Noble Gases in Ice Cores: Indicators of the Earth's Climate History

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Abstract

Polar ice cores constitute excellent archives of past environmental conditions and provide us with glimpses into the Earth's climatic history over hundreds of thousands of years. For the past two decades, noble gases, used as conservative tracers, have played a substantial role in extracting information from these archives. Noble gas analysis can be performed on two types of ice core samples. First, atmospheric air, trapped in bubbles in polar ice, can be extracted and analyzed for its noble gas composition. Variations in the isotopic and elemental composition of noble gases trapped in air bubbles can be used to infer ancient environmental conditions at the surface of the ice sheets, adding to understanding of the controls on Earth's climate. For example, thermal fractionation allows for the creation of a 'gas isotope thermometer' in ice cores. Second, particles that were deposited on the surface snow and incorporated in the ice matrix can be analyzed for their noble gas isotope composition. These analyses reveal information about the input and origin of both terrestrial aerosols and extraterrestrial dust. The conservative nature of noble gases, ensuring that such fingerprints are preserved over long periods of time, and the exceptionally good dating of polar ice cores make noble gas analysis of ice cores a versatile tool to study a wide spectrum of geochemical and paleoclimatic processes: from constraints on the magnitude of temperature changes during abrupt climate transitions in the Earth's history, to determining the rate of Argon-40

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degassing from the solid Earth over its history, or quantifying variations in the accretion of extraterrestrial dust on the Earth's surface. Below, we present case studies to review some of the applications of noble gas analysis in the polar ice archive, both in trapped air bubbles and in particles incorporated in the ice matrix.

1 Introduction

Polar ice cores are arguably the most powerful tool for reconstructing the timing and extent of changes in earth's environment over the past 800,000 years. Because ice cores represent continuous and well-datable archives, they have dramatically advanced our understanding of how the earth's climate has changed in the past.

Ice cores collected from Greenland have revolutionized our notion of climate variability during the past 123,000 years (e.g., Dahl-Jensen et al. 2002; Grootes et al. 1993; Johnsen et al. 1997; NGRIP Project Members 2004), and have been instrumental in characterizing climate transitions from glacial to warm conditions as well as identifying and understanding past abrupt climate change (e.g., Alley et al. 2009; Severinghaus and Brook 1999).

Antarctic ice core records extend even further into the past; the longest ice core drilled in East Antarctica represents an archive going back to ~800,000 years before present, covering the past eight glacial cycles since the Mid-Pleistocene Climate Transition (EPICA Community Members 2004). The information extracted from these ice core records can provide insight into a variety of climate forcing mechanisms and provide a basis for assessing the range of natural variability of climate, and for testing regional and global climate models under a wide range of conditions.

Perhaps most importantly, polar ice cores contain remnants of ancient atmospheric air. Snow accumulating on a polar ice sheet gradually compacts under its own weight to form a layer of recrystallized and porous snow called firn, which then further compacts to form ice. In the upper part of the firn layer, the entrapped air can still mix with the atmosphere. At the base of the firn layer, at about 50–100 m, as the firn becomes impermeable ice however, the air gets occluded in bubbles in the ice and preserved over long periods of time (Schwander 1989).

Air trapped in bubbles in polar ice has been used for a variety of paleoenvironmental studies, primarily to document the variability in the composition of past atmospheres. Analyses of the trapped air bubbles have proven to be particularly useful for reconstructing the variability of greenhouse gases, such as CO_2 and CH_4, over the earth's history (e.g., Loulergue et al. 2008; Luethi et al. 2008; Petit et al. 1999).

In addition, these air bubbles contain gases such as noble gases and nitrogen, whose atmospheric concentrations and isotopic ratios have—in contrast to the greenhouse gases CO_2 and CH_4—stayed unchanged on the 100,000 year to 1 Myr time scale spanned by ice cores (Allegre et al. 1987). Variations in the isotopic ratios of these gases in the trapped air bubbles, caused by either physical processes such as thermal or gravitational fractionation within the firn or by large-scale redistribution between the atmosphere and ocean, can be used to infer climate-related processes.

An example for this is the thermal diffusion-based noble gas thermometer. Transient temperature gradients, such as a sudden cooling or warming, fractionate the air within the firn by thermal diffusion (Leuenberger et al. 1999; Severinghaus et al. 1998). The resulting gas-isotope anomalies are then locked into and preserved in the air bubbles in the ice; precise measurements of these noble gas isotope anomalies in the trapped air bubbles allow to infer the underlying transient temperature change and, thus, allow unprecedented insights into the magnitude and abruptness of past climate change (Severinghaus and Brook 1999).

Analyses of the heavy noble gas isotopes, krypton and xenon, in the air bubbles trapped in ice cores can be used to reconstruct past mean ocean temperature. This method takes advantage of the strong temperature dependence of the solubility of krypton and xenon in water (Weiss and Kyser 1978), analogous to paleotemperature reconstructions from groundwater (Aeschbach-Hertig and Solomon 2013). As the total inventory of krypton and xenon in the atmosphere and ocean is conserved through time, variations in mean ocean temperature modulate their atmospheric abundances. Krypton and xenon, measured in ice core air, allow us to reconstruct their paleoatmospheric histories, which can then be interpreted to reflect the magnitude and timing of variations in the mean ocean temperature in the past (Headly and Severinghaus 2007).

Noble gas analysis of gas bubbles trapped in ice cores is not limited to heavy noble gases but also includes helium isotopes. Unlike the other atmospheric noble gases, helium enters the ice not only at the firn/ice transition, but also at the ice/bedrock interface. Due to its small molecular diameter, helium can readily diffuse through the ice, complicating its interpretation in the archive. Despite this caveat, analysis of helium isotopes in polar ice cores allows reconstruction of processes acting at the base of the ice sheet (e.g., Craig and Scarsi 1997; Jean-Baptiste et al. 2001a), including assessing the stratigraphic integrity of the basal ice, but—given the focus of this chapter on climate-related processes—will not be described here in detail.

In addition to trapped ancient air, polar ice cores also contain small amounts of impurities that can be important indicators of past climate and environmental conditions. Examples of such impurities are mineral dust particles from deserts that are transported thousands of kilometers in the atmosphere and deposited on the ice, ash particles from volcanic eruptions, sea salt aerosols and cosmic dust particles.

In the late 1990s, Brook pioneered the development of helium isotope analysis of particles trapped in the ice (Brook et al. 2000). Helium isotope analysis allows the relative proportions of particles of cosmic, as well as of terrestrial origin to be identified. Interplanetary dust particles (IDPs), the fine fraction of extraterrestrial matter reaching the earth that is derived from cometary and asteroid debris, is highly enriched in ^{3}He, whereas terrestrial dust is dominated by radiogenic helium (^{4}He).

When combined with snow accumulation rates—a parameter typically well known in ice cores—we can determine extraterrestrial ^{3}He fluxes and reconstruct the variability of the flux of interplanetary dust particles (IDPs) to the earth (Brook et al. 2009, 2000; Winckler and Fischer 2006). On the other hand, the ^{4}He signal measured in the particles from the ice can be used to identify terrestrial dust and—by combining it with complementary terrigenous proxies—provides information about the provenance of the mineral dust deposited on the ice.

Noble gas analyses in air bubbles trapped in the ice and in the particulate matter, respectively, represent two modern analytical techniques that are motivated by a spectrum of different objectives. In this chapter we review both techniques by presenting specific climate-related case studies and discuss their impact, limitations and future potential.

2 Background: Ice Cores in Greenland and Antarctica

The fundamental idea of using ice cores to study past climate was conceived in the 1950s by the Danish scientist, Willi Dansgaard. Several deep ice cores (Fig. 1) have been retrieved from the Greenland ice sheet, among them the GRIP, GISP-2 and North GRIP cores which reach back up to 123,000 years (NGRIP Project Members 2004). The newest deep drilling project in Greenland, the North Greenland Eemian Ice Drilling (NEEM), commenced in 2007 with the goal of retrieving an undisturbed record of the full Eemian interglacial period 115,000–130,000 year ago.

The longest ice cores, however, have been drilled in Antarctica (Fig. 1). In the 1970s, ice core drilling at the Russian station 'Vostok' began, and more than 25 years later, a more than 3,500 m long ice core was drilled above Lake

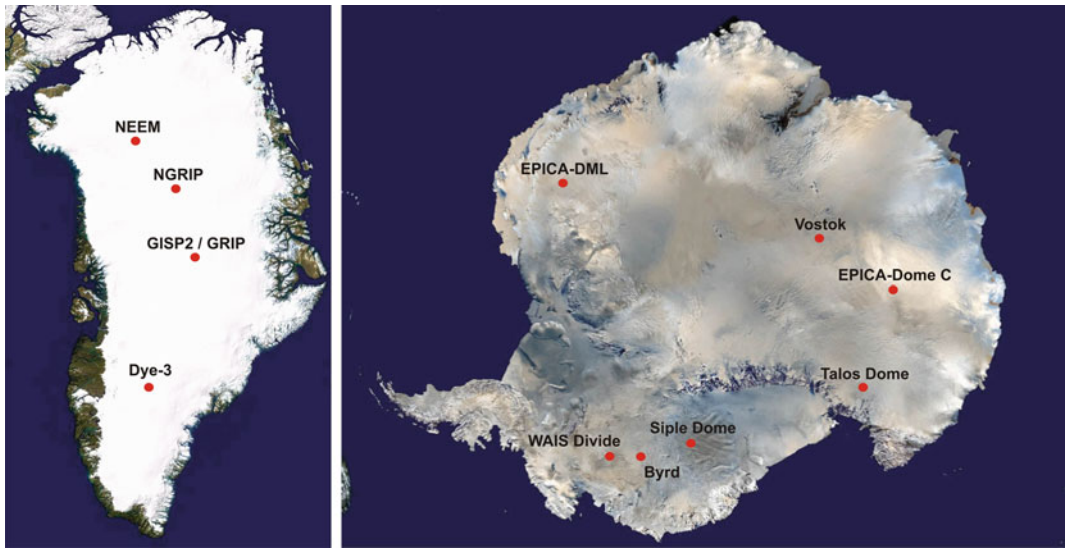

Fig. 1 Map of both polar regions indicating selected ice core drilling sites in Greenland (NEEM, NGRIP, GRIP/GISP2; and Dye 3) and in Antarctica (EPICA DML, Dronning Maud Land; Vostok; EPICA Dome C, Siple Dome; Talos Dome, Byrd and WAIS) where noble gas measurements have been performed

Vostok (78.5°S, 107°E, 3,488 m above sea level) reaching back about 400,000 years. Recently as part of the EPICA (European Project for Ice coring in Antarctica) project, a deep drill core at Dome C (EDC, 75°S, 123°E, 2,882 m above sea level) reached a record-holding 800,000 year. Another EPICA core was drilled in Dronning Maud Land (EDML, 75°S, 0°E, 3,233 m above sea level), which covers about 160,000 year and—due to its higher snow accumulation rate—allows for reconstruction of higher resolution atmospheric and climate records than previous ice cores from the East Antarctic plateau. The latest major ice coring project in Antarctica is the West Antarctic Ice Sheet Divide ice core (WAIS Divide, 79.5°S, 112°W, 1,766 m above sea level). The WAIS Divide ice core, recently completed at a length of 3,400 m, provides the first Southern Hemisphere climate and greenhouse gas records of comparable time resolution and duration to the Greenland ice cores, which will enable detailed comparison of environmental conditions between the northern and southern hemispheres.

Noble gases in trapped air bubbles have been measured in Greenland at the GISP-2 ice core (Headly and Severinghaus 2007; Kobashi et al. 2008a, b, 2009; Severinghaus and Brook 1999; Severinghaus et al. 1998), at GRIP (Landais et al. 2004b) and North Grip (Landais et al. 2004a, 2006). In Antarctica, noble gases have been measured at the Siple Dome ice core in West Antarctica (Severinghaus et al. 2003) as well as in firn air from Siple Dome (Severinghaus and Battle 2006) and at Vostok (Bender et al. 2008; Caillon et al. 2001, 2003) and Dome C (Bender et al. 2008; Dreyfus et al. 2010) in East Antarctica.

Helium isotopes in particles from ice have been measured at GISP-2 in Greenland (Brook et al. 2000) and at Vostok (Brook et al. 2009, 2000) and EDML in Antarctica (Winckler and Fischer 2006).

3 Analytical Techniques

3.1 Preparation of Ice Samples for Noble Gas Analysis

Ice cores capture a record of air bubbles as well as particulates (e.g., mineral dust, volcanic particles, and comic dust). The two types of

analyses—air bubbles and particulates—require different preparation and extraction methods.

3.1.1 Noble Gases in Trapped Air Bubbles

Typically, ice samples are taken from the inner portion of the ice core to minimize possible adverse effects of gas loss due to temperature fluctuations during core retrieval and handling. The air trapped in the bubbles is released using a designated vacuum extraction line. The early extraction method was based on a melt-refreeze technique (for details see Severinghaus et al. 1998); subsequent noble gas analyses were done using a 'wet extraction' technique (e.g., Severinghaus et al. 2003), partially based on the extraction method developed by Sowers et al. (1989). Briefly, the ice samples are placed in pre-chilled stainless steel extraction vessels containing a glass-covered magnetic stirrer. After evacuation, the vessels are warmed to room temperature releasing the trapped gas by melting. Gases are then transferred through a water trap to a collection vessel, kept at 10 K, effectively using the water vapor as carrier gas. The wet extraction method has subsequently been optimized for combined argon and nitrogen isotope measurements (Kobashi et al. 2008b) as well as for the Kr/N_2 method (Headly and Severinghaus 2007) to ensure quantitative extraction of the heavy noble gases. The extracted gas is then exposed to a hot getter to absorb N_2, O_2 and other reactive gases. A detailed overview of different gas extraction techniques can be found in Landais (2011).

3.1.2 Noble Gases in Particles from Ice Cores

The samples for the pioneering helium isotope analyses of particulate matter in ice were derived from melting subsections from the GISP-2 and Vostok ice core (Brook et al. 2000). This technique is the most direct analysis of particulates in ice cores and has been used in a subsequent study by Brook et al. (2009).

As access to ice core samples is limited and relatively large samples of ice (on the order of kilograms) are required, an alternative technique has been developed. This approach samples the excess water stream of continuous flow chemical melt-water analysis (CFA), a routine analysis in modern ice core research (Kaufmann et al. 2008). Briefly, for CFA the ice core (typically a 3×3 cm cross section) is melted on a specially designed melt head, where only the innermost section of the ice core is used for the analysis to prevent contamination. Then, the melt is directly led to a continuous flow analysis system. After the CFA, the excess water (which used to be discarded) is saved and stored in polyethylene (PE) containers.

For both techniques, directly melting the ice or using the excess water stream, the water is subsequently filtered and the particulate dust (extraterrestrial and terrigenous dust) is collected on 0.45 μm silver filters (manufactured by Osmotics–Poretics).

Each filter is then wrapped in aluminum foil. Aluminum foil balls (including the silver filter) are melted in a classical double-vacuum high temperature furnace, as shown in Fig. 10 in Burnard et al. (2013), to extract the helium. During extraction the furnace is kept exposed to a liquid nitrogen cooled charcoal trap in order to remove CO_2, H_2O and organic compounds. Further purification is performed by exposure to a getter. The gas is then collected on a cryogenically cooled charcoal trap held at $\sim$13 K and helium is separated from neon by heating the trap to 45 K. Abundance and isotopic analyses are measured using static noble gas mass spectrometry (e.g., Winckler et al. 2005; Kurz et al. 1996). Helium isotopes remain the only noble gas system measured in the particles from ice cores.

3.2 Mass Spectrometry

Two different mass spectrometric techniques are used for analyzing noble gases in trapped atmospheric air bubbles or particulates trapped in the ice, respectively.

3.2.1 Noble Gas Mass Spectrometry of Trapped Air

Isotopic ratios of noble gases in trapped air bubbles are analyzed on a multi-collector

isotope ratio mass spectrometer (Severinghaus et al. 2003, 1998). This type of mass spectrometer (e.g., Finnigan MAT 252) differs from traditional static mass spectrometers typically used to measure noble gases (e.g., Burnard et al. 2013) in that it is a dynamic-inlet instrument that uses far more sample (on the order of 1 cm^3 STP). The mass spectrometric analysis follows conventional procedures of dynamic isotope ratio mass spectrometry, with modifications designed to minimize any fractionating effects, such as thermal diffusion during volume splitting steps.

Precision is attained by bleeding sample and standard gases through two capillaries that are alternately fed into the mass spectrometer or into a waste line at high vacuum, with rapid switching between sample and standard minimizing the effect of instrument drift (McKinney et al. 1950). Mass spectrometric results must be corrected for pressure differences between sample and standards, and for the sensitivity of isotopic measurements to the elemental ratios (the so-called ''chemical slope''). The overall precision for measuring the $^{40}Ar/^{36}Ar$ ratio obtained for duplicate analyses of a 100 g ice sample is 0.012 ‰ (1 standard error of the mean, Severinghaus et al. 2003).

3.2.2 Noble Gas Analysis of Particles

Noble gases in particulates trapped in the ice are measured with a sector-field mass spectrometer and analyzed in a static mode [i.e., 'standard' configuration, as described in Burnard et al. (2013)].

4 The Noble Gas Record from Trapped Air Bubbles in Ice Cores

4.1 Paleothermometry from Thermal Diffusion: Estimate of Abrupt Temperature Change Magnitude

Quantitative estimates of temperature change in the past are instrumental to understanding the mechanism of climate change, yet classical temperature proxies suffer from numerous drawbacks. In ice cores, the oxygen isotopes of ice are affected by processes other than temperature and have been shown to underestimate the Greenland temperature changes between the last glacial period and the present by up to a factor of two. A persistent problem with many proxies is that they require an assumption that the present observed sensitivity of the proxy to temperature was also the sensitivity back through time—for example the assumption that the "spatial slope" and the "temporal slope" in temperature reconstructions from water isotopes are equal (e.g., Jouzel et al. 1997)—which is an often untested or controversial assumption. Here noble gases offer an advantage because their sensitivities are fundamental physical laws, which do not change with time. One such application of noble gases is the thermal-diffusion based gas thermometer in ice cores, which was developed over the past two decades.

Atmospheric gases are steadily trapped in bubbles in glacial ice by compaction of the 50–100 m thick layer of snow (typically called firn) on top of a polar ice sheet. Analysis of these air bubbles in ice cores drilled from the polar ice caps has yielded a cornucopia of useful information on past changes in greenhouse gas content of the atmosphere. In addition, gases whose atmospheric ratios are constant on relevant timescales ($\sim$100,000–1,000,000 year), such as the isotopes of noble gases and N_2, can reveal the impact of fractionation processes occurring within the firn. These processes include thermal diffusion (the separation of gases in a temperature gradient), and gravitational fractionation (the settling of heavier species towards the bottom in a gravitational field).

Thermal diffusion was first predicted theoretically in 1917 with the solution to the Boltzmann equation by Sydney Chapman and David Enskog, and was experimentally verified shortly thereafter (Chapman and Dootson 1917). Thermal diffusion is not to be confused with the diffusion of heat, but is rather the transport of mass by a temperature gradient, with the heavier molecules generally moving toward colder

regions. A temperature gradient exists in the firn for several centuries following a change in surface temperature due to the fact that firn is an excellent thermal insulator and the heat capacity of the ice sheet is large. This temperature gradient fractionates the air within the firn by thermal diffusion, due to the fact that the atmosphere represents a virtually infinite reservoir that cannot change. A key point is that gases diffuse about 10 times faster in firn than heat, which allows the gas composition to approach near-equilibrium with the temperature at any one depth (Severinghaus and Brook 1999; Severinghaus et al. 1998).

As the bubbles are continually closing and trapping the fractionated air at the base of the firn, an ice core contains the equivalent of a tape recording of the firn air composition over time. The noble gas isotopes record an abrupt step-function warming as a sudden positive spike in the heavy isotope followed by a gradual decay over several centuries as the firn becomes isothermal once again. The amplitude of the spike is proportional to the magnitude of the abrupt surface warming. Abrupt cooling is likewise recorded as a negative spike. Laboratory measurements of air equilibrated in a carefully controlled, known temperature gradient are used to calibrate the method, as theoretical predictions are not sufficiently accurate (Grachev and Severinghaus 2003a, b).

A complication is that gravitational fractionation also occurs in the firn, due to the settling of heavy gas species to the bottom of the stagnant column of air (Craig et al. 1988; Schwander 1989; Sowers et al. 1989). To isolate the signal due to temperature change, it is necessary to measure two different isotope pairs that have differing sensitivity to temperature, such as $^{15}N/^{14}N$ of N_2 and $^{40}Ar/^{36}Ar$ (Fig. 2). When scaled by the mass difference so that their gravitational effects are equal, their difference, known as $\delta^{15}N_{excess}$, is nominally a function of temperature only (Severinghaus and Brook 1999).

$$\delta^{15}N_{excess} = \delta^{15}N_{meas} - \delta^{40}Ar_{meas}/4 \quad (1)$$

The temperature difference between the top and bottom of the firn layer is denoted ΔT.

$$\begin{aligned}\Delta T &= \delta^{15}N_{excess} / \left(\Omega^{15} - \Omega^{40}/4\right) \\ &= \delta^{15}N_{excess} / 0.0047\,‰\,K^{-1}\end{aligned} \quad (2)$$

where Ω^{15} and Ω^{40} are thermal diffusion sensitivities of the argon and nitrogen isotope pairs.

In practice, a time-dependent numerical model of heat transport in the firn is generally used to interpret the data, because heat diffusion and advection does warm or cool the base of the firn slightly on the gas diffusion timescale and thus reduces the amplitude of the thermal diffusion signal by about 10 % depending on the firn thickness. The thermal diffusion tool is insensitive to gradual temperature changes, of order 1 K/century or less, because the firn becomes thermally equilibrated on these timescales. Diffusion of gas occurs on a timescale of a decade or so, preventing the air bubbles from recording higher frequencies than this, so this tool is only sensitive to decadal-to-centennial scale temperature variations. Fortunately, this happens to be a timescale of interest in paleoclimate research due to the wide interest in the Dansgaard/Oeschger events of the last glacial period, recorded in Greenland ice cores (Fig. 3).

4.2 Paleothermometry from Solubility: A Time Series of Mean Ocean Temperature

A persistent mystery in paleoclimate research has been the cause of the observed rise in atmospheric carbon dioxide at the ends of glacial periods. Understanding this puzzle is important because future climate depends in part on the natural feedback response of the earth system to human perturbation. A massive body of circumstantial evidence points to the deep ocean as the key reservoir for carbon dioxide variations, but basic quantitative information such as the temperature of the deep ocean over time is still lacking. A major reason is that the classical proxy for ocean temperature, the oxygen isotope ratio of benthic foraminifera, is also affected by the oxygen isotope ratio of the water. This

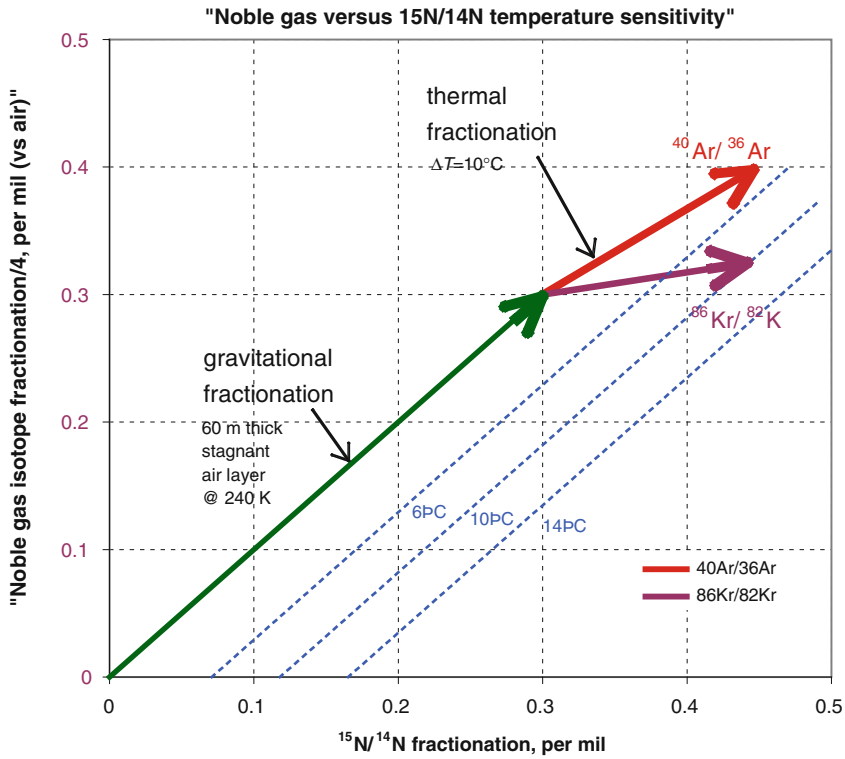

Fig. 2 Schematic of the basis for the thermal diffusion paleotemperature change indicator in trapped gases from ice cores. Thermal fractionation causes heavy isotopes to migrate toward colder regions, but the response is weaker for the noble gas pairs $^{86}Kr/^{82}Kr$ and $^{40}Ar/^{36}Ar$ than for $^{15}N/^{14}N$ of N_2 on a per-mass-unit-difference basis. Gravitational fractionation also affects gases in polar firn, with the same response for all gas pairs on a per-mass-unit-difference basis. Measurement of both a noble gas pair and $^{15}N/^{14}N$ thus permits the separation of gravitational and thermal effects (Severinghaus et al. 1998). The coloured arrows show the nominal effect of an abrupt 10 °C surface warming on the gas at the *bottom* of a 60 m thick firn column initially at 240 K. Isotherms for the ^{15}N-^{86}Kr system are shown in *blue*

fundamental ambiguity has been overcome for certain unique times such as the last glacial maximum, by directly measuring the water isotopic ratio, but a highly-resolved time series of deep ocean temperature still eludes us. Such a time series would place constraints on proposed mechanisms of carbon dioxide variation. Ice cores have the unique property that they trap samples of the atmosphere in a highly resolved time series, so a deep ocean temperature proxy contained within an ice core would be the ideal means to test these hypotheses. A further benefit of this would be that there is no relative age uncertainty between two proxies measured in the same core.

The heavy noble gases krypton and xenon are highly soluble in liquid water, and their solubility has a strong temperature dependence (Fig. 4), a principle that is also used in groundwater paleothermometry (see Aeschbach-Hertig and Solomon 2013). This fact is the basis for the mean ocean temperature paleoindicator based on measured krypton and xenon in trapped air bubbles from ice cores (Headly and Severinghaus 2007).

Because the total number of krypton, xenon, and N_2 molecules in the ocean–atmosphere system is essentially constant, a warming ocean will outgas and must cause an increase in the atmospheric inventory. The solubility of N_2 is low, and its temperature dependence is weak, making it respond much less than the noble gases. Thus the krypton/N_2 and xenon/N_2 ratios

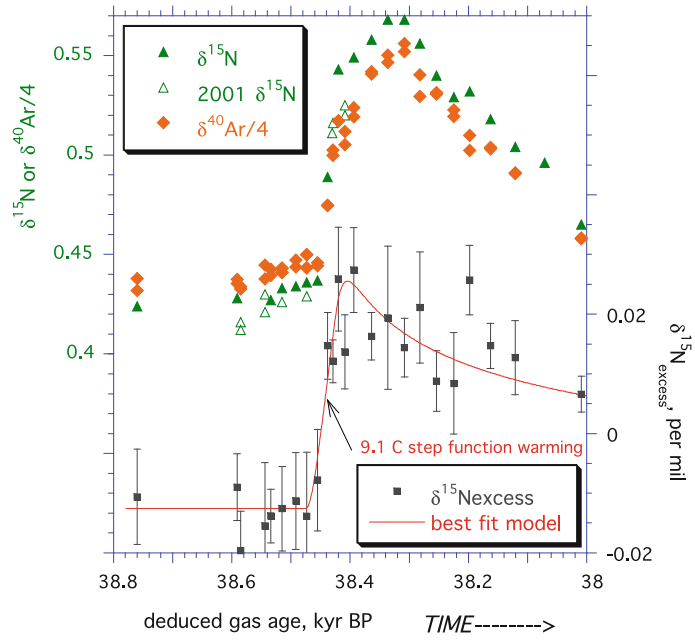

Fig. 3 Noble gas isotopic ratios in the Greenland (GISP2) summit ice core, across an abrupt warming event known as Dansgaard-Oeschger event 8 (Orsi et al. 2009). A heat transfer model forced by step function in surface temperature finds a best fit solution of 9 ± 3 °C for the warming amplitude, although considerable scatter in the data suggests some experimental artifacts. This approach also yields an estimate of the gravitational fractionation signal, which is related to the change in firn thickness. The method gives ~6 m of firn thickening, which is reasonable for this event considering that accumulation rate doubled abruptly along with the temperature change

in trapped air should record mean ocean temperature, albeit slightly weighted toward the cold end of the temperature distribution due to the nonlinearity of the solubility (Fig. 4). This nonlinearity is captured in a model that is used to interpret measured atmospheric change in terms of ocean temperature change.

Argon would be a natural choice for the less-soluble gas to which Kr and Xe are compared, however firn air studies show that the atmospheric Ar/N_2 ratio is not well retained in glacial ice due to preferential exclusion of argon from overpressured bubbles during the air entrapment process at the base of the firn. In contrast, these studies show that the atmospheric Kr/N_2 and Xe/N_2 ratios are well preserved during this process (Severinghaus and Battle 2006).

A key assumption that must be made is that the inventory of N_2 in the ocean–atmosphere system is sufficiently constant on 100,000 year timescales that its atmospheric abundance only responds significantly to solubility, despite the fact that biological denitrification and nitrogen fixation are sources and sinks of N_2. Support for this assumption is provided by the fact that the total denitrifiable pool of N amounts to less than 0.01 % of the atmospheric inventory. Bubble injection causes a ~1 % supersaturation of dissolved N_2 in the ocean (Hamme and Emerson 2004), but because only ~0.6 % of total N_2 resides in the ocean, even the extreme case of eliminating this supersaturation would cause only a 0.06 per mil fractional increase in atmospheric N_2. For comparison, the experimental error of the Kr measurement is 0.2 per mil, and that of Xe is 0.4 per mil. There is also no reason to expect that bubble injection would be reduced in a glacial climate.

To gain insight into the expected signal in atmospheric Kr/N_2 and Xe/N_2 ratios from mean ocean temperature change, it is helpful to first consider a simple isothermal box model of the

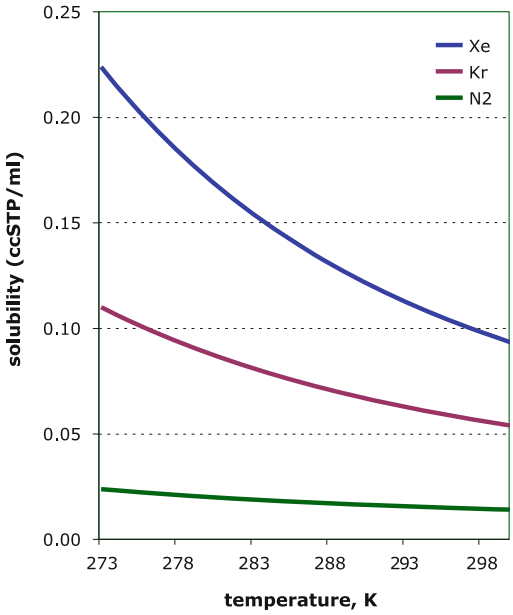

Fig. 4 Equilibrium solubility of xenon, krypton, and N_2 in seawater of salinity 35 psu, expressed as the Bunsen coefficient, in ccSTP of gas per ml of seawater (Hamme and Emerson 2004; Weiss 1970; Weiss and Kyser 1978; Wood and Caputi 1966). The equation for xenon has been corrected per (Hamme and Emerson 2004), and the underlying equations for solubility are available on the website http://web.uvic.ca/~rhamme/download.html

ocean in gas-solubility equilibrium with an overlying atmosphere. Ocean temperature T is the only variable changed; salinity, ocean volume, and sea surface atmospheric pressure are held constant. Mass conservation requires that the total number of Kr atoms in the ocean–atmosphere system before and after the temperature change must be equal (the 'superscript indicates the state after the change).

$$Kr_a + Kr_o = Kr'_a + Kr'_o \tag{3}$$

The inventory of krypton in the ocean Kr_o may be represented by the temperature-dependent Bunsen solubility coefficient $\beta(T)$ times the surface partial pressure of krypton pKr and volume of the ocean V_o (the Bunsen coefficient, in cm^3STP/cm^3STP water, describes the volume of pure gas at 1 atmosphere that will dissolve in a volume of water at equilibrium, see Fig. 4). The atmospheric inventory may likewise be simply represented as the surface partial pressure of krypton times the volume V_a that the atmosphere would have if it were at standard temperature and pressure.

$$Kr_o = \beta_{Kr}(T) p_{Kr} V_o$$

$$Kr_a = p_{Kr} V_a \tag{4}$$

$$Kr'_o = \beta_{Kr}(T') p_{Kr'} V_o$$

$$Kr'_a = p_{Kr'} V_a \tag{5}$$

Substituting (4–5) into (3), and repeating the analogous steps for N_2, then solving for the observed atmospheric quantity $\delta Kr/N_2$ yields

$$\delta Kr/N_2 + 1 = \frac{\frac{p_{Kr'}}{p_{N'_2}}}{\frac{p_{Kr}}{p_{N_2}}} = \frac{\frac{V_a}{V_o} + \beta_{Kr}(T)}{\frac{V_a}{V_o} + \beta_{N_2}(T)} \Big/ \frac{\frac{V_a}{V_o} + \beta_{Kr}(T')}{\frac{V_a}{V_o} + \beta_{N_2}(T')} \tag{6}$$

The actual mean ocean temperature is +3.5 °C presently. For illustration, let us consider the effect of cooling the model ocean from 3.0 to 0 °C. Taking V_o as $1.37 \cdot 10^{18}$ m^3 and V_a as $1.77 \cdot 10^{20}$ mol air $\cdot$ 0.02241 m^3STP $mol^{-1} = 3.97 \cdot 10^{18}$ m^3STP, the ratio V_a/V_o is 2.90 m^3STP m^{-3} (another way of saying this is that the atmosphere is effectively about 3 times bigger in volume than the ocean). Inserting the respective Bunsen coefficients, one obtains a $\delta Kr/N_2$ value of −2.1 ‰. The corresponding xenon value is −5.4 ‰. At current measurement precision, these values correspond to a signal-to-noise ratio of about 10.

A more detailed and realistic model gives a smaller change of −1.5 ‰ for krypton, largely due to the smaller volume and increased salinity of the glacial ocean (Headly and Severinghaus 2007). For comparison, preliminary measurements on ice cores using this method do show a colder glacial ocean, as expected, with a mean temperature about 3 ± 1° colder than present (Headly and Severinghaus 2007). The uncertainty quoted here is larger than the formal experimental uncertainty due to possible

systematic error in the large corrections that must be made for gravitational and thermal fractionation.

Corrections to measured values of $\delta Kr/N_2$ and $\delta Xe/N_2$ in ice core samples must be made to recover the true atmospheric values due to the physical processes occurring in the firn layer, which include gravitational settling, thermal diffusion, turbulent convection, and slow downward advection due to snow accumulation and bubble closure. Isotopic ratios ($^{15}N/^{14}N$ of N_2 and $^{86}Kr/^{82}Kr$) are measured in the same ice sample in order to make these corrections, with appropriate scalings, based on the assumption that these values do not change in the atmosphere. Convection and advection create disequilibrium, making the actual gravitational settling somewhat less than theoretically predicted (Severinghaus et al. 2010). Disequilibrium is more pronounced for slower-diffusing gases (such as xenon) than fast-diffusing gases (such as N_2) and thus must be considered carefully. A firn gas transport model incorporating all four processes with realistic estimates of past convection and snow accumulation is used to develop empirical scaling relationships between the isotopic ratios and the values to be corrected (Severinghaus et al. 2010).

Although this proxy is still under development, it is anticipated that the uncertainties will be substantially reduced as multiple records from different ice cores are compared. Because the atmosphere is well-mixed, all records should agree, providing a critical test of method reliability. Future work also includes testing the degree to which this proxy is representative of the deep ocean. Taking all waters colder than 4 °C as a working definition of the deep ocean, more than 80 % of the ocean volume lies in the deep ocean. The greater solubility at cold temperatures and the nonlinearity of the solubility-temperature relationship also contribute to dominance of the variation in this proxy by the deep ocean. Thus it seems likely that this proxy will be effectively a very good deep ocean thermometer but this needs to be quantitatively explored.

4.3 Triple Argon Isotope Composition in Trapped Air: Constraining the Outgassing Rate of ^{40}Ar from Earth's Interior

Understanding the origin of volatiles on Earth's surface is one of the fundamental problems of earth science. The volatile budget of the atmosphere and the degassing history of the earth are related to a range of fundamental processes of geodynamics, including heat production in the earth' interior and mantle mixing (e.g., Zhang and Zindler 1989; Porcelli and Wasserburg 1995).

The atmospheric concentrations of most noble gas isotopes, including the argon isotopes ^{36}Ar and ^{38}Ar, are constant on timescales of 100,000 year to millions of years (e. g., Porcelli and Wasserburg 1995; Allegre et al. 1987; Zhang and Zindler 1989). The ^{40}Ar concentration of the atmosphere, by contrast, is not constant, because ^{40}Ar is produced from radioactive decay of ^{40}K in the earth' interior and outgassed to the atmosphere. Therefore, the $^{40}Ar/^{38}Ar$ ratio of the atmosphere will increase monotonically with time.

Analyses of the isotope composition of argon in trapped air from deep Antarctic ice cores can be used to reconstruct the evolution of the paleoatmospheric $^{40}Ar/^{38}Ar$ ratio. In order to accurately reconstruct the paleoatmospheric $^{40}Ar/^{38}Ar$ ratio, one has to correct for gravitational fractionation in the firn, described in Sect. 4.1 (Craig and Wiens 1996; Schwander 1989; Sowers et al. 1989). This effect is more than an order of magnitude larger than the increase in the $^{40}Ar/^{38}Ar$ ratio of the atmosphere but it can be corrected by scaling to the gravitational fractionation of $^{38}Ar/^{36}Ar$ ratio, which is otherwise constant. Because the fractionation scales with mass difference (1.002, the ratio of the mass difference between ^{40}Ar and ^{38}Ar, and ^{38}Ar

and ^{36}Ar, respectively), the paleoatmospheric ^{40}Ar/^{38}Ar ratio can be calculated as follows

$$\delta^{40/38}Ar_{paleoatmosphere} = \delta^{40/38}Ar_{sample} - 1.002 \cdot \delta^{38/36}Ar_{sample} \quad (7)$$

Bender et al. (2008) reconstructed the paleoatmospheric ^{40}Ar/^{38}Ar history for the last ~780,000 year by analyzing samples from the Vostok and Epica Dome C ice cores (Fig. 5). The ^{40}Ar outgassing rate can be determined from the slope of the regression to be ($1.1 \pm 0.1 \cdot 10^8$ mol year^{-1}), consistent with simple models summing the outgassing from the continental crust and the upper mantle (Albarede 1998; Zhang and Zindler 1989).

Besides the significance of constraining the ^{40}Ar outgassing rate to understand the present and past geodynamics of the earth, the knowledge of the rate has important implications for ice core research itself. Tripe isotope composition of argon in trapped air allows ice samples of unknown age to be dated by dating the trapped air. Although current uncertainties of this method are fairly large [on the order of 180,000 year or 11 % of the age whichever is greater, Bender et al. (2008)], this independent dating technique could be of particular interest for dating old ice bodies of unknown age such as the rock glaciers in Mullins Valley or for future deep ice core drilling projects in Antarctica in search of very old ice.

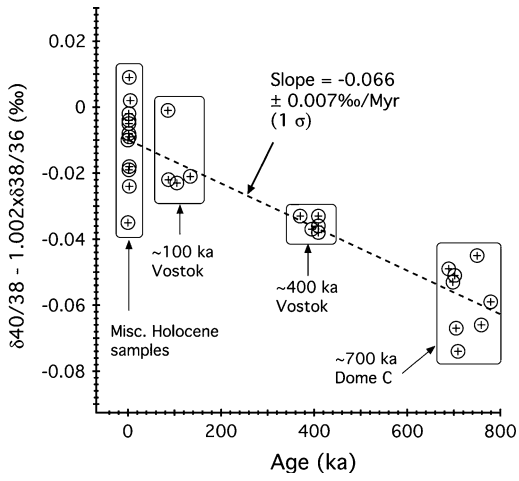

Fig. 5 Paleoatmospheric ^{40}Ar/^{38}Ar ratio, reconstructed from trapped air from the Vostok Ice core and Epica Dome C ice core, vs time. Figure from Bender et al. (2008). The results imply a contemporary rate of increase in the ^{40}Ar/^{38}Ar ratio of 0.066 ± 0.007/Myr, and a ^{40}Ar outgassing rate of (1.1 ± 0.1) · 10^8 mol yr^{-1}

5 The Noble Gas Record from Particulate Matter in Ice Cores

5.1 Reconstructions of the Flux of Interplanetary Dust from Ice Cores

Based on its specific helium isotope signatures, most notably high ^{3}He concentrations and ^{3}He/^{4}He ratios, extraterrestrial ^{3}He has been identified in a variety of climate archives: Quaternary sediments (e.g., Marcantonio et al. 1996; Takayanagi and Ozima 1987), sediments spanning the Cenozoic (Farley 1995), sedimentary rocks as old as 480 Ma (Patterson et al. 1998), loess deposits (Du et al. 2007) and, most recently, in polar ice cores. Tracing the extraterrestrial flux provides insights into a variety of questions, among them the variability of the extraterrestrial input and its relation to astronomical events, such as break-up of asteroids and comet showers, the potential impact of extraterrestrial dust on the earth' climate, and the potential use of the extraterrestrial ^{3}He signal as 'constant flux proxy' to constrain mass accumulation rates (for details, see McGee and Mukhopadhyay (2013).

Particles filtered from ice core samples represent a binary combination of a terrestrial and extraterrestrial dust component. Helium isotope analyses are uniquely suited to deconvolve the contributions from these two dust components because the helium isotopic composition of these two mixing components varies by about a factor of 10^4. Applying a simple two-component mixing model (e.g., Marcantonio et al. 1995; Patterson and Farley 1998), the fraction of extraterrestrial helium is

$$\left[{}^3\mathrm{He}_{\mathrm{ET}}\right] = \left[{}^3\mathrm{He}_{\mathrm{meas}}\right]\left(\frac{1-\frac{{}^3\mathrm{He}/{}^4\mathrm{He}_{\mathrm{TERR}}}{{}^3\mathrm{He}/{}^4\mathrm{He}_{\mathrm{meas}}}}{1-\frac{{}^3\mathrm{He}/{}^4\mathrm{He}_{\mathrm{TERR}}}{{}^3\mathrm{He}/{}^4\mathrm{He}_{\mathrm{IDP}}}}\right) \quad (8)$$

where $^3\mathrm{He}_{\mathrm{ET}}$ and $^3\mathrm{He}_{\mathrm{meas}}$ are the extraterrestrial and the measured ^{3}He concentration, respectively, and $^3\mathrm{He}/^4\mathrm{He}_{\mathrm{TERR}}$ and $^3\mathrm{He}/^4\mathrm{He}_{\mathrm{IDP}}$ denote the ratios assumed for the terrigenous ($\sim$0.01 R_a, where R_a is the helium isotope ratio of atmospheric air, 1.384 10^{-6}) and extraterrestrial endmembers ($\sim$200 R_a), respectively.

Extraterrestrial ^{3}He is delivered to the earth surface by cosmic dust [for more details, see McGee and Mukhopadhyay (2013)]. The interplanetary dust particles (IDPs) consist of a combination of asteroid and comet debris (Dohnanyi 1976) and acquire their characteristic helium signature from implantation of solar wind (e.g., Nier and Schlutter 1990). However, most IDPs $>$ 35 μm suffer severe heating during entry into the earth's atmosphere and loose their helium signal (Farley et al. 1997; Fraundorf et al. 1982). The atmosphere effectively acts as a filter, allowing only fine IDP, corresponding to about 0.5 % of the total IDP mass flux, to retain their helium signal. Thus, extraterrestrial ^{3}He data from ice cores (and other climate archives) offer a view of cosmic fluxes that is distinct from and complementary to that provided by other common extraterrestrial tracers, such as iridium or osmium, which trace the total extraterrestrial mass flux (Peucker-Ehrenbrink 1996).

^{3}He/^{4}He isotope ratios measured in particles from ice cores are typically relatively high. ^{3}He/^{4}He ratios from Greenland ice core range between 7 and 48 R_a (Brook et al. 2000); helium isotope ratios measured in particles from Antarctic ice cores are even higher than in Greenland and can be as high as 200 Ra (Brook et al. 2009, 2000; Winckler and Fischer 2006) because they are less diluted with terrestrial dust.

The high ^{3}He/^{4}He ratios measured in the particles are close to that of the extraterrestrial end-member, indicating that nearly all the ^{3}He in the ice is of extraterrestrial origin. According to Eq. (8), at least 99.8 % of the total ^{3}He is of extraterrestrial origin in all ice samples analyzed. This result is robust with respect to variations in the exact isotopic ^{3}He/^{4}He composition of both endmembers.

Ice cores offer the advantage compared to other terrestrial and marine climate archives that accumulation rates are well known. By multiplying the ^{3}He concentration with the snow accumulation rates, the flux of extraterrestrial ^{3}He can be determined

$$f_{He_{ET}} = \left[{}^3He_{ET}\right] \cdot AR_{ice} \quad (9)$$

where ^{3}He is the extraterrestrial ^{3}He concentration and AR_{ice} is the snow accumulation rate of the ice.

Figure 6 shows the reconstructed extraterrestrial ^{3}He fluxes from three different ice cores, GISP2 in Greenland (Brook et al. 2000) and Vostok (Brook et al. 2000) and EDML (Winckler and Fischer 2006) in Antarctica, covering the past 100,000 years. The studies from GISP 2 and Vostok directly used ice core samples, while the record from EDML was reconstructed with the excess water method (see Sect. 3.1.2).

Late Holocene samples from Vostok as well as from GISP 2 are replicates from the same or immediately adjacent depth levels in the ice core. The deeper samples from Vostok as well as the record from EDML represent time series. The range of ^{3}He fluxes for the replicate samples from Vostok and GISP 2, respectively, is relatively large and is thought to reflect the statistical effect of sampling a small number of IDPs in a given ice sample (Farley et al. 1997). The number of IDPs in a sample is proportional to the sample size and inversely proportional to the accumulation rate, known as the area-time product. Because ice cores tend to have relatively large accumulation rates, resulting area-time products are small. Even though large ice samples, of the order of hundreds of grams to several kilograms, are analyzed, this does not fully compensate for the effect of the high accumulation rates. The observed reproducibility between replicates or variability between adjacent samples is for all ice core studies equal to or better than the expected statistical distribution of ^{3}He data based on an atmospheric

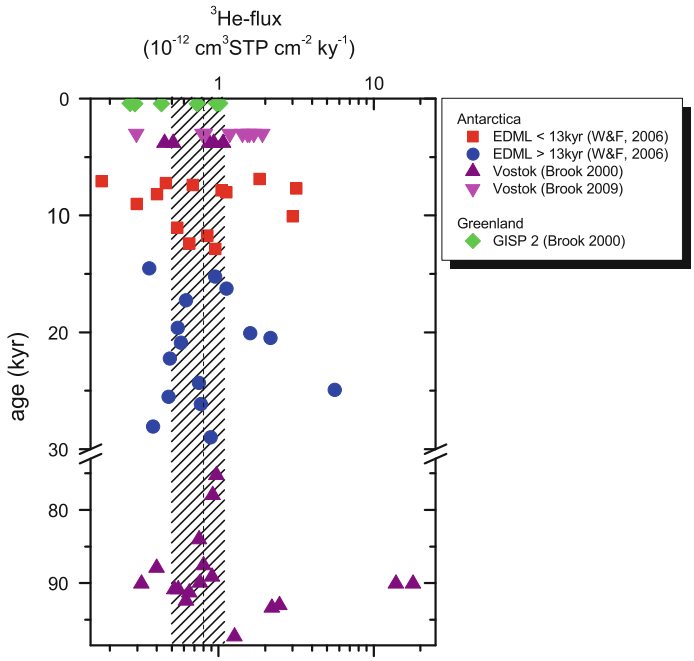

Fig. 6 Compilation of all ^{3}He flux data from polar ice cores vs age. Data are from EPICA DML (Winckler and Fischer 2006), Vostok (Brook et al. 2000, 2009) and GISP-2 (Brook et al. 2000). Please note the break on the age-axis, as no data are available between 30 and 75 kyr. High values may reflect rare large, ^{3}He-rich IDPs or short-term variability in the dynamics of IDP production, transport or accretion. The solid line and the shaded area represent an estimate of the extraterrestrial ^{3}He flux based on marine sediment [(8 ± 3) 10^{-13} cm^3 ^{3}He cm^{-2} kyr^{-1}, McGee and Mukhopadhyay 2013]

entry model [Farley et al. 1997, for details see McGee and Mukhopadhyay (2013)].

The over-all temporal and spatial variability of the reconstructed ^{3}He fluxes, as reflected by the three studies covering different time periods (Fig. 6), is in the same range as the scatter between replicate samples. This is particularly noteworthy because the three ice cores represent very different polar settings in Greenland and Antarctica, respectively, for example widely varying snow accumulation rates between 1 g cm^{-2} yr^{-1} in marine isotope stage (MIS) 5 ice from Vostok and 22 g cm^{-2} yr^{-1} at GISP2.

Perhaps most importantly we do not observe any significant change in the ^{3}He flux from interglacial (MIS 5, Vostok) to glacial (MIS 2 at EDML) to interglacial (Holocene at Vostok, GISP2 and EDML) conditions. The median extraterrestrial ^{3}He flux of all data is (8.10 ± 3.15) 10^{-13} cm^3 ^{3}He cm^{-2} kyr^{-1}. This flux is in good agreement with the best estimates of the extraterrestrial ^{3}He flux from mostly low-latitude marine sediments, (8 ± 3) 10^{-13} cm^3 ^{3}He cm^{-2} kyr^{-1} (McGee and Mukhopadhyay 2013; dashed line in Fig. 6). The consistency between the ice core based ^{3}He flux with the estimate from marine sediment cores supports a spatially and temporarily uniform deposition of IDPs on Earth.

The finding of a quasi-constant flux of extraterrestrial dust to Earth allows us to test a recent, stunning climate forcing hypothesis: Muller and MacDonald (1995, 1997) suggested that the 100,000 year climate cycles of the Quaternary are driven by fluctuations in the extraterrestrial dust accretion due to variability in the inclination of the earth (Muller and MacDonald 1995, 1997). The lack of variability in the ^{3}He flux on glacial-interglacial timescales over the past 100,000 yr is inconsistent with this hypothesis (Winckler and Fischer 2006; Brook et al. 2009) and rules out the input of

interplanetary dust as a driver of the late Pleistocene 100,000 year glacial cycles.

5.2 Reconstructions of Terrestrial Dust and Its Provenance

In addition to tracking cosmic dust, helium isotopes measured in particles from ice cores provide a record of atmospherically transported mineral aerosols (dust). Mineral dust is thought to have significant effects on the earth' radiation budget, both directly by influencing the radiative balance of the atmosphere (e.g., Arimoto 2001; Harrison et al. 2001) as well as indirectly by supplying micronutrients to the ocean (e.g., Martin 1990), thereby influencing the biological productivity of the surface ocean and, potentially, the biological uptake of CO_2 by the ocean (e.g., Bopp et al. 2003; Falkowski et al. 1998; Moore et al. 2002; Watson et al. 2000).

Polar ice cores provide an unambiguous record of dust fluxes; in particular, they show that dust deposition from the atmosphere to the polar ice sheets was about 20 times greater during glacial periods (e.g., EPICA Community Members 2004; Lambert et al. 2008; Petit et al. 1999). These dust flux records, based on major ions (non-sea salt Ca), coulter counter or laser measurements, show almost perfect agreement between individual sites across Antarctica or Greenland, to the extent that these records can be used to synchronize age scales. However, much less is known about the geographical origin of the terrestrial dust emitted and even less regarding the processes leading to increased dust mobilization.

The mineralogy, chemistry and isotopic composition of particulate dust in ice can in principle be used to identify the source areas from which the aeolian material is derived. In the past, the most successful approach has been based on radiogenic isotopes, such as neodymium, strontium and lead, and matching the observed isotopic composition of the particulate matter in the ice core with the isotopic fingerprint of potential source areas (e.g., Basile et al. 1997; Grousset et al. 1992).

The prevailing view until now has been that the source of dust to Antarctica is Southern South America, based largely on characterization of dust recovered from glacial sections of ice cores (Basile et al. 1997; Delmonte et al. 2004; Grousset et al. 1992).

Characterizing the provenance of interglacial dust has been analytically challenging due to the extremely low dust levels during interglacial periods. Recent radiogenic isotope analyses of interglacial dust samples, from the Holocene and MIS 5e, indicate that dust deposited in Antarctica during interglacial time periods may be derived from a mixture of dust sources rather than a single source. Potential sources include different regions within southern South America and other sources like Australia (Delmonte et al. 2007; Revel-Rolland et al. 2006) or possibly the Puna-Altiplano area (Delmonte et al. 2008). However, no definite conclusions have yet been drawn due to the limited data set and overlap of potential source areas (PSAs) in Sr–Nd space.

Helium isotopes measured in the EDML core in Antarctica provide a record of the dust flux and dust provenance and represent a new provenance tool that can potentially be helpful in answering this question. The ^{4}He signal in ice cores is typically dominated by the terrigenous component while the ^{3}He signal is mostly of extraterrestrial origin. Terrigenous ^{4}He has successfully been used to reconstruct dust fluxes to late Pleistocene marine sediments (Patterson et al. 1999; Winckler et al. 2008, 2005) and to modern corals (Mukhopadhyay and Kreycik 2008). Within the terrigenous fraction, resistant trace phases, such as zircons and apatite, are rich in U and Th and have consequently high concentrations of ^{4}He. Volcanic material, in contrast, has very low ^{4}He concentrations, typically 3 orders of magnitude lower than in continentally derived material (Patterson et al. 1999). Because terrigenous ^{4}He is produced from alpha-decays of U and Th within the rock matrix, it is expected to increase with the formation age of the source rock (disregarding variable helium retention characteristics of different rock types). Consequently, when paired

with another relatively constant terrigenous proxy [X] (such as Ca or ^{232}Th), the $^{4}He_{terr}$/[X] ratio is to a first order a function of the rock formation age. Conceptually, geochemical fingerprints of ^{4}He/[X] in ice core samples can then be matched up with distinct ^{4}He/[X] ratios between potential dust source areas, thus allowing tracing the provenance of the dust deposited.

Terrigenous ^{4}He can be calculated from the same data presented in the Sect. 5.1 using a simple two-component mixing model (Patterson et al. 1999)

$$\frac{^{4}He_{terr}}{^{4}He_{meas}} = \frac{(^{3}He/^{4}He)_{meas} - (^{3}He/^{4}He)_{ET}}{(^{3}He/^{4}He)_{terr} - (^{3}He/^{4}He)_{ET}}$$

where *terr* and *ET* denote the terrigenous and extraterrestrial component, respectively. Terrigenous ^{4}He-fluxes, calculated by multiplying the terrigenous ^{4}He concentration with the ice accumulation rate, are generally greater during the last glacial period than during the Holocene. However, the decrease from glacial to interglacial values is only by a factor of 2, in sharp contrast to the interglacial/glacial decrease of a factor of about 20 that is commonly observed from particulate dust flux measurements (EPICA Community Members 2004; Fischer et al. 2007; Petit et al. 1999).

A likely explanation is that the ^{4}He concentrations of the glacial dust source is smaller than that of the interglacial dust. This is supported by the isotope mixing diagram with nss Ca^{2+} as terrestrial dust reference (Fig. 7). Glacial and interglacial samples lie on well-defined mixing lines. While both mixing lines are anchored in the same extraterrestrial endmember (intercept with the ^{4}He/^{3}He-axis), their slopes are significantly different, indicating distinct terrestrial end-members. Glacial ice shows much lower ^{4}He/nssCa^{2+} ratios than interglacial ice.

Thus, the last glacial to Holocene shift in ^{4}He/nssCa^{2+}—together with the moderate decrease of the ^{4}He-flux—points to a glacial to interglacial shift in terrestrial dust sources.

There are two scenarios that could potentially explain this shift:

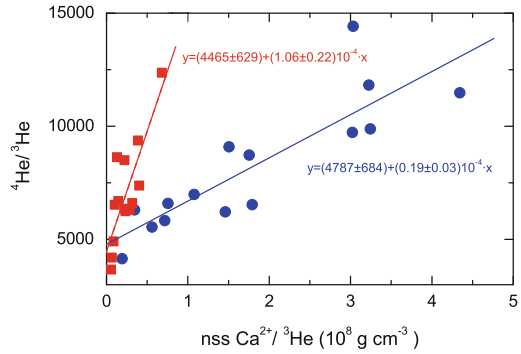

Fig. 7 Isotope mixing diagram with non sea salt Ca^{2+} (nss Ca^{2+}) as terrestrial dust reference species. Glacial (*blue symbols*) and interglacial (*red symbols*) ice samples fall along two well-defined mixing lines with matching y-intercepts (^{4}He/ ^{3}He ratio of the extraterrestrial endmember) and distinct slopes suggesting a glacial-interglacial change in terrestrial dust source distribution (Winckler and Fischer 2006)

a. Taken at face value, the ^{4}He fluxes and ^{4}He/nssCa^{2+} ratios (Fig. 7) observed across Termination 1 appear to imply a younger (and therefore less radiogenic) source of dust in glacial times, compared to interglacials. Southern South America represents a relatively young orogenic environment. Australia or South Africa, in contrast, are part of the Precambrian shield and are expected to show higher radiogenic ^{4}He concentrations.
b. Alternatively, the glacial/interglacial shift in the ^{4}He/nssCa ratio could reflect a change in the dominant dust source within South America. A possible scenario could be a change from fresh glacial outwash material, during glacial periods, with little chemical weathering to a loess/dessert dust source, during interglacials, which has been exposed to chemical weathering for a longer time. Calcium is known to be an element which is highly susceptible to chemical weathering (e.g., Taylor and McLennan 1985). The main carrier for ^{4}He is zircon (Patterson et al. 1999) which is resistant to chemical weathering. Therefore, He is expected to be retained better than calcium, and accordingly the interglacial dust is likely to show higher ^{4}He/Ca.

Comprehensive characterization of the helium isotopic composition and ^{4}He/Ca ratios of all potential source areas, including different regions in South America, Australia and possibly local Antarctic dust sources, is needed to differentiate between the two scenarios. Such work is currently in progress.

6 Summary and Future Work

Analyses of noble gases of air bubbles, trapped in ice cores, have provided important insights into the environmental record of the earth and underlying mechanisms of climate change. Additionally, helium isotope measurements of particles trapped in the ice core provide a record of the influx of extraterrestrial dust to the earth and of varying terrestrial dust input. Noble gas studies in ice core research are still a relatively new field and several lines of future research offer promising avenues of research:

- To what extent can future records of Kr/N_2 and Xe/N_2 ratios from different ice cores reduce the uncertainty in the deep ocean paleo temperature estimate? Because the atmosphere is well-mixed, records from different ice cores should agree, providing a critical test of method reliability. If successful, a precise time series of the deep ocean temperature will provide a key parameter for global climate models.
- How old is the oldest ice in Antarctica? In addition to argon isotopes (Sect. 4.3), the long-lived krypton isotope ^{81}Kr, with a half-life of 229 kyr, represents a promising tracer for dating old ice ranging from 200 kyr to 1.5 Myr. Recent breakthroughs in the atom trap trace analysis (ATTA) technique for measuring krypton isotopes (Jiang et al. 2012), combining both significant reduction in sample size and much improved counting efficiency, may pave the way for radiometric dating of old ice, complementing Ar-based dating methods.
- How did the extraterrestrial ^{3}He input vary over the Late Pleistocene? Limited availability of larger ice samples from traditional ice coring projects has so far hampered our ability to accurately determine the extraterrestrial ^{3}He flux. However, horizontal ice core sites from Greenland and Antarctica (e.g., Taylor Glacier), replicate coring and sampling excess water from CFA—together with analyzing different grain size fractions—may be helpful in providing sufficient ice for more precise ^{3}He flux estimates.
- What is the origin of dust deposited in Antarctica? A major investigation of the ^{4}He/Ca fingerprint of source areas in the Southern hemisphere is underway and will provide the background information needed to constrain the dust sources and, by doing so, help to increase our understanding of the role of dust in climate.

The case studies presented in this chapter illustrate the wide spectrum of noble gas applications in ice core research. The range of applications is even wider, but, given our focus on climate-related studies, we have not covered further noble gas studies, such as the use of helium isotopes in ice to (a) constrain basal ice dynamics from radiogenic ^{4}He diffusion from the bedrock (Craig and Scarsi 1997) or (b) to determine the accretion of lake ice in the Vostok record (Jean-Baptiste et al. 2001b) as well as the search for missing xenon in polar ice sheets (Bernatowicz et al. 1985). The potential for future advances of noble gas analyses in ice core research is very large, as a result of the drilling of new ice cores in unexplored regions and new ice cores reaching further back in time, exploration of re-exposed old ice at ice margins and blue ice areas, increases in the range of chemical and isotopic proxies measured and increasing temporal resolution of the analyses.

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