6. INTERSTITIAL WATER STUDIES, LEG 15 – INERT GASES

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ABSTRACT

Inert gases (He, Ne, Ar, Kr, and ${}^{4}\text{He}/{}^{3}\text{He}$) have been measured in fourteen samples of pore water from sections of core at three locations (Sites 148, 149, and 150) in the Caribbean Sea. Ne, Ar, and Kr are severely depleted relative to solubility values, with considerably less depletion observed for ${}^{3}\text{He}$ and ${}^{4}\text{He}$. Four samples show excess ${}^{4}\text{He}$ and all samples show ${}^{4}\text{He}/{}^{3}\text{He}$ greater than the atmospheric value. The depletion of the heavy inert gases almost certainly occurred during shipboard sampling. The depletion for Ne in each sample has been used to correct the ${}^{3}\text{He}$ and ${}^{4}\text{He}$ results. When this is done, every sample contains excess ${}^{3}\text{He}$ and ${}^{4}\text{He}$ relative to solubility. Also, there are definite trends of ${}^{3}\text{He}$ and ${}^{4}\text{He}$ contents with depth—below 100 meters, both isotopes are a factor of 2 above solubility, with less enrichment at depths above 100 meters.

INTRODUCTION

Inert gases dissolved in natural waters are tracers for the origin, residence time, and temperature history of the water. Recent discussions are to be found in papers by Revelle and Suess (1962), Bieri et al. (1967), Clarke et al. (1969), and Craig and Clarke (1970). Examination of the helium isotopes is particularly interesting because of the continuous flux of ³He and ⁴He from the oceanic crust and mantle and the production of ⁴He in sediments from U and Th decay. Determination of ³He in pore waters may shed light on the problem of excess ³He in the oceans, while ⁴He measurements may provide a means of determining the residence time of the pore waters, if the U and Th contents of the sediments are determined so that the release rate of ⁴He into the water is known. The other inert gases (Ne, Ar, Kr, and Xe) may possibly be indicators of past ocean temperature because of the temperature-solubility effect for each gas. It was with these possibilities in mind that this work was initiated.

EXPERIMENTAL

Sampling Method

The pore water samples were obtained as follows. Six-inch sections of the core were taken in the plastic core liner, capped, and taped. These were then transferred to the N_2 dry box for loading into the squeezer. Within the dry box the samples were removed from the liner, trimmed to eliminate surface contamination, and loaded into the squeezer. The squeezer was then taken from the dry box and placed in the press. As shown in Figure 1, the exit port of the press was connected via tygon tubing to one and in a

few cases two copper sampling tubes mounted in series. The tubes were placed in a vertical position so that water would enter from the bottom and flow out through the top. The tubing was thoroughly flushed with N_2 and then sealed with clamps. A syringe was placed above the last copper tube to receive the overflow water. As pore water began to emerge from the squeezer, the clamps were opened and water allowed to flow through the tubing until at least one copper sampler volume (10 ml) had entered the syringe. The tygon tubes adjacent to the copper tube were then clamped off and the tube removed from the system. It was then crimped at both ends with pinch clamps (Imperial Eastman Corp. No. 105 FF pinch-off tool). These sealed copper tubes were then sent to McMaster for mass spectrometric analysis.

The greatest source of difficulty comes from the N_2 gas trapped in the squeezer during loading. Such entrapment is an unavoidable part of the present squeezing method. During the initial compression of the sample in the press, most of this gas is driven off ahead of the water. The residual gas comes out as a series of bubbles, which then move up the column and out. The most likely source of gas loss is via these bubbles. Their number varied from sample to sample. Only in one case (Sample P-12) was there none. We see, however, no correlation between the neon deficiency discussed below and the degree of bubbling (a result that puzzles us).

In some cases duplicate samples were taken by placing a second tube above the first. Since the bubbling subsided as the run progressed, the water in the lower tube (I) should be less subject to gas loss into the bubbles than the water in the upper tube (II). Further details of the squeezing procedure are given in the paper by Horowitz et al. in this volume.



Figure 1. Shipboard sampling method.

Inert Gas Analysis

The water samples were processed in a vacuum line constructed of Corning 1723 glass, with pyrex stopcocks, and a Toepler pump made of Pb-glass. The He-Ne fraction was sealed in a break-seal sample tube of 1723 glass, and the Ar, Kr, Xe fraction condensed on activated charcoal in a pyrex sample tube (after purification with Ti metal held at 800°C). Extraction time was about 30 min for the He-Ne fraction and about 60 min for the Ar-Kr-Xe fraction. Blanks were collected before and after this series of samples-the procedure was identical to the usual method except that there was no water in the sample container. In one case, immediately after the pore water extraction, the section of the line containing the water was isolated, new sample tubes sealed on, and the gases collected in the usual manner. These samples served to test the efficiency of gas release.

The mass spectrometer used is a 10-inch radius static instrument of high sensitivity. ${}^{4}\text{He}{}^{-3}\text{He}$ measurements were carried out first, then the magnetic field was increased and the ${}^{20}\text{Ne}$ signal recorded. Pore water He-Ne measurements were interspersed with analyses of aliquots of air of known volume. In this way absolute values for the 4 He- 3 He ratio and the He-Ne contents were determined. The Ar-Kr-Xe fraction was sealed to a sample line connected to the mass spectrometer volume via a capillary leak. 40 Ar and 84 Kr ion currents were measured relative to signals from known volumes of air (purified with Ti). Xe was not measured because of a large Xe "memory" in the instrument at the time of these measurements.

RESULTS AND DISCUSSION

The inert gas data are summarized in Table 1. Figure 2 shows the results expressed relative to solubility values at 4° C and $35^{\circ}/_{\circ\circ}$ salinity from a water-saturated atmosphere (Weiss, 1970, 1971; König, 1963). We assume that the depletions observed for Ne, Ar, and Kr occurred during shipboard sampling. In all but one case, bubbles of N₂ traversed the water column during the squeezing process (see Figure 1) and must have resulted in partial "stripping" of the dissolved inert gases. It appears-assuming that Ne, Ar, and Kr were originally close to solubility equilibriumthat these gases have all been depleted by about the same fractional amount. We have therefore assumed that the neon depletion factor for each sample is equal to the depletion factor for ³He and ⁴He. Corrected helium results are given in Table 2. It should be pointed out that these corrected results probably represent lower limits since loss of ³He and ⁴He, originally above solubility equilibrium, could occur with only minor loss of Ne, Ar, and Kr. For example, this may have occurred during the time the core was on its way from the sea bottom to the ship, or while the sediment was exposed to the atmosphere prior to loading in the N₂ glove box. We estimate, however, that such losses amounted to less than 10 per cent for ³He and 4He.

Figure 3 shows plots of ³He and ⁴He (corrected contents) versus depth. The data for Site 149 appear to define profiles with a rapid increase in concentration from 0 meters to 80 meters, and with practically not concentration gradient below 80 meters.

³He Profile

The observed profile cannot be explained by assuming a source of ³He benneath the sediments. If this were so, one would expect the concentration gradient for ³He to be constant or increase slightly with increasing depth. It seems to us that the only plausible explanation of the observed profile is to suppose that the ³He content in the Atlantic Ocean was about 12×10^{-14} cc STP/g until t years ago, when the content decreased to the present-day value of about 6×10^{-14} cc STP/g as measured by Jenkins et al. (1972). If we take a concentration of 9×10^{-14} cc STP/g at 40 meters (see Figure 3), then t ig given by

$$\frac{1}{2} = \operatorname{erf} \frac{x}{2\sqrt{Dt}}$$
, where $x = 40$ meters

The diffusion coefficient for helium in water at 0°C is 1.7 \times 10⁻⁵ cm² sec⁻¹ according to Boerboom and Kleyn (1969). Manheim (1970) has compiled data which shows

Sample ^a	Site	Depth (m)	⁴ He/ ³ He × 10 ⁻⁶	³ He cc STP/g × 10 ^{14c}	He cc STP/g × 10 ^{8c}	Ne cc STP/g × 10 ^{8c}	Ar cc STP/g × 10 ^{4c}	Kr cc STP/g × 10 ^{8c}
P-5	148	209	1.43±0.05	3.39	4.85	5.44	0.99	2.40
P-4	148	246	1.51±0.06	3.90	5.88	5.18	0.95	2.27
P-10	149	17	1.08±0.03	2.39	2.58	5.70	1.64	2.98
P-13 (I)	149	17	0.98±0.03	2.65	2.60	6.49	1.54	5.06
P-2 (II)	149	17	0.93±0.03	2.50	2.33	5.41	1.18	3.17
P-14	149	78	0.90±0.03	3.56	3.20	5.74	0.97	2.88
P-9	149	173	0.79±0.02	3.00	2.38	3.53	0.33	0.49
P-1	149	254	0.81±0.02	3.76	3.04	5.54	0.61	1.03
P-11	149	301	0.85±0.03	4.24	3.59	5.81	0.76	1.79
P-6	149	354	0.91±0.03	4.27	3.87	6.21	0.88	2.07
P-3 (I)	150	91	0.91±0.02	5.35	4.87	9.66	1.52	3.61
P-7 (II)	150	91	0.89±0.04	4.85	4.29	8.87	1.37	4.57
P-12	150	91	0.75±0.02	4.60	3.45	7.10	0.91	2.40
P-8	150	113	0.72±0.03	2.31	1.65	2.49	0.79	2.15
Solubility	Values	(4 C, 3	5 °/00)	5.40	3.90	17.06	3.44	7.40

TABLE 1 Inert Gas Contents

^aNumbers 1 to 14 indicate the sequence of extraction and analysis. Samples labeled I and II are pore water splits from one squeezing (see the text). Water samples weighed 9.7 to 10.4 g.

^bAtmospheric ⁴He/³He is 0.715 × 10⁶ (Mamyrin et al., 1970). Quoted errors are the sum of the standard deviation for a pore water determination plus the standard deviation of the mean ⁴He/³He for eight air aliquots analyzed during this series.

^cEstimated precision for He, Ne, and Ar data is about $\pm 5\%$ and $\pm 10\%$ for Kr. Blank corrections varied from 3% to 10% for He, 2% to 8% for Ne, and <1% for Ar and Kr. Extraction efficiency was better than 99.5% for all gases.



Figure 2. Inert gas concentrations relative to solubility at $35^{\circ}/_{\circ\circ}$ and $4^{\circ}C$ equivalent to 1.00. Lines on chart represent measurements on individual samples. Mean values for Ne, Ar, and Kr are 0.35 ± 0.09 , 0.30 ± 0.11 , 0.36 ± 0.16 respectively. Errors are one standard deviation.

that diffusion coefficients in sediment pore water, 50 per cent porosity, are about a factor of 7 lower than in free solution. Thus, if a value of 2.4×10^{-6} cm² sec⁻¹ is taken for $D(^{3}\text{He})$ at 0°C, we obtain,

$t \simeq 0.3 \times 10^6$ years

We estimate also from the shape of the ³He profile below 100 meters, that an average oceanic ³He concentration of about 12×10^{-14} cc STP/g must have been maintained for at least 10 m.y. The profile is, of course, not sufficiently well defined to determine exactly how rapidly the oceanic decrease occurred or to preclude fluctuations about the average values during the two "constant" periods. Indeed, even major fluctuations could escape detection if they were of sufficiently short duration. Atlantic Ocean measurements (Jenkins et al., in press) have shown that the present-day ³He excess in the deep water is approximately 5 percent of total ³He. Thus the above interpretation of the pore water profile requires that prior to 0.3 m.y. ago, the ³He excess was ~20 times the present value. It seems to us that there are only three possible explanations:

1) The ³He residence time in the Atlantic changed by a factor of ~ 20 , with no change in the ³He flux into the ocean.

2) The ³He flux into the ocean changed by a factor of \sim 20, with no change in the residence time.

3) The atmospheric ³He content decreased by a factor of $\sim 2, 0.3$ m.y. ago.

The first explanation requires a drastic change in the circulation pattern of the Atlantic. As far as we are aware, there is no independent evidence to support this view.

TABLE 2 Corrected Helium Contents

Sample	Depth (m)	^{3}He cc STP/g \times 10 ^{14a}	He cc STP/g × 10 ^{8a}
P-5	209	10.6	15.2
P-4	246	12.8	19.4
P-10	17	7.1	7.7
P-13 (1)	17	6.9	6.9
P-2 (II)	17	7.9	7.3
P-14	78	10.5	9.6
P-9	173	14.5	11.5
P-1	254	11.6	9.4
P-11	301	12.4	10.5
P-6	354	11.8	10.7
P-3(1)	91	9.5	8.6
P-7 (II)	91	9.3	8.3
P-12	91	11.1	8.3
P-8	113	15.8	11.3
Solubilit	y V	5 40	3.90

^aWe estimate that the corrected data is reliable to about $\pm 30\%$.

Oceanic ³He measurements only provide estimates of the present-day (<1000 years) flux into the oceans, and we have no way of knowing whether the ³He flux has been constant. Thus we cannot say whether explanation 2) is correct. The third possibility requires a change in ³He escape rate from the atmosphere to space or that the decrease in ³He flux into the Atlantic *caused* a factor of 2 decrease in atmospheric ³He content. Since the present ³He flux into the Pacific is ~5.5 atoms cm⁻² sec⁻¹ (Craig and Clarke, 1970), and the ³He escape rate is ~7.2 atoms cm⁻² sec⁻¹ (Johnson and Axford, 1969) it seems likely that oceanic flux changes would lead to alterations in atmospheric ³He content.

None of the above explanations seems very satisfactory at present. If, however, the depth effect we have indicated is indeed real, then some aspect of the ³He cycle must have undergone a major change in the last few hundred thousand years.

The flux of ³He from sediment to ocean at Site 149 is given by

$$J(^{3}\text{He}) = \frac{DC^{*}}{\sqrt{\pi DT}}$$

Where C^* is the difference between the ³He concentration in the pore water at the sediment surface and below 100 meters $= 6 \times 10^{-14}$ cc STP/g = 1.9×10^6 atoms/g. If we take $D(^{3}\text{He}) = 2.4 \times 10^{-6}$ cm² sec⁻¹ and $t = 0.3 \times 10^{6}$ years than $J(^{3}\text{He}) = 5 \times 10^{-4}$ atoms cm⁻² sec⁻¹. This value is four orders of magnitude lower than the ³He flux into the Pacific Ocean, ~5.5 atoms cm⁻² sec⁻¹. Measurements in the Atlantic (Jenkins et al., in press) indicate that the ³He flux into that ocean is probably within a factor of 2 of the Pacific flux, with the differences in excess ³He in the deep water being due, most probably, to residence time differences. Thus it seems that the present locations' samples for pore waters is far from the source regions for ³He input to the Atlantic. Future ³He-⁴He analyses of pore waters, which we are continuing, may help identify these source regions.

⁴He Profile

The fact that the shape of the ⁴He profile (Site 149) is so similar to the ³He profile, is very puzzling. ⁴He, unlike ³He, is being produced at a constant rate in the sediments, and we would expect to observe an approximately constant gradient of ⁴He concentration. The present-day ³He excess in the Atlantic is 5 percent of total ³He, and the radiogenic ⁴He excess is <1 per cent of total ⁴He (Craig and Weiss, 1971; Bieri, 1971; Jenkins et al., in press). Thus, if the ⁴He profile is to be explained in a similar way to the ³He profile, we must assume at least a factor of 100 change in ⁴He flux into the ocean, or a similar factor for the oceanic ⁴He residence time. Alternatively, it must be supposed that the ⁴He content of the atmosphere decreased by about a factor of 2, 0.3 m.y. ago. It should be pointed out that the atmospheric escape mechanisms for ⁴He and ³He are different. ⁴He escapes predominantly by a nonthermal mechanism (Axford, 1968), while ³He escapes mainly by a thermal mechanism (Johnson and Axford, 1969). Thus in order to significantly alter the ⁴He and ³He contents of the atmosphere, the escape rates for both mechanisms must change. It is also noteworthy that the atmospheric residence times of ³He and ⁴He are quite long, on the order of 10⁶ years (Axford, 1969).

An alternative explanation of the shape of the ⁴He profile may be that below 100 meters some process of sediment diagenesis greatly decreases the rate of release of ⁴He to pore water. It seems significant that the two ⁴He points for Site 148 fall far from the curve defined by the Site 149 data. This difference could be accounted for if the (U + Th) contents, or ⁴He release rates, differ by about a factor of 2 between 150 meters and 250 meters at the two sites. The fact that the two ³He points for Site 148 fall close to the Site 149 curve tentatively suggests that the ³He profile does reflect a past oceanic or atmospheric change. If the above reasoning is correct, then ³He profiles should be similar from place to place (except near source regions), but ⁴He profiles should vary markedly depending on local conditions. This question can only be answered by further sampling.

The flux of ⁴He from sediment to ocean at Site 149 is calculated to be approximately 10^3 atoms cm⁻² sec⁻¹. This value may be compared to the production rate in the sediment. If we consider a column 100 meters long, 1 cm² in area, water density = 1.0, sediment density = 3.0, with porosity = 50%, U = 1.5 ppm, and Th = 6 ppm, then the ⁴He production rate in the column is ~2.5 × 10³ atoms sec⁻¹. Thus, at Site 149, the ⁴He flux can probably be accounted for by production in the upper 100 meters, and there is no need to assume the existence of a flux from beneath the sediments.

In summary, these measurements represent the first attempt at determining inert gas contents of sediment pore waters. Even though gas loss occurred during sampling, the fact that the apparent depletions for Ne, Ar, and Kr are so



Figure 3. ³He and ⁴He profiles (corrected values).

similar leads us to believe that the corrected helium contents (based on neon) are probably within 30 per cent of the unperturbed contents. We are presently planning extensive sampling with improved methods at other locations on the sea floor. It is hoped that some of the questions raised by the present work can be answered in this way.

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REFERENCES

- Axford, W. I., 1968. The polar wind and the terrestrial helium budget. J. Geophys. Res. 73, 6855.
- Bieri, R. H., 1971. Dissolved noble gases in marine waters. Earth Planet. Sci. Letters. 10, 329.
- Bieri, R. H., Koide, M. and Goldberg, E. D., 1967. Geophysical implications of the excess helium found in Pacific waters. J. Geophys. Res. 72, 2497.
- Boerboom, A. J. H. and Kleyn, G., 1969. Diffusion coefficients of noble gases in water. J. Chem. Phys. 50, 1086.



- Clarke, W. B., Beg, M. A. and Craig, H., 1969. Excess ³He in the sea: evidence for terrestrial primordial helium. Earth Planet. Sci. Letters. 6, 213.
- Craig, H. and Clarke, W. B., 1970. Oceanic ³He: contribution from cosmogenic tritium. Earth Planet Sci. Letters. 9, 45.
- Craig, H. and Weiss, R. F., 1971. Dissolved gas saturation anomalies and excess helium in the oceans. Earth Planet. Sci Letters, 10, 289.
- Jenkins, W. J., Beg, M. A., Clarke, W. B., Wangersky, P. J. and Craig, H., in press. Excess ³He in the Atlantic Ocean. Earth Planet. Sci. Letters.
- Johnson, H. E. and Axford, W. I., 1969. ³He in earth's atmosphere. J. Geophys. Res. 74, 2433.
- König, H., 1963. Über die Löslichkeit der Edelgase in Meerwasser. Z. Naturforschg. 18, 363.
- Mamyrin, B. A., Anufrier, G. S., Kamensky, I. L. and Tolstikhin, I. N., 1970. Determination of the isotopic composition of helium in the atmosphere. Geokhimiya 6, 721.
- Manheim, F. T., 1970. The diffusion of ions in unconsolidated sediments. Earth Planet. Sci. Letters. 9, 307.
- Revelle, R. and Suess, H. E., 1962. Interchange of properties between sea and atmosphere. *In* The Sea, Volume 1, Hill, M. N. (Ed.). New York (Interscience).
- Weiss, R. F., 1970. The solubility of nitrogen, oxygen and argon in water and sea water, Deep-Sea Res. 17, 721.
- Weiss, R. F., 1971. The solubility of helium and neon in water and sea water. J. Chem. Eng. Data. 16, 235.