Reports

Noble Gases in Sea Water

Abstract. *Concentrations of noble gases in samples of sea water obtained at depths to 3437 meters from a Pacific Ocean station were measured by mass spectrometry. An excess of helium, in relation to concentrations of the other noble gases, is attributed to influx of atoms of this gas from the sediments where it is produced by the natural radioactive decay of members of the uranium and thorium series. On the basis of a steady-state model, the escape of helium from the earth is calculated at* 6.4×10^{13} *atoms per square centimeter per year.*

Definitive analyses of the concentrations and isotopic compositions of all noble gases in sea water have not yet been made, although several important problems in earth science depend upon such results. For example, the escape of helium-4 and argon-40 from the lithosphere, where these nuclides are produced in the natural radioactive decay series of uranium and thorium and by the decay of potassium-40, respectively, might be established if concentration gradients existed within the water column. Also, if the concentrations of noble gases in a sea water mass were established through equilibrium with the atmosphere and determined by the water temperature, when the water mass was at the ocean surface, then unmixed sea waters should yield an appropriate temperature based upon noble gas contents, while mixed water masses would not give a unique value (*1*). It is assumed that there have been no significant gains or losses of noble gases since the time of atmospheric equilibration of the water mass in question.

Previous work on concentrations of noble gases in sea water (*1, 2*) has yielded results lacking either high analytical precision or a complete spectrum of analyses of these gases. We have attempted to improve and extend the cited work in various ways: (i) analyses were made for most of the isotopes of the noble gases and for all the concentrations in which they occur; (ii) a highly sensitive and high-precision mass spectrometer was used; and (iii) a sea water sampling device that encapsulates water *in situ* and allows direct introduction of the water to the extraction apparatus was constructed (*3*).

An omegatron mass spectrometer was used (*4*) which can detect very small amounts of the noble gases; 5.5 ml of sea water were used for a single analysis of the five gases. Table 1 illustrates the precision of the measurements on a set of four air samples after normalization to standard temperature and pressure and subtraction of the water vapor. For the He, Ne, and Ar analyses, a sample of gas was expanded directly into the mass spectrometer immediately after extraction of dissolved gases from the liquid and removal of such interfering substances as water vapor, N_2, CO_2, and O_2. The Kr and Xe are measured after these gases have been separated from Ar; most of the fluctuations in the concentration of Kr, Xe, and Ar result from slight differences in yield in separation. Differences between the air samples collected on Mount Palomar and over the ocean can be attributed to the inadequacy of the corrections for pressure and humidity, which are inexact inasmuch as these parameters were not precisely determined for the Mount Palomar sample.

A sampling device in which aluminum tubing is sealed *in situ* by an electrically driven pinching mechanism was used to recover water samples from oceanic depths to 3400 m. This sampler completely eliminated problems entailed in transferring water samples from conventional recovery devices, such as Nansen bottles, to the analyzing apparatus.

Samples of sea water were collected at a station off California (31°24'N, 120°04'W; water depth, 3700 m) and transferred to the extraction apparatus in the laboratory. Details of the laboratory techniques will be published elsewhere. The results are given in Table 2.

Concentrations of the noble gases were converted to temperatures in the following ways. The temperature dependence of the solubility of argon in sea water has been determined by Douglas (*5*); our argon concentrations were compared directly with his curves to give the temperature cited in Table 3. The temperatures based on the relative concentrations of Ne and Ar, Kr and Ne, and Xe and Ne, were ascertained by using the pure water solubility data as functions of temperature [determined by Morrison and Johnstone (*6*)] and the quotients of the solubility of a given noble gas in sea water to the solubility of the same gas in fresh water (*7*) to obtain the curves of the ratio of the solubility of noble gas 1 to the solubility of noble gas 2, versus the temperature. The temperatures based on the above three ratios are also given in Table 3.

The temperatures based on the relative concentrations of Ne and Ar and Kr and Ne agree with the recorded temperatures to within several degrees in five of the eight samples of the pro-

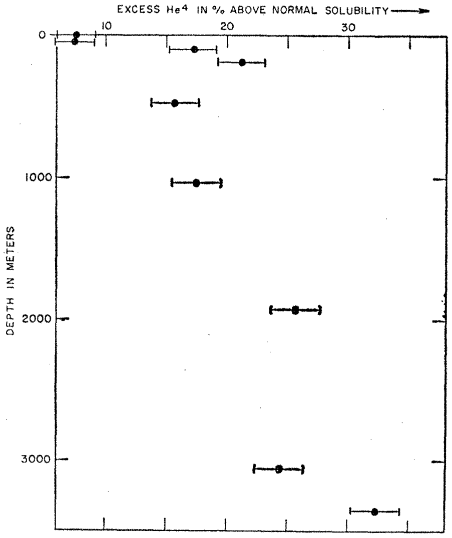

Fig. 1. Excess helium in sea water samples as a function of depth. Plotted is the average excess as determined by the ratio of Ne to Ar and Kr to Ne.

Table 1. Precision of measurements on four samples of air. The results cannot be compared directly with the atmospheric data given in Table 2 inasmuch as the noble gas measurements in this table are derived from samples of different sizes from the total sample.

Date of analysis (1964)	Sample No.	Size of sample* (cm^3)	Measurements in air (arbitrary units)					
			He^4 ($\times 10^6$)	Ne^{20} ($\times 10^6$)	Ne^{22} ($\times 10^7$)	Ar^{40} ($\times 10^5$)	Kr^{84} ($\times 10^{10}$)	Xe^{136} ($\times 10^9$)
3 March	128/AI†	0.258	1.31	4.12	4.21	1.05	6.9	4.2
23 March	131/AII†	.257	1.31	4.12	4.21	1.06	6.7	4.1
2 April	136/AIII†	.255	1.30	4.15	4.21			
6 April	138/A‡	.236	1.27	4.03	4.07	1.04	6.8	5.3

* Corrected to standard temperature and pressure. † Collected over the Pacific. ‡ Collected at Mount Palomar.

Table 2. Concentrations of noble gases, and the excess of helium in samples of sea water collected at 31°24′N, 120°04′W. Results expressed as cm^3 corrected to standard temperature and pressure. Conversion of the relative isotopic values measured with the omegatron spectrometer to the total rare gas content was based on the atmospheric concentrations (Atm.) shown at the end of the table and the isotopic compositions of Nier (*11*).

Depth (m)	He $\times 10^5$	Δ He $\times 10^6$	Ne $\times 10^4$	Ar $\times$ 10	Kr $\times 10^5$	Xe $\times 10^6$
46	4.4	2.9	1.74	3.10	7.0	7.7
93	3.6	6.6	1.23	2.15	4.8	10.0
189	3.7	8.2	1.24	2.25	5.1	7.9
462	3.1	5.8	1.06	1.78	3.7	4.4
1039	3.2	6.3	1.04	1.50	2.6	3.7
1930	4.6	11.0	1.54	3.28	7.9	12.5
3065	4.5	9.5	1.54	2.91	6.0	7.4
3437	5.0	13.4	1.62	3.28	7.4	11.0
Atm.	524		182	93.2	114	86

file (excluding depths of 462, 1039, and 3065 m). Temperature measurements of samples of surface water taken off the Scripps Institution of Oceanography pier indicate that the temperatures for the Ne and Ar and Kr and Ne concentrations are within 2°C of the measured temperatures (Table 4). The temperatures for the Xe and Ne relative concentration follow the same general pattern, but are the least accurate because of experimental difficulties in determining the concentrations of xenon.

The temperatures based upon the Ar concentrations alone for the pier waters are too low, indicating about 25 percent supersaturation. The profile samples in general give much too high temperatures for Ar; we cannot explain this anomaly.

In the two samples nearest the surface in the profile, the temperatures based on the relative concentrations of Ne and Ar and Kr and Ne closely accord with the measured temperatures. These two samples, both above the thermocline, probably reflect in their temperatures a close approach to equilibrium of the waters with atmospheric gases. The deeper samples also show correspondence of the temperatures (based on the noble gas ratios) with the measured temperatures, the values being slightly above 0°C. The sample from 3065 m shows a derived temperature slightly higher than measured temperature; this may have resulted from a pretripping of the sampler at a shallower depth.

The high temperature determined by measurements of noble gases at two intermediate depths (462 and 1039 m) deviate considerably from accepted concepts that the noble gases should reflect in their concentrations a surface water temperature at the time of equilibration with the atmosphere. This anomaly is unresolved; any loss of gases during collection, storage, and processing of the samples seems improbable. However, there are some indications that extraction of the gases from the liquid, and their transfer, may have been incomplete.

Temperatures based on a ratio involving helium are considerably and systematically higher than those of Table 3, suggesting an excess of helium. Such excess is to be expected if the rate of removal of helium from the lithosphere (helium produced by the decay of members of the uranium and thorium series) is (i) of the same magnitude as the production rate, or (ii) high, relative to the rates of mixing of oceanic water masses with each other and exchange with the atmosphere. Helium excess may also be generated by systematic fractionation of helium with respect to all other noble gases, but this is extremely unlikely.

Since the absolute solubilities of helium as functions of temperature in sea water are ill-defined, and our measured concentrations are in general below saturation, the amount of excess helium in sea water, as cm^3/liter, was determined by normalizing the helium concentrations to those of either neon or argon in the following equation, similar in concept to Eq. 6 of Benson and Parker (*1*):

$$\Delta \mathrm{He} = \left[\frac{A_{\mathrm{He}}}{A_{\mathrm{NG}}} - \frac{\alpha_{\mathrm{He}}}{\alpha_{\mathrm{NG}}}\right] \times A_{\mathrm{NG}} \times C_{\mathrm{He}}^{\mathrm{Air}}$$

Table 3. Temperatures (°C) of sea water observed or calculated from the concentrations and ratios of noble gases. Water collected at 31°24′N, 120°04′W.

Derivation of temperature	Depth (meters)							
	46	93	189	462	1039	1930	3065	3437
Observation	13.5	11	8.5	5.7	3.7	2.1	1.7	1.6
(Ne/Ar)	12	14	12	17	29	1	8	4
(Kr/Ne)	9	12	10	19	>30	<0	11	0
(Xe/Ne)	24	<0	7	27	>30	<0	18	3
(Ar)	11	>30	>30	>30	>30	8	14	8

Table 4. Comparison of observed temperatures of surface water off La Jolla pier with temperatures calculated from noble gas ratios (°C).

Derivation of temperature	Date of collection (1963)							
	4 Dec	4 Dec	4 Dec	5 Dec	5 Dec	5 Dec	6 Dec	6 Dec
Observation	15.5	16.0	16.3	15.5	15.8	15.6	15.8	16.3
(Ne/Ar)	12	15	16	12	16	14	15	16
(Kr/Ne)	13	17	21	13	17	13	16	18

where *A* refers to the measured gas concentration in sea water, normalized to 1 atm partial pressure of the gas, α is the solubility coefficient, and $C^{\text{Air}}_{\text{He}}$ is the concentration of helium in air. The values of the solubility coefficients were taken for the temperature corresponding to an average temperature based upon the concentration ratios of Ne to Ar and Kr to Ne. The values for the excess helium (Table 1) are plotted in percentages above normal solubility at the corresponding temperature in Fig. 1.

The highest values (around 32 percent) are found in samples taken from depths nearest the bottom. Surface samples gave values close to 8 percent which can be attributed to either incomplete exchange of helium with the atmosphere or systematic error in the solubility data for helium. The two samples (462 and 1039 m) which gave calculated temperatures for the noble gases higher than measured temperatures also show a minimum in the helium excess.

If excess helium found in sea water is attributable to influx of helium from the lithosphere (helium production in the water column itself from dissolved uranium and thorium is negligible), it is possible to consider quantitatively the problem of the helium escape from the upper atmosphere, with the assumption of steady-state conditions. The injection of helium into the water column will occur at the sediment-water interface and the gas will be distributed both horizontally and vertically by convective mixing processes; such a mixing is suggested in Fig. 1. An average value of the excess can be appropriately obtained from the deep water samples (those below the thermocline); after subtraction of the excess found in surface water it is 6.1×10^{-6} cm^3/liter or 1.64×10^{11} atom/cm^3. Fourteen samples of surface water give an average helium excess of 2.9×10^{-6} cm^3/liter. Since the time elapsing between contact of a water mass with the atmosphere and its present location in deep water is of the order of 1000 years (*8*) on the basis of radiocarbon studies, and with an assumed average depth of 3900 m for the ocean, one can derive a rate of efflux from the lithosphere into the water or an "atmospheric production rate" (*9*) for helium of $(1.64 \times 10^{11} \times 3.9 \times 10^5)/10^3 = 6.4 \times 10^{13}$ atom cm^{-2} year^{-1}. The mean lifetime for a helium atom in the atmosphere is then found to be 1.8×10^6 years, assuming that the "atmospheric production rate" from the continents is the same as the oceanic value and that the helium content of the atmosphere is 1.13×10^{20} atom/cm^2.

Although we agree that more knowledge of the distribution of excess helium in the oceans and of the age of water below the thermocline is desirable, we think that discussion of this novel approach to the helium escape problem in relation to other investigations is justified. The problem of helium escape from the terrestrial atmosphere is considered in two recent papers (*9, 10*). Nicolet arrives at a figure of $\leq 5.5 \times 10^{13}$ atom cm^{-2} year^{-1}, based on observations of the terrestrial heat balance and assuming that the generation rate of helium is essentially equivalent to the "atmospheric production rate."

On the other hand, Wasserburg and co-workers (*10*) derive an "atmospheric production rate" for helium from observations made on terrestrial natural gases and from certain assumptions on the origin of atmospheric argon. They find a production rate between 4.4×10^{12} and 2.2×10^{14} atom cm^{-2} year^{-1} with 10^{11} atom cm^{-2} year^{-1} as a best estimate. It can be seen that our rate for the atmospheric production of helium, derived from the accumulation of helium during the average time the water spends below the thermocline, is slightly above Nicolet's upper limit and agrees well with Wasserburg's statement that the true value probably lies closer to the higher production rate.

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References and Notes

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Solar X-Ray Spectrum below 25 Angstroms

Abstract. *Below 25 Å, the solar spectrum consists primarily of the emission lines of Fe* XVII, *O* VIII, *O* VII, *and N* VII. *The lines of the more highly ionized atoms, Fe* XVII *and O* VIII, *originate in localized active regions. Lines of O* VII *and N* VII *emanate from the full disk.*

On 25 July 1963 spectral measurements of solar x-ray emission were made with a Bragg crystal spectrometer carried in an Aerobee Rocket. The spectrometer consisted of a single crystal of potassium acid phthalate (KAP) as the diffracting element, a Geiger counter detector, and a mechanism to rotate the crystal and detector in a 1:2 ratio. Wavelengths were determined from the Bragg equation:

$$n\lambda = 2d \sin \theta \qquad (1)$$

where n is the order of diffraction, λ the wavelength, d the grating constant, and θ the angle of diffraction. The instrument was kept pointed at the sun by a biaxial pointing control. Potassium acid phthalate has a $2d$ spacing of 26.633 Å. The angle θ was varied continuously during flight to provide one full spectrum scan and a partial repeat. The accuracy of wavelength determination was about ± 0.1 Å and was limited primarily by the precision of mechanical alignment and by pointing excursions. No collimation was used. Consequently the angular width of an observed line was a direct measure of the angular width of the x-ray emitting region.

The observed spectrum was dominated by emission lines which contained at least 85 percent of the integrated flux between 10 Å and 25 Å. No line was detected below 13 Å with an intensity as great as 10^4 photons/cm^2 per second. All the observed lines are listed in Table 1 together with their respective identifications and in-