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Stable isotope studies of secondary carbonates of the Süttő loess-paleosoil sequence, Hungary

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Research on secondary carbonates in loess-paleosoil sequences is of great importance because it provides detailed paleoenvironmental information, and might serve as proxies for climate. Different secondary carbonate subtypes (e.g. calcified root cells, hypocoatings) reflect detailed signals on the extension and intensity of leaching processes.

In the formation of secondary (authigenic) carbonates different processes take part, like the flow of the bicarbonate soil solutions and biomineralization. During dust accumulation the soil development remains mostly continuous, but can be inhibited by higher sedimentation rates, whereas secondary carbonates remain in the deposits. Secondary carbonate subtypes and their distribution help to recognize and characterize environmental and pedosedimentary processes.

Multidisciplinary investigations have been carried out recently on the loess-paleosoil sequence at Süttő (e.g. luminescence dating, granulometry and malacology). For a combined (micro)morphological and stable isotope study, samples were taken in 10 cm vertical resolution from the approximately 15 m thick sequence. Secondary carbonates were separated by using wet sieving and stereomicroscopy prior to stable isotope analysis.

Carbon and oxygen isotope composition of calcified root cells shows mean values of –21.6‰ for $\delta^{13}C$ and –13.7‰ for $\delta^{18}O$, respectively. For hypocoatings mean values of –6.7‰ and –6.6‰, for carbonate-coatings –7.3‰ and –7.5‰, and for calcite crystal aggregates –12.1‰ and –6.7‰ were measured for $\delta^{13}C$ and $\delta^{18}O$, respectively.

Stable isotope clusters will help to describe genetic processes of secondary carbonates and vertical patterns in the loess sequence might serve as more reliable environmental indicators than stable isotope compositions of bulk samples.

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Calcite carbon and oxygen stable isotopes in riverine tufas as paleoclimatic records of Interglacials: the sequence of Condat-sur-Vézere (MIS 5, South-western France)

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Calcareous tufas result from calcite precipitation under open-air conditions in streams, rivers and lakes. In Europe, they are characteristic of Interglacials and common in almost any area with carbonate bedrock where mean annual air temperature is above 5 °C. Their composition (95% of $CaCO_3$) makes them suitable for oxygen and carbon stable isotopes ($\delta^{18}O$ and $\delta^{13}C$) investigations. These parameters have been shown to be important palaeoclimatic proxies in Holocene tufas. At decadal-scale sampling resolution, in modern and Holocene tufas, $\delta^{18}O$ of calcite records variations in $\delta^{18}O$ of regional rainfall. Thus, it reflects mainly air temperature variations, as source or amount effects (particularly continentality), depending on locality, should not change at a given site. $\delta^{13}C$ of tufa calcite indicates rainfall intensity and moisture availability (linked to biomass type/abundance).

We have recently investigated the suitability of $\delta^{18}O$ and $\delta^{13}C$ as palaeoclimatic proxies in Pleistocene tufas. The 'Condat tufa' (commune of Condat-sur-Vézère, South-Western France) was first attributed to the Last Glacial Maximum by radiocarbon dates. This attribution was refuted in the 1980s as its molluscan and ostracod faunas show clear temperate attributes. Two new dates by U/Th-TIMS around 100–110 ky now clearly assigned the Condat tufa to MIS 5 although not to the full interglacial Eemian (MIS 5e, from c. 130 to c. 115 ky). Tufa was sampled continuously at 5 cm resolution along the 6 m high Condat profile. Neither $\delta^{18}O$ nor $\delta^{13}C$ show important climatic variations in temperature or rainfall intensity, except at the bottom of the sequence where a relative cooler and drier episode is recorded. In the upper 5 m, $\delta^{18}O$ indicates a constant low warming whereas stable humidity is recorded by $\delta^{13}C$. No wet and warm climatic optimum is identified. This climatic reconstruction is coherent with the U/Th dates that attribute the 'Condat tufa' to an advanced phase of the MIS 5, younger than the Eemian.

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Isotope hydrological and geophysical studies on the perennial cave ice deposit of Saarhalle (Mammuthöhle, Dachstein Mts, Austria)

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The largest perennial ice deposit of the Mammuthöhle cave system is located in the "Saarhalle" chamber. Its extension is 40 m by 15 m and the maximum ice depth is 6 m. The cave system can be classified as a dynamic cave, but within this large dynamic system Saarhalle can be regarded as a static chamber. The ground penetrating radar data show that the base of the ice in Saarhalle is dominated by large boulders, and that the ice is stratified. A multitude of reflection bands is visible down to depths of 4–6 m. These reflection signatures are interpreted as thin layers of sediments and might help to understand the ice formation by representing isochrones. A 5.28 m long ice core was extracted from the Saarhalle ice block and sectioned into 105 samples. Tritium activity, $\delta^{18}O$ and δD compositions were analysed. Tritium activities of 12 non-neighbouring samples distributed along the upper 1.65 m were measured by ^{3}H–^{3}He ingrowth method applying the ^{4}He spike technique. The pattern of tritium activities along the studied profile suggests that an "old" and a "modern" water are mixing. The stable isotope composition of the ice core samples showed relative enrichment and d-excess values were characteristically lower compared to the potential sources (local precipitation, karstwater) indicating the fractionation effect of the freezing process. However the cave ice water line provided a slope coefficient of 8.13. These isotopic characteristics reflect a mixed-component open-system freezing model. Our previous opinion about the age of the uppermost cave ice layers needs revision as the tritium activities provided by the more sensitive ^{3}H–^{3}He ingrowth method clearly indicate contribution of modern water at least down to 1.21 m depth. GPR data show layering parallel with subsurface topography. Major shifts in stable isotope values show some correspondence to reflector zones observed in the GPR profile. Both tritium activities and stable isotopic characteristics suggest that cave ice has been formed from more than one water source.

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Stable O-isotope record of Holocene freshwater tufa in Lake Valgejärve, Estonia – an interpretation of postglacial climate changes

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High-resolution stable oxygen isotope data from 3.1 m long freshwater tufa section in Lake Valgejärve, northwestern Estonia reveals changes in palaeoclimate and -hydrological conditions between ca. 10 500 and 2 000 cal yr BP.

$\delta^{18}O$ values fluctuate in a 3.17‰ (V-PDB) wide interval and reflect several warming and cooling episodes throughout the time of lake marl precipitation. Gradual increase in $\delta^{18}O$ in the tufa deposited between 10 500 and 9000 cal yr BP is caused by postglacial rapid warming and the $\delta^{18}O$ values reach their first maximum at around 9000 cal yr BP. Since then onwards the $\delta^{18}O$ values decrease (with several fluctuations) by 1‰ until 4800 cal yr BP. This trend includes small peak of relatively negative $\delta^{18}O$ values at ca. 8200 cal yr BP. In tufa deposited between 4800 and 2200 cal yr BP there is another clear increase in $\delta^{18}O$ values of ca. 2.5‰. The youngest analysed tufa sequence, representing 2200–2000 cal yr BP, shows once again a decrease in $\delta^{18}O$ values. However, in general the recorded fluctuations in $\delta^{18}O$ values do not directly correlate to up to now known changes in temperature and lake water levels in the region. For example, if the recorded $\delta^{18}O$ values attribute only to temperature changes, then the TMJJA varies approximately 10 °C, being highest between 6500–4000 cal yr BP.

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The isotopic memory of fossils

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Oxygen isotope compositions of invertebrate (carbonate) and vertebrate (phosphate) skeletons are able to record both temperature of mineralization and isotopic composition of the aqueous solution. In the case of 'cold–blooded' vertebrates, temperature is close to that of their environment (air, water) whilst in the case of 'warm–blooded' vertebrates, temperature is close to that of their body. The oxygen isotope composition of body water can match that of ambient water (invertebrates, fish) or it can be ^{18}O-enriched by several ‰ (e.g. 4–5‰ in Human Beings). The amplitude of body water ^{18}O-enrichment relative to ambient water depends on the mass balance between input (diet) and output (sweat, breathing, faeces) fluxes in relationship to the residence time of body water.

Isotopic fractionation equations may be experimentally determined. Oxygen isotope compositions of structural carbonate in apatite are commonly used to track climate changes in the continental environment, however, the knowledge of a temperature–dependent isotopic fractionation between carbonate and water is needed to quantify paleotemperatures. The oxygen isotope fractionation between the structural carbonate of inorganically-precipitated hydroxyapatite and water was determined in the range 10 °C–37 °C. Values of $1000\ln\alpha(CO_3^{2-}\text{–}H_2O)$ are linearly correlated to the inverse of the temperature (K) according to the following equation: $1000\ln\alpha(CO_3^{2-}\text{–}H_2O) = 25.19\ (\pm 0.53).10^3.T^{-1} - 56.47\ (\pm 1.81)$ ($R^2 = 0.998$). This fractionation equation has a slightly steeper slope than those already established between calcite and water even though measured fractionations are of comparable amplitude in the temperature range of these experimental studies. It is consequently observed that the oxygen isotope fractionation between apatite carbonate and phosphate increases from about 7.5‰ up to 9.1‰ with decreasing temperature from 37 °C to 10 °C. A compilation of $\delta^{18}O$ values of both phosphate and carbonate from

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modern mammal teeth and bones confirms that both variables are linearly correlated, despite a significant scattering up to 3.5‰, with a slope close to 1 and an intercept corresponding to a $1000\ln\alpha(CO_3^{2-}–PO_4^{3-})$ value of 8.1‰. This apparent fractionation factor is slightly higher or close to the fractionation factor expected to be in the range 7–8‰ at the body temperature of mammals.

Two case studies are also presented to illustrate how continental seasonal changes in past air temperatures and the metabolic status of extinct marine vertebrates may be inferred from the oxygen isotope composition of tooth enamel phosphate:

– Continuous tooth growth and absence of enamel remodeling in bovid teeth ensures a reliable record of the intra-annual variability of air temperature through an incremental $\delta^{18}O$ analysis from apex to cervix. This method has been applied to *Bison priscus* dental remains of Late Middle Pleistocene from the fossiliferous level of a cave at Coudoulous I in South-Western France. The stacked oxygen isotope signal obtained by combining nine bison teeth shows sinusoidal variations (15.0‰ to 19.1‰ V–SMOW) of seasonal origin over 2.5 years. The corresponding computed mean annual temperature of 9±3 °C is about 4 °C lower than at present. Seasons appear more contrasted in Coudoulous I during level 4 deposition with summers as warm as present ones (19±3 °C) and significantly colder winters about 0±3 °C compared to 6±1 °C at present.

– Thermoregulation and body temperature of extinct vertebrates are central questions for understanding their ecology and evolution. The thermophysiologic status of the great marine reptiles is still unknown, even though some studies suggested that thermoregulation may have contributed to their exceptional evolutionary success as apex predators of Mesozoic aquatic ecosystems. We have tested the thermal status of ichthyosaurs, plesiosaurs and mosasaurs by comparing their oxygen isotope compositions of tooth phosphate to those of co-existing fish. Data distribution reveals that these large marine reptiles were able to maintain a constant and high body temperature from tropical to cold temperate oceanic environments. Their estimated body temperatures, in the range 35±2 °C–39±2 °C, suggest high metabolic rates required for predation and fast swimming over large distances offshore.

Oxygen isotope compositions of vertebrate apatite are considered to represent valuable proxies of past climate changes including the determination of mean annual air temperatures, sea surface temperatures, seasonal changes in air or water temperature, and latitudinal thermal gradients. The study of faunal assemblages also opens possibilities to decipher the metabolic status of extinct vertebrates such as the Mesozoic great marine reptiles and the contemporaneous dinosaurs.

Semi-continuous online isotope and elemental ratio measurements of high time resolution on Greenland ice cores for temperature reconstruction

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Greenland temperature variations on millennial time scales were characteristic for the last ice age. Abrupt warmings, known as Dansgaard-Oeschger (DO) events, can be traced in $\delta^{18}O_{ice}$ records of Greenland ice cores. However, it has been shown that $\delta^{18}O_{ice}$ is not only influenced by temperature but also by seasonal precipitation changes. Therefore, independent temperature estimates are requested. Measurements of the isotopic composition of gases trapped in the ice, namely $\delta^{15}N$, $\delta^{17}O$, $\delta^{18}O$ and $\delta^{40}Ar$ can be used to calibrate the paleo-thermometer. Since atmospheric nitrogen and argon isotopes are stable over very long time periods, corresponding changes are solely due to separation processes occurring within the firn column – the uppermost part of an ice sheet. The firn column can be classified into three parts, (i) the convective zone, (ii) the diffusive zone and (iii) the non-diffusive zone. The height of the latter zone is given by the depth difference of the lock in depth (LID) and the close-off depth (COD). Whereas at the LID diffusion stops the air is closed off and conserved in bubbles at the COD. The convective zone is mainly governed by wind-driven convection but it is generally limited to only a few meters. The diffusive zone, though, is the dominating part of the firn column and leads to changes in the isotope and elemental ratios due to gravitational settling and thermal diffusion separation. Additionally, an already existing gradient within the firn column that originates from a temporal evolution of any concentration in the atmosphere leads to a diffusive flux. For nitrogen and argon isotopes this is not the case and the observed values can be interpreted as combined signal from gravitational enrichment and thermal diffusion effect. The combination of nitrogen and argon isotopes allows a separation of these two processes, this has been applied in a number of study up to now. For the atmospheric oxygen isotope ratios ($\delta^{17}O$ and $\delta^{18}O$) the situation is different since they change as a function of time representing on the one hand an isotope signal of sea-water (mainly through ice

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buildup or ice melting) or on the other hand a varying exchange of atmospheric oxygen with the biosphere (terrestrial as well as oceanic) associated with respiration fractionations. Both oxygen isotope ratios are believed to change rather smoothly with time due to the large reservoir of atmospheric oxygen. These allow us to disentangle the gravitational and thermal diffusion effects from the atmospheric signals with a triple isotope approach, namely the use of $\delta^{15}N$, $\delta^{17}O$ and $\delta^{18}O$. A record for the last 100 kyrs will be shown measured on the NorthGRIP ice core. Temperature shifts in the range of 8 to 12 degree Celsius are common for DO events, but values as high as 16°C were estimated.

This powerful tool of short-term temperature reconstruction has been discovered about two decades ago and will be discussed in detail based on different published examples. Its potential, limitations and implications will be presented. Particularly, the influence of the measurement uncertainty onto the temperature estimate will be discussed. Conclusions based on obtained temperature estimates during rapid climate change events involving hydrology and biogeochemical cycles are drawn. In addition, the influence of thermal diffusion effect over a transition phase glacial-interglacial, exhibiting a strong temperature gradient over an extended time period, will be discussed.

Carbon and oxygen isotopes in Baltic Early Palaeozoic geology: some results and trends

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Carbon and oxygen isotopes were introduced into Baltic early Palaeozoic geology by Brenchley and co-workers in 1994. The Institute of Geology, Tallinn University of Technology, has played a decisive role in the following progress in that field. More than 3000 whole rock analyses from Estonia, Latvia, Lithuania, Russia (St. Petersburg and Far East areas), Ukraine (Podolia), Norway (Oslo area, Farsund) and Sweden (Dalarna) have been made, mostly from the Ordovician-Silurian, but a few also from the Devonian. Recently new equipment was purchased, allowing further developments.

The quality of whole rock analyses compared to those of brachiopod shell calcite has been discussed repeatedly. Baltic sedimentary rocks are, as a rule, weakly altered diagenetically and the results of analyses are therefore trustworthy, but show slightly lower values compared to brachiopod shell calcite.

Carbon isotopes are mainly used in chemostratigraphy, but together with oxygen (brach.) isotopes also applied for interpretations in palaeoenvironmental and biodiversity studies.

Recently Ainsaar et al. established a standard curve for most of the Ordovician section with a series of $\delta^{13}C$ excursions. Medium-sized excursions (from the bottom) are Mid-Darriwilian, Guttenberg (GICE), Rakvere, Saunja, Moe and Paroveja. Detailed studies in the uppermost Ordovician, displaying a major carbon isotope excursion (Hirnantian) triggered by global climate change, have revealed causal links between cooling and glaciation with sea level changes and a severe mass extinction of biota. The succession of excursions indicates differences in carbon cycling in pre- and post-GICE time.

The Silurian carbon isotope trend is in general lines similar to that in the Ordovician. The first half of the period shows rather weak perturbations (only two medium excursions in the Llandovery), the second half (beginning with the early Wenlock) four major $\delta^{13}C$ excursions. The 3rd of the latter, in the late Ludlow, is among the strongest in the whole Phanerozoic. The suggested glacial origin of those excursions remains disputable.

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Stable isotopes of rainfall and dripwater at Ursilor Cave (Romania): the path to reliable speleothems paleoclimate reconstructions

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The Ursilor (Bears) Cave is located on the western edge of the Bihor Mountains (NW Romania) at 482 m asl and is highly decorated with a variety of speleothems, making it the most important show cave in Romania. The cave's main passage develops ~150 m beneath the surface. The mean annual temperature in the cave area is 9.7 °C, whereas in the cave temperature is constant year around (9.8 °C). The overall climate conditions are mild and humid (~950 mm/year). Paleoclimate reconstructions based on speleothems from this cave have already produced some interesting results. However, it is crucial to understand the long-term relationship between the isotopic composition of modern precipitation and the key climatic parameters (temperature, precipitation amount, source of precipitation etc.). Equally important is to decipher how the isotopic signal is altered while the meteoric water is stored or travels thorough the soil and epikarst above the cave. A two-year monitoring study (here we report results of the first 9 months) that implies collection of precipitations (on weekly basis) and cave drip water sampling at 4-day intervals was initiated in July 2010. The surface meteorological station (within one km from the cave) is also recording the amount of rainfall, air temperature, and relative humidity. In-cave water collection device is located at the far end of the touristic path. Data loggers at the cave water collection site measure the cave temperature, relative humidity, and drip rates at one-hour interval. The local meteoric water line (LMWL) obtained from 15 values of δ^2H and $\delta^{18}O$ of rainwater samples collected nearby Ursilor Cave has a slope of 7.95 ($\delta^2H = 7.952*\delta^{18}O+8.46$; $R^2 = 0.986$), which is very close to the global meteoric water line (GMWL; $\delta^2H = 8*\delta^{18}O + 10$). By contrast, the δ^2H in cave drip water reflects a narrow range (average = –10.60‰; n = 34), indicating an attenuation of the seasonal rainfall isotopic variation due to mixing between the water in the soil/epikarst storage and recharge water from different rain events. This phenomenon is not expressed in such a well-visible way in the δ^2H values. However, the limited data set (mid-July to early March 2010) precludes us in explaining such differences.

From our current data, the mean *d*-excess value for the first 9 months is 8.85‰ in rain water and 10.20‰ in cave drip water, both values being typical of Atlantic air masses.

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Modelling the effects of melting and refreezing on the original isotopic signal in cave ice

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A series of recent studies have targeted oxygen and hydrogen stable isotopes in cave ice as proxies for past air temperatures, but the results are far from being as straightforward as they are in high latitude and altitude glaciers and ice caps. The main problems emerging from these studies are related to the mechanisms of cave ice formation (i.e. freezing of water) and post-formation processes (melting and refreezing), which both alter the original isotopic signal in water. Different methods have been put forward to solve these issues, and a fair understanding of the present-day link between stable isotopes in precipitation and cave ice exists now. However, the main issues still lays unsolved: 1) is it possible to extend this link to older ice and thus reconstruct past changes in air temperature?; 2) to what extent are ice dynamics processes modifying the original climatic signal and 3) what is the best method to be used in extracting a climatic signal from stable isotopes in cave ice?

To respond to these questions, we have conducted a modelling experiment, in which a theoretical cave ice stable isotope record was constructed using present-day observations on stable isotope behaviour in cave ice and ice dynamics, and different methods (presently used for both polar and cave glaciers), were used to reconstruct the original, known, isotopic values. Our results show that it is possible to remove the effects of ice melting and refreezing on stable isotope composition of cave ice, and thus reconstruct the original isotopic signal, and further the climatic one.

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Correlating $\delta^{18}O$ values of Barbary sheep tooth enamel and environmental waters: Implications for North African palaeoclimate reconstructions

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The climate of North Africa is known to have been highly variable during the most recent 100,000 years. Over the same time period archaeological sites show significant changes in human behaviour, leading to suggestions that climate change was a driving force behind human behavioural developments. However, a direct link between climate and humans remains to be established, in part due to a lack of directly comparable archaeological and climatological records. The isotopic analysis of mammalian remains, which accumulate through human hunting and butchery practices, provides a means to address this problem.

The $\delta^{18}O$ of mammalian tooth enamel can be correlated with the $\delta^{18}O$ of local meteoric water because 1) teeth mineralise in isotopic equilibrium with body water, and 2) the diet and drinking water of an animal determines the $\delta^{18}O$ of its body water. This relationship allows the $\delta^{18}O$ of tooth enamel to be used as a palaeoclimatic proxy. Furthermore, quantitative palaeoclimatic reconstructions are possible if a numerical relationship between modern species and modern climate can be established, and applied to the fossil record. As the isotopic enamel-climate relationship varies between species a species-specific relationship must be derived.

This paper presents data from modern Barbary sheep populations, demonstrating a link between the $\delta^{18}O$ of the species tooth enamel and the $\delta^{18}O$ of local environmental waters. These results are then applied to Barbary sheep teeth from archaeological contexts in the Gebel Akhdar of northeast Libya. Results show patterns of climate change over the last 100 ka that can be correlated to the archaeological record, providing the means to assess the impact of such changes on human populations.

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Recent achievements and future prospects of ice core science

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Since the early 1960s the ice core community has produced a wealth of scientific results from a still relatively limited number of deep drilling sites in Greenland and Antarctica with the longest record extending back to the last interglacial in Greenland and covering eight glacial-interglacial cycles in Antarctica. Although measurements performed on the first ice cores, Camp Century and Byrd, largely focused on the isotopic composition of the ice as an indicator of climate change, the number of studied parameters has steadily increased encompassing numerous measurements performed on the entrapped air bubbles, on various impurities as well as on the ice itself. The climatic information provided by these various paleodata is extremely rich. The relationships between forcing factors and climate, about the importance of carbon cycle feedbacks, about the occurrence of abrupt climate variability, and about the interplay between polar climate, ice sheet dynamics, and sea-level variations are examples that are highly relevant to future climate change.

With the completion of major projects in Greenland and Antarctica over the last 15 years, the international ice coring community is planning for the next several decades. The costs and scope of future work create the need for coordinated international collaboration. Developing this international collaboration is the charge of IPICS, International Partnerships in Ice Core Sciences, a planning group currently composed of ice coring scientists, engineers, and drillers from 19 nations. By now the discussions have lead to an ambitious four-element framework that both extends the ice core record in time and enhances spatial resolution.

The four projects were defined as:

1) A deep ice coring program in Antarctica that extends through the mid-Pleistocene transition, a time period where Earth's climate shifted from 40,000 year to 100,000 year cycles.

2) A deep ice core in Greenland recovering an intact record of the last interglacial period.

3) A bipolar network of ice core records spanning approximately the last 40,000 years.

4) A global network of ice core records spanning the last 2,000 years.

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Pleistocene seasonal temperature reconstructions from $\delta^{18}O$ of bison teeth, Ural Russia

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The aim of present study is the reconstruction of seasonal temperature variations during the late Pleistocene in Nether-Polar Urals, Russia. For this purpose, we analysed the $\delta^{18}O$ values of the carbonate component in enamel of tooth from fossil bison (Bison priscus Boj.). The lower jaw with fully preserved tooth sequences and fragments of cranium from adult bison have been collected from a grot located in the Urals, Russia (56°23´N, 57°37´W). The age of remains is estimated by a time interval from 17 to 23 thousand years according to radiocarbon datings of bones from upper and lower covered layers.

Oxygen isotope composition of the carbonate component in tooth enamel was analysed from five teeth (M1, M2, M3, P3 and P4). Enamel samples were collected by drilling of grooves from the cervix to the apex of tooth crown. Sample preparation for $\delta^{18}O$ analysis was performed using 105% phosphoric acid at 95 °C. The evolved CO_2 was cryogenically purified. The oxygen isotope ratio of CO_2 was measured with a Finnigan MAT 253 mass spectrometer in a continuous flow mode with He as the carrier gas. Standard deviation of the $\delta^{18}O$ analysis is ±0.15‰.

The intra-tooth $\delta^{18}O_{V\text{-}SMOW}$ values of enamel displayed variations: M1 (from 16.6 to 18.0)‰; M2 (from 16.8 to 20.5)‰; M3 (from 16.2 to 20.7)‰; P3 (from 15.5 to 17.9)‰; P4 (from 16.9 to 20.9)‰. The temporal record of $\delta^{18}O$ variations over 2.5 yr obtained by connection of individual intra-tooth $\delta^{18}O$ variations on a time scale. The connection was performed according the eruption sequence of M1, M2, M3, P3, P4 tooth. The temporal $\delta^{18}O$ record reproduces the seasonal $\delta^{18}O$ variations with amplitude from 15.5‰ to 20.9‰. Adjusted for dampened $\delta^{18}O$ values due to the mineralization process, the seasonal $\delta^{18}O$ values ranged from 13.7‰ to 23.1‰. This data has allowed us to estimate the $\delta^{18}O$ values of environmental waters in range from –10.0‰ to –23.4‰. Winter and summer temperatures were estimated to be respectively –25°C and +10°C. Pleistocene winter temperature was about 9 °C lower then at present and summer temperature was about 7 °C lower then at present.

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