One way to look at the Kr anomaly is that the heavier Kr—and therefore also slower diffusing gas in the firn air column—deviates from the lighter N_2 and Ar isotopes towards a smaller gravitational enrichment. This could be related to the relatively fast transformation of the WAIS Divide firn air column, which could lead to disequilibrium in the firn air such that the slow diffusing gases would not be able to 'catch up' with the fast downward advection of the ice matrix. This effect would be stronger the more slowly the gases diffuse through the firn air, which is (to first order) related to the weight of the molecule; hence N_2 and Ar would be less affected than the heavier gases like Kr and Xe. By using the isotopes of a light molecule to correct for gravity (δ^{40}Ar in our case) the gravitational component of the heavier molecules might be overestimated. This would be consistent with the depletion in the reconstructed atmospheric δ^{86}Kr (Extended Data Fig. 1a), and potentially also δKr/N_2, δXe/N_2 and δXe/Kr. If this were the case, however, we would expect an even stronger 'anomaly' for Xe isotopes (δ^{132}Xe (^{132}Xe/^{129}Xe)) than for Kr isotopes (by about a factor of two, based on the diffusivity in air/total mass). For the data obtained in the last campaign (see Methods subsection 'Deriving noble gas elemental and isotope ratios from ice cores') we changed the mass spectrometer method so that we were able to obtain δ^{132}Xe (not shown here), though with much worse precision[10] than for δ^{86}Kr. The data indicates no anomaly for δ^{132}Xe, which is not what we expected, but the data are sparse and further work is needed to rule this out.

That a Kr anomaly (or δ^{86}Kr$_{excess}$) is indicative for disequilibrium effects in the firn air column is shown by the firn air transport modelling study of ref. 61. The model, however, currently lacks experimental support, for which reason further firn air studies at different sites with different firn transformation characteristics are needed. For our purposes, such work would also need to include the effects on the heavy noble gases (isotopes and mixing ratios), in particular δKr/N_2, δXe/N_2 and δXe/Kr. This has the potential to strongly reduce the current uncertainty of our MOT data, both on the absolute and relative scale.

Box model to infer MOT. To derive MOT from the heavy noble gas data, a box model is used as described in ref. 10. The basic assumption in the model is that N_2, Kr and Xe are conserved in the ocean–atmosphere system and that these gases are in solubility equilibrium between the two reservoirs. Hence, any change in ocean temperature changes the well defined equilibrium state of the noble gases. Since the solubilities of the individual gases are not equally sensitive to water temperature changes, the ocean temperature change leads to a change in atmospheric mixing ratio, which can be observed with ice cores. Here, the model is used backwards, using the measured atmospheric ratios as input and deriving the corresponding MOT by iteration. We use the same solubility functions as used in ref. 15 (which uses the solubility function of ref. 62 for N_2, of ref. 63 for Kr, and of ref. 64 for Xe) with the same 2% correction for the original Xe solubility function.

The first rough validation of this simple box model comes from the work of ref. 9, which showed an agreement of MOT derived from their noble gas ratios measurements in ice cores with the MOT independently derived from ocean sediment core proxies. Furthermore, the simple box model has been tested against a climate model with intermediate complexity[11] and also showed a negligible difference between the two models despite the large complexity difference. The same study also confirmed that the only non-surface heat source for the ocean—geothermal heating—is too small to affect the noble gas–MOT relation noticeably. However, in ref. 11 a sea ice gas-exchange effect is also implemented, which resulted in different noble-gas-to-MOT relationships from those of the non-sea-ice case. From the new noble gas data of this study, we can now conclude that their sea-ice effect is overestimated, as the corresponding δXe/N_2 scaling would suggest an unrealistically low MOT for LGM of at least 4 °C below today (our −4‰ value for the LGM is no longer covered by their results).

Owing to the much higher quality of the noble gas data presented in this study, smaller effects not considered in ref. 9 can become relevant. Therefore, we implemented and tested different model elements to assess all possible sources of uncertainties within our box model. An overview of the different elements is shown in Extended Data Table 1, including the corresponding effects onto the LGM–Holocene MOT difference. The effects were derived by successively implementing the elements from top to bottom of the table.

The most minimalist model consists only of one ocean and one atmosphere box and uses only the measured noble gas ratios (δKr/N_2, δXe/N_2 or δXe/Kr) to infer MOT. This model setting suggests the LGM MOT to be roughly −2.0 °C colder than the Holocene, which seems too low compared to the −2.5 °C to −3.5 °C suggested by sediment core proxies and model studies[4,5,7,11]. Nevertheless, we can assess the uncertainties of our MOT estimate within this minimalist model. The only source of uncertainty here is the analytical uncertainty which we propagate into the total MOT uncertainty using 3,000 Monte-Carlo simulations (3,000 realizations of MOT values while changing the noble gas ratios within their analytical uncertainties). The corresponding MOT uncertainty is on average

±0.26 °C for δKr/N_2, ±0.15 °C for δXe/N_2 and ±0.17 °C for δXe/Kr, respectively, comparable to what is reported in ref. 10 for the individual methods.

As ref. 9 has already pointed out, sea-level change has an important effect on the noble gas distribution in the ocean–atmosphere system owing to the associated changes in ocean volume, ocean salinity and sea surface pressure. Salinity and sea surface pressure affects the solubility equilibrium state and the ocean volume defines the total storage capacity of the ocean. Here we use the sea-level change record from ref. 14 to derive these elements. Implementing the sea-level change effects increases the LGM–Holocene difference by 0.5 °C, with the largest contribution by the volume effect and the other two effects roughly compensating each other (see Extended Data Table 1). The uncertainty of the sea-level change record is also propagated into our total MOT uncertainty estimate; however, its contribution is below 10% of that of the analytical uncertainty.

The two elements included so far correspond to what has been implemented in the previous works already. We now investigate further elements that potentially have a considerable effect on our MOT reconstruction. The colder glacial climate is known to be drier than the interglacial/modern climate because of its lower water content. A lower water content also means a lower total mass of the atmosphere and hence, a lower average sea surface pressure. We estimate this effect using the current atmospheric H_2O concentration of about 2.5% (ref. 65) and a Clausius–Clapeyron relation of atmospheric H_2O concentration and temperature[66] while taking our MOT differences relative to today to be the effective surface temperature change. This approach might slightly underestimate the effective change in H_2O concentration/sea surface pressure because the average surface temperature change might have been slightly larger[6,67]; however, considering the small effect on the MOT reconstruction and the uncertainties related to such global surface temperature estimates, this approach is justified. For the sake of completeness, we implemented a linear change of this effect from the LGM to the beginning of the Holocene in our final MOT record.

The majority of the ocean volume gets its temperature and noble gas imprint, respectively, in the high latitudes around Antarctica where the largest portion of the deep water is formed[21]. In these regions the average sea surface pressure is slightly lower by about 3% compared to the average ocean surface[68]. We therefore assume a time-independent offset of the effective sea surface pressure by 3% to calculate the solubility equilibrium state in our box model. This slightly reduces the noble gas amounts dissolved in the ocean and causes the noble gas ratios to be less sensitive to MOT changes. Hence, this effect requires a slightly lower LGM temperature of −0.05 °C to compensate for the reduced sensitivity. Regional sea surface pressure changes between glacial and interglacial climate are simulated to be in the range of a few hectopascals[69], which is one to two orders of magnitude smaller than the global sea surface pressure effect from changing sea levels. Therefore we can assume this pressure bias to be time-independent.

As shown in refs 15 and 16, deep waters today are slightly undersaturated in Kr and Xe with respect to the water temperature. This phenomenon is explained by the strong cooling rate these waters experience before they sink into the deep ocean, preventing the noble gases from fully equilibrating with the waters before they sink[15]. The observed undersaturation is roughly 2% for Xe and 1.3% for Kr, respectively. Owing to the large differences expected in the glacial deep-water circulations compared to today[22], it is possible that this undersaturation pattern was different for glacial periods. As the general overturning of the deep circulation is expected to have been slower, it is likely that the cooling rate was smaller in glacial times and, hence, the undersaturation smaller. The most extreme case—where noble gases were in full equilibrium in glacial times—leads to unrealistically large discrepancies between the MOT derived from the different ratios. The change of undersaturation that keeps MOT differences roughly within the allowed uncertainty range is 50% (meaning that Xe undersaturation at LGM could have been 1% and Kr accordingly). This causes the LGM temperature derived from the different ratios to be up to 0.4 °C warmer as with a constant undersaturation (Xe/Kr being most sensitive followed by Xe/N_2, and almost no effect for Kr/N_2). Since the effective change in undersaturation is unknown, we calculate MOT realizations for the case with constant undersaturation at all times and a 50% change (linear) over the course of the LGM–Holocene transition (17,900–11,550 yr BP) and combine the two scenarios for our best-estimate record. This leads to a slight shift of the average MOT towards warmer temperatures and an increase in the uncertainty range for the earlier part of the record (see also LGM–Holocene MOT change estimate below).

AABW and NADW—which together represent more than half of the global ocean volume today and probably occupied even more in glacial times[22]—have different characteristics with regard to temperature and salinity (see also Fig. 1). Using only one ocean box in our model as done so far implies that the global temperature distribution in the ocean was the same as today and that all water masses changed their temperature equally. However, AABW is −0.88 °C today[20]