Krypton-85 in the Ocean

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A method is described to determine for the first time the ^{85}Kr concentration in seawater. Samples of 220 l of seawater are degassed aboard a research vessel. The krypton contained in the gas sample is isolated in the laboratory and its ^{85}Kr activity is measured in a gas counter. The background of the lowel-level counting-array is 0.026 cpm; surface water samples yield a netto count-rate of 0.13 cpm. The reproducibility of the method was checked by gas standards (krypton-air mixtures) and moreover by three surface water samples; both sets agree within $\pm 1\,\sigma$, or $\pm 5\%$. The mean value of three samples of great depths (1600, 2000, 2000 m) is 5% of the surface water concentration. This figure represents the possible contamination of the samples by atmospheric ^{85}Kr during the various preparation stages (blank value). Two profiles have been measured from the North Atlantic (about 40°N, 18°W, November 1972). A strong decrease of the ^{85}Kr concentration is found in the upper 1000 m. In a simple one-dimensional vertical diffusion-advection model the profiles can be simulated with a coefficient of apparent vertical eddy diffusion of 5 cm²/sec in the depth range of 300 to 1000 m (main thermocline). A possible application of oceanic ^{85}Kr data is the combination of depth profiles with those of other tracers, in particular ^{3}H. Another application of the ^{85}Kr method is the dating of groundwaters younger than 20 years.

Introduction

For the last 15 years natural or man-made radionuclides have been used to investigate the motions of water masses in the interior of the world ocean [1, 2]. As these radionuclides enter the ocean by gas-exchange, rainout, fallout, or liquid discharge at the atmosphere-ocean interface their "intrinsic clock" (radioactive decay) gives information on the time necessary for the surface water to reach oceanic depths. According to their different halflives the various radionuclides are suitable for different mixing phenomena: ^{14}C for large scale mixing like the renewal of the oceanic deep water [2]; ^{3}H [3, 4], ^{137}Ce [2], and ^{90}Sr [2, 5] for the mixing across the main thermocline, the region of the sharpest temperature gradient (boundaries between 300 and 1000 m depth approximately, varying with geographic latitude), and ^{222}Rn for the gas exchange rates in the surface water layer [1, 6].

Water transport in the ocean is described by two phenomena: directed motion and turbulent exchange. The more tracers are studied the more critical examinations are possible of these ideas and of the relative contributions of both phenomena to water mixing [7–9]. Oceanic ^{3}H profiles have been measured in this laboratory for about 10 years [3, 10]. Prospecting for a new tracer, ^{85}Kr was selected as a potential candidate.

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^{85}Kr is a β^--emitter of 10.76 years halflife. It is produced by man's nuclear activities on the earth's surface; military Pu-production and civilian nuclear power production are the main sources [11]. Figure 1 presents roughly the course of the ^{85}Kr concentration with time in the North Atlantic surface water at about 50 °N, calculated under the assumption that the gases in the surface water layer are in equilibrium with those of the marine troposphere. Also indicated is the calculated course of the ^{3}H concentration, the bulk of which originated from atmospheric nuclear weapon tests in the early sixties [11]. Water leaving the surface of the ocean and entering the subsurface layers is marked by a time-specific ^{85}Kr to ^{3}H concentration ratio. The halflives of both radionuclides being similar (halflife of ^{3}H 12.3 6years) this ratio scarcely changes in time. As directed water motion preserves the tracer concentration ratios (cf. Fig. 1) whereas turbulent exchange smears them, one should thus be able to disentangle the mechanisms of directed water motion (advection, upwelling, downwelling) and turbulent exchange (eddy diffusion) in the region of the main thermocline, pursuing as well ^{85}Kr as ^{3}H profiles. A first step to this goal was the development of an experimental technique to measure ^{85}Kr in the ocean.

Experimental Procedure

a) *On board of a research vessel* seawater samples are taken from shipboard. The samplers are

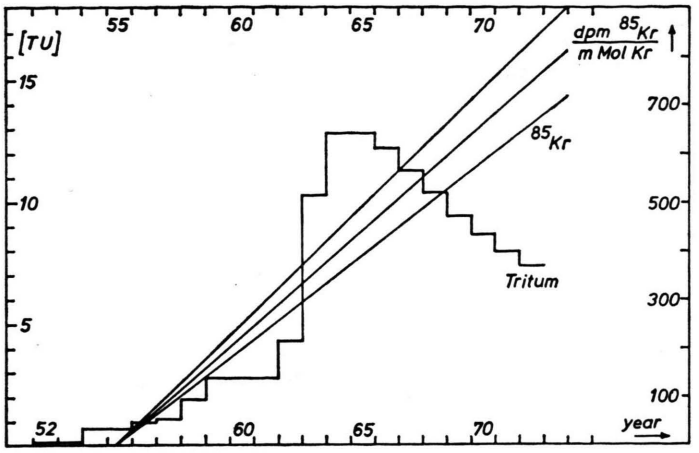

Fig. 1. ^{85}Kr and ^{3}H concentration in North Atlantic surface water. *Straight lines:* Rough pattern of the calculated increase of ^{85}Kr concentration in the surface water of the North Atlantic at 50° N (linear approximation, cf. [11, 29]). The scattering of the atmospheric values is represented by the upper and the lower straight line (±10% deviation). Note: the ^{85}Kr concentration decreases slightly from North to South (cf. [30, 31]) but there is zonal homogeneity (cf. [32, 29]). The *histogram* shows the calculated ^{3}H concentration course in the same water body (values from [20]). The unit of the ^{3}H concentration is 1 TU = 1 ^{3}H atom per 10^{18} ^{1}H atoms.

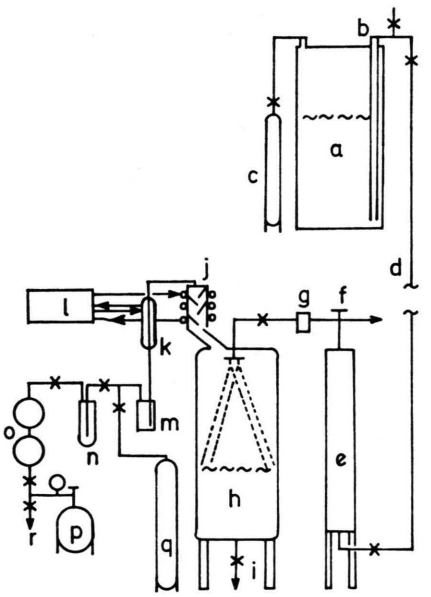

Fig. 2. Degassing array for 220 l of seawater on shipboard. a, Gerard-Ewing large-volume water sampler (stainless steel, 270 l); b, standpipe (stainless steel); c, CO_2 gas cylinder; d, tube "Heliflex" (50 m long, evacuated); e, water heater (12 kW, evacuated); f, three-way cock; g, thermometer; h, tank (stainless steel, evacuated, 220 l); i, to the water and the vacuum pump; j, reflux cooler for condensation of water vapour; k, cooler for penetrating water; l, cooling unit; m, water trap; n, water trap (dry-ice cooled); o, compressor; p, commercial propan-butan gas cylinder as sample-container (bellows sealed valves) together with thermometer and manometer; q, pure nitrogen gas; r, to the vacuum pump.

gas-tight; whilst they are emptied, CO_2 gas is admitted to prevent access of air. Figure 2 shows the degassing array. The seawater passes the water heater (e) and is degassed by being expanded into a vacuum tank (h). From there the gases are continuously pumped (o) into the sample-container (p). Within 40 to 45 min 220 l of seawater are degassed with an overall efficiency of (78±5)%, which value is determined by comparison with equilibrium gas solubilities. After degassing the water is pumped off (i) and the degassing array is filled with pure nitrogen gas (q), whereafter the system is evacuated (i, r) (for further explanation see [21]). One run takes 2 hours.

During the cruises No. 27 and 29 of the German research vessel "Meteor" several casts each of about five 270 l samples were taken with Gerard-Ewing water samplers [12]. A total of 54 gas samples was collected.

b) *In the laboratory* the Kr gas contained in the gas samples (3 to 4 l STP with 3 ppm Kr) is isolated in one step by fractionated adsorption on charcoal. Figure 3 shows the gas separation system. The gas sample (a) is pumped by the Toepler-pump (g_1) through the charcoal-column (h) at dry-ice temperature and a pressure of 350 Torr (flux 1 l STP per hour). After the sample cylinder (a) is evacuated, the charcoal (h) is pumped slowly to 10 Torr within 3 hours. Then the charcoal is heated to 350 °C and the desorbed gases are expanded through the trap (n) (at liquid nitrogen temperature, to freeze out the CO_2 contained in the gas sample) into the calcium oven (j) where the remaining reactive gas components are bound chemically. After this treatment the sample has a volume of about 0.5 cm^3 STP and contains besides argon about (82±9)% of the extracted Kr gas, i.e. 8 mm^3 STP; the efficiency of recovery was determined by gas standards of known Kr content. The sample is transferred by means of the Toepler-pump (g_2) to a small-volume counting tube mounted at (k). Before entering the Toepler-pump (g_2) the gas passes the trap (o) (at liquid nitrogen temperature) where traces of H_2O, CO_2 and ^{222}Rn are

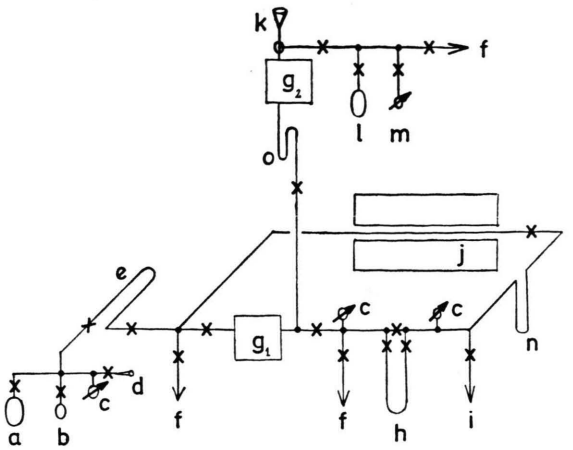

Fig. 3. Gas separation system in the laboratory. a, sample cylinder; b, krypton addition for the preparation of gas mixtures; c, Bourdon manometer; d, valve; e, molecular sieve for sample-drying (50 gr, 3 Å); f, to the vacuum pump; g_1, g_2, Toepler pumps; h, charcoal column (10 g, Desorex F 10, length 150 cm, diameter 6 mm); i, to the vacuum pump via dosing-valve; j, calcium oven (700 °C); k, connection to the counting tube; l, argon-methane mixture (80/20); m, precision manometer (Wallace and Tiernan); n, trap for freezing out CO_2 (at liquid N_2 temperature); o, trap for adsorbing traces of H_2O, CO_2 and ^{222}Rn (at liquid N_2 temperature).

adsorbed. This is necessary as the α-emitter ^{222}Rn may be produced in the charcoal (h) and in the molecular sieve (e) [13–15]. Most of the Xe is retained in the two traps (n) (o). Argon-methane (80/20) (l) is added to the sample to a total pressure of 670 Torr (m) at 0 °C.

After counting the composition of the gas filling is analysed mass-spectrometrically; the Kr content is determined by comparison with gas standards of similar and known composition. The reproducibility of the sample preparation and of the ^{85}Kr activity measurements was checked by five gas mixtures of known Kr content (stable Kr) and of known ^{85}Kr activity; the ^{85}Kr activity was about 0.2 cpm (typical surface water value 0.13 cpm). Good agreement within these five samples was found. The mean standard deviation (1 σ) of a single measurement is 4%. Intercalibration measurements with Stockburger [16] and the ^{14}C laboratory of this institute (^{14}C counters of known sensitive volume) allowed an absolute calibration of the counting tube (cf. conversion factor in Table I). Suitable choice of the materials of the counting tube (the body consists of quartz-glass, the kathode of hyperm-steel; 20 μm anode-wire of Wo) and the use in a low-level counting array with a lead shield of 15 cm thickness and a plastic scintillator as anticoincidence-ring [17, 18] brought the background down to 0.026 cpm at a lower threshold energy of 0.5 keV, i. e. 0.00214 cpm/cm² surface (cp. [19]). The internal counter works in the proportional region, the energy calibration is performed by an external ^{55}Fe source (K-capture, 5.9 keV). The working voltage is 1400 Volt. The slope of the plateau for ^{55}Fe is 3.5% per 100 Volt, the length of the plateau is 200 Volt. From the energy spectra of the background and of the samples the lower threshold energy was selected to be 0.5 keV.

Table I. ^{85}Kr concentration values from seawater samples.

Position: 39° N, 21.75° W.	Date: 25. 11. 1972	
depth (m)	^{85}Kr concentration *	
0005	0.0738	(05)
0005	0.0800	(04)
0800	0.0075	(37)
1600	0.00435	(25)
Position: 42° N, 14.5° W.	Date: 21./22. 11. 1972	
depth (m)	^{85}Kr concentration *	
0005	0.0743	(05)
0400	0.0507	(05)
0800	0.0078	(13)
1200	0.0063	(19)
2000	0.0016	(57)
Position: 42.75° N, 14.5° W.	Date: 22. 11. 1972	
depth (m)	^{85}Kr concentration *	
0400	0.0436	(07)
2000	0.0065	(50)

* The unit is: cpm ^{85}Kr/Torr Kr at 0 °C in the counting tube at a lower threshold energy of 0.5 keV. The conversion factor to absolut activities is 8040 dpm ^{85}Kr/mMol Kr per cpm ^{85}Kr/Torr Kr at 0 °C (1 σ error 3%). The values in brackets show 1 σ in %.

Results

Table I presents the measured ^{85}Kr values together with the positions, depths, and dates of sampling. In Fig. 4 the values of Table I are plotted against depth. A sharp decrease of the ^{85}Kr concentration with depth is found in the upper 1000 m. The three surface water values agree within the experimental precision. Considering the different positions and the errors, the two pairs of values of 400 m and of 800 m depth agree well. The mean value of the three samples of great depths is about 5% of the surface water value (detection limit for a five days measuring time). This figure represents the upper limit of the contamination of the samples by atmospheric ^{85}Kr during processing.

Although one of the samples of 2000 m depth corresponds to about 8% of the surface value, it is highly unlikely that this is a real effect, eventually caused by leakage or production of ^{85}Kr in situ:

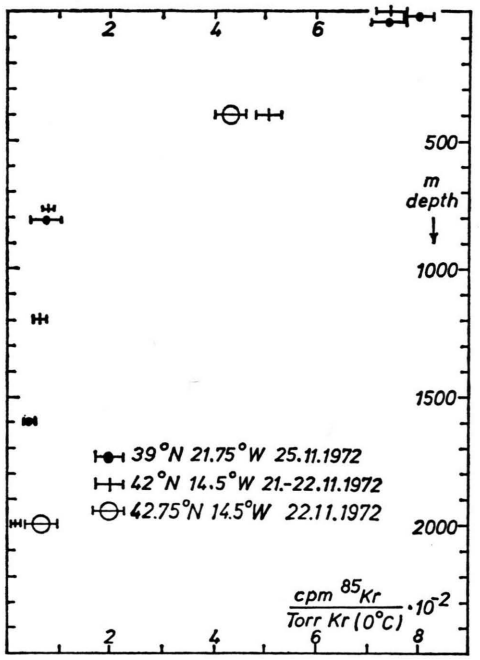

Fig. 4. ^{85}Kr depth profile. The samples were taken during cruise No. 29 of the German research vessel "Meteor". The three surface values are staggered a little bit for clearness, the two 800 m values as well. Error bars correspond to $\pm 1\,\sigma$.

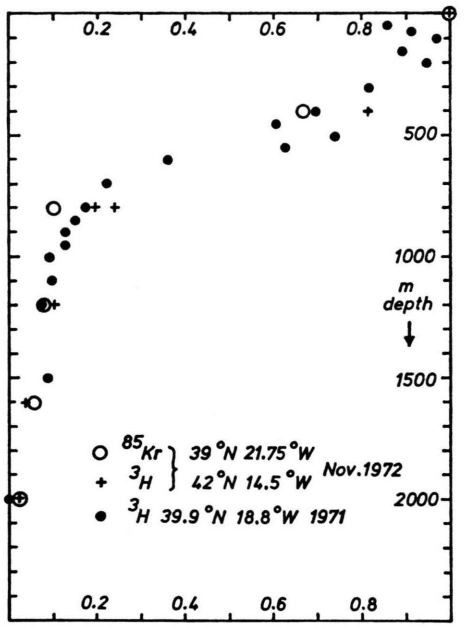

Fig. 5. Normalized ^{85}Kr and ^{3}H profiles. ^{85}Kr values of Table I (the last two values of Table I are not shown here) normalized at the surface (open circles) together with tritium values of the same samples (crosses). The full circles are ^{3}H values of a neighbouring station taken in 1971 (cp. [11]).

the sampling position lies within an area where radioactive waste has been sunk into the Iberian Deep Sea (water depth 5000 m approximately). Further ^{85}Kr samples of this region are not available at present.

The obvious decrease of the ^{85}Kr concentration in the upper 1000 m corresponds to the accepted ideas of water transport in the region of the main thermocline [2, 4, 20]. Figure 5 shows the ^{85}Kr profile (open circles) normalized to surface water concentration together with similarly normalized profiles of ^{3}H for the same samples (crosses) as well as samples from a neighbouring station (full circles) [11]: in the region of the main thermocline the ^{85}Kr values are lower than those of ^{3}H; this fact is reasonable in view of Fig. 1, which shows that the bulk of the ^{85}Kr has had less time than that of the ^{3}H to penetrate to the interior of the ocean.

Interpretation

To get an idea of the magnitude of the coefficient of apparent eddy diffusion in the region under study, a simple model of the ocean is sketched (cp. [21–23]).

The surface water layer is assumed to be well mixed and its gases are in equilibrium with the atmosphere (renewal time by gas exchange is some months [6, 24, 25]). The depth of this well mixed layer is supposed to be approximately that of the winter convection, which is about 300 m in the sampling area [26]. This depth happens to be that of the 12 °C isotherme [27, 28]. The region below, till about 1000 m depth, is the so-called main thermocline. Assuming that there is but vertical water transport, the tracer concentration changes only by vertical water exchange (characterized by the coefficient D of apparent vertical eddy diffusion), by directed water motion (characterized by a velocity w), and by radioactive decay (decay constant λ). Taking the depth as the $+z$ coordinate with the origin in 300 m depth, the relevant differential equation in the region of the main thermocline is:

$$\partial_t c = D\,\partial_z^2 c - w\,\partial_z c - \lambda c$$

where $c(z, t)$ is the concentration of the tracer under study. For a linear increase of $c(z=0, t)$ in time t, starting in 1955.4 from zero (cf. Fig. 1) the solution is (cf. [33]):

$$c(z,t)/c(z=0,t) = 0.5 \exp(z\,w/2\,D)$$
$$\cdot\{(1-z/2\,t\,\beta)\exp(-z\,\beta/D)\ \mathrm{erfc}\,[(z-2\,t\,\beta)/2\sqrt{D\,t}]$$
$$+(1+z/2\,t\,\beta)\exp(+z\,\beta/D)$$
$$\mathrm{erfc}\,[(z+2\,t\,\beta)/2\sqrt{D\,t}]\}$$

where

$$\beta = (\lambda D + w^2/4)^{1/2},\ \mathrm{erfc}(x) = 1-\mathrm{erf}(x) \text{ and}$$
$$\mathrm{erf}(x) = 2/\sqrt{\pi}\int_0^x \exp(-r^2)\,\mathrm{d}r\,.$$

A theoretical profile with $D = 5\ \mathrm{cm^2/sec}$, $w = 0\ m/a$ and $z = 0$ in 300 m depth reasonably simulates the measured profile.

A similar D value results from the ^3H profile measured at the same samples (cf. Fig. 5) using the same model but considering the different input function of ^3H into the ocean surface water: the histogram of Fig. 1 is approximated by a sudden increase from zero in 1962.9 and an exponential decrease in time with the halflife of ^3H.

Literature values of D are $4\ \mathrm{cm^2/sec}$ from combined ^{90}Sr and ^3H profiles [5] and $4.34\ \mathrm{cm^2/sec}$ from combined ^{90}Sr and ^{137}Ce profiles [2] for the North Atlantic main thermocline. Thus describing the rate of mixing in this region by one-dimensional models, one finds that other tracers produce mixing parameters similar to those calculated from the ^{85}Kr profiles. The profiles differ in shape (cf. Fig. 5) due to the different time course of the input of the radionuclides into the ocean surface water (cf. Figure 1). ^{85}Kr to ^3H ratios should allow to gain new information of the physical reality and the relative contributions of the different water transport phenomena (characterized by D and w) in the region of the main thermocline.

One must be aware of the fact, however, that the model described here neglects an alteration of the tracer concentration due to lateral transport processes. It is now generally accepted that horizontal advection on isopycnic surfaces from the North may be even dominant (cf. [4]). Thus the model here describes but the apparent response of the ocean to the input of an atmospheric gas-phased inert tracer but not the real physical features of the water motions in the interior of the ocean [21].

Conclusions

A new experimental technique has been developped to measure a new tracer in oceanography, viz. ^{85}Kr. The method is shown to produce consistent results and the same coefficients of apparent eddy diffusion as ^3H, ^{90}Sr, and ^{137}Ce profiles. The accuracies of the ^{85}Kr and the ^3H method are comparable for samples down to 10% of the surface water concentration. The processing and the measuring time for a ^{85}Kr sample is about ten times that of ^3H (the statements refer to the ^3H laboratory of this institue). 24 hours for processing and 5 days for measuring are necessary for one ^{85}Kr sample. This difference is justifiable only as the combination of ^{85}Kr profiles with those of other tracers, e. g. ^3H, can give new information on the contributions of water exchange and water advection to water transport. The quantitative aspects of this have to be looked into more thoroughly before starting extensive research programs.

As the gases dissolved in continental surface waters are in equilibrium with the tropospheric gases, dating of groundwaters younger than 20 years (cf. Fig. 1) should be another application of the ^{85}Kr method.

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