



Impact of diapycnal mixing on the saturation state of argon in the subtropical North Pacific

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[1] Diapycnal mixing plays an important role in both physical and biogeochemical processes in the oceans, yet the rate of tracer mixing has not been adequately quantified. A theoretical analysis predicts that diapycnal mixing should raise the saturation state of noble gases in the thermocline, at a rate proportional to diapycnal diffusivity. We apply this theory to existing measurements of argon in the ventilated thermocline, where the increase in the saturation state should be proportional to the integrated effect of diapycnal mixing. Combining argon observations from time-series stations in the North Pacific with freon ventilation age, we tentatively estimate the regional diapycnal diffusivity at $0.35 \pm 0.21 \cdot 10^{-4} \text{ m}^2\text{s}^{-1}$. Major sources of uncertainty include spatial and temporal variability and sparse sampling. These uncertainties could be significantly reduced using measurements of several noble gases in a transect from the isopycnal outcrop to the interior gyre. **Citation:** Ito, T., C. Deutsch, S. Emerson, and R. C. Hamme (2007), Impact of diapycnal mixing on the saturation state of argon in the subtropical North Pacific, *Geophys. Res. Lett.*, *34*, L09602, doi:10.1029/2006GL029209.

1. Introduction

[2] Mixing across the ocean's pycnocline controls the upwelling of waters in the middle and low latitudes, and impacts the global transport of heat, nutrients and carbon in the oceans. However, the distribution and magnitude of diapycnal diffusivity (κ) is poorly known. Recent field studies show that κ may vary by more than two orders of magnitude in the interior ocean [Polzin *et al.*, 1997], while tracer release experiments [Ledwell *et al.*, 1998] and microstructure measurements [Gregg, 1987] suggest that κ is only on the order of $10^{-5} \text{ m}^2\text{s}^{-1}$ in the thermocline.

[3] Noble gases are not affected by biology and can be useful tracers of physical ocean processes. Unlike transient inert tracers, noble gases such as argon have a constant atmospheric history, so that their distribution in the ocean is governed by the time-mean structure of ocean transport and processes that occur at the air-sea interface.

[4] The thermodynamic solubility of dissolved argon is a nonlinear function of temperature; thus ocean mixing processes can raise the saturation state of argon as depicted in Figure 1a. Bieri *et al.* [1966] were among the first to suggest

that the saturation state of argon might reflect diapycnal mixing in the water column, and this mechanism has been demonstrated in numerical simulations [Henning *et al.*, 2006] and in equatorial field measurements [Gehrie *et al.*, 2006].

[5] Ito and Deutsch [2006] (hereinafter referred ID06) derived a mathematical relationship between the saturation state of argon (ΔAr) and diapycnal diffusivity. The theory predicts that the magnitude of ΔAr will be sensitive to the rate of diapycnal mixing in the subtropical thermocline where ΔAr should be controlled by the interplay between isopycnal ventilation and diapycnal mixing. Dissolved noble gases integrate the effect of diapycnal mixing through the history of a water parcel, so that the gas's saturation state in the interior ocean is elevated relative to the isopycnal outcrop. Thus, the difference in ΔAr between the interior ocean and the outcrop may be used as a regional measure of κ averaged over the timescale of thermocline ventilation. This theoretical prediction was in agreement with a suite of numerical experiments using an explicit argon cycle and ocean general circulation model where diapycnal diffusivity in the thermocline was varied over a wide range.

[6] In contrast, the sensitivity of ΔAr to the rate of diapycnal mixing in the tropical thermocline is weak because the tracer distribution is dominated by the vertical advective-diffusive balance, which involves two end-members only. Although the observed supersaturation in the tropical thermocline reflects the existence of diapycnal mixing, Gehrie *et al.* [2006] demonstrate that the magnitude of ΔAr has little predictive power for the rate of diapycnal mixing in this location.

[7] In this paper, we use existing observations of ΔAr in the ventilated thermocline (1) to test the theoretical prediction that ΔAr increases along ventilation pathways in the thermocline and (2) to make a preliminary estimate for the temporally averaged diapycnal diffusivity in the region based on the theoretical relationship between the rate of increase in ΔAr and the diapycnal diffusivity.

[8] In section 2, we present a brief summary of Ito and Deutsch's [2006] theory and its application to field observations. In section 3, we analyze existing argon data in the light of the theory, and calculate a provisional diapycnal diffusivity. Section 4 examines the uncertainties involved in such estimates and implications for the use of noble gases as a measure of ocean mixing.

2. Theoretical Background

[9] The saturation state of Ar is commonly expressed as

$$\Delta\text{Ar} = \frac{\delta\text{Ar}}{[\text{Ar}_{sat}]} \times 100(\%) \quad (1)$$

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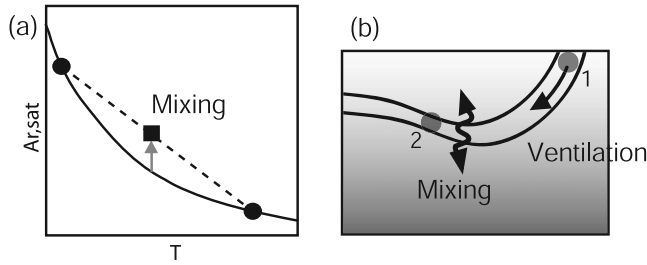


Figure 1. A schematic diagram illustrating the impact of diapycnal mixing on argon saturation. (a) Mixing of two water masses (filled circles) produces temperature and Ar properties along a conservative mixing line (dash line) which lies above the Ar saturation line (solid line, curvature exaggerated for clarity). (b) While diapycnal mixing tends to increase ΔAr , horizontal ventilation brings ΔAr in the interior ocean back toward its surface value. The relative strength of the two competing processes determines the large-scale gradient of ΔAr along a density surface.

where $\delta Ar = [Ar] - [Ar_{sat}]$ is the difference between measured and saturated Ar concentrations. Supersaturations (undersaturations) are represented by positive (negative) values of both δAr and ΔAr . Combining the tracer equations for T and Ar , the governing equation for δAr in a stratified, three-dimensional ocean can be written (ID06):

$$\frac{D\delta Ar}{Dt} = F + \text{diff}(\delta Ar) + \text{SPR} \quad (2)$$

where $\frac{D}{Dt}$ is the Lagrangian derivative following the mean circulation. F is the net surface flux including the effects of air-sea gas and heat transfer. Diffusive transport ($\text{diff}(\delta Ar)$) redistributes δAr through eddy mixing both along and across isopycnals. The effect of diapycnal mixing also gives rise to a positive source of δAr ; the saturation production rate (SPR). SPR is defined as $(\frac{\partial^2 Ar_{sat}}{\partial T^2}) \kappa (\frac{\partial T}{\partial z})^2$; thus the source of δAr is proportional to the second derivative (curvature) of the solubility of argon, to diapycnal diffusivity, and to the thermal stratification squared. Note that SPR vanishes if $[Ar_{sat}]$ is a linear function of T .

[10] Scale analyses and numerical simulations (ID06) suggest that advective transport of δAr dominates over diffusive transport in the subtropical, ventilated thermocline. Under typical thermocline conditions, supersaturation caused by $\text{diff}(\delta Ar)$ is less than 20% of that caused by SPR, so the former is neglected in this study. The effects of air-sea heat flux and gas exchange are not relevant after subduction into the interior thermocline, and have also been neglected. Heating due to short wave radiation can reach below the base of mixed layer in low latitudes causing a shallow, local source of δAr [Spitzer and Jenkins, 1989], but this effect is not important in the subtropical thermocline below 200 m. Based on these arguments we approximate equation (2) as

$$\frac{D\delta Ar}{Dt} \cong \left(\frac{\partial^2 Ar_{sat}}{\partial T^2} \right) \kappa \left(\frac{\partial T}{\partial z} \right)^2. \quad (3)$$

This relationship describes the increase of δAr along the trajectory of a water parcel in the subtropical, interior

thermocline. If the ΔAr at the isopycnal outcrop is stationary in time, the magnitude of ΔAr is predicted to increase from the outcrop to the interior thermocline along an isopycnal surface. The along-isopycnal gradient of ΔAr is determined by the balance between advective transport and the internal source due to mixing (Figure 1b).

3. Estimating Diapycnal Diffusivity From Observations of ΔAr

[11] Our approach to applying equation (2) to the limited existing Ar observations involves an assumption that the trajectory of the selected water parcel remains very close to the same isopycnal. We can then approximate the Lagrangian derivative of δAr by contrasting the observed Ar and the ventilation ages (τ) at two locations on the same density surface.

$$\frac{D\delta Ar}{Dt} \cong \left| \frac{\delta Ar^{(2)} - \delta Ar^{(1)}}{\tau^{(2)} - \tau^{(1)}} \right|_{\sigma_0} \quad (4)$$

where $\delta Ar^{(1)}$ and $\delta Ar^{(2)}$ are observations from the two stations on the same isopycnal, and $\tau^{(1)}$ and $\tau^{(2)}$ represent corresponding ventilation ages.

[12] By taking the difference in argon saturation and ventilation age between two points on an isopycnal surface, we can estimate the rate of increase in argon saturation as the water becomes older along the isopycnal. Then we can solve for κ by inverting equation (3).

$$\kappa \cong \left(\frac{\partial^2 Ar_{sat}}{\partial T^2} \right)^{-1} \left(\frac{\partial T}{\partial z} \right)^{-2} \left| \frac{\delta Ar^{(2)} - \delta Ar^{(1)}}{\tau^{(2)} - \tau^{(1)}} \right|_{\sigma_0} \quad (5)$$

[13] In order to estimate diapycnal diffusivity, we need to determine ΔAr , ventilation ages, and thermal stratification from the observations. The only location where it is currently possible to make this estimate using existing high-quality data is on the isopycnal surface $\sigma_0 = 26.6$ in the North Pacific, which outcrops in the northwestern Pacific close to the location of the time-series station KNOT (155E 44N, see Figure 2), and reaches a depth of 500 m at the subtropical time-series station HOT (158W 23N). Field measurements of Ar in the potential density range 26.5 to 26.7 at the KNOT and HOT time-series sites (Figure 3) are compared to evaluate the change in ΔAr from an outcrop region to the central subtropical gyre. Ratios of Ar/O₂ were measured by mass spectrometry and O₂ concentrations by Winkler titration to obtain absolute Ar saturations [Emerson *et al.*, 1999; Hamme and Emerson, 2004]. All samples were measured in duplicate and quality controlled for less than a 0.5% difference between duplicates. The mean of duplicate measurements is treated as a single data point, and then the mean and standard deviation of ΔAr at each station are calculated in the density range of $\sigma_0 = 26.6 \pm 0.1$. We used KNOT data collected in January, February and May 2000 because these times are closest in the seasonal cycle to the ventilation of this water mass and least likely to be affected by subsurface heating. At HOT, the 26.6 isopycnal is at approximately 500 m depth, and we used samples from all seasons collected during 2000 and 2001. There is a clear difference between ΔAr values at the two stations (see

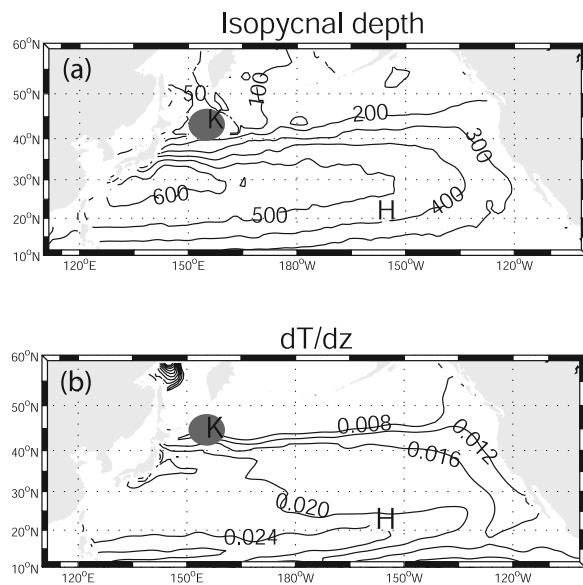


Figure 2. Properties on the isopycnal layer $\sigma_0 = 26.6$ based on the World Ocean Atlas [Conkright *et al.*, 2002]: (a) isopycnal depth and (b) thermal stratification, $\frac{\partial T}{\partial z}$. Shaded oval marks the region of the winter-time outcrop. Approximate positions of the KNOT and HOT station are marked with K and H, respectively.

Figure 3) with Ar more supersaturated at HOT, as predicted by the theory. The difference in mean ΔAr between the two stations is statistically significant, with a magnitude and estimated error at the 95% confidence interval of $0.82 \pm 0.49\%$. We discuss the possible sources of errors in the section 4.

[14] We evaluate the ventilation age (τ) of the thermocline water based on pCFC11 from Warner *et al.* [1996] as adjusted by the analysis of Mecking *et al.* [2004]. We assume that the age of waters at the outcrop of the isopycnal is zero. The uncorrected pCFC-11 age of $\sigma_0 = 26.6$ waters at the HOT station is approximately 18 years. Mecking *et al.* [2004] showed that freon ages were biased toward younger values due to tracer mixing along isopycnals in the North Pacific. This bias is larger in older waters (>20 years) than in younger waters, leading to a corrected age of 20.7 years at the HOT station.

[15] Finally, we use the World Ocean Atlas climatology [Conkright *et al.*, 2002] to calculate vertical stratification (Figure 2b). The climatological temperature distribution on the $\sigma_0 = 26.6$ surface reveals a spatially-averaged thermal stratification of 0.020 degree m^{-1} in the subtropical thermocline. The spatial variability of the thermal stratification is smaller than the mean by an order of magnitude, so its impact is neglected in this study.

[16] Applying the theory to these observational data yields a diapycnal diffusivity of $\kappa = 0.35 \pm 0.2110^{-4} m^2 s^{-1}$ using a second derivative for Ar_{sat} of $0.013 \mu M deg^{-2}$ in the T-S range of the $\sigma_0 = 26.6$ surface. This estimate is of the same order of magnitude with the $\sim 10^{-5} m^2 s^{-1}$ values derived from microstructure and tracer release experiments in the thermocline [Gregg, 1987; Ledwell *et al.*, 1998]. Despite the limited, currently available observations of ΔAr , application of the theory to the measurements does yield diapycnal diffusivity estimates which are of reasonable magnitude. So

far, the error estimate only reflects the error in the mean ΔAr difference between the two stations. In the following section, we discuss other sources of uncertainty and the possibilities for improving the signal to noise ratio in future studies.

4. Conclusions, Caveats, and Suggestions for Future Measurements

[17] The above, provisional estimate of diapycnal diffusivity contains a number of potential caveats. We show here that some are probably not serious and that others can be addressed with future sampling programs.

4.1. Theoretical Issues

[18] The theory applied to the argon data assumes that the effects of along-isopycnal mixing are negligible. The impact of isopycnal mixing can be roughly estimated by replacing κ with K_I and $\frac{\partial T}{\partial z}$ with $\frac{\partial T}{\partial x}$ in equation (3), where K_I represents the isopycnal eddy diffusivity. Assuming $K_I = 2000 m^2 s^{-1}$ and an isopycnal temperature gradient of $4 \cdot 10^{-7}$ degree m^{-1} , isopycnal mixing can only increase ΔAr by 0.04% over the ventilation timescale, which is small compared to the observed ΔAr difference of 0.8%. Thus, we suggest that isopycnal mixing can only play a minor role in the variation of ΔAr in the thermocline.

[19] We also assumed that the interannual variability in ΔAr at the isopycnal outcrop is small. A large interannual trends in air-sea heat fluxes at the outcrop could impact our measurements of the ΔAr difference between stations as well as the along-isopycnal gradient of ΔAr , and therefore the estimate of diapycnal diffusivity. The initial ΔAr is sensitive to meteorological forcing at the isopycnal outcrop including air-sea heat fluxes, atmospheric pressure and gas exchange rates [Hamme and Emerson, 2002; Ito and Deutsch, 2006]. In order to evaluate variability in outcrop conditions, we calculated the winter-time ΔAr at station KNOT from NCEP-NCAR reanalysis data [Kalnay *et al.*, 1996] using the model of ID06. The inferred ΔAr did not

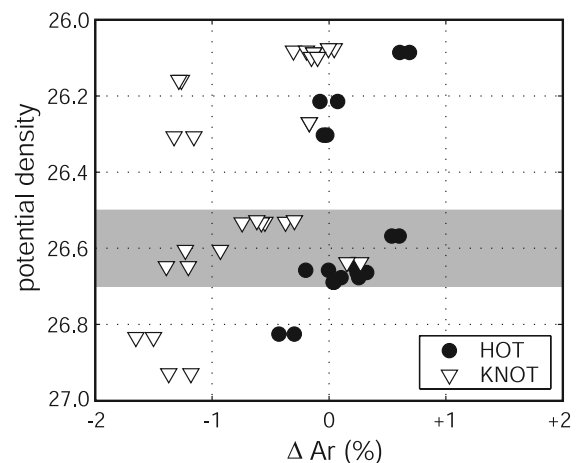


Figure 3. Observed argon saturations at the HOT and KNOT stations are plotted against potential density. HOT data is shown for all seasons sampled in 2000–2001. KNOT data is shown for January, February, and May 2000 cruises. Data from potential densities less than 26.5 are not plotted for the May KNOT cruise, as these waters could have been affected by seasonal heating.

show any significant interannual trend in the last 55 years, but instead exhibited random variability with a standard deviation of 0.23%, which is comparable to the ΔAr variability observed in the data. Given the inference from the available data, we conclude that the interannual variability of ΔAr at the outcrop is likely to be small with respect to the mean ΔAr difference of $0.82 \pm 0.49\%$ between the two stations, and cannot explain the observed ΔAr difference.

[20] Uncertainty in ventilation ages due to isopycnal eddy stirring can introduce both systematic bias and random errors. The young ventilation age bias has been corrected in our calculation following Mecking *et al.* [2004]. However, we have not determined the random error in the ventilation age, which would have required the measurement of multiple transient tracers [Vaugh *et al.*, 2002].

4.2. Analytical Issues and Strategy for Future Measurements

[21] Inter-cruise variability in the accuracy of our measurements is a potential source of error to this analysis. Measurements at HOT are particularly vulnerable, because the accuracy of O_2 measurements decreases in the thermocline where O_2 concentrations are low. Data sets from both stations used here contain data from more than one cruise, which limits the impact of this issue on our conclusions here. However, analytical errors of this type need to be addressed in future sampling programs.

[22] In this study, the large-scale gradient in ΔAr was inferred from point measurements at two stations that are both influenced by strong mesoscale variability. Multiple stations between the mid-latitude outcrop and the interior gyre would significantly improve the estimate of large-scale ΔAr gradients. In addition, analytical error in Ar measurements in water masses with low O_2 concentrations can be resolved using isotope dilution method [Gehrie *et al.*, 2006; Hamme and Severinghaus, 2007]. Finally, the impact of diapycnal mixing on noble gas saturations increases with the curvature of the solubility-temperature relationship. The solubility of xenon (Xe) is more strongly curved than that of argon, so the impact of diapycnal mixing must be more strongly expressed in Xe [Hamme and Severinghaus, 2007]. Therefore, the signal to noise ratio would improve significantly if we make measurements of several noble gases along a transect from the isopycnal outcrop to the interior gyre. Multiple noble gas measurements will also allow us to constrain the impact of interannual variability in certain surface processes, including bubble-mediated gas fluxes.

4.3. Final Remarks

[23] As dissolved gas tracers, noble gases naturally integrate the effect of diapycnal mixing over the ventilation timescale of water masses in the thermocline. Inferences from noble gas distributions are complementary to other measures of diapycnal diffusivity such as microstructure measurements [e.g., Gregg, 1987], purposeful tracer release experiments [e.g., Ledwell *et al.*, 1998] and large-scale inversions [e.g., Ganachaud and Wunsch, 2000]. The decadal ventilation timescale of subtropical gyres is intermediate between that of tracer release experiments (months to a year timescale) and inferences from basin-scale heat and tracer budgets (century to millennium timescale). Thus noble gases provide a unique measure of regional diapycnal mixing

averaged over decadal timescales, which impacts the uptake of heat and CO_2 in the middle and low latitudes and contributes to the supply of nutrients from the thermocline maintaining biological productivity in the surface ocean.

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