

## METHODS

**Deriving noble gas elemental and isotope ratios from ice cores.** The analytical method we used to analyse the trapped air in the ice samples is described in ref. 10. Briefly, about 800 g of ice are melted in an evacuated vacuum vessel and the released air is cryo-trapped in a dip tube cooled with liquid helium. In a second step, the air is split into two subsamples and from one of them all non-noble gases are removed via a Zr/Al getter. Then, each of these two subsamples is analysed separately on a specific dual-inlet isotope ratio mass spectrometer. The two machines provide high-precision deviations (usually expressed in  $\delta$ -notation) from a standard, which is in our case the current atmospheric composition. Specifically, the two machines provide the following main isotope ratios (mass ratios):  $\delta^{15}\text{N}$  ( $^{29}\text{N}_2/^{28}\text{N}_2$ ),  $\delta^{40}\text{Ar}$  ( $^{40}\text{Ar}/^{36}\text{Ar}$ ) and  $\delta^{86}\text{Kr}$  ( $^{86}\text{Kr}/^{82}\text{Kr}$ ); as well as the following main elemental ratios:  $\delta\text{Ar}/\text{N}_2$  ( $^{40}\text{Ar}/^{28}\text{N}_2$ ),  $\delta\text{Kr}/\text{Ar}$  ( $^{84}\text{Kr}/^{40}\text{Ar}$ ) and  $\delta\text{Xe}/\text{Ar}$  ( $^{132}\text{Xe}/^{40}\text{Ar}$ ). The elemental ratios of  $\delta\text{Kr}/\text{N}_2$  ( $^{84}\text{Kr}/^{28}\text{N}_2$ ),  $\delta\text{Xe}/\text{N}_2$  ( $^{132}\text{Xe}/^{28}\text{N}_2$ ) and  $\delta\text{Xe}/\text{Kr}$  ( $^{132}\text{Xe}/^{84}\text{Kr}$ ), which are used for the MOT reconstruction, are derived by combining the machine elemental ratios accordingly. The isotope ratios are used to correct for gravitational and thermal fractionation in the firn column as described in Methods subsection 'Inferring atmospheric noble gas ratios from the raw data'.

The dataset presented here was obtained over the course of three measurement campaigns in 2014 and 2015. The first campaign applied method 1 described in ref. 10 during which 21 samples of the WAIS Divide ice core were analysed. The results of two of the samples were fully or partly rejected owing to measurement artefacts or artefacts occurring in the bubble-to-clathrate-transition zone (BCTZ) of ice cores (see Methods subsection 'Sample rejection and the data gap from 4,000–7,500 yr ago') below). The second and third campaigns applied method 2 of ref. 10, in which 42 and 15 samples, respectively, from the same core were analysed. Six samples of the second campaign were partly or fully rejected for the same types of reasons as mentioned above; two rejections were required in the third campaign samples.

**Sample rejection and the data gap from 4,000–7,500 yr ago.** 10 out of the 78 samples we measured for this study are subject to sample rejections. For 3 of them, however, the entire set of data did not have to be rejected (partial rejections). Partial rejections can occur when a measurement error occurs after the sample splitting<sup>10</sup>, thus affecting only the corresponding dataset. Another possibility is that a minor error only affects the parameters that are most sensitive to it: for example, a thermal gradient during the splitting process will affect  $\delta\text{Ar}/\text{N}_2$  the most because of its strong thermal diffusion sensitivity<sup>43</sup> relative to the precision obtained<sup>10</sup>. Depending on the amplitude of such an error, some parameters might appear as outliers, while others do not. It is therefore important to check all parameters thoroughly and individually and put them into the context (if possible) of the whole record, as done for the example of the BCTZ in ref. 10. For the first case (affecting one subsample), we have two such cases where the primary heavy noble gas data was lost owing to a failure of the corresponding mass spectrometer. For the second case of single parameter outliers, we rejected the data including Xe, but kept the remaining parameters. These affected samples could be replaced by measuring a neighbouring sample.

The full rejections affect 7 samples, of which one is related to operational errors during the measurement procedure and another one to a contaminant in the sample. These two samples could also be replaced by measuring a neighbouring sample. The remaining 5 of these full rejections are related to gas fractionation in the BCTZ, which creates a data gap<sup>10</sup> in our record from about 4,000–7,500 yr BP that can only be filled with measurements from another core. In the BCTZ, gases are fractionated due to gas-loss and fractionation processes between the bubbles and clathrates occurring in this zone<sup>44,45</sup>. We identified this zone primarily by inconsistencies or outliers in  $\delta\text{Ar}/\text{N}_2$  with respect to  $\delta^{40}\text{Ar}$  ( $^{40}\text{Ar}/^{36}\text{Ar}$ ) as seen in ref. 44, but we also looked for inconsistencies in all other observed isotope and element ratios<sup>10</sup>. The BCTZ is also known as the brittle ice zone<sup>46</sup> because of the very brittle behaviour of the ice core and is often reported as such by the drilling team. However, the way we observe the BCTZ through the gas measurements does not necessarily line up with the observation via the core quality or the appearance/disappearance of clathrates and bubbles in the ice. The reason is that at the upper end of the BCTZ some fractionation has to build up in order to obtain noticeable effects from the gas diffusion processes in the extracted air, and at the lower end, the gas fractionation can 'tail' into the fully clathrated ice zone<sup>45</sup>. Hence, we expect the alterations in the gas record due to the BCTZ which we observe via the gas measurements to be shifted downwards in depth compared to the zone defined by the core quality and inclusion observations; however, it is not clear to what extent. It was a goal of this study and of ref. 10 to identify the BCTZ-affected zone for the parameters we obtained.

The top end of the BCTZ-affected zone was found between 922 m and 1,120 m depth and the bottom end was found between 1,510 m and 1,572 m depth<sup>10</sup>, while the core quality and inclusion observations find the BCTZ or 'brittle ice zone' at

520–1,310 m depth<sup>47,48</sup>. This large shift of several hundred meters is surprising and has not been observed so far in other gas records; however, it is specific for the ice core and the gases we observe here and could also vary between different methods for the same gas species. Nevertheless, it is interesting to note that we find gas fractionation effects of the BCTZ to affect our data in a depth interval that is considerably deeper and slightly narrower than what the ice observations suggest.

A further quality control was done by comparing the reconstructed atmospheric  $\delta^{18}\text{O}$  ( $^{34}\text{O}_2/^{32}\text{O}_2$ ) values with the record of ref. 49. However, it turned out that this control is not very sensitive and did not uncover more outliers than those already identified with the parameters mentioned above. Nevertheless, it is important to check all these parameters to ensure the consistency of the great wealth of data the method provides, because many elements of this complicated method can alter the measurement<sup>10</sup>. The high quality of the record (outside the BCTZ) is probably attributable to careful core handling and processing under cold conditions (the ice-processing tent in the field was actively cooled to  $-25^\circ\text{C}$ )<sup>50</sup> and our subsamples were kept in a  $-50^\circ\text{C}$  freezer whenever possible to prevent outgassing<sup>51</sup>.

**Potential biases in MOT from noble gases in ice core samples.** Concentration or ratio changes in the most prominent gases in the atmosphere ( $\text{CO}_2$  and  $\text{O}_2$ ) are the result of a combination of complex biogeochemical processes reacting or adapting to changing climate<sup>49,52</sup>. Therefore, these well studied gases contain an intrinsic delay and low-pass filtering behaviour with respect to climate change that are dependent on the inertia of the underlying mechanisms. In contrast, the noble gases analysed in this study are not subject to any biogeochemical process and their atmospheric changes are dependent only on their physical transportation in the atmosphere–ocean system. For our application here the relevant physical transportation processes are (1) the exchange between ocean and atmosphere, (2) the mixing within the atmosphere and (3) the transport from the atmosphere into the ice. We discuss these three elements in detail to show that they do not create a temporal modulation of the observed noble gases with respect to MOT.

All the heat fluxes in and out of the ocean take place at the ocean–atmosphere interface. There is no internal heat source in the ocean, and geothermal heating (the most potent heat source for the ocean besides the atmosphere/surface) is negligible compared to the forcing at the surface<sup>11</sup>. Hence, if the noble gas transport across the ocean–atmosphere interface is following the equilibrium solubility function as assumed here, for each joule going in or out of the ocean a corresponding number of noble gas molecules gets released from or dissolved in the ocean, respectively. Internal mixing of water masses with different temperatures mixes joules and noble gases in the same way. Although this would lead to local solubility disequilibrium in these mixed waters owing to the nonlinearity in the solubility functions, it does not affect the measured atmospheric composition, because this process takes place inside the ocean.

The assumption of gas equilibrium is justified because the gas transfer velocity between surface ocean and atmosphere of the observed gases lies in the range  $13\text{--}16\text{ cm h}^{-1}$  ( $3^\circ\text{C}$  water temperature,  $10\text{ m s}^{-1}$  wind speed)<sup>53</sup>, which translates into an equilibration timescale for these gases of one to two months with a mixed layer of 200 m thickness as found in polar regions (shorter equilibration in other regions). This is short enough to capture the strong seasonality in the hemispheric ocean heat fluxes as evidenced by atmospheric measurements<sup>54</sup> of  $\text{Ar}/\text{N}_2$ , and is also much shorter than the residence time of water parcels in the mixed layer, in particular in the Southern Ocean, where gas equilibration is most critical<sup>55</sup>. There is a slight disequilibrium of noble gases in the deep ocean<sup>15,16</sup>, but this does not affect the relatively fast equilibration timescales of the surface ocean. However, it has implications for the absolute scale of our proxy, as discussed below in Methods subsection 'Box model to infer MOT'. For these reasons, the ocean–atmosphere gas exchange does not create any delay or low-pass filtering behaviour of atmospheric noble gases with respect to climate change/ocean temperature changes in our record. This is also supported by the model simulation of ref. 11, which includes physical gas exchange processes and ocean circulations in a three-dimensional model. The ocean circulation perturbation experiments done in this study do not show any temporal modulation between the modelled ocean temperature and atmospheric noble gases.

Mixing within the atmosphere also takes place on timescales of months to a year, for which reason the studied gas mixing ratios probably contain geospatial differences on seasonal timescales<sup>54</sup> comparable to  $\text{Ar}/\text{N}_2$ . However, these seasonal variations are smoothed in the trapped air in ice core samples because of the low-pass filtering of the stagnant firn air column through which atmospheric signals have to be transported before they are trapped in the ice<sup>56</sup>. The filter time characteristic for the WAIS Divide ice core varies<sup>29</sup> between 20 yr and 50 yr, meaning that the trapped air in the ice is an average value over these time periods. This filter characteristic is in fact exceptionally low for Antarctic ice core standards and is a