCMs basically well represent global distribution of water isotopes in precipitation, as well as their seasonal cycle, they sometimes poorly describe meteorology and isotopic distribution in inland Antarctica [54]. In particular, two systematic biases are typical for GCMs: 1) a lack of isotopic depletion for central Antarctica, even in the models providing a correct range of near-surface temperatures, and 2) an underestimation of moisture supply to inland Antarctica. Several physical reasons may be invoked to explain these biases. State-of-the-art atmospheric GCMs do not resolve very shallow inversion layers due to their representation of boundary layer processes; they usually have no specific simulation of diamond dust formation and effects; the simulated atmospheric dynamics may be affected by grid point singularities at South Pole; their representation of polar cloud distribution and microphysics may be problematic [54]. These drawbacks might be eliminated by incorporating water isotopic transformations into the meso-scaled atmospheric models with better geographical and vertical resolution (e.g., [31, 48]).

In our study we use a simple Rayleigh-type isotope model developed by Salamatin et al. [70] on the basis of the theory of isotopic fractionation along the entire trajectory from the air mass formation above the tropical ocean to central Antarctica [6, 9, 11, 13, 15, 27, 34, 36, 41, 47, 57, 80]. The model has some improvements compared to the previous studies, e.g., the involvement of the outer water vapor into the area of air mass formation, optimization of microphysical processes approximations for mixed and solid clouds, as well as multi-trajectory scheme of simulations of isotope depletion in precipitation. The model was tuned using experimental data on isotopic distribution in the whole Antarctic continent (Fig. 3), along the Patriot-Hills – Vostok traverse (Fig. 2), as well as on the seasonal isotope-temperature changes at Vostok Station (Fig. 5, Section 4).

After tuning, the model parameters are fixed (except for those describing the source conditions, which could have changed in the past) and model is used for paleo-climate reconstructions as presented in Section 5.

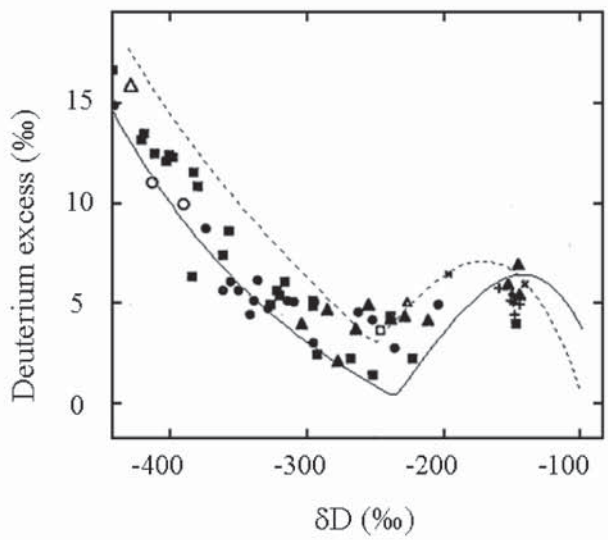

Fig. 3. Comparison of dxs/δD curve simulations for Antarctica with available experimental data (from [70])

In this section we have briefly considered the theoretical basis of the isotope-temperature method of paleo-reconstructions and presented simple Rayleigh-type isotopic model adjusted to simulate the isotopic

composition of precipitation in the polar regions. The isotope-condensation temperature geographical slope of 10‰ $^{o}C^{-1}$ has been deduced for Antarctica, which seems to be in agreement with the experimental data. Next sections (3 and 4) will be devoted to the discussion of the recent temporal and spatial isotopic variability at Vostok aiming to derive the local isotope-temperature calibration coefficient needed for paleo-reconstructions, and to estimate the signal-to-noise ratio of the vertical isotopic profiles.

3. Spatial variability of snow isotopic content. Signal-to-noise ratio in isotopic series

In this section we discuss the small-scale spatial variability of snow isotopic composition in the vicinities of Vostok station in order to determine to which extent the isotopic variations observed in a single ice core may be attributed to climatic signal.

The typical area of an ice core cross-section is of the order of 10^2 cm^2, which makes ice core properties highly subjected to a variety of local small-scale processes. The question arises about applicability of the ice-core data to characterize the isotope (climate) changes of different temporal and spatial scales.

The distribution of snow accumulation rate, as well as of snow physical and chemical properties, is known to be highly uneven on the local and regional scales. It has been demonstrated in a number of publications (e.g., [1, 23, 29, 32, 79, 84]) that the quasi-periodical spatial variability of snow accumulation with the wavelength of 2 to 40 km, often observed in different parts of Antarctic continent, is caused by drifting undulations of the snow surface. These large-scale undulations are conventionally known as "mega-dunes" [30]. Also well known are micro-relief features with typical wavelengths of tens meters (or less) and vertical scale of few (tens) of cm. The influence of micro-relief on ice core records reveals itself in high level of white (or rather blue, i.e., with maximum energy in high frequency) noise, so-called "stratigraphic noise" [22, 23, 28, 29]. The amount of this noise for low accumulation sites is estimated to be about 90% of the total variance of accumulation time-series observed in a single point [22, 23]. Intermediate-scale surface undulations (few hundred meters) have recently been found in the vicinity of Vostok Station [23] and named "meso-dunes" (Fig. 4).

A leveling of the snow surface which was performed in December 1999 at the Vostok stake network (two profiles, each 1 km long, located 1.5 km to the north from the station) made it possible to directly compare the spatial distribution of the snow accumulation with the snow surface height. In Figure 4, the snow surface relief along the NS profile of the stake network is shown together with the 2-year (1998–99) snow build-up profile. One can see a covariation between snow relief forms and the spatial oscillations of snow accumulation.

In Fig. 4 the profile of isotopic composition of the upper 10-cm layer of snow is also shown. The negative correlation between this profile and that of accumulation is remarkable (r = -0.68), with the slope (regression coefficient) of -3.45 ‰ cm^{-1}. Such an isotope pattern may be explained by non-uniform wind-driven redistribution of snow precipitating in different seasons. For example, winter (isotopically lighter) snow may be preferentially accumulated in hollows due to smaller snow crystal particles and higher wind speed. This is supported by the fact that the amplitude of isotopic variability shown in Fig. 4 is similar to that of seasonal changes (Fig. 5, next Section). Also note the negative correlation between δD and dxs (Fig. 4), which is typical for seasonal changes, too (Fig. 5).

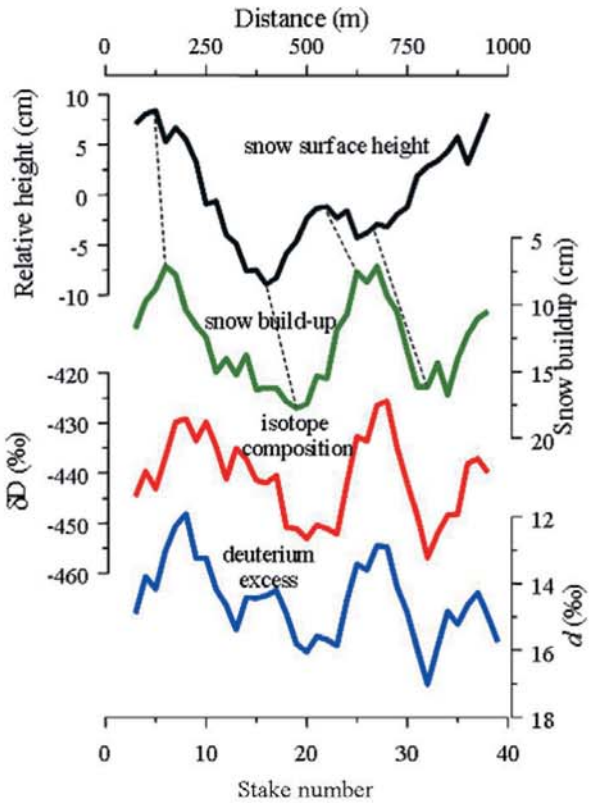

Fig. 4. The surface profile in December 1999 (black), the two-year (1998–99) snow build-up (green), and the δD and dxs profiles (red and blue, respectively) measured in the upper10-cm layer of snow. All the profiles represent a 125 m running mean. Note that the general slope of the snow surface is subtracted from the surface profile (from [23]).

Another possible reason for the accumulation-isotope correlation is post-depositional isotopic changes, i.e., changes of initial isotopic composition of snow which take place in the upper snow thickness due to mass and isotopic exchange with deeper snow or with atmospheric water vapor. Indeed, accumulation rate is an important factor determining the rate of post-depositional changes [82]: the lower is snow build-up rate, the longer is snow exposure to the surface

processes, the stronger are post-deposition changes. It is expected that such changes in central Antarctica lead to the enrichment of snow isotope composition [82], which is in agreement with the observed negative correlation between isotopic content and snow build-up (Fig. 4).

It has been shown [22, 23] that the spatial variations of δD and accumulation rate are reflected in time series of these parameters due to the drift of the involved dunes. For example, the dunes shown in Fig. 4 are associated with the accumulation wave in temporal series with the length of about 20 years. We call such variations, not directly attributed to climate variability of the studied snow characteristics, "relief-related" variations [21]. The overall noise in isotopic time-series due to these variations is estimated to represent about 80% of the total variance (which corresponds to a signal-to-noise ratio of 0.25).

In [21] several non-direct indications of presence of mega-dunes in the area of Vostok Station are given. The corresponding "relief-related" temporal variations attributed to mega-dunes that can be found in the time-series of accumulation rate and snow isotope composition are of the order of 1000 years in wavelength. This conclusion highlights the importance of the results presented in this section for the ice core record interpretation. How to extract the climatic signal from the relief-related variations? In the case of a single time-series available for an area, the smoothing of the series may be applied with the averaging window wide enough to erase possible relief noise. For example, the period of smoothing needed to suppress the influence of meso-dunes (Fig. 4) at Vostok Station is 20 years [25]. Another method to separate climatic and relief-related variations is based on using band-pass filtering techniques. Also, non-climatic oscillations can be suppressed by constructing stacked series of studied parameter using the data from several pits (stakes, cores) due to the fact that relief-related temporal variations are not generally correlated in adjacent sites located in the same area. See an example of such study in Section 4.2.

Distinguishing between climatic and relief-related temporal oscillations is straightforward and is based on the following principles: 1) relief-related temporal variations (unlike climatic ones) always have their counterparts in the surface (spatial) profiles of studied parameter; 2) climatic variations are synchronous at all the sites located in the area and thus they should be well preserved in the stacked series of studied parameter; 3) additional confirmation of the climatic origin of observed temporal changes in the climate proxy may be obtained through its comparison with available instrumental data (e.g., data on air temperature).

As for the post-depositional changes of snow isotopic composition, the influence of this factor on the isotope-temperature paleo-reconstructions would be zero provided that those changes remained constant in the past. However, since both involved parameters (temperature and accumulation rate) varied with time, the effect of the post-deposition changes may have varied, too. At present, it is not possible to quantify the influence of this factor, but we assume it is comparatively small, because the past variations of temperature and accumulation rate caused opposite effects on the post-depositional isotopic changes [82].

In this section we discussed the local spatial variability of snow isotopic composition in the vicinity of Vostok Station, which appears to be very high and likely related to uneven snow re-distribution by wind. Corresponding "relief-related" variability in isotopic time-series accounts for roughly 80% of total variance and therefore a 20-year running mean smoothing is needed to isolate the climatic signal. Alternatively, if several temporal series are available for the studied area (as it is the case for Vostok), constructing stack series is the best solution. If an ice core drilling site is located in a mega-dunes area, "relief-related" oscillation may be as long as about 10^3 years. However, in the case of Vostok Station the resolution of deep ice core isotopic record (500 years) is low enough to exclude the impact of mega-dunes.

4. Recent temporal variability of isotopic content in the vicinity of Vostok Station

In this section we discuss the temporal variability of the Vostok snow isotopic composition on the time-scale from seasonal to centennial. Available isotopic data are calibrated against instrumental temperature data, on seasonal (Section 4.1) and multi-year scale (Section 4.2). The calibration coefficients are then used to reconstruct temperature variations in the vicinity of Vostok Station over the past 200 years (Section 4.3), using the data from deep snow pits, with the aim to demonstrate that isotopic composition may indeed be successfully used for paleo-temperature reconstructions.

4.1. Seasonal changes of snow precipitation isotopic composition

In Figure 5 the mean monthly values of precipitation isotopic composition are shown as measured in the samples collected during the period from December 1999 to December 2000. The δD values reveal clear seasonal cycle (with an annual average of -453 ‰) consistent with the annual cycle of local air temperature. The corresponding annual mean of $\delta^{18}O$ (not shown) is -58.4 ‰.

Also shown in Figure 5 are seasonal changes of *dxs*. This parameter reveals minimum values in summer and maximum in winter, being in anti-phase with δD and air temperature. Such behavior of *dxs* is mainly caused by opposite trends of δD and *dxs* in ice clouds precipitation (Fig. 3), but may also be related to seasonal changes of the moisture source conditions (T_{OC}). It is assumed that summer minimum of deuterium excess in precipitation is due to the southward shift of the major moisture source [7, 17, 18, 54, 81]. This assumption is supported by our simple isotope model [70], which suggests that the average weighted summer temperature for the

source region is about 1.5ºC lower than the winter one, likely due to reducing sea ice extent around Antarctica.

The correlation coefficient between the mean monthly values of δD and near-surface air temperature (T_2) for the period December 1999 – December 2000 is significant and equals 0.89±0.14, whereas the regression slope equals 2.12±0.35 ‰ °C^{-1}. This value is considerably lower than corresponding geographical slope of 6 ‰ °C^{-1} discussed in Section 2. The difference is partly explained by significant change of moisture source between summer and winter periods as pointed above. But the main reason for the observed discrepancy is considerable seasonal changes of local conditions, in particular, the temperature inversion strength (due to changes in radiation and heat balance), which governs relationship between condensation and near-surface temperatures.

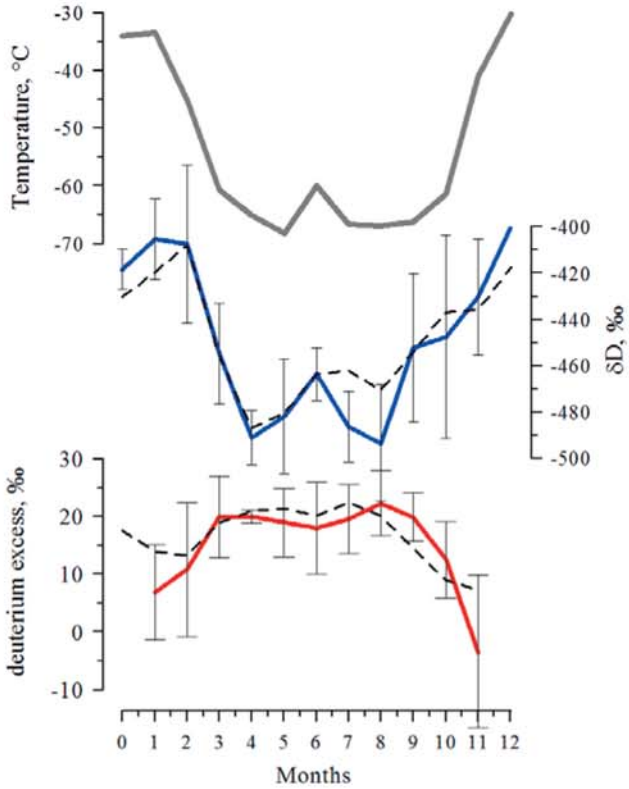

Fig. 5. Seasonal variations of isotopic composition (δD and dxs) of precipitation (solid lines), blowing snow (dashed lines) and air temperature at Vostok Station. Error bars represent standard deviation (1 σ) of isotope composition in the precipitation samples collected in the same month (from [20]).

We cannot determine relationship between δD in precipitation and T_C or T_i, in 2000 because the balloon-sounding observations have not been carried out. To estimate the isotope-temperature slope we took the mean monthly values of T_i for the period 1963–1991 keeping in mind comparatively low inter-annual variability of this temperature [20]. Using these data and δD values measured in 2000 leads to a $\delta D/T_i$ slope of 6.2±1.1 ‰ °C^{-1}, which is lower than 10 ‰ °C^{-1} obtained for the $\delta D/T_C$ slope with our simple isotopic model [70]. We attribute this difference to the significant deviation of the temperature on the top of the inversion layer from the weighted condensation temperature. Our model simulation suggests that the observed winter-summer δD changes in precipitation from -490‰ to -410‰, accompanied by *dxs* shift from 22‰ to 7‰, may be interpreted as T_C change from -48ºC to -40ºC, and T_{OC} change from 19.5ºC to 18ºC.

4.2. Isotope-temperature calibration on multi-year scale

In this subsection we discuss the results of detailed isotopic studies performed in snow pits dug in the vicinities of Vostok Station. Understanding the formation of isotopic composition of the upper snow layers should give a clue for interpreting the isotopic profiles measured along the deep ice core.

The data discussed in this Section have been obtained as a result of detailed snow thickness study in 6 shallow and 3 deep pits dug in 1980-2000. In addition to isotope snow sampling, stratigraphic (Fig. 6) and geochemical observations have been carried out, which allowed accurate dating of snow, as described in [20].

The main feature of the vertical profiles of snow isotopic composition is the regular oscillations (Figs. 6 and 8) with the total magnitude of about 60–80 ‰ for δD (that is, about 70–90% of the seasonal change of isotopic composition of precipitation at Vostok, see Section 4.1). Note that this value is larger than the magnitude of δD change during LGM-Holocene transition (about 50–55 ‰ [63]).

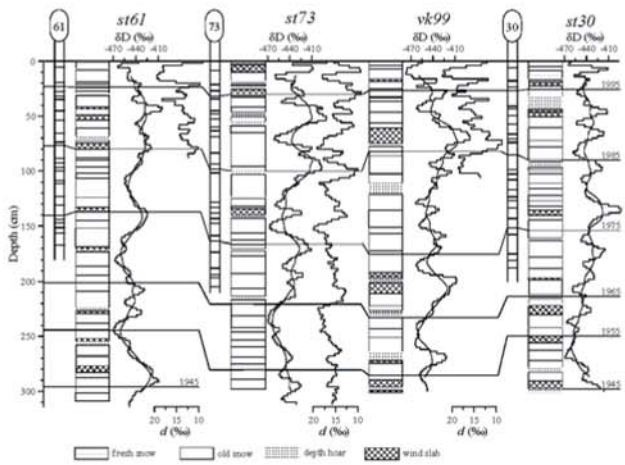

Fig. 6. Stratigraphic studies in 4 shallow pits in the vicinity of Vostok Station([20].

As shown in Section 3 (see also [20, 21, 23]), these oscillations are mainly related to the drift of different types of snow surface relief forms (micro-relief and meso-dunes) rather than to climatic variations. The signal-to-noise ratio [28], determined from the mean correlation coefficient of the δ time-series from 8 individual shallow pits studied in the vicinity of Vostok Station [23], is 0.25, which suggests that "stratigraphic

noise" accounts for about 80 % of the total variance of snow isotope composition in a single point. This noise, typical for low-accumulation sites, was previously found when investigating the snow accumulation at the Vostok snow-stake network [22]. To reduce the noise, we constructed the stacked δD time-series using the data from all the eight pits. In Fig. 7 we show this series for the period 1946-1995 together with the mean annual and summer temperatures at Vostok Station, as obtained from instrumental observations.

In Section 3, we have established that the sensible resolution of the climatic δ time-series obtained in a single point at Vostok should not be better than 20 years. This period is needed to sufficiently reduce the relief-related variations linked with the drifting meso-dunes (Fig. 4). For the stacked series the corresponding period was estimated to be 7 years [23]. Further smoothing decreases the variance of the series insignificantly but does not increase the signal-to-noise ratio.

According to Fig. 7, the isotopic composition of snow changed significantly during the last 60 years with the minimum in 1953–1964 and maximum in the 1980s followed by a decrease during 1990s with assumed minimum around 2000. The correlation (r) between snow isotope composition and near-surface air temperature (for smoothed series) is statistically significant and equals nearly 0.6. Thus, the local temperature at Vostok accounts for about 40 % of the isotope inter-annual variability. The corresponding regression coefficient is 17±4 ‰ °C^{-1}. This value is almost 3 times larger than the geographical $\delta D/T_2$ slope. Similar value (20.3 ‰ °C^{-1}) was obtained by Jouzel and others [43] for the South Pole precipitation.

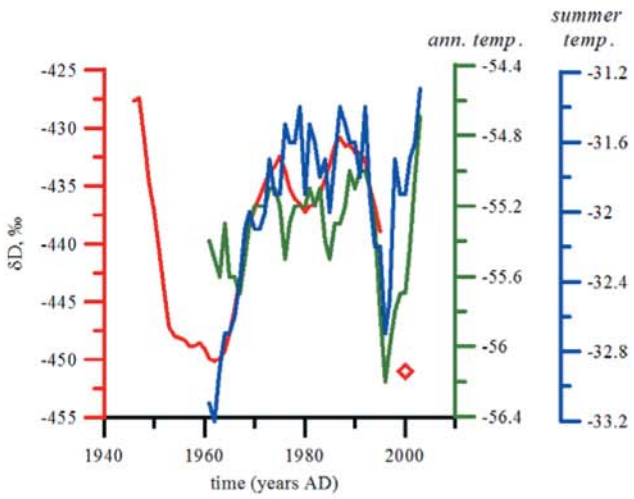

Fig. 7. Stacked record of δD of snow in the vicinity of Vostok Station based on the data from 8 shallow pits (red) shown along with mean annual (green) and mean summer (blue) temperatures. All series are 7-year running means. Diamond depicts mean isotope composition of surface snow in 2000.

Interestingly, the snow isotopic composition appears to be much closer related to the summer temperature than to the mean annual temperature (Fig. 7). The correlation coefficient between δD and summer T_2 is 0.92 with the slope of 10.2±0.8 ‰ ºC^{-1}. The latter value corresponds to the predicted model slope between precipitation isotopic composition and condensation temperature (see Section 2). This could be explained if most of precipitation at Vostok occurs during the summer, which is not the case [20, 25]. The other possible reason for this phenomenon is possibly strong post-deposition effects in this low-accumulation region of Antarctica, which considerably changes the initial isotopic composition of snow precipitation and occurs mostly in the warm part of the year. This assumption is consistent with the fact that the Vostok snow pit isotopic record closely covariates with the "effective snow surface temperature" derived from the shallow borehole temperature analysis [50].

4.3. Vostok temperature history over the past 200 years based on the isotope data from deep pits

In this sub-section we use the isotope-temperature calibration established above to reconstruct the Vostok temperature history on centennial scale based on isotope data from deep pits.

In 25th and 45th summer seasons of Russian Antarctic expedition snow stratigraphy was studied in three deep snow pits dug at Vostok Station, *vk10* (1980, 10 m deep), *vk99* and *st30* (1999/2000, both 12 m). Aside from stratigraphic observations, detailed (2-5 cm) isotope sampling was carried out in the two latter pits. Snow thickness was dated based on layer counting corrected by absolute age markers of 1955, 1965 (high beta-activity) and 1816 (Tambora layer of high acidity) and by correlation to snow build-up at the accumulation stakes [20, 25]. The results of studies carried out in *vk99* and *st30* are presented in Fig. 8.

Based on the results of the deep pits studies, temporal series of snow isotopic composition and accumulation rate have been reconstructed for the last 225 years (1774–1999). Stacked δD and accumulation (a) series are presented in Figure 9. One should note a high level of stratigraphic noise in the variability of both parameters. The required smoothing to sufficiently suppress this noise is estimated to be 11 years for both δD and a. Note that for δD series the contribution of high-frequency noise is less than for accumulation due to diffusive isotope smoothing (see also fading of the isotopic oscillations in the deeper parts of the profiles shown in Fig. 8) [28, 37].

The reconstructed series of temperature and accumulation rate (Fig. 9) correlate with each other (r = 0.2 but statistically significant; for the 20th century r = 0.6), and also with the data presented in Fig. 7.

In general, Vostok deep pit isotopic data suggest that 11-year means of T_2 have changed over the past 200 years within the range of 1ºC (using the $T_2/\delta D$ slope established above). The magnitude of corresponding changes of effective weighted condensation temperature is about 2ºC (according to the slope of 10‰ ºC^{-1}), which may likely correspond to variation of summer

temperature rather than mean annual temperature (see also Fig. 7).

The pattern of small-scale climatic changes presented in Figs. 7 and 9 is likely common for the whole East Antarctica (see, for example, [59, 66]). According to M. Pourchet with co-authors [66], who obtained snow accumulation values in 14 sites by snow β-radioactivity measurements, the mean snow accumulation rate in East Antarctica in 1965–1977 was 30 % higher than during the previous decade.

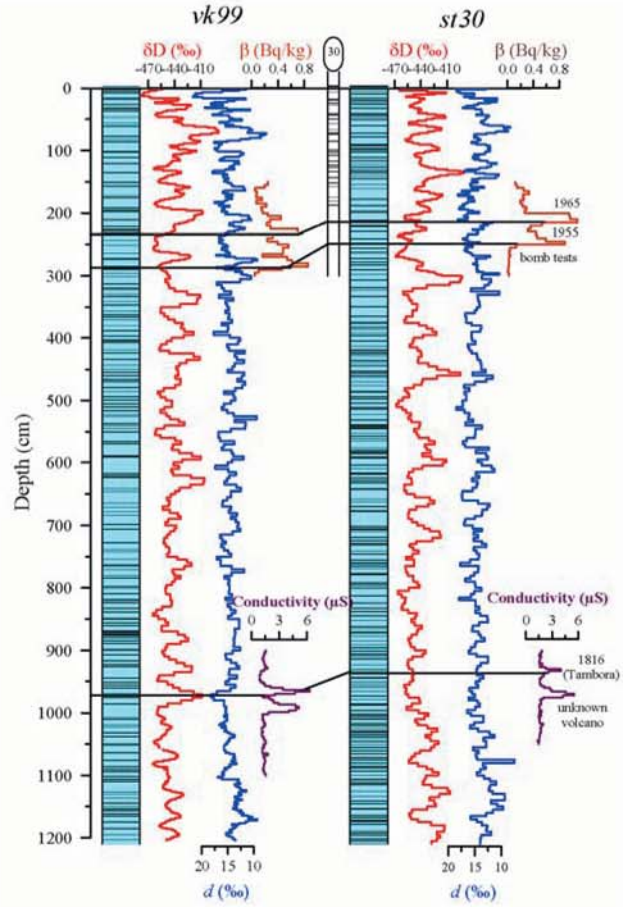

Fig. 8. The results of snow thickness studies (annual layer boundaries, isotope composition (δD and dxs), total beta-radioactivity and snow liquid conductivity) in pits vk99 and st30. Values of annual snow build-up at stake 30 are corrected for snow settling. The horizontal lines represent reference levels of 1955, 1965 and 1816 (from [20]).

During the 1990s all the series reveal a clear decrease of their values, especially well marked for air temperature. This agrees with cooling observed at the most Antarctic stations (except for Antarctic Peninsula) during this period [19].

The observed changes are likely related to the variations of cyclonic activity in Antarctic [26, 59, 73], since cyclones bring both moisture and heat to the interior of the continent.

Another interesting feature of the 200-year Vostok climatic data is an apparent 50-year cycle of both temperature and accumulation rate. It has been shown [25] that these variations correlate with the so-called Pacific Decadal Oscillation (e.g., [77]), which suggests a tele-connection between central Antarctica and tropical Pacific.

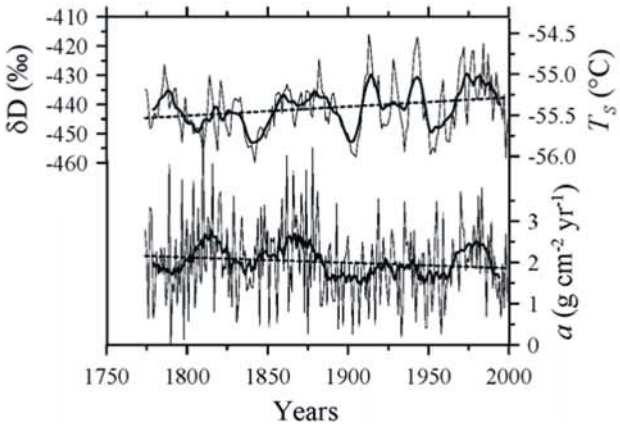

Fig. 9. Stacked records of δD and accumulation rate from deep pits. Thin lines are original time- series, whereas the thick ones represent 11-year running means. ([20].

In general, the comparison of the series of isotopic composition and snow accumulation rate from deep pits with other Vostok and Antarctic data on δD, a and T allows to conclude that the reconstructed 200-year series (Fig. 9) reliably represent climatic variability in the studied area of Antarctica. For the present study this implies that isotopic composition of snow thickness can, indeed, be used for paleo-temperature reconstructions.

In this Section we summarized the data on temporal variability of snow isotopic composition at Vostok Station and discussed its relationship with instrumentally obtained air temperature. On both seasonal and multi-year time scales the strong correlation between δD and T_2 is observed. The regression coefficient (slope) of this relationship is, however, significantly different from that of geographical correlation (Section 2), which likely reveals different near-surface/condensation temperature relationships for various temporal and spatial scales. This fact implies that the present-day geographical $\delta D/T_2$ slope in Antarctica can hardly be directly used for paleo-temperature reconstructions based on the deep ice core data. The problem is additionally complicated by possible offset between firn temperature, that is used as a proxi of near-surface air temperature T_2, and T_2 itself, as mentioned in Section 2. On the other hand, we have not found any evidence that the theoretical $\delta D/T_C$ slope (10‰ ºC^{-1}, Section 2) does not hold true for the temporal (seasonal to multi-year) isotopic variability, which encourages using it for paleo-reconstructions. It has also been demonstrated that snow isotopic composition at Vostok is rather related to summer, than to the mean annual temperature, which likely reflects noticeable post-depositional changes of initial snow

isotopic content. Finally, in this Section we used the isotopic data from deep snow pits in order to reconstruct local paleo-temperature over the past 225 years. The correlation of this record with available climatic data for East Antarctica suggests that the isotopic profiles of Antarctic snow can be used for paleo-climatological studies.

5. Paleo-temperature interpretation of Vostok deep ice core isotopic data

In this Section we use the results obtained in the previous Sections to reconstruct long-term temperature changes using isotope record from the deep Vostok ice core.

First, we note that, as described in Section 3, a detailed isotopic time-series obtained in a single point (pit or ice core) reflects "relief-related" noise (representing 80% of the total variance) rather than climatic signal. The wavelength of this noise may be as large as 10^3 years in the case of mega-dunes influence. For shallow cores, and for intermediate and deep cores drilled in the high-accumulation areas, where a high-resolution record is intended, the effect of relief-related variations will be a critical issue. The results of shallow coring at Dronning Maud Land clearly illustrate this notion [61]. Individual cores located here in climatically uniform area reveal quite different trends over the last 200-year period. It underlines the fact that only constructing stack record on the base of the data from several cores may produce reliable climatic series for the area.

The described effect however will unlikely be visible in the low-resolution (500 years) Vostok isotopic record. Another source of noise in isotopic series is related to the post-depositional changes of initial snow isotopic content (Section 3). The contribution of this noise to the deep ice core isotopic series is supposed to be relatively low because the past changes of temperature and accumulation rate tend to compensate their influence on the post-depositional processes. As it has been shown in Section 4, the values of the isotope/near-surface temperature slopes for the geographical, seasonal and inter-annual variations are different. In contrast, the isotope-condensation temperature slope appears to be constant (about 10‰ $^{o}C^{-1}$) in all cases. The latter, however, is difficult to confirm empirically due to the lack of the data on the condensation temperature.

The first attempt to quantitatively estimate past changes in near-surface air temperature using the ice core isotopic data was made in 1979 by C. Lorius and others [52] on the basis of the present-day geographical δ/T_{10} slope. Twenty years after, the same approach with only minor corrections was used to reconstruct the air temperature changes over the last 420 ka at Vostok Station [63]. In the latter paper the changes of inversion temperature in the past (compared to its present-day value), ΔT_i, are calculated from changes of isotopic composition of ice, $\Delta\delta D$:

$$\Delta T_i = \frac{\Delta\delta D - p\Delta\delta^{18}O_{oc}}{C_i}, \qquad (11)$$

where $\Delta\delta^{18}O_{oc}$ is correction for the changes of mean isotopic composition of sea water in the past due to changes of water volume trapped in Earth's glaciers. T_i is related to the near-surface air temperature T_2 by equation (10) and is supposed to be a proxy of T_C (Eq. 9). The coefficient p was first taken equal to 8 [63] (following Eq. (7)). However, it was shown later that p has smaller value [46] due to the fact that the influence of isotopic change at the ocean surface weakens as an air mass becomes isotopically depleted, which can easily be demonstrated with a Rayleigh model. According to this approach, during LGM (δD is about -483 ‰, see fig. 10) T_i and T_2 were, respectively, 5.5 and 8.5°C lower than at present (δD is about -410 ‰).

The comparison of isotope method with the results of independent paleo-temperature approaches has shown that the former likely underestimates the amplitude of past climatic changes in the polar regions (see the review in [20, 39, 46]). Among these independent approaches, the most elaborated one is the deep borehole thermometry method that allows extracting paleo-temperature history from the ice sheet temperature field (see the method overview in [69]). In particular, for Greenland this method shows that LGM-Holocene surface snow temperature shift was about two times larger than predicted from the isotopic approach [12, 38]. This discrepancy has been explained by considerable change of atmospheric circulation between glacial and present time, accompanied by strong change of precipitation seasonality [83]. In particular, in Holocene the contribution of winter precipitation has increased, which reduced apparent LGM-Holocene isotope shift recorded in ice core.

As for Antarctica, the difference between the two methods should be less (up to 30%) [69, 71, 78], likely due to a weaker change in precipitation seasonality [46]. Also, for Antarctica the borehole method is less straightforward and requires very high precision of borehole temperature data, which leads to a lower accuracy of the obtained results [69]. Together with uncertainty of the isotopic method, this means that paleo-temperature estimations produced by both methods for central Antarctica do not differ significantly [46].

Another important factor responsible for the difference between isotopic and bore-hole thermometry methods (or, in other words, between present-day geographical and long-term temporal isotope-temperature slopes) is changing conditions in the moisture source region [3, 20, 46].

As shown in Section 2 (see Eq. (1)), the precipitation isotope composition is related to the source-condensation temperature difference, rather than to the T_C alone. Thus, simultaneous climatic change in the tropics and polar region reduces the isotopic content of the polar precipitation.

The relationship between geographical and temporal isotope-temperature slopes can be expressed as:

$$(d\delta/dT_C)_{temporal} = (C_T + C_{OC}/m), \quad (12)$$

where C_T and C_{OC} are geographical slopes between precipitation isotope content (δ), and condensation (T_C) and source temperature (T_{OC}), while m – "amplification factor" describing the ratio of the amplitudes of paleo-climate change in polar regions and tropics [46]. For C_T and C_{OC} equal 10 and -2.8 ‰ °C^{-1}, respectively, as follows from the isotope model [70], the 15 % difference between geographical and temporal slopes corresponds to m value of 1.9, which seems to be reasonable [80].

In order to account for the moisture source effect using only ice core isotopic data, K. Cuffey and F. Vimeux developed a method combining the data from the both isotopes, δD and $\delta^{18}O$ [13, 80]. The method is based on the fact that both δD and deuterium excess (dxs) are dependent on both condensation and source temperatures. Solving the system of two linear equations one can come to the following formulas [80]:

$$\Delta T_{OC} = a\Delta\delta D + b\Delta dxs + c\Delta\delta^{18}O_{oc} \quad (13a)$$

$$\Delta T_C = d\Delta\delta D + e\Delta dxs + f\Delta\delta^{18}O_{oc}, \quad (13b)$$

where the linear coefficients can be derived from the simple isotopic model. The application of this method to the Vostok isotopic data gives 20 % stronger amplitude of LGM-present day temperature shift than "classical isotopic method", which only uses geographical δ/T slope (Eq. 11) [63].

As a result, using the method described by Eq. (13) and applying coefficients obtained from our simple isotope model [70], we estimate that T_C and T_2 during LGM time at Vostok Station were, respectively, about 6 and 10ºC lower than their present-day values.

The isotope-paleotemperature reconstruction based on Vostok ice core data is presented in Fig. 10.

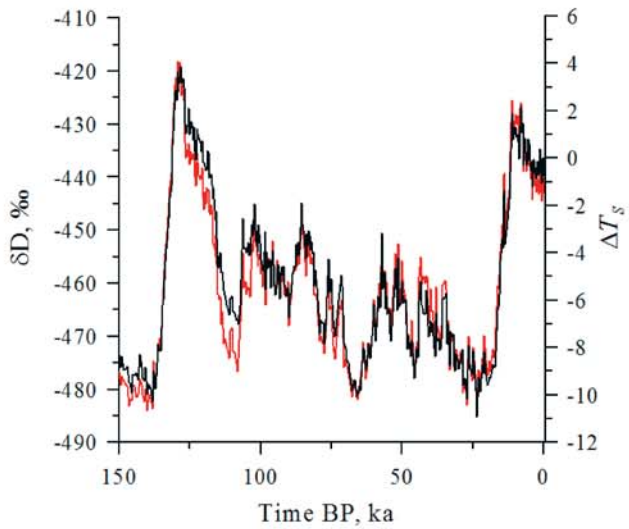

Fig. 10. Deuterium content in Vostok deep ice core (red) and inferred paleo-temperature (T_2) (black) for the last 150 ka.

The paleo-temperature reconstruction obtained by improved isotopic method (Eq. 13), as presented in Fig. 10, is consistent with the results of recently refined borehole thermometry method [78] (see also paper by Salamatin and others in this volume). We thus consider these values (LGM and Holocene optimum ΔT_2 of -10 and 2 ºC compared to present day) as the most reliable paleoclimatic estimations for the Vostok Station. The same LGM T_2 has been recently deduced from the Dome C deep isotope record [40] using similar refined isotopic method (Eq. 13).

This result implies that the moisture source influence is the most (and probably the only) important factor affecting isotope-temperature paleo-reconstructions in central Antarctica.

We should note that direct comparison of the "isotope" and "borehole thermometry" methods of paleo-reconstructions is somewhat problematic, since the first deals with condensation temperature T_C (which is further transformed to near-surface air temperature T_2, as demonstrated in Section 2), while the second does with "effective snow surface temperature", which roughly corresponds to T_S. We should also note that effective condensation temperature (T_C) may not be equal to mean annual air temperature at any atmospheric level. As an example, in Section 4 it has been demonstrated that snow isotopic composition closer related to summer temperature, which likely reflects the post-depositional changes of initial snow isotopic content.

In this section we have demonstrated that "classical isotopic method" (based on the present-day geographical isotope-temperature slope) is not able to correctly reproduce the amplitude of past temperature changes in Greenland and Antarctica, which is evident from the results of the alternative approach, borehole thermometry. For Antarctica, the main reason for this discrepancy is the past changes in the moisture source conditions. The refined isotopic method has been applied instead, with the moisture-source correction based on the use of dxs data. Assuming that Vostok deep ice core isotopic record reliably represents climatic signal (i.e., relief-related or post-depositional noise is negligible), we obtain the following estimations of ΔT_2 in the past (comparing to present-day value): -10ºC for LGM and 2-2.5ºC for the Holocene optimum. These figures are in agreement with the results of the borehole thermometry method.

6. Isotopic composition of the basal part of the Vostok ice core

Below 3538 m the Vostok ice core comprises frozen water of subglacial lake Vostok [44]. A number of studies have been devoted to the isotopic [24, 62, 75] microbiological [4], gas [49, 56] and chemical [16, 55, 72, 76] content of the lake ice, as well as to its physical properties [58].

The scheme of water balance in Lake Vostok and lake ice formation is supposed to be as follows [45, 74, 75].

The lake has two main water sources, glacier melt and hydrothermal water. Melt water comes from the northern part of the lake where energy balance allows glacier ice to fuse. Fresh melt water is lighter than slightly salty deeper lake water, so it seeps southward along the tilted glacier sole, mixing with lake water. In the southern part of the lake (where Vostok Station is situated) the freezing takes place involving two main mechanisms, frazil crystal formation and slow freezing in equilibrium with ice.

In [24] we developed a simple model describing the isotopic composition of lake ice and taking into account possible non-steady-state of lake Vostok, not complete mixing of glacier melt water with the deeper lake water, and the presence of the second lake water source (hydrothermal) in addition to glacier melt [4, 62].

At present, the depth of the deep 5G-1 borehole at Vostok is 3668 m. Ice core down to 3650 m is being now investigated, and here we present isotopic profile down to the depth of 3623 m (Fig. 11).

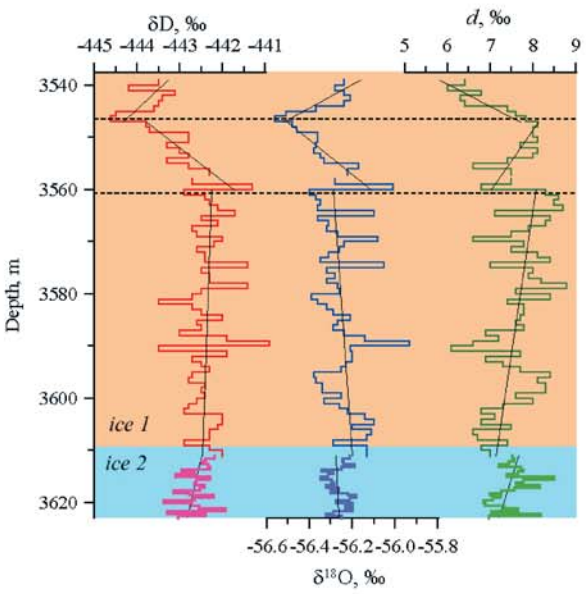

Fig. 11. Isotopic composition of the Lake Vostok ice as measured on the Vostok ice core (3538-3623 m).

The main feature of the lake ice isotopic profile is its extremely low variability, about 1-2 orders of magnitude less than for meteoric snow and ice, which requires very high measurement precision. The highest variability is characteristic for upper section of lake ice profile, which was formed in the conditions of strong water super-cooling, due to contact of cold glacier with relatively warm lake water [78].

Another feature of the lake ice is very low deuterium excess value: 7-8‰ instead of 15‰ typical for the Vostok meteoric ice. However, if the lake is in steady-state, the isotopic composition of income water (glacier melt) and outcome water (lake ice) has to be the same. Thus, the low deuterium excess in lake ice suggests non-equilibrium state of the lake Vostok, or, more likely, the presence of an additional water source. Actually, low *dxs* of Vostok lake ice is considered to be one of the evidences for the presence of the hydrothermal water sources in the lake [62], as hydrothermal water is usually enriched in oxygen 18 [10, 35].

The whole thickness of the lake ice may be divided into 2 layers, lake ice 1 and 2, with the boundary at 3609 m. For lake ice 1 the high concentration of visible mineral inclusions is typical, while ice 2 is extremely clean [44]. It is supposed that ice 1 was formed in the shallow part of Lake Vostok, probably in a strait between western shore and small island upstream of Vostok Station [65], whereas ice 2 likely originates from the deep central-southern part of the lake.

At first glance, from isotopic point of view, the ices 1 and 2 are very similar in terms of mean isotopic content and variability (Fig. 11). The only difference between them seen by now is comparatively poor δD-$\delta^{18}O$ correlation in ice 2. This phenomenon is still awaiting for explanation.

Using lake Vostok isotopic model [24] it is possible to estimate the isotopic content of the lake water. The latter depends on several factors, but for the most likely scenario of lake ice formation (50% of frazil crystals formed under reasonable super-cooling conditions and sufficient mixing of melt-water with residence lake water) it is characterized by δD of -450 ‰ and $\delta^{18}O$ of -58 ‰.

7. Conclusions

In this paper we discussed the main factors responsible for the formation of the isotopic composition of an ice core. The overview of theory and a range of experimental data strongly suggests that the snow (ice) isotopic content is a proxy of the temperature conditions that occurred during the precipitation and deposition of this snow in the remote past. On the other hand, the quantitative temperature interpretation of the isotopic record is not straightforward. On the short time scales a number of factors (local meteorology, wind-driven snow-redistribution, post-depositional processes, etc.) may alter or weaken the isotope-temperature relationship. On the longer time-scale, the change of moisture source conditions and atmospheric circulation may affect the isotopic composition of precipitation in the polar regions. In particular, for Vostok Station the difference between present-day geographical isotope-temperature slope and corresponding long-term temporal slope is as much as about 20% and may be explained by the past changes of the temperature in the tropical oceans where the precipitating air mass has been formed.

In the last section of the paper we have briefly reviewed the formation of the isotopic composition of the lower part of Vostok ice core that comprises frozen water of subglacial lake Vostok.

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