Determining the Thermal Diffusion Factor for $^{40}Ar/^{36}Ar$ in Air To Aid Paleoreconstruction of Abrupt Climate Change

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The thermal diffusion factor (α_T) of $^{40}Ar/^{36}Ar$ in air has been measured in the laboratory for the first time. The mean values of $\alpha_T \times 10^3$ that we find at −30.0 °C are 9.85 ± 0.04 for air and 11.25 ± 0.03 for pure argon. The latter value is more precise than the data found in the literature. The temperature dependence of the thermal diffusion factor in air in the range −60 to −10 °C can be described by an empirical equation $\alpha_T \times 10^3 = 26.08 - 3952/\langle T \rangle$ (±1%), where $\langle T \rangle$ is the effective average temperature. Results of this study are valuable for reconstruction of magnitudes of abrupt climate change events recorded in Greenland ice cores. For one abrupt warming event ~15,000 years ago, near the end of the last glacial period, these results yield a warming of 11 ± 3 °C over several decades or less. Theoretical calculations are not yet able to provide the needed accuracy, and the experimental results for the thermal diffusion factor in air should be used for paleoenvironmental studies.

Introduction

The cold, dry conditions of the last glacial period were frequently interrupted by sudden transitions to warmer, more humid conditions, which persisted for several centuries to millennia.[1] The transitions typically took place in somewhere between 1 and 50 years.[2] The temporal pattern of abrupt climate changes is revealed by the Greenland ice cores[3] (Figure 1). The changes were widespread, taking place nearly synchronously over much of the Northern Hemisphere.[2] The physical mechanism of these changes is currently debated.[4] Reliable data concerning paleoclimate serves as a testground for climate models employed in attempting to predict future climates.[5] In fact, these models currently underpredict the magnitudes of the observed warmings, implying that further model refinement is needed.[2] Knowledge of the precise magnitudes of the abrupt climate change events would be valuable from that perspective, and would increase our understanding of the sensitivity of Earth's climate to future perturbations.

Determination of the magnitudes of abrupt climate change events is ambiguous when the conventional ice-core paleotemperature proxy, $\delta^{18}O$ in H_2O of the ice, is used.[6] Factors other than temperature affect this proxy, and its exact relation to temperature is difficult to know for times in the past. An alternative approach involves searching for isotopic anomalies in the fossil air from the bubbles in ice cores.[7−10] Prior to becoming trapped in the ice, the air is isotopically enriched or depleted by the process of thermal diffusion.[7] (Another process fractionating isotopes, gravitational settling,[7] is well understood and easily quantified using the barometric equation and will not be discussed here.) Thermal diffusion (called the "Soret effect" for liquids) is an unmixing of gaseous mixtures subjected to a temperature difference.[11,12] The direction of the unmixing is generally toward lower temperature for the heavier species, and toward higher temperature for the lighter species.

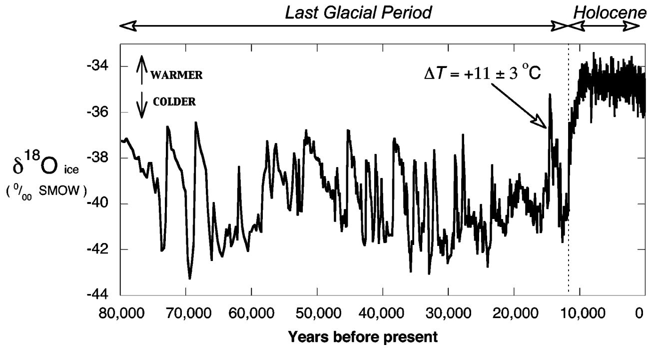

Figure 1. Record of climate change in Greenland during the past 80,000 years. (Data archived at the World Data Center for Paleoclimatology, Boulder, CO: GISP2 Stable Isotopes (Oxygen) (Stuiver, M.) http://www.ngdc.noaa.gov/paleo.) The quantity $\delta^{18}O_{ice}$ [3] measured on the ice core samples serves as the classical proxy for temperature. The Last Glacial Period was punctuated by ~22 abrupt warming events. The magnitude of the abrupt warming event marked with an arrow (the "Bølling warming") of +11 ± 3 °C was deduced using the fossil air paleothermometer with the coefficients found in this work (compared to a previous value of +9 °C found using the old, poorly known coefficients[9]). The abrupt warming at the end of the Younger Dryas is marked by the dotted line (see Discussion section).

The origin of the isotopic anomalies in fossil air from glacial ice is as follows.[7] A 50 to 100 m thick porous layer of compressed snow ("firn") on top of an ice sheet acts as a buffer zone between the free atmosphere and the deep-firn/ice transition, where new ice forms continuously and encloses air in bubbles. (Deep firn is transformed into ice because of the added weight of freshly precipitated snow at the surface.) An abrupt warming at the surface creates a difference of temperatures across the firn layer, because the insulating properties of the firn hamper propagation of heat downward. Thermal diffusion drives the heavier components of air in the firn downward, toward colder temperatures. As a result, the air at the bottom of the firn becomes enriched in the heavier isotopic species. Enclosure of the deep-firn air into bubbles in ice takes place

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subsequently, which preserves the isotopic anomaly by sealing the air and preventing further mixing.

An isotopic anomaly observed in the fossil air extracted from a section of an ice core can be used to find the magnitude of the corresponding abrupt climate change. This is achieved using a model of heat transfer, ordinary molecular diffusion, and thermal diffusion in the firn layer.[9,13] Thickness and porosity of the firn, effective gas diffusivity, temperature at the site, and the rate of snow accumulation at the time of interest are prescribed in the model. To calculate the extent of isotopic unmixing of air in the firn due to thermal diffusion, the value of a phenomenological coefficient known as the "thermal diffusion factor"[12] is needed. The literature supplies such values for ^{40}Ar/^{36}Ar in pure argon[14−22] rather than in air, which is the relevant mixture for paleoreconstructions. Values of the thermal diffusion factor for an isotopic pair in pure and in mixed gas are often found to be rather different.[23,24] The effect of adding a third gas to an isotopic mixture is commonly to reduce the thermal diffusion factor. As Van der Valk and De Vries[23] wrote in 1963: "Perhaps we may say that in most cases the original separative collisions are diluted by non- or at least less-separative collisions due to the added gas".

The goal of the present work is to experimentally obtain the values for the thermal diffusion factor for ^{40}Ar/^{36}Ar in air in the range of temperatures relevant for paleoreconstruction purposes, −60 to −10 °C. It must be emphasized that no porous medium (firn) was used in the experiments. It may be argued that since the mean free path of the molecules is 3 orders of magnitude smaller than the typical diameter of the pores in the firn (∼1 mm), collisions with the walls are negligible. Hence, the values of the thermal diffusion factors should remain unchanged in the natural environment to which they are applied. However, it would be desirable to prove this statement experimentally in future work. Isotopic fractionation due to selective adsorption on the surfaces of the pores in the firn has already been demonstrated to be negligible in an experiment.[25]

The thermal diffusion factor is determined in a laboratory by maintaining a desired mixture in a known temperature difference and detecting the imposed steady-state difference of isotopic composition.[25,26] The latter can be expressed using the "delta" notation conventional in geochemistry as follows:

$$\delta^* = \left[\frac{([^{40}\mathrm{Ar}]/[^{36}\mathrm{Ar}])_{T_{\mathrm{COLD}}}}{([^{40}\mathrm{Ar}]/[^{36}\mathrm{Ar}])_{T_{\mathrm{HOT}}}} - 1\right] \times 10^3\ {}^0\!/_{00} \tag{1}$$

where $1^0/_{00}$ ("per mil") = 0.1%, and [^{40}Ar] and [^{36}Ar] are the mole fractions of ^{40}Ar and ^{36}Ar in the part of the vessel maintained at a lower temperature "T_{COLD}" (numerator) or a higher temperature "T_{HOT}" (denominator). The choice of T_{HOT} as a reference temperature is arbitrary: if T_{HOT} is put in the numerator and T_{COLD} in the denominator, δ^* reverses its sign but its magnitude remains unchanged. Unlike in other geochemical studies, no reference gas needs to be used when determining the difference in isotopic composition, but rather the composition of the "cold" gas is directly compared to the composition of the "hot" gas. To indicate that no reference is used, the asterisk accompanies the "delta" character. The expression for the thermal diffusion factor is given in these terms as[25]

$$\alpha_{\mathrm{T}} = \frac{\ln(1 + \delta^* \times 10^{-3})}{\ln\left(\dfrac{T_{\mathrm{HOT}}}{T_{\mathrm{COLD}}}\right)} \tag{2}$$

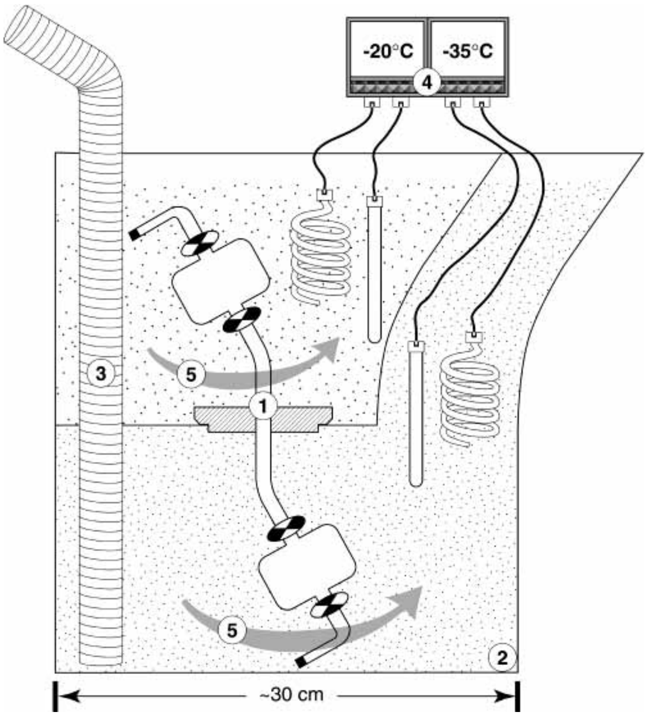

Figure 2. Setup used in our thermal diffusion experiments. The gas mixture is maintained in a precisely controlled temperature difference until a steady state with respect to thermal diffusion is reached. The cell (1) is filled with gas and inserted in a bath (2); a chiller probe (3) cools ethanol in both sections of the bath; a temperature controller (4) maintains temperatures in sections at their set values; the bath fluid in both sections is mixed vigorously (5).

The thermal diffusion factor is also dependent on absolute temperature according to an approximate equation:[11,12,25]

$$\alpha_{\mathrm{T}}(\langle T\rangle) \cong a - b/\langle T\rangle \tag{3}$$

where a and b are arbitrary constants and $\langle T\rangle$ is the effective average temperature. This effective average temperature is given as[12]

$$\langle T\rangle = \frac{T_{\mathrm{COLD}}T_{\mathrm{HOT}}}{T_{\mathrm{HOT}} - T_{\mathrm{COLD}}} \ln\left(\frac{T_{\mathrm{HOT}}}{T_{\mathrm{COLD}}}\right) \tag{4}$$

Although various equation forms have been proposed to describe the temperature dependence of α_{T},[12] we favor eq 3 proposed from theoretical considerations in 1940[27] because of its simplicity and because it has been shown to adequately describe a high-precision thermal diffusion data set.[25] The experimental value of the thermal diffusion factor of eq 2 is assigned to the effective average temperature of eq 4. Throughout this paper, units of Kelvin are implied for temperature, unless indicated otherwise.

Experimental Methods

The experimental arrangement shown in Figure 2 was used to maintain a desired mixture in a set temperature difference (constant to within ±0.1 °C). A gas-tight stainless steel vessel (1), referred to as a "cell", was filled with gas and inserted inside the two-section bath (2). The opening in the partition between the two sections was closed off by a cover attached to the cell in the middle. Ethyl alcohol served as a bath fluid and was vigorously mixed. It was chilled at a constant rate by a chiller probe (3) that went through both sections. The two heaters were connected to PID (proportional-integral-derivative) temperature controllers (Omega) (4), and were automatically turned on and off as required to keep the temperatures at desired values with minimal temperature fluctuations. The experimental gas mixture was allowed a sufficient amount of time to reach a steady state with respect to thermal diffusion (see below). A screwdriver-shaped tool with pins at its tip matching holes on valve handles was used to close off the inner valves on a cell and thus terminate the experiment. The latter procedure was performed quickly and with a minimal perturbation to the temperatures in the bath. Finally, the cell was removed from the bath, dried, and brought to a uniform room temperature.

At the end of an experiment the gas isolated in spaces between the inner and outer valves of a cell (in "sample" volumes) was characterized by a different isotopic composition on one side relative to the other. Two cells were employed in the experiments: the "big" cell (~26.2 cm^3 sample volume) and the "small" cell (~1.2 cm^3 sample volume).[25] The former was used in experiments with dry tank air (pumped at ground level in La Jolla, CA), and the latter in experiments with pure argon [commercial ultrahigh purity Ar].

To provide a control for the thermal diffusion experiments, "blank" experiments were performed with the same regularity. The latter experiments were designed to mimic the thermal diffusion experiments in all aspects (including sample treatment and analysis, see below), with the exception of the applied temperature difference, which was zero in that case. An isothermal water tank was used in the blank experiments instead of the two-section bath. The definition of $\delta*$ of eq 1 for a blank experiment is modified by assigning the numerator and denominator to the "lower" and "upper" portions of a cell, respectively (Figure 2), rather than to T_{COLD} and T_{HOT}. Note, that in case of the thermal diffusion experiments the upper section of the bath was always the warmer one in order to avoid thermal convection in the cell.

Three different groups of experiments were performed that were distinguished on the basis of the cell that was used, the gas pressure inside the cell, and the amount of time allowed to reach a steady state, as follows: "*Air-1*" (big cell, 0.2 atm, 2 h), "*Air-2*" (big cell, 1 atm, 10 h), and "*Pure-Ar*" (small cell, 1 atm, 2 h). The indicated times do not include the time needed to reach the set values of temperatures in the bath. The steady state of a thermal diffusion experiment is defined as the state when the flux due to thermal diffusion is equal and opposite to the flux due to ordinary diffusion and the maximum separation of isotopes is reached. It is approached exponentially with a relaxation time τ.[28] The thermal diffusion relaxation time (τ) is approximately 5 min for the small cell and 90 min for the big cell for a pressure of 1 atm.[25] These values have been determined experimentally by measuring the induced fractionation at 0.5τ, 1τ, 2τ, etc. The values decrease when lower pressures are used, the relaxation time being proportional to pressure.[11] The amount of time needed to reach ~99% of the steady-state value is ~4.5τ. Since the cells in the experiments were maintained at the set temperatures for at least 6τ in all experiments, the time was always sufficient to reach the steady state.

The temperatures in thermal diffusion experiments were monitored using a pair of surface thermistors with digital indicators (Newport, INFCH-series), separate from the PID controller. The thermistors were attached to the sample volumes of a cell on both sides. An additional temperature reading was obtained from a thermistor in the bath fluid (experiments of groups *Air-2*, *Pure-Ar*). Another crosscheck of the surface temperature readings was performed on several occasions by measuring the bath fluid temperatures using the certified individually calibrated mercury thermometers (Fisher). The thermometer readings were persistently 0.1 °C higher than the surface-thermistor readings. This reflects either a real difference between fluid temperature and the cell's temperature, or a calibration offset (which would not affect the magnitude of the measured temperature difference but would slightly bias the effective average temperature). The average values of the 21 readings of surface temperatures (collected at 30 s intervals during the final 10 min of an experiment) are reported as the experimental temperatures "T_{COLD}" and "T_{HOT}" (see Results section).

A dual-inlet Finnigan MAT 252 mass spectrometer was used to determine the values of $\delta*$ (see eq 1). Gas was expanded into the sample-side and standard-side bellows of the mass spectrometer, either directly from the sample volumes of a cell (group *Pure-Ar*), or from the tubes containing the processed samples (groups *Air-1* and *Air-2*, see below). The pressures in the bellows were adjusted to ~38 mbar prior to the analysis. The δ-values were obtained 144 times for each pair of samples from group *Air-1*, and 216 times for those from groups *Air-2* and *Pure-Ar*. Precise balancing of ion currents on the standard and sample sides was performed either manually or automatically throughout the run. Less than 2% of values collected in a run were typically rejected as outliers by the mass spectrometer's ISODAT software (through the use of a Dixon-3 statistical test, 90% confidence limit). A correction for pressure imbalance[29] amounted to $0.002^{0}/_{00}$ or less for the δ-values of group *Air-1*, and $0.0004^{0}/_{00}$ or less (negligible) for the values of groups *Air-2* and *Pure-Ar*. The correction for the isotopic discrimination due to major gas abundance ("chemical slope")[29] for groups *Air-1* and *Air-2* had a magnitude of $\leq 0.005^{0}/_{00}$ and $\leq 0.002^{0}/_{00}$, respectively. The average δ-values corrected for both effects are reported in the Results section.

A treatment of samples from groups *Air-1* and *Air-2* was performed prior to the analysis in order to remove oxygen from the samples. This step was necessary because $^{18}O_2$ interferes with ^{36}Ar in a mass-spectrometric measurement. All gases other than noble gases were eliminated from the samples by exposing them to sheets of an aluminum/zirconium alloy at 900 °C.[29] Tank nitrogen (commercial ultrahigh purity N_2) was added to the residual samples in prescribed proportions (~10× for group *Air-1* and 3× for group *Air-2*). This was done in order to bring the bulk of the samples to the optimal size for a mass spectrometric analysis. The analysis-ready gas samples were finally collected in ~10 cm^3 tubes by submerging the latter in liquid helium. A more in-depth treatment of the experimental details is contained in refs 29 and 25.

Results

The results of experiments are summarized in Table 1. Note that a temperature difference of ~15 °C (similar to the magnitudes of the biggest recorded abrupt climate changes[8]) was employed in all cases. This value was chosen because it is big enough to produce a precisely measurable signal without sacrificing representativeness. Three groups of experiments are distinguished: *Air-1*, *Air-2*, and *Pure-Ar* (see Experimental Methods section). Experiments with air (*Air-1*, *Air-2*) were the major focus of this study, whereas experiments with argon (*Pure-Ar*) were intended to establish a common ground with the data available in the literature and serve as a check on our technique. The early results for air (*Air-1*) are considered preliminary, since a major improvement in reproducibility was achieved for the later results (*Air-2*). The factors that contributed to the improvement were a larger sample size, a greater number of measurements for each analysis on the mass spectrometer, and a subtle refinement of the various experimental steps.

TABLE 1: Data from Our Thermal Diffusion Experiments with Air and Pure Argon

GROUP	*SUBSET* [$\langle\delta^*_0\rangle$]	#	δ^*_0 ($^0/_{00}$)	δ^*_{TD} ($^0/_{00}$)	T_{COLD} (°C)	T_{HOT} (°C)	$\langle T\rangle$ (°C)	$\alpha_T\times10^3$
Air-1 [preliminary] air, ~0.2 atm	*1* [+0.016]	*1)*	0.014	0.624	–38.2	–22.6	–30.6	9.45
		2)	0.016	0.649	–38.2	–22.5	–30.5	9.78
		3)	0.016	0.634	–38.1	–22.4	–30.4	9.56
		4)	0.010	0.697	–38.4	–22.5	–30.6	10.39
		5)	0.021	0.629	–38.3	–22.4	–30.5	9.35
		6)	0.013	0.647	–37.9	–22.7	–30.5	10.08
		7)	0.025	0.638	–38.0	–22.4	–30.4	9.68
		8)	0.006	0.661	–38.3	–22.5	–30.6	9.90
		9)	0.024	0.633	–38.1	–22.5	–30.5	9.60
	2 [+0.013]	*1)*	0.018	0.619	–49.3	–33.9	–41.8	9.11
		2)	0.027	0.633	–49.8	–33.9	–42.0	9.01
		3)	0.010	0.661	–49.8	–33.9	–42.0	9.42
		4)	0.018	0.642	–49.5	–33.8	–41.8	9.27
		5)	0.011	0.629	–49.8	–33.7	–41.9	8.85
		6)	0.018	0.633	–49.5	–33.6	–41.7	9.02
		7)	–0.013	0.627	–49.7	–33.7	–41.9	8.88
		8)	0.022	0.623	–49.9	–33.8	–42.0	8.76
		9)	0.009	0.632	–49.6	–33.7	–41.8	9.01
		10)	–0.006	0.617	–50.0	–33.7	–42.0	8.56
		11)	0.024	0.651	–50.0	–33.8	–42.1	9.10
		12)	-	0.654	–50.3	–33.8	–42.2	8.97
Air-2 air, ~1 atm	*1* [+0.014] [+0.004]	*1)*	0.014	0.637	–37.9	–22.6	–30.4	9.88
		2)	0.011	0.618	–37.3	–22.5	–30.1	9.92
		3)	0.018	-	-	-	-	-
		1)	0.009	0.602	–37.4	–22.5	–30.1	9.75
		2)	–0.006	0.595	–37.3	–22.6	–30.1	9.77
		3)	–0.005	0.623	–37.8	–22.9	–30.5	10.08
		4)	0.009	0.595	–37.4	–22.6	–30.2	9.70
		5)	0.004	0.602	–37.6	–22.7	–30.3	9.75
		6)	0.010	0.606	–37.7	–22.7	–30.4	9.74
		7)	-	0.626	–38.0	–22.7	–30.5	9.86
	2 [+0.007]	*1)*	0.002	0.602	–50.8	–35.2	–43.2	8.77
		2)	0.006	0.623	–51.1	–35.2	–43.3	8.90
		3)	0.009	0.622	–51.1	–35.3	–43.4	8.94
		4)	0.002	0.623	–50.9	–35.0	–43.1	8.91
		5)	0.014	0.611	–50.8	–35.2	–43.2	8.90
	3 [+0.004]	*1)*	0.001	0.538	–65.3	–50.4	–58.0	7.71
		2)	0.002	0.539	–65.5	–50.4	–58.1	7.62
		3)	0.010	0.537	–65.1	–50.3	–57.9	7.75
	4 [+0.005]	*1)*	0.002	0.629	–19.8	–4.9	–12.5	10.92
		2)	0.007	0.613	–19.4	–4.7	–12.2	10.79
		3)	0.007	0.619	–19.5	–4.9	–12.3	10.97
Pure-Ar argon, ~1 atm	*1* [+0.009]	*1)*	0.007	0.712	–38.2	–22.8	–30.7	11.07
		2)	0.013	0.727	–38.3	–22.9	–30.8	11.30
		3)	0.005	0.704	–37.9	–22.7	–30.5	11.10
		4)	–0.001	0.713	–38.0	–22.7	–30.5	11.16
		5)	0.003	0.714	–38.1	–22.8	–30.6	11.18
		6)	0.011	0.709	–37.6	–22.6	–30.3	11.33
		7)	0.012	0.702	–37.4	–22.4	–30.1	11.23
		8)	0.011	0.702	–37.4	–22.4	–30.1	11.23
		9)	0.016	0.712	–37.4	–22.4	–30.1	11.39

Thermal diffusion experiments at the given temperature conditions were repeated multiple times and interspersed with complementary blank experiments. The overall sequence of such experiments constitutes a subset in a group (Table 1). A stable and undisturbed functioning of the mass spectrometer was generally characteristic of the period of time required to complete all of the experiments that form a subset (i.e., ~1–6 weeks). During that time no changes were made to the setting parameters of the mass spectrometer, and no tuning or repairs were needed (subset 1 of group *Air-2* is an exception, see below).

The parameters directly measured in a thermal diffusion experiment were the temperatures (T_{COLD}, T_{HOT}) at which a mixture was maintained, and the induced difference of isotopic composition (δ^* of eq 1), denoted as δ^*_{TD} in this case. No temperature difference was used in blank experiments, hence the difference of isotopic composition in that case (denoted as δ^*_0) is expected to be zero.

The changing, nonzero values of δ^*_0 (Table 1) indicate the presence of a small time-varying offset from the "true" zero in a mass spectrometer's reading. The offset is arbitrarily considered to have remained the same throughout the time period corresponding to a given subset. The offset is estimated by the quantity $\langle\delta^*_0\rangle$ (Table 1), which is the average of all δ^*_0 values in a subset. Two different values of $\langle\delta^*_0\rangle$ are shown for subset 1 of group *Air-2*, because the corresponding sequence of experiments was incidentally interrupted after the third thermal diffusion experiment (a repair was needed because of a short circuit). The first $\langle\delta^*_0\rangle$ value in that case corresponds to the first two thermal diffusion experiments (and is the mean of the first three δ^*_0 values), and the second to the remaining experiments.

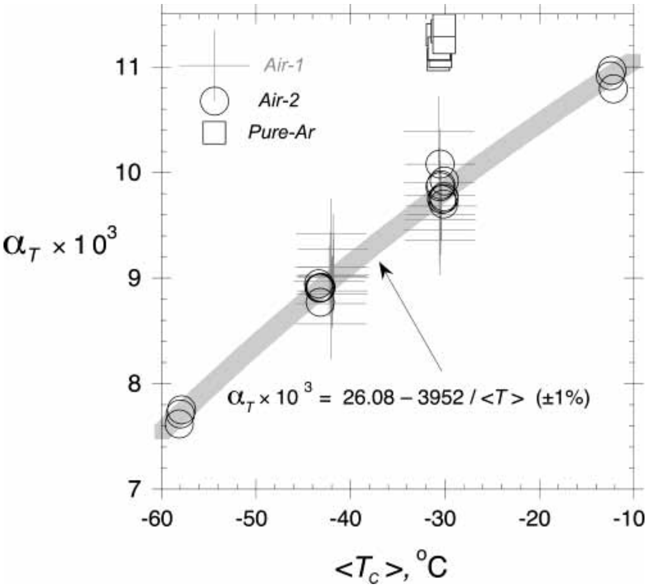

Figure 3. Thermal diffusion factor α_T for air and argon obtained in our experiments. Temperature dependence of α_T for air is described by an empirical equation indicated on the plot (eq 5). The curve is a least-squares fit to the *Air-2* data. Thickness of the curve corresponds to the uncertainty of ±1%.

The effective average temperature $\langle T \rangle$ for a thermal diffusion experiment (Table 1) was calculated using eq 4. The corresponding value of the thermal diffusion factor α_T was obtained by substituting the quantity ($\delta^*_{TD} - \langle \delta^*_0 \rangle$) in place of δ^* in eq 2. (The value of $\langle \delta^*_0 \rangle$ corresponds to the same subset as that of δ^*_{TD}). Hence, the varying offset of the zero reading of the mass spectrometer has been taken into account when calculating α_T. The magnitude of the "zero-offset correction" to the quantity δ^*_{TD} typically amounted to ~1% and never more than ~2% of its value.

The thermal diffusion factor obtained from our experiments is plotted as a function of the effective average temperature in Figure 3. The size of the data points for each group of experiments corresponds to the uncertainties of respective α_T values (2σ), as determined below. A least-squares fit to the data of group *Air-2* of the form given by eq 3 yields the following empirical equation:

$$\alpha_T(\langle T \rangle) \times 10^3 = 26.08 - 3952/\langle T \rangle \qquad (5)$$

Most of the experimental results correspond to the value of $\langle T \rangle$ of approximately −30 °C (Table 1). It would be desirable to "scale" them to that exact temperature in order to find the average values of α_T and the standard deviations for groups *Air-1*, *Air-2*, and *Pure-Ar*. The "scaling" is performed by using the local value of the derivative to $\alpha_T(\langle T \rangle) \times 10^3$ of eq 5 at −30.0 °C, which is 0.067/K. For example, the value of $\alpha_T \times 10^3$ of 9.88 at −30.4 °C translates to the value of 9.91 at −30.0 °C. Mean values of $\alpha_T \times 10^3$ scaled to −30.0 °C are 9.79, 9.85, and 11.25 for groups *Air-1*, *Air-2*, and *Pure-Ar*, respectively (the number of values averaged was nine in each case). For group *Pure-Ar*, it was assumed that the derivative value at −30 °C is the same for pure argon as for air. The raw standard deviations (1σ) for the respective groups of results are 0.33, 0.13, and 0.10, corresponding to relative raw standard deviations of ~3%, ~1%, and ~1%. Hereafter, we present both raw standard deviations (σ) and the standard deviations of the mean values $\sigma_m \equiv \sigma/\sqrt{N}$, where N is the number of repeated experiments.

Discussion

The scatter of the experimental values of the thermal diffusion factor α_T at −30.0 °C serves to indicate the overall raw experimental uncertainty (~1% for *Air-2* and *Pure-Ar*). The calculation of this uncertainty (given in Results section) can also be approached differently, using the typical uncertainties in the parameters entering eq 2. The values of temperatures reported in Table 1 are typically known to ±0.1 °C, whereas the difference of isotopic composition (δ^*_{TD} or δ^*_0) is characterized by an error ($1\sigma_m$) of $\pm 0.007^0/_{00}$ (group *Air-1*), $\pm 0.003^0/_{00}$ (group *Air-2*), or $\pm 0.001^0/_{00}$ (group *Pure-Ar*). Here σ_m is the standard deviation of the mean δ^* value for repeated determinations on the same thermal diffusion or blank gas sample. The combined errors translate into a projected raw standard deviation of ±0.19 in the values of $\alpha_T \times 10^3$ for group *Air-1*, ±0.12 for *Air-2*, and ±0.11 for *Pure-Ar*. The similarity of the projected error and the measured error in the latter two argues against the presence of any major unaccounted-for sources of error. On the other hand, the actual observed error in α_T is larger than expected in the case of group *Air-1*, likely due to errors associated with unsophisticated gas handling.

The average values of the thermal diffusion factor at −30.0 °C (denoted $\langle \alpha_T \rangle$; see Results section) are not significantly different for groups *Air-1* ($\langle \alpha_T \rangle \times 10^3 = 9.79 \pm 0.11$) and *Air-2* ($\langle \alpha_T \rangle \times 10^3 = 9.85 \pm 0.04$) at the 95% *t*-test confidence limit ($N = 9$ in each case). A preferred result for air is that of group *Air-2*, since the uncertainty of the preliminary group *Air-1* results is greater. The difference of 1.40 between the average values of $\alpha_T \times 10^3$ at −30.0 °C for groups *Air-2* and *Pure-Ar* ($\langle \alpha_T \rangle \times 10^3 = 11.25 \pm 0.03$) is found to be statistically significant (95% confidence limit). Evidently, the presence of N_2, O_2, and other gases in air reduces the value of the thermal diffusion factor for $^{40}Ar/^{36}Ar$ through "nonseparative collisions" (see Introduction section). A similar reduction has been observed by Van der Valk and De Vries[23] on other mixtures.

The uncertainty in the deduced empirical equation for the temperature dependence of the thermal diffusion factor for air may be estimated from the departure of the data from eq 5. The pooled standard deviation (psd) of the data points of group *Air-2* from the curve corresponding to eq 5 (see Figure 3) is equal to 0.10 (psd is defined as the square root of the sum of squared differences between a data point and a corresponding curve value, divided by the number of degrees of freedom). This value has a magnitude similar to that of the overall raw uncertainty of the $\alpha_T \times 10^3$ values of group *Air-2* (i.e. ±0.13). Hence, eq 5 can be used to obtain the values of the thermal diffusion factor for air at selected temperatures from the range −60 to −10 °C, with an uncertainty of ~1%.

Figure 4 shows the literature data for pure argon in the temperature range 100 to 800 K, with our average results shown for comparison. Clearly, the offset between the thermal diffusion factor for air and for argon that we find (i.e., 1.40 ± 0.05, in terms of $\alpha_T \times 10^3$) is beyond the resolution capability of the published results. The magnitude of the offset is similar to the typical uncertainty of the literature data, which is ±1 in terms of $\alpha_T \times 10^3$. Our average result for pure argon at −30.0 °C (see Figure 4) is characterized by a precision >10 times greater than the previously available data, and may serve as an intercomparison point for future studies.

It is instructive for comparison purposes to calculate the desired thermal diffusion factors from theory.[30] Three examples for pure argon constants based on considerations found in the literature are given. An attractively simple approximation to the

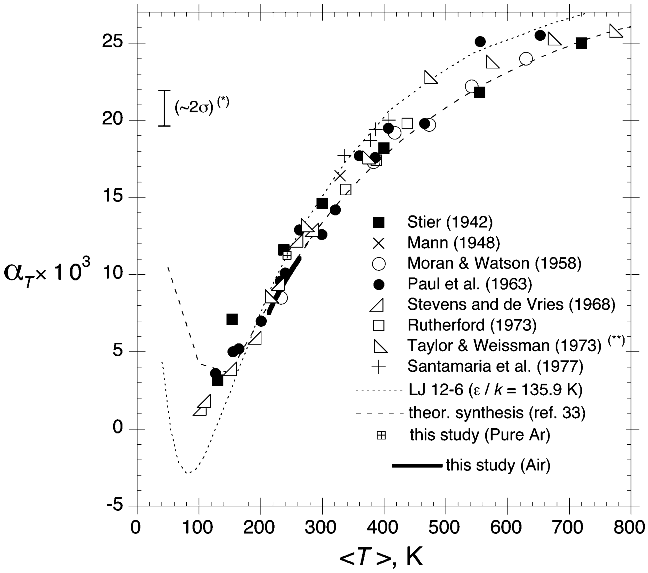

Figure 4. Literature data for the thermal diffusion factor of ^{40}Ar/^{36}Ar in pure argon. Our average results for pure argon and air are shown for comparison. The error bar for our data point for pure argon (11.25 ± 0.03) is ~7 times smaller than the size of the data point. The thickness of the curve representing our data for air roughly corresponds to the uncertainty of ±1%. Dashed lines correspond to theoretical calculations (see Discussion section). The force constant for the Lennard-Jones potential ($\epsilon/k = 135.9$ K) was chosen such that the calculated α_T would fit through our average data point for pure argon. $^{(*)}$The typical error (~2σ) of the data from the literature. $^{(**)}$The original value for one of the data points has been corrected in the companion paper.[21]

isotopic thermal diffusion factor can be written as[31]

$$\alpha_T \cong 1.69\left(2-\frac{\partial \ln D}{\partial \ln T}\right)\left(\frac{M_1-M_2}{M_1+M_2}\right) \qquad (6)$$

where D is the self-diffusion coefficient of the gas, and M_1 and M_2 are the masses of isotopes of that gas. The roughly correct magnitude of α_T of 13×10^{-3} for ^{40}Ar/^{36}Ar in pure gas is obtained when the somewhat poorly known quantity ($\partial \ln D/\partial \ln T$) is taken to equal 1.85. The Lennard-Jones 12-6 interatomic potential for argon with a force constant ϵ/k set to 135.9 K yields a curve for α_T shown in Figure 4 (the so-called second Kihara's approximation was employed[32]). Also plotted in Figure 4 are theoretical results of Kestin et al.,[33] who constructed an elaborate internally consistent database of noble gas transport properties on the basis of the simultaneous fitting of all available transport data and interrelations between them known from theory. A theoretical calculation of the effect of dilution of ^{86}Kr/^{84}Kr and some other isotopic pairs by a third gas on their α_T values has been undertaken by Kincaid et al.,[24] yielding in some cases reductions similar to those we have found for argon in air (i.e., ~14%). Importantly, theoretical calculations such as these do not constrain the constants to the needed level of precision for paleoenvironmental studies.

The significance of the newly available thermal diffusion factors for isotopic argon, combined with those for isotopic nitrogen[25] in air, lies in the fact that they provide improved confidence in reconstructions of the magnitudes of past abrupt climate changes that may recur in the future.[2] The application of the gas-isotope method has been hampered by the lack of appropriate thermal diffusion constants.[7] For example the magnitude of the abrupt warming at the end of the Younger Dryas cold interval in Greenland (Figure 1) was estimated at 5−10 °C as the method was first developed,[7] whereas the new constants allow refinement of this number to 9 ± 3 °C (unpublished). That value can be constrained even further if fresh ice is analyzed using the more precise analytical procedures now available. Precise temperature information about past climates is critical in validating and calibrating climate-prediction models. Most current climate models apparently do not capture some of the essential physics of abrupt climate change, because they underestimate their known magnitudes.[2]

Conclusions

The values of the thermal diffusion factor α_T of ^{40}Ar/^{36}Ar in air have been determined for the first time. They are represented by an empirical equation $\alpha_T \times 10^3 = 26.08 - 3952/\langle T \rangle$ (±1%) in the range of temperatures −60 to −10 °C. The values of the thermal diffusion factor differ significantly for air and for pure argon: at −30.0 °C they are 9.85 ± 0.04 and 11.25 ± 0.03 for air and argon, respectively. Experimental techniques used in this study employed a modern mass spectrometer and allowed a precision much greater than was previously possible. It would not be appropriate to use the pure-gas literature data for paleoreconstruction purposes because of the ~14% offset between air and pure argon values. Results reported here enable more accurate reconstructions of abrupt climate change magnitudes, which are valuable for assessing the validity of climate-prediction models.

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