THE MARINE GEOCHEMISTRY OF ARGON

By

David Frank Bolka

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ABSTRACT

An extensive literature search has been made with the attempt to collect all references to the solubility of argon in distilled water, aqueous salt solutions and sea water except for untranslated Russian literature. The bibliography is considered to be a significant collection of work up to the present time concerning, not only the solubility of argon, but the sources and the distribution of argon in the cosmos, lithosphere, atmosphere, biosphere and hydrosphere.

The properties and processes of formation of argon isotopes are discussed and the decay of potassium-40 to argon-40 is treated at length with calculations of the amounts of argon-40 introduced into the oceans by this process. These amounts are shown to be negligible for any conceivable residence time of deep water.

The solubility of argon in distilled water and in sea water is discussed with references to original papers of all investigators who have been concerned with this problem. The effect of hydrostatic pressure on the solubility of argon is discussed theoretically and figures are given to show that the equilibrium model of the argon cycle in the sea is incorrect.

The conclusions that the solubility of argon in distilled water has been well determined and that the solubility in sea water is not known well enough are made. It is also concluded that much more work is necessary in the distribution of argon in the oceans and that too few data have been gathered to give any insight into the argon cycle in the marine environment except that sea water appears to be near saturation with respect to dissolved argon. The variations from saturation can be explained by variations in atmospheric pressure, heating or cooling of the water after equilibration with the atmosphere, mixing, or supersaturation because of trapped bubbles.

Utilization of the dissolved argon content of sea water samples as indicators of the conditions under which solution took place and as a means of determining the amounts of nitrogen and oxygen that have been consumed in biological and chemical reactions is considered. The use of variations in the dissolved argon content of water samples because of the differing surface conditions from summer to winter as an indicator of the mean drift velocity of a water mass is proposed. Antarctic bottom water is used as an example.

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INTRODUCTION

Since the discovery of argon (Rayleigh and Ramsay, 1895) investigators have been intrigued and puzzled by its "nobility." Only recently has argon been shown to combine chemically with other elements and that it is not inactive, but possesses a relatively high ionization potential (Selig, et al. 1964). However, the chemical reactions involving the noble gases take place under conditions of temperature, pressure and catalysis that are not found in the sea and in this presentation argon will be considered to be chemically inert.

This thesis is the result of a comprehensive literature search and an attempt to collect all of the published material relating to argon in the marine environment and much of the material dealing with the terrestial abundance and distribution of argon. As will be seen, little work has been done in the determination of argon concentrations and distribution in the sea and this is a field that deserves much more investigation. As an inert gas in the sea, argon could presumably be used as a tracer in water masses and as an in situ indicator of the history of a parcel of water.

In this thesis the characteristics of the isotopes of argon will be considered, its cosmic and terrestial distribution will be discussed and the argon cycle in the sea will be treated in considerable detail. The utilization of the dissolved argon content of sea water as a tracer and autobiographical indicator will be discussed.

PROPERTIES AND FORMATION OF ARGON ISOTOPES

Eight isotopes of argon have been discovered or prepared; of the eight, with consecutive mass numbers from 35 through 42, three, argon-36, 38 and 40 are naturally occurring in the earth and its atmosphere. Some of the others may exist in stellar bodies and in the upper portions of the earth's atmosphere where cosmic ray activity is more intense than it is near the earth's surface. The significant properties of the isotopes of argon are collected in table 1.

The hard-sphere model for the atoms of gaseous argon describes the behavior of the gas phase. Argon, while monotomic and inert, is not perfect; it follows van der Waal's equation

$$(P + n^2a/V^2)\,(V-nb) = nRT \qquad (1)$$

quite well with the coefficients a = 1.345 liters atm/mole^2 and b = 0.03219 liters/mole. The density of argon (of terrestial isotopic composition) is 1.7837 g/liter and its specific gravity is 1.3796 (air = 1). Its melting point is -189.2° C and its boiling point is -185.7° C.

The most striking irregularity in the distribution of argon is the prepanderance of argon-40 in the earth. Theoretically, the isotope of mass number 36 should be the most abundant because mass number 36 is one of the "magic numbers" of filled nucleon shells (Rankama, 1963). This, however, is not the case on earth because of the decay of potassium-40 to argon 40 (von Weizsacker, 1937; Thompson and Rowlands, 1943).

Gerling and Shukolyukov (1959), in analysis of seventeen uranium minerals showed that argon-38 was present in amounts greater than could be accounted for by adsorption of atmospheric argon and concluded that it could be produced as one of the spontaneous fission products of uranium-238. They also hypothesized that a radioactive "mother" substance with a half life of about 6.9×10^8 years was the intermediate member of the decay chain, but were unable to isolate it. Their calculations for the yield ~3.7% from spontaneous fission of uranium-238 and 3% from neutron-induced fission of uranium-235 of argon-38 in these minerals are now considered to be several orders of magnitude too high (Wasserberg & Bieri, 1958; Signer & Nier, 1959), although Gerling's figures may be approached in materials that have been enriched in uranium-238 and chlorine-35. Fleming and Thode (1953) found that the argon-36/argon-38 ratio in pitchblende varies by more than 300% and never reaches that in air (5.35). They deduced the process of formation of argon-38 to be either

$$Cl^{35}\,(\alpha\,,p)\ Ar^{38}$$

or

$$Cl^{35}\,(\alpha\,,n)\ K^{38} \xrightarrow{\beta^+} Ar^{38}$$

and state that the extent of the reaction depends on the uranium-238 content, the amount of light elements contained in the material and the age of the sample. The thermal neutron cross section for chlorine-35 is 30 ± 20 barns.

Rankama (1963) proposes the reaction

$$Fe^{56} \xrightarrow{SP} K^{38} \dashrightarrow Ar^{38}$$

and a similar reaction from calcium for the formation of argon-38 in iron meteorites with a yield from a meteorite of 10 cm radius of 1.7×10^{18} atoms or $0.06\ cm^3$ (STP) in a period of 10^9 years. In terms of yield per gram of iron-56 he states that $1.0 \times 10^{-15}\ cm^3$ (NTP) of argon-38 are produced per gram of iron per year and that about 3.2×10^{-15} cm^3 (STP) of argon-38 are produced per gram of calcium per year.

Rankama also lists the fission products from atomic and thermonuclear bomb explosions and from the table presented (pp. 104-105) it appears that little of the immediate activity and none of the longer lasting activity is attributable to nuclides of argon or nuclides that decay to produce argon in detectable amounts. Friedlander and Kennedy (1949), in figure III-2, page 70, show that the yield of fission products extends from mass number 70 to mass number 165. Thus, for fission, mass numbers of forty will be produced in exceedingly small amounts if, indeed, at all. Thus, the bomb input of argon into the atmosphere and hydrosphere may be ignored.

Ehhalt, et al (1963) have proposed that argon-37 is produced in the atmosphere through the neutron capture of argon-36. In normal air the activity of the argon-37 produced in this manner is less than 2.5 dpm/mole Argon and they conclude that the argon-37 produced is about 10 % of the natural carbon-14 in the atmosphere. Furthermore, they state that the argon-37 produced decays by K electron capture to chlorine-37, the half-life of the reaction being 34 days. The chlorine-37 then decays spontaneously to stable chlorine-36, the half life of this reaction being on the order of 1 second.

Argon-36 Production

In areas of high neutron flux, argon-41 is formed through neutron capture by argon-40 (L. N. Frey, personal communication).

$$Ar^{40} (n) \longrightarrow Ar^{41}$$

This reaction is unimportant in natural surroundings because of the short half-life of argon-41 and the absence of areas of high neutron flux.

See fiqure 1 for a schematic representation of formation of argon isotopes.

THE COSMOCHEMISTRY OF ARGON

Argon is the fifth most abundant element in the universe with a calculated abundance of 1.5×10^5 atoms per 10^6 atoms of silicon (Cameron, 1959). Brown (1949) has calculated the cosmic abundance of argon-36 to be 10^5 atoms per 10^6 atoms of silicon from lognormal abundance curves of the elements. He also states that in planetary nebulae the ratio of argon to oxygen is 0.0060 in the absence of silicon and that this same ratio is 0.1 in γ-Pegasi which has a silicon/oxygen ratio of 0.09. From solar and stellar data Brown calculates an abundance of 1.30×10^4 to 2.2×10^5 atoms per 10^6 atoms of silicon. Aller (1957), from examinations of planetary nebulae has found a mean argon/oxygen ratio of 130/104, but the actual values are widely scattered (236, 91, 180, 91, 310, 68, 100, 81, 106, 123). Suess and Urey (1956) have found the following abundances for argon (per 10^6 atoms Si) in β-type stars and nebulae.

Argon-36	1.50×10^5
Argon-38	1.26×10^5
Argon-40	2.4×10^4

They state that the above figures are probably no more accurate than within a factor of ten. They also have excluded radiogenic argon-40. Brown (1949) gives argon-36 and argon-38 abundances of 4.50×10^4 and 8.7×10^3, respectively per 10^6 atoms of silicon and considers all argon-40 as radiogenic and excludes it.

Alpher and Herman (1953), in a comprehensive and critical review of the mechanisms of element formation have concluded that the nucleon capture in the non-equilibrium state of the expanding universe suffers from fewer difficulties than other theories. An extremely thorough treatment of interstellar nucleogenesis, including detailed discussion of the several processes that have been hypothesized as well as proved, has been published by Burbridge, Burbridge, Fowler, and Hoyle (1957). Their evidence is most impressive in explaining the formation of the elements. They maintain that genesis of the light nuclei takes place in first generation stars where major elements of carbonaceous substances as well as the elements up to atomic number about 25 are synthesized. Following instabilities in the star and eventual return of the stellar material to interstellar space, stars of later generations are formed. It is in these that elements of higher atomic weight are synthesized. Although many theories explain portions of the creation of the elements, none is as thorough and complete as that of the Burbridges, Fowler and Hoyle. These theories will not be discussed here and the reader is referred to their paper for a comprehensive and extremely interesting discussion.

Menzel (1960) has stated that the atmosphere of Venus is composed of carbon dioxide (90 - 100%), nitrogen (0 - 9%) and argon (0 - 1%). Kuiper (1947) in a theoretical consideration of the ability of a planet to hold its primordial gaseous constituents based on the calculation of escape velocity for each of the lighter gases has predicted that argon should be the fifth most abundant gas in the atmospheres of Jupiter and Saturn and the fourth most abundant on Neptune; although in the latter it would probably exist in the solid state. He also compares the planets in declining ability to retain their atmospheres for periods of at least 10^9 years. The evidence given by Menzel (1960) shows that argon exists in the atmosphere of Venus; it should also be present in the atmospheres of Uranus, Mars, Triton, the third moon of Jupiter and possibly Pluto.

Isotopic ratios of argon in the cosmos have been discussed by Suess (1949). He concludes that cosmic argon consists of 85.6% argon-36, 14.1% argon-38 and about 0.4% argon-40. Thus, cosmically, it appears that argon abundance ratios follow the theoretical predictions that argon-36 should be the most abundant isotope of argon.

THE ABUNDANCE AND DISTRIBUTION OF TERRESTIAL ARGON

Argon in the Lithosphere:

The argon content of the lithosphere consists of two distinct phases: the argon that is trapped in the crystal lattice of minerals and that which is contained between grains and/or crystals. The argon which is held between the grains of crustal material is released when the material is weathered and is added to the supply of argon in the atmosphere. That which is found in the crystal lattice is generally held tightly enough so that it is carried along with the weathered material and is exsolved into the atmosphere or hydrosphere only very slowly, if at all. In most work on the crustal abundance of argon these two forms are determined together and the results reported as if argon were contained in rocks and minerals only between grains. Thus, the figures given for the crustal occurrence of argon usually consider only the argon that can be liberated by weathering and its cycle in the lithosphere. These figures are helpful, however, in considering the role of argon in the lithosphere and in potassium - argon dating.

Mason (1958) has estimated the amount of argon in crustal rocks to be 0.04 g/ton and the argon/silicon ratio in the whole earth to be 5.9×10^{-8}. Brown (1947) estimated that, on the average, each gram of rock in the earth contains 3.9×10^{-8} grams of argon. Brown's figure must be treated as an approximation because the argon content depends on the potassium content and the age of the rock as well as the size of the grains of which the rock is composed as will be seen later. Brown, using the above average, estimates that the minimum amount of argon in the lithosphere is 6.6×10^{19} grams and that the maximum is 3.0×10^{20} grams.

Rayleigh (1939) and Elerson and Polykovskii (1963) have investigated the gaseous constituents of rocks. Their figures are listed in tables 2 and 3. The argon content of basalt cored in the Mohole project's Guadelupe site has been reported by Krueger (1964); he reports 0.00019 parts per million as the average argon content in a sample with an age of 15 ± 7 million years and 0.0030 parts per million in a sample with an age of 32 ± 10 million years. Brown (1949) has reported the argon content of meteoritic phases to be 0.12% by weight. This percentage is highly variable from siderites to chondrites and also between two meteorites of the same type and should be considered only in the light of its usefulness as an order-of-magnitude type figure.

Argon in the Atmosphere:

The argon content of the atmosphere has been determined many times and with very good accuracy. The accepted value is 0.9343% by volume as shown in table 4, the U.S. Standard Atmosphere (1962). Moissan (Gluekauf, 1951) determined the argon content of atmospheric air at twelve widely scatterred locations. His figures, shown in table 5, illustrate the constantcy of argon in the atmosphere.

In most theories of atmospheric evolution it is assumed that all of the argon of proto-atmosphere as well as water and most other lighter gases escaped before the earth solidified and that the present atmpspheric gases have been released from the earth over the last approximately 10^9 years (Russell and Menzel, 1933; Rubey, 1951).

The argon and other gases that have been outgassed in the course of geologic time have either emanated from volcanic and fumarolic activity or have slowly diffused upward through the crust and been released through weathering of crustal material. Cady and Cady (Brown, 1947) and Matsuo (1961) have analysed volcanic gases for argon. Their figures are collected in tables 6 and 7. Allen (1922) investigated the nitrogen and argon content of volcanic gases in many regions of the world and found an overall average of 0.42% argon. The amount of argon varied widely, with an average value of 0.26% in Hawaii, the West Indies and South America, 1.23% in Iceland and 0.13% in the Katmai region of Alaska. Some of the volcanic gases in Hawaii were found to contain no argon. Allen concludes that the argon comes from crustal rocks and that it is primordial, but he does admit the possibility of atmospheric contamination and recycling of argon through the hydrosphere. Rankama (1954) has estimated that boriferous volcanic gases near Larderello, Italy, supply about 4.4 x 10^6 grams of argon annually. He does not state, however, if the total amount is primordial or if there is a possibility of atmospheric contamination or recycling. From the results of the preceding investigations it may be concluded that outgassing of the primordial argon of the crust and, perhaps, of the mantle as well, is still in progress.

The role of Potassium-40 Decay:

Of the 6.55 x 10^{18} grams of argon in the atmosphere, 6.53 x 10^{18} grams is argon-40 (Rankama, 1954). Let us now consider the role of the radioactive decay of potassium-40 in supplying the theoretically anomalous proportion of argon-40 in the earth and its atmosphere.

Because of the abnormal abundance of argon-40. This reaction was observed by Thompson and Rowlands (1943 and has since been utilized in potassium-argon dating by many investigators. Wasserburg (1954) has written a comprehensive and elucidating article on this method of dating; it will be discussed briefly here.

Potassium-40 undergoes a dual decay to argon-40 through K shell electron capture and to calcium-40 through emission of an electron, as shown in figure 2. The relevant decay constants are collected in table 3.

The following equations can be written describing the decay of potassium-40. If N_o is the number of K^{40} atoms at time t = 0, N' is the number of Ar^{40} atoms formed in time, t, and N is the number of atoms of K^{40} left at time, t, and assuming N' = 0 at t = 0, and a decay constant λ,

$$dN/dt = -\lambda N \tag{2}$$

$$N = N_o e^{-\lambda t} \tag{3}$$

$$N' = N_o - N = N(e^{\lambda t} - 1) \tag{4}$$

$$N'/N = \frac{N(e^{\lambda t} - 1)}{N} = e^{\lambda t} - 1 \tag{5}$$

If λ_β and λ_K are the decay constants for β -decay and K capture, respectively, then

$$N'/N = \frac{\lambda_K}{\lambda_K + \lambda_\beta} \left[e^{(\lambda_\beta + \lambda_K)} - 1 \right] \tag{6}$$

and

$$t = \frac{1}{\lambda_K} \quad \frac{N'}{N} \tag{7}$$

where this is the age of the material as determined by measuring the ratio N'/N. Expressing the production of argon-40 in terms of the branching ratio, R,

$$N' = \frac{R}{1 + R} \quad N(e^{\lambda t} - 1) \tag{8}$$

Values for the branching ratio, R, of potassium-40 range from 0.06 to 0.13 with the best value being 0.123 (Rankama, 1963). Ahrens (1954) has estimated the cosmic abundance of potassium to be about 0.2%. Potassium-40 comprises 1.18 x 10^{-2}% ± 1 x 10^{-2}% of terrestial potassium (Reutersward, 1951). Table 9, contains the observed abundances of potassium in different rivers of the world (Livingstone, 1963) and tables 10 and 11 contains analyses of pelagic sediments for potassium (El Wakeel and

Riley, (1961) and the content of potassium-40 calculated from Reutersward's data.

Turekian (1959) using the model of Shillibeer and Russell (1955) has calculated the production of argon-40 in the crust and release into the atmosphere to amount to 3.02×10^{32} atoms/year, while Damon and Kulp (1958) have computed the production in the crust to be 4.0×10^{31} atoms per year and that in the mantle to be 3.08×10^{32} atoms/year at the present time, but that the maximum amount of outgassing from the crust at present is 1.5×10^{30} atoms per year. If this rate had been constant for the last 4.5×10^{9} years only about 1% of the present amount of argon-40 in the atmosphere would have been supplied. Damon and Kulp, therefore, assume that the crust and mantle must have lost about 30% of their argon-40 during the first billion years of geologic time. This conclusion is in opposition to that of Turekian, possibly because Turekian assumed the composition of the earth to be the same as that of chondrites and based his calculations on the fact that both the crust and the mantle are outgassing argon-40 at the present time. His conclusion is that the rate of outgassing has been constant over the course of geologic time. It appears unlikely that the mantle is outgassing argon-40 to any appreciable extent at the present time since an atom of argon-40 is emitted with an energy of only 30 ev during the decay process (Rankama, 1963). This energy is several orders of magnitude lower than that needed for the argon-40 to escape from the crystal lattice. Krylov and others (1962) have found that radiogenic argon-40 is fully preserved in particles of feldspars and micas less than 0.001 mm in radius; Murin, et al (1962) have found it necessary to anneal microcline perthite in order to outgas more than a fraction of one per cent of the argon-40 it contains; Fechtig, et al (1961) have found that the diffusion from sanidine, phonolithe, augite and moldavite at room temperature is so small that it need not be corrected for in potassium- argon age determinations; and Hurley (private communication) has stated that argon-40 is completely retained by sediment particles at temperatures below about 150° C. Equally impressive evidence of the ability of materials to retain radiogenic argon-40 is presented by Khutsaidze (1962) who states that after heating for eight hours at 500° C less than 2% of the argon-40 contained in microcline escaped and none escaped from biotite. These values for the diffusion, or rather non-diffusion, of argon-40 from various materials tend to support the conclusions of Damon and Kulp (1958).

Thus, while the decay of potassium-40 has supplied most, if not all, of the argon-40 in the earth, its atmosphere and hydrosphere, the rate of production is such that it is only noticeable over periods of the order of the age of the earth.

ARGON IN THE MARINE ENVIRONMENT

Argon, in contrast to most of the other gases dissolved in sea water, may be considered to be introduced from three distinct sources: the atmosphere, the decay of potassium-40 in the sediments and outgassing of argon-40 into the sea, and the decay of potassium-40 in the salt of the sea itself. Two simple calculations will serve to illustrate that the latter two sources are negligible in comparison with the atmosphere.

Using the following values for oceanic parameters and constants:

1. Percentage of K_2O in the sediments = 2.10% (El Wakeel & Riley, 1961)
2. Average sediment density = 2.00 gm/cm^3 (Nafe and Drake, 1963),
3. Area of all oceans = 3.61×10^8 km^2,
4. Volume of all oceans = 1.37×10^{21} liters (Sverdrup, et al, (1942),
5. Branching ratio of K^{40} = R = 0.123,
6. Total decay constant of $K^{40} = \lambda = 5.33 \times 10^{-9}$ yr^{-1} (Rankama, 1963);

and making the following assumptions:

1. An average sediment thickness of 1 km extending over the bottom of all oceans,
2. The constitution of the sediments and the oceanic salt has remained the same over geologic time,
3. An average chlorinity of 19°/oo (density = 1.023 g/cm^3),
4. An average potassium content of sea water of 0.038% (Miyake, 1939; Webb, 1939),
5. All the argon-40 produced has been released into the ocean, and

substituting in equation (8) we arrive at the following contributions of argon-40, in 4×10^9 years. From the sediments, 0.018 ml/l of argon-40 has been outgassed into the sea and from the potassium in the sea salt, 0.002 ml/l of argon-40 has been produced in sea water. However, the residence time of potassium in sea water is only the order of 10^7 years (Barth, 1961; Goldberg and Arrhenius, 1958) and in this period of time only 1.4×10^{-7} ml/l of argon-40 would have been produced in sea water, a truly negligible amount. The composition of silt interstitial waters has been studied by Shishkina (1959) and Shishkina and Bykova (1962). They find that the compostition of the interstitial waters of pelagic sediments is very nearly the same as that of sea water with respect to chlorine and potassium. If assumption 5, above, is revised in the light of diffusion evidence cited in the preceding section (Rankama, 1963; Krylov, et al, 1962; Murin, et al, 1962, Fechtig, et al, 1961; Hurley; Khutsaidze, 1962) the contribution of argon from the sediments may be lowered by at least two orders of magnitude and is truly negligible.

One other consideration which has been neglected so far in the contribution of argon-40 to the sea by sediments is the concept of oceanic overturning and the residence times of deep water masses. Broecker, et al (1961), through the use of carbon-14 dating methods have determined the residence times of deep water masses. These data are collected in table 12. The longest residence time of any water mass is on the order of a few thousand years. It is evident that in this short period of time no appreciable contribution of argon-40 could be supplied by the sediments. Thus, we may conclude that a negligible amount of argon-40 is supplied through the radioactive decay of potassium-40 in the sea and sediments. The only source of argon in the sea that it is necessary to consider (except, perhaps biological activity) is the atmosphere.

Argon in the Marine Biosphere:

Before considering the mechanism of solution and the amount of argon supplied by the atmosphere, let us consider the role of argon in the biosphere. Vinogradov (1953) in his monumental work on the elementary composition of marine organisms quotes only two sources, Tolomei (1897) and Schloesing and Richard (1896) The former having detected argon in plants and the latter two investigators having found it in the swimbladders of fish in the same proportions as in air. They concluded that there was no biochemical process influencing the presence of argon but that it was due to the "simple penetration from air." Larimer and Ashley (1962) found that the gas in floats of Portuguese Men-of-war consisted of 1.1% argon, 74.4% nitrogen, 14.4% oxygen, 8.9% carbon monoxide and 0.4% carbon dioxide. He concluded that the argon is slightly selectively diffused into the floats from the atmosphere and from' sea water. From this meager evidence and from the new work on the chemical reactions of the noble gases (Selig, et al, 1964) it may be concluded that the biosphere does not play an important role in the argon cycle in the sea.

The Physical Chemistry of Solution of Argon:

The solubility of any gas in distilled water depends on the partial pressure of the gas in the atmosphere, the temperature, and the total pressure. In dilute solutions, Henry's Law describes the gross characteristics of the solubility; that is

$$C_i = K \times p_i \qquad (9)$$

where C_i is the concentration of the i-th constituent in the solution,

p_i is the partial pressure of the i-th constituent in the vapor phase

and K is the constant governing the solubility, in general a function of temperature, total pressure and composition of the solvent.

In considerations of the solubility of gases in distilled water, the Bunsen absorption coefficient is usually given as the figure for the solubility. The Bunsen coefficient, α, is defined as the amount of gas in cm^3 at standard temperature & pressure that is dissolved in one liter of water when the pressure of the gas over the solvent is 760 mm Hg. Another quantity sometimes used (Lannung, 1930) is the Ostwald coefficient, l, which is the equilibrium ratio of volume concentrations of the gas in the solution and in the vapor phase. The relation between α and l is

$$l = \frac{\alpha T}{273} \qquad (10)$$

Most investigators report either the Bunsen coefficient or the solubility in milliliters (STP)/liter of water. To change from to the solubility in ml/l, s_o, the following relation can be easily derived.

$$s_o = \frac{\left[(760 + p\ water) - p_i\right]}{760}\alpha_q \qquad (11)$$

where p_{water} is the vapor pressure of water at the temperature of solution

p_i is the partial pressure of the gas in millimeters of mercury in a dry, standard atmosphere

and q is the percentage of the gas in a dry, standard atmosphere.

Another expression which is useful in considering the solubility of argon, especially when older investigations are encountered is the following due to Coste (1927), first proposed by Winkler (1906),

$$\alpha_{Ar} = 1.435\,\alpha' \qquad (12)$$

in which α_{Ar} is the Bunsen solubility coefficient of argon.

α' is the Bunsen coefficient for "atmospheric nitrogen" (A mixture comprised of 98.815% nitrogen and 1.185% argon with negligible amounts of the other rare gases).

The earliest work on the solubility of argon in distilled water was done by Rayleigh and Ramsay (1895) and many investigators have redetermined the values. The best values available today are probably those due to Klots and Benson (1963a) and Douglas (1964) and these are tabulated in table 13. The fine agreement between the two lends credibility to their accuracy. König (1963) has also recently investigated the solubility of argon in distilled water but his values do not agree well with those of Klots and Benson or Douglas (See table 13). Throughout the sixty-five years of investigation of the solubility very little agreement has occurred between workers especially at lower temperatures. All the values that were found are collected in table 13, with references to the original papers. The values obtained by Klots and Benson (1963) and Douglas (1964) are plotted in figure 3. Koyama (1958) has also described a method of direct determination of argon and nitrogen in which calcium metal is used to remove nitrogen and an alkaline pyrogallol solution is used to remove the oxygen and carbon dioxide from a mixture of gases. The fraction of gas remaining is considered to be argon. The amounts of argon and nitrogen are determined by measurements of the gas pressure before and after removal of each constituent. An accuracy of 3% is claimed, but no data are given.

Eley (1939, 1944) and Klots and Benson (1963b) have investigated the mechanism of solution of argon. The enthalpy of solution is negative with the value -2.97 kcal/mole (Eley, 1939) or -3.015 kcal/mole (Klots and Benson, 1936) at 20° C. The entropy of solution is also negative with a value of either -22.6 kcal/deg· mole (Eley, 1939) of -32.0 kcal/deg· mole (Klots and Benson, 1963b) at 20° C. Both Δ H and Δ S become less negative with increasing temperature. The specific heat at constant pressure, ΔC_p, is 46 ± 10% cal/deg· mole as determined by Klots and Benson, at 20° C and decreases with increasing temperature.

Eley (1941) has proposed the following mechanism for the solution of inert gases in water. A cavity the size of the gas molecule is made in the water and the gas molecule is inserted in the cavity. The energy of cavity formation is low because the molecules of water retain their polarization around the cavity. Presumably the structure of the gas-water solution is more ordered than that of the gas alone or of the water in the absence of the dissolved gas molecules, hence the negative entropy of solution. Only a certain degree of order can be attained at any temperature; less ordering occurs at higher temperatures so there are a limited number of sites available to be filled by the gas molecules. Thus, this theory qualitatively explains the decrease in solubility with increased temperature.

Valentiner (1927, 1930) proposed the equation

$$\log_{10} \alpha = A (1/T) + B \log_{10} T - X \qquad (13)$$

for the dependence of the Bunsen coefficient on temperature (in degrees Kelvin). Using von Antropoff's (1910) values be concluded A = 3069, B = 20.01, and X = 61.230. These values fit the data used to within 1%, thus validating the form of the equation. New determinations, especially those of Klots and Benson (1963a) and Douglas (1964) are of such accuracy (0.2% and 0.25%, respectively) that any least squares fit of the data points is much less accurate than a smooth curve drawn through the experimental values. Also, since the values of Klots and Benson and Douglas do not agree within the stated accuracies, it is not profitable to revise the coefficients of (13) at this time. More, definitive, work on the relationship between the Bunsen coefficient and temperature is needed.

Klots (1961) has investigated the effect of hydrostatic pressure on the solubilities of gases and has found that the solubilities of nitrogen and oxygen decrease with increasing hydrostatic pressure. The effect of pressure as being a second order effect on the solubility is also discussed by Guggenheim (1949).

A straightforward treatment of the effect of hydrostatic pressure can be derived by considering the partial molal free energy of a solute in an equilibrium model (Klotz, 1963). I

If equilibrium is attained the partial molal free energy, $\overline{F}$ is identical at the surface and at depth, or $F_o = F_d$, where the subscripts o and d refer to the surface and to a depth, d, respectively.

Then $d\overline{F} = 0$.

$$\overline{F} = \text{fxn}(z, P, \ln m) \qquad (14)$$

z is the vertical axis, positive downward

P is the hydrostatic pressure

and m is the amount of solute dissolved.

Thus, $$0 = d\bar{F} = \left(\frac{\partial \bar{F}}{\partial z}\right)_{P,\ln m} dz + \left(\frac{\partial F}{\partial P}\right)_{z,\ln m} dP + \left(\frac{\partial \bar{F}}{\partial \ln m}\right)_{z,P} d\ln m \qquad (15)$$

and $$\left(\frac{\partial \bar{F}}{\partial \ln m}\right)_{Pz} d\ln m = -\left(\frac{\partial \bar{F}}{\partial z}\right)_{P,\ln m} dz - \left(\frac{\partial \bar{F}}{\partial P}\right)_{z,\ln m} dP \qquad (16)$$

$$\left(\frac{\partial \bar{F}}{\partial z}\right)_{P,\ln m} = -Mg\,;\quad \left(\frac{\partial \bar{F}}{\partial P}\right)_{z,\ln m} = \bar{V}$$

m = molecular weight of the solute

g = acceleration of gravity

$\bar{V}$ = partial molal volume of the solute

using Henry's Law, $\bar{F} = RT\ln m + B$

$$\left(\frac{\partial \bar{F}}{\partial \ln m}\right)_{P,z} = RT$$

Then $$RT\, d\ln m = Mg\, dz - \bar{V}\, dP \qquad (17)$$

$$dP = \rho\, g\, dz$$

ρ = density of water

and $$RT\, d\ln m = Mg\, dz - \bar{V}\rho\, g dz \qquad (18)$$

$$\bar{V} = M\bar{v}$$

$\bar{v}$ = partial specific molal volume (cm^3/g)

$$RT\, d\ln m = Mg\, dz - M\rho\bar{v} g dz = Mg\,(1 - \rho\bar{v})\, dz \qquad (19)$$

Assuming $\bar{v}$ and ρ are not functions of depth and integrating (19) from the surface to depth, d:

$$RT \ln\frac{m_o}{m_d} = Mg\,(1 - \bar{v}\rho)\, d \qquad (20)$$

From (20) it can be seen that if $\bar{v}\rho > 1$, $m_o > m_d$ and the solubility will decrease with depth. For nitrogen $\bar{v}\rho = 1.47$ and the solubility decreases with depth. No values for the partial molal volume of argon are available (Kritchevsky and Iliinslaya, 1945), but the value of b in van der Waals' equation is a reasonable approximation. From (1), $b = 32.19\ cm^3/mole$ and then $\bar{v} = 0.806\ cm^3/g$. For any value of the density less than 1.240, $\bar{v}\rho < 1$; thus the solubility of argon should increase with depth in contrast to that of nitrogen. This treatment also leads to the conclusion that the solubility of oxygen is constant with increasing pressure ($\bar{v}_{o2} \cong 1.00$, $\bar{v}_{O_2} = 0.97$), just the opposite result as that given by Klots (1961) using the dependence of solubility on pressure given by Guggenheim (1949).

Sisskind and Kasarnowsky (1931) have investigated the effect of pressure on the solubility of argon. Their results are collected in table 15 and show that the solubility decreases with increasing pressure. The assumptions made in integrating equation (19) are not strictly true since the density is a function of temperature, salinity and pressure. Density in the ocean generally increases slightly with depth but seldom, if ever becomes greater than 1.040. Thus, it must be concluded that either the value for the van der Waals b coefficient is not a good approximation to the partial specific molal volume or that the assumption of equilibrium is not valid. According to Klots (1961) the fact that a parcel of water will be supersaturated at depth if it was saturated at the surface means that a small vertical gradient in the chemical potential will exist and equilibrium will not be attained. A small upward molecular diffusion of the excess gas should occur which may be of importance in mass transport studies. The effect of conditions under which a bubble may form and the decrease of solubility of gas with depth has also been studied by Miyake (1951).

The Solubility of Argon in Sea Water:

The solubility of argon in sea water of various salinities has been studied by very few people. Åkerlof (1935) and Eucken and Herzberg (1950) have determined the solubility of argon in aqueous salt solutions. Their data are collected in table 16. The first determinations of dissolved argon in sea water were made by Fox (1907, 1909) who measured the solubility of "atmospheric nitrogen" which consisted of nitrogen (98.815%) and argon (1.185%) with negligible amounts for the other inert gases. From his data the solubility of argon can be calculated by means of equations (11) and (12). Rakestraw and Emmel (1938b) have made the most complete series of determinations of the solubility of argon in sea water, but they estimated their accuracy to be only about 5%. Their data are collected in table 16 and figure 4. Benson and Parker (1961a) have determined the ratios of the solubilities of nitrogen and argon by mass spectrometric techniques with an accuracy approaching 0.1%, but have reported argon solubilities for only one salinity as calculated from their ratios and values of "atmospheric nitrogen" solubilities as reported by Fox and Rakestraw and Emmel. The values of Fox and Rakestraw and Emmel as determined by Benson and Parker are collected in table 17, and figure 5. König (1963) has also determined the solubility of argon in water of salinity 34.54°/oo. His values are also contained in table 18 and figure 5.

One puzzling feature of the solubility curves as reported by various workers is the fact that the slopes are different. This leads to the inference that the ratio of the solubilities of nitrogen and argon is temperature dependent. This was shown to be true by Benson and Parker (1961a) with N_2/Ar solubility ratio increasing from 37.48 to 39.05 over a temperature range of 0 to 30 degrees C. Thus, equation (12) must be corrected for the effect of temperature. In correcting "atmospheric nitrogen" solubility data for argon, the ratios given by Benson and Parker should be used rather than equation (12), but what is really needed is a complete set of determinations of solubility of pure argon in water of all salinities and temperatures commonly found in the sea.

The mechanism of solution and distribution of argon in the sea can best be illustrated by a simple model of the ocean. If it is assumed that a parcel of water and the atmosphere above it are in equilibrium several factors influence the solubility. These can be separated into surface factors and body factors (Benson and Parker, 1961b).

Surface factors:

1. Water temperature
2. Salinity
3. Atmospheric pressure
4. Atmospheric humidity
5. Surface conditions (waves, etc.)
6. Kinetics of near-surface mechanisms

Body factors:

1. Radioactive decay (already seen to be negligible)
2. Mixing
3. Radiative heating from below
4. Influx (or efflux) through the sea floor
5. Hydrostatic pressure (already considered)

If equilibrium is attained at the surface

$$C_i = S' \frac{P_a - P_w}{760} \tag{21}$$

C_i = concentration of gas dissolved (cm^3/l)

S' = solubility of gas

P_a = atmospheric pressure

P_w = saturation vapor pressure of the water at the ambient temperature and salinity.

Benson and Parker state the relative humidity cannot be 100% nor can it be zero, but this is not true. For some small distance above the surface, $\delta /$, the relative humidity must be 100%, but the gradient is very great. This means the argon passes through a fluid phase before it is dissolved in the liquid.

Then

$$C_i = S' \frac{P_a - q(P_w)}{760} \qquad (22)$$

q = relative humidity at some arbitrary distance from the surface.

At the surface, equation 21, is true.

If breaking waves are present, bubbles will be formed and will be dissolved, thus supersaturating the water to some extent depending on the size of the waves and their duration in the area. König, et al (1964) have estimated supersaturation because of trapped bubbles may exceed 10%.

As the parcel of water sinks, if it retains its initial temperature and salinity, the concentration of dissolved argon will be an indicator of its history. If it is heated or cooled after it leaves the surface it will be either supersaturated or undersaturated and the dissolved argon can be used as an indicator of the extent of either process. k If, however, it mixes with water of a different temperature and salinity, the mixture will be supersaturated in argon since the curves for solubility versus temperature are not straight lines. Consider the mixing of two equal volumes of water, the first at 25° C. and the second at 5° C., both having a salinity of 36.13^{o}/oo, and each having been separately equilibrated with the atmosphere at standard pressure. The mixture at 15° C. will contain

0.2895 ml (STP)/l dissolved argon as contrasted with the concentration as deduced from the data of Rakestraw and Emmel of 0.2785 ml (STP)/l that a sample of water at 15° C. would have if it had been independently equilibrated with the atmosphere. This would indicate a supersaturation of nearly 4%, the same degree of supersaturation as would have occurred if solution had taken place at 13° and the water had been heated to 15°.

Variations in the atmospheric pressure would tend to alter the concentration also. In the winter the average atmospheric pressure is higher in high latitudes than it is in the summer. Since the average temperature is also lower during this period, the amount of gas dissolved in water at the surface will be significantly greater in winter. As this colder water sinks and moves toward the equator the concentration of dissolved argon, since it is chemically inert in the sea, will remain the same in the absence of heating and mixing. If a section were made toward the equator the concentration of dissolved argon should fluctuate quite regularly with distance away from the source area. The maxima would be winter water and the minima would be water formed in the summer. This, then, would enable one to calculate a mean drift velocity for water masses such as Antarctic Bottom Water and North Atlantic Deep and Bottom Water.

As an example, consider the case of the Antarctic Bottom Water. This water is formed in the Weddell Sea during the winter when surface temperatures are near -1° C (Makintosh, 1946). Extrapolating the curve of figure 5 from the data of Rakestraw and Emmel plus Benson and Parker the concentration of dissolved argon in the winter should be 0.390 cm^3 (STP)/liter of sea water. (The concentration may be higher depending on the salinity of the water.) Mean summer temperatures of the surface water of this area are one to two degrees higher than those in winter. If 1.5° C is chosen as a reasonable summer surface temperature, the concentration of dissolved argon in summer should be 0.367 cm^3 (STP)/liter of sea water. This is a difference of 0.023 cm^3 (STP)/liter (6.3%) and should be detectable by any of the methods used in recent years to determine inert gases in sea water. The least accurate of these methods (König, et al. 1964) has an accuracy of at least 3%, and the method used by Goldberg (personal communication) is accurate to a few tenths of one per cent.

If a section is made northeastward from the Weddell Sea and concentration of dissolved argon in the bottom water is plotted versus distance, a sinusoidal curve should be obtained on which each maximum represents winter water and each minimum summer water.

The effect of variations in atmospheric pressure as discussed by Carritt (1954) would tend to increase the maxima on the curve and to decrease the minima because the most intense and most prolonged high pressure periods occur in the winter. If a mean pressure difference of 30 mb exists between summer and winter, the difference in the maxima and minima will be nearly doubled.

The Distribution of Argon in the Oceans:

The direct determination of the dissolved argon content of sea water has been made by few investigators and only four stations are available. These are stations A2893, A2899 and A2901 from Rakestraw and Emmel (1938a) and one station made by Goldberg (unpublished data). See tables 18 and 19 and figures 6 - 9. The determinations made by Goldberg should be treated as preliminary results since they are from the only station run so far (Goldberg, personal communication), but they are useful in exhibiting the range of the concentration of dissolved argon in water off the coast of Southern California. No temperature or salinity data were included with the argon values. Rakestraw and Emmel's values in the Western North Atlantic are perhaps more useful in spite of the limited accuracy of the determinations because the dependence on the temperature and salinity can be seen. In station A2893, the value of 0 320 at 300 meters is significantly greater than can be accounted for through an experimental error and must be considered to be real. This high value could be explained if a strong high pressure cell were over the area of solution or if the surface were strongly agitated by a storm when solution took place. The same processes may explain the apparently high values at 23 and 46 meters on station A2899. In deeper water, as would be expected, the concentration of dissolved argon is higher because of the lower temperature and salinity. In station A2893 the temperature and salinity decrease gradually from 1000 meters to the bottom and the argon concentration increases slightly in the same depth interval, the curves being nearly mirror images. The same effect is seen in station A2899 between 1200 and 3800 meters, with the argon value at 2690 meters being slightly lower than would be expected. However, no evidence of introduction from the bottom is evident in the argon curves and the increase with depth can be explained by the decreased temperature and salinity and surface conditions at solution can be used to explain the seemingly anomalous values. The scarcity of data precludes drawing any conclusions about the general distribution of argon in the sea, but it appears safe to assume that the dissolved argon concentration indicates the temperature and salinity of the water at the time of solution.

Revelle and Suess (1962) have published one determination of the dissolved argon content of sea water. They found 0.32 ml(STP)/l of dissolved argon at a depth of 5350 meters at 14° - 12' N, 155° - 08' W. No accuracy was given for the measurement. König, et al (1964) have recently published a number of determinations of the dissolved argon concentration in waters of the Pacific and Indian Oceans. An accuracy of 2% is claimed. Their values are collected in table 20, but since no complete stations were made, no figure has been prepared from these data.

Oana (1957) and Sugawara and Tochikubo (1955) have determined the concentration of dissolved argon versus depth in some Japanese Lakes. Their data support the conclusion that the argon content is an indicator of the conditions under which solution took place. Oana (1957) has also determined the dissolved argon concentration of river waters and ground waters and has found that the argon in ground waters is a maximum in the winter. He observed that the maxima were displaced in time and suggested the use of the argon concentration as an indicator of the velocity of movement of the ground water.

It should be possible to determine the amounts of oxygen and nitrogen that have been consumed in biological and chemical reactions since a sample of water left the surface by determining the content of argon, oxygen and nitrogen and using the argon value to calculate an original content for the other two gases. This would be possible if the assumptions that no mixing took place and that the original amounts of the gases were the saturation amounts can be demonstrated to be valid. Again, too little data are available to demonstrate the usefulness of this hypothesis.

CONCLUSIONS

First, it must be concluded that much more work needs to be done, both in the determination of the solubility of argon in sea water and in the measurement of the argon content of the sea. It appears that argon in the sea can be utilized as a tracer of water movements and as an indicator of the conditions under which solution occurred. The argon content of a sample of sea water may also be utilized to determine the amount of oxygen and nitrogen consumed in biological and chemical processes since the water left the surface.

The mechanism of solution and the solubility in distilled water appear to be adequately understood as evidenced by the excellent agreement between Klots and Benson (1963a) and Douglas (1964). See Figure 3.

It is believed that all available data on the solubility of argon in distilled water, aqueous salt solutions, and sea water have been collected except for untranslated Russian literature. The bibliography is considered to be a significant collection of work up to the present time concerning the solubility of argon, its sources and distribution in the cosmos, lithosphere, atmosphere and hydrosphere, except for some work on potassium - argon dating. Enough references to the latter are included so the reader may find most of the other work cited in the literature included in this paper.

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Table 1

Properties of Argon Isotopes

(from Hodgeman, 1962)

Isotope	Natural Abundance (%)	Atomic Mass.	Half-Life	Radiation	Energy (Mev)
Ar^{35}	-	34.9850	1.84 sec	β^+	4.4
Ar^{36}	0.34	35.9780	stable		
Ar^{37}	-	36.9777	34.1 days	K	no γ
Ar^{38}	0.06	37.974	stable		
Ar^{39}	-	-	2.4 min. 265 yr	β^- β^-	2.1 0.565
Ar^{40}	99.600	39.9756	stable	β^-	1.25
Ar^{41}	-	40.9774	1.8 hr	γ	1.3
Ar^{42}	-	-	7200 days		

Table 2

Argon Content of Rocks
(after Rayleigh, 1939)

Material	Argon Content (cm^3 . 10 5/gm rock)
Granite	2.8
"	1.2
"	3.2
Dunite	3.7
"	1.9
"	1.1
Eclogite	2.2
Obsidian	1.8
Pumice powder	0.9
Pumice lumps	3.7

Table 3

Gaseous Content of Rocks
(after Elerson & Polykovskii, 1963)
gas contents in milliliters/ kilogram

Type of Rock	CO_2	H_2	CH_4	Ar	He	N_2	Total
Pink granite	25. 2	11. 2	1. 4	1. 40	-	60. 3	99. 50
" "	18. 0	0. 0	0. 0	0. 93	-	42. 5	61. 43
Granite porphyry	5. 0	10. 0	5. 0	4. 50	-	135. 0	159. 50
" "	4. 5	4. 5	1. 5	0. 25	-	21. 0	31. 75
Greisen I	2. 3	0. 0	0. 0	0. 49	0. 0016	41. 6	44. 39
" II	1. 2	0. 0	0. 0	1. 20	0. 0020	72. 0	74. 40
Microcline	4. 8	0. 0	0. 0	0. 80	-	32. 0	37. 60
Vein Quartz	16. 4	30. 8	0. 0	1. 36	0. 0130	162. 5	211. 07
Citrine 1st generation	12. 8	0. 0	0. 0	4. 30	0. 0270	405. 0	422. 13
" 2nd "	5. 2	0. 0	0. 0	0. 83	0. 0083	143. 0	149. 03
" 1st "	54. 5	13. 5	0. 0	8. 90	0. 0270	337. 8	414. 73
" 2nd "	3. 2	0. 7	0. 0	1. 30	0. 0190	32. 1	37. 32
" 2nd "	4. 7	2. 1	0. 0	1. 18	0. 0032	101. 1	109. 08
Averages	12. 13	5. 6	. 61	2. 11	-	119. 05	142. 46

Table 4
The U.S. Standard Atmosphere
(NASA, 1962, page 9)

Constituent	% by volume	variable constituents marked by *
Nitrogen	78.084	-
Oxygen	20.9476	-
Argon	0.9343	-
Carbon Dioxide	0.0314	*
Neon	0.001818	-
Helium	0.000524	-
Krypton	0.000114	-
Xenon	0.0000087	-
Hydrogen	0.00005	?
Methane	0.0002	*
N_2O	0.00005	-
Ozone	0 to 0.000007 (summer)	*
	0 to 0.000002 (winter)	*
Sulfur Dioxide	0 to 0.0001	*
NO_2	0 to 0.00002	*
Ammonia	0 to trace	*
Carbon Monoxide	0 to trace	*
Iodine	0 to 0.000001	*

Table 5

Argon Content of the Atmosphere
(after Gluekauf, 1951)

Location	Ar (% by volume)
Odessa	0.935
Leningrad	.933
Athens	.935
Ionian Sea (37° N, 15°E)	.936
Vienna	.938
Berlin	.932
Venice	.936
Mt Blane	.935
Paris	.934
London	.933
Atlantic Ocean (37° N, 24° W)	.932
Atlantic Ocean (43° N, 22° W)	(.949)*
Average (omitting *)	0.9343 ± 0.0006
Standard deviation (omitting *)	± 0.002% (0.2% of Ar content)

Table 6

Rare Gas Content of Natural Gases

(after Cady & Cady, 1939)

(in Brown, 1947)

Sample number	He	Ne	Ar	(Kr + Xe) $\cdot 10^5$
1	7.55	-	0.890	3.3
2	6.00	-	0.530	5.4
3	1.73	-	0.196	5.5
4	0.047	0.0008	0.290	8.2
5	0.19	< 0.991	0.124	3.6
6	0.052	-	0.0356	1.7
7	0.55	-	0.140	5.3
8	2.20	-	0.078	-
9	0.074	0.002	0.93	-
10	0.305	-	0.035	0.066

Table 7

Argon in Fumarolic Gases in Japan
(after Matsuo, 1961)

Sample number	Nitrogen (ml/l)	N_2/Ar	Argon
1	167	334	0.50
2	258	290	0.89
3	189	255	0.74
4	132	367	0.36
5	210	328	0.64
6	214	324	0.66
7	516	(419)	(1.23)
8	648	239	2.71
9	290	271	1.07
10	258	347	0.74

Table 8

Decay Constants of K^{40}

(after Rankama, 1963)

Constant	Minimum value	Maximum value	Best value
Specific gamma activity (γ)	2.96 γ/sec·g	3.63 γ/sec·g	3.4 γ/sec·g
Specific beta (β^-) activity	27.4 β^-/sec·g	29.6 β^-/sec·g	27.6 β^-/sec·g
Branching ratio	0.06	0.13	0.123 (γ/β^-)
λ_{β^-}	$4.60 \cdot 10^{-10} yr^{-1}$	$5.16 \cdot 10^{-10} yr^{-1}$	$4.73 \cdot 10^{-10} yr^{-1}$
λ_e	$5.6 \cdot 10^{-9} yr^{-1}$	$5.8 \cdot 10^{-9} yr^{-1}$	$5.82 \cdot 10^{-9} yr^{-1}$
Total λ	$5.28 \cdot 10^{-10} yr^{-1}$	$5.58 \cdot 10^{-10} yr^{-1}$	$5.31 \cdot 10^{-10} yr^{-1}$
Half-life	$1.25 \cdot 10^{9}$ yr	$1.33 \cdot 10^{9}$ yr	$1.31 \cdot 10^{9}$ yr

Note: Half-life calculated from λ

Table 9

Mean Composition of River Waters of the World

(after Livingstone, 1963)

Area	HCO_3	SO_4	Cl	NO_3	Ca	Mg	Na	K	Fe	SiO_2	Σ
North America	68	20	8	1	21	5	9	1.4	0.16	9	142
South America	31	4.8	4.9	0.7	7.2	1.5	4	2	1.4	11.9	69
Europe	95	24	6.9	3.7	31.1	5.6	5.4	1.7	0.8	7.5	182
Asia	79	8.4	8.7	0.7	18.4	5.6	- 9.3 -		0.01	11.7	142
Africa	43	13.5	12.1	0.8	12.5	3.8	11	-	1.3	23.2	121
Australia	31.6	2.6	10	0.05	3.9	2.7	2.9	1.4	0.3	3.9	59
World	58.4	11.2	7.8	1.0	15	4.1	6.3	2.3	0.67	13.1	120
Anions[1]	0.958	0.233	0.220	0.017	-	-	-	-	-	-	1.428
Cations[1]	-	-	-	-	0.750	0.342	0.274	0.059	-	-	1.425

---

[1] millequivilants of strongly ionized species

Table 10
Analyses of Pelagic Sedemints for K_2O and K^{40}

(after El Wakeel & Riley, 1961)

Sample number	Depth(m)	Latitude	Longitude	Type	%K_2O by wgt	%K^{40} X10^5 (calculated)
1	5400	24° 20'N	24° 28'W	Calcareous ooze	1.34	5.90
2	4800	20° 39'N	50° 33'W	Globigerina ooze	0.57	2.51
3	5820	30° 22'N	154° 56'W	Red Clay	3.68	16.23
4	5130	03° 48'S	152° 56'W	Globigerina ooze	1.43	6.31
5	4700	45° 26'N	09° 20'W	Globigerina ooze	1.48	6.52
6	3195	26° 08'S	14° 36'W	Globigerina ooze	0.16	0.70
7	4402	46° 35'S	24° 15'W	Diatom ooze	2.15	9.48
8	3956	35° 55'N	17° 29'E	Globigerina ooze	1.35	5.95
9	3956	35° 55'N	17° 29'E	Globigerina ooze	1.49	6.57
10	4464	01° 06'N	85° 36'E	Globigerina ooze	1.40	6.18
11	1395	38° 55'N	31° 35'W	Globigerina ooze	0.46	2.02
12	4710	48° 52'N	15° 00'W	Buff colored clay	3.05	13.45
13	5582	34° 11'N	55° 32'E	Calcareous clay	3.52	15.52
14	5949	24° 30'N	64° 47'W	Red Clay	3.70	16.31
15	3200	22° 07'S	115° 10'W	Calcareous manganiferous ooze	0.10	0.44
16	4793	06° 52'N	67° 13'E	Red Clay	3.08	13.58
17	5395	24° 35'N	64° 02'W	Red Clay	3.63	16.00
18	5200	04° 04'S	152° 53'W	Red Clay	1.49	6.57

Table 10 (con't)

19	5500	04° 02'N	172° 19'W	Red Clay	1.48	6.52
20	5170	11° 28'S	102° 24'E	Red Clay	1.93	8.51
21	4405	01° 00'S	64° 00'E	Red Clay	1.50	6.62
22	5500	10° 12'N	26° 36' W	Red Clay	2.05	9.04
23	5480	14° 32'N	55° 05'W	Red Clay	2.95	13.01
24	4685	16° 44'S	161° 22'W	Chocolate volcanic Clay ore	2.90	12.78
25	4940	31° 05'N	135° 24'W	Red Clay	3.65	16.09
26	3110	40° 56'N	125° 38'W	Green Mud	2.30	10.14
27	4090	43° 45'N	137° 06'W	Brown-grey Mud	2.68	11.82
28	4270	43° 49'N	143° 07'W	Tan Clay	3.55	15.65
29	5080	09° 09'N	144° 26'W	Siliceous Clay	3.25	14.33
30	359	19° 46'N	154° 58'W	Volcanic muddy sand	0.36	1.58
31	5408	20° 27'N	154° 55'W	Volcanic Clay	1.20	5.30
32	3460	29° 24'N	153° 06'W	Brown Clay	3.95	17.42
33	6140	42° 29'N	162° 08'W	Brown Clay	3.60	15.87
34	6	53° 22'N	04° 15'W	Light Brown Clay	2.55	11.25
35	5	53° 18'N	04° 02'W	Light Brown Clay	3.10	13.67

Average Compositions

Type	%K_2O	%$K^{40} \times 10^5$
Calcareous	1.48	6.52
Argillaceous	3.26	14.38
Siliceous	1.90	8.38
Oceanic average	2.10	9.26

(48.7% Calcareous, 37.8% Argillaceous, 13.5% Siliceous)

Note: all samples washed to remove soluble ions and salts

Table 11

K_2O and K^{40} Content of Core Sample 17

24° 35'N 64° 02" Depth 53$_9$5 no
(after El Wakeel & Riley, 1961)

Red Clay

Depth in core (cm)	K_2O%	$K^{40} \cdot 10^5$ (%)
Top 4 cm	3. 61	15. 89
50	3. 79	16. 69
100	3. 76	16. 56
150	3. 72	16. 38
200	3. 65	16. 07
250	3. 54	15. 59
300	3. 61	15. 89
350	3. 61	15. 89
400	3. 64	16. 03
450	3. 63	15. 98
500	3. 43	15. 10
Average	3. 63	15. 98

Table 12

Residence Times of Water Masses from Carbon - 14 dating (after Broecker, et al., 1961)

Water mass	Residence Time (years)
Arctic	45
North Atlantic Surface Water	10
South Atlantic Surface Water	10
North Atlantic Deep Water	600
Antarctic	100
Pacific + Indian Surface Water	25
Pacific + IndianDeep Water	1300

Age of Deep Water (after Broecker, et al., 1961)

Deep Water of North Atlantic Origin

Depth (m)	Number of Samples	Crude Age (years)
Surface	19	—
200-400	3	300
800-1100	8	600
122-2500	7	650
1200-2500 (western boundry)	10	350
2500-4000	15	700
>400	15	650

Deep Water of South Atlantic Origin

Depth (m)	Number of Samples	Crude Age (years)
200-400	6	120
600-1200	6	300
1200-2500	3	75
>500	3	200

Table 13

Solubility of Argon in Distilled Water

(Numbers given are Bunsen Coefficients)

$(\alpha \cdot 10^3)$

Investigation Temperature & Date	0	1	2	3	4	5	6	7	8	9
(a) Rayleigh and Ramsay (1895)										
(b) Estreicher (1899)	57.80	56.12				50.80				
(c) Winkler (1906)	53									
(d) Fox (1909)										
(e) von Antropoff (1910)	56.1									
(f) Valentiner (1927)	57.8									
(g) Lannung (1930)	50.5$^{1.65}$									
(f) Morrison and Johnstone (1954)										
(i) Oana (1957	52.51	51.09	49.78	48.40	47.10	45.90	44.74	43.65	42.50	41.52
(j) Klots and Benson (1963)			51.27	49.76	48.36	47.13	45.96	44.85	43.78	42.79
(k) Konig										
(l) Hamberg + Benson & Parker	52.88					46.22				
(m) Winkler + Benson & Parker	51.42					45.21				
(n) Fox + Benson & Parker	51.53					45.58				
(o) Douglas (1964)						46.89	45.84	44.73	43.69	42.72

Table 13 (con't)

10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
		39.4		13.90 40.5											
45.25					40.99					37.90					34.70
42										35					
43.8										37.9					
46.9										40.0					
		12.4 38.7			37.1			34.9		33.4					31.5
10.7 40.9					14.3 37.2				18.2 34.6						24.4 31.1
40.49	39.51	38.60	37.67	36.92	36.00	35.19	34.38	33.74	33.05	32.36	31.67	30.98	30.36	29.68	29.11
41.82	40.88	40.03	39.18	38.29	37.59	36.80	36.17	35.51	34.84	34.21	33.61	33.01	32.43	31.89	31.37
37.9					35.8					32.5					
41.21					37.11					33.88					31.43
40.03					35.98					32.74					30.17
40.77					36.98					33.88					31.32
41.80	40.86	40.00	39.15	38.33	37.53	36.77	36.04	35.35	34.68	34.05	33.42	32.84	32.28	31.74	31.23

Table 14

The Effect of Hydrostatic Pressure on the Solubility of Argon

(after Sisskind & Kasarnowsky, 1931)

Pressure (atm)	$\alpha \cdot 10^3$
1	51.5
25	51.6
50	50.4
75	46.7
100	43.5
125	40.5

Note: Data from Lannung, 1930; for 1 atmosphere

Table 15

Solubility of Argon in Aqueous Salt Solutions

(a)

Salt	m	
	0	0.0332
KCl	3.00	0.0220
	4.55	.0174
NaCl	3.23	.0216
	5.98	.0149
LiCl	3.35	.0248
	6.78	.0187
$NaNO_3$	3.51	.0204
	7.37	.0123
Perchloric acid	4.05	.0411
	9.32	.0521
$CaCl_2$	2.95	.0216
	5.37	.0180
$SrCl_2$	2.10	.0203
	3.56	.0150
$BaCl_2$	1.25	.0185
	1.74	.0141
$MgCl_2$	3.02	.0248
	5.02	.0228
$AlCl_3$	0.98	.0247
	1.56	.0179

(b)

Salt	T(° c)	m	α
NaCl	0	0	0.0526
NaCl	0	0.43	.0443
NaCl	0	1.005	.0343
NaCl	0	1.07	.0337
NaCl	0	2.26	.0208
NaCl	0	3.06	.0147
NaCl	20	0	0.0387
NaCl	20	0.54	.0319
NaCl	20	1.13	.0259
NaCl	20	1.91	.0196

References:

(a) Akerlof (1935)
reduced to 0° C and 760 mmHg

(b) Eucken & Hertzberg (1950)

α = vol of gas in liters @ 0° & 760 mm Hg in solution containing 1000g of solvent.

m = molality (moles of salt/1000g solvent)

Table 16

Solubility of Argon in Sea Water
in ml/l at STP from normal atmosphere of 760 mm Hg
(after Rakestraw & Emmel, 1938b)

	Cl(^{o}/oo)	15	16	17	18	19	20	21
Temp.	S(^{o}/oo)	27.10	28.91	30.72	32.52	34.32	36.13	37.94
2		0.405	0.400	0.395	0.389	0.384	0.379	0.373
4		.384	.379	.374	.369	.363	.358	.352
6		.365	.360	.355	.350	.345	.340	.335
8		.347	.343	.338	.333	.329	.324	.319
10		.331	.327	.323	.318	.314	.310	.305
12		.317	.313	.309	.304	.300	.296	.292
14		.304	.300	.296	.292	.288	.284	.280
16		.292	.288	.284	.280	.277	.273	.269
18		.282	.278	.274	.270	.267	.263	.259
20		.272	.268	.264	.260	.256	.253	.249
22		.262	.258	.255	.251	.247	.244	.240
24		.253	.249	.246	.242	.238	.235	.231
26		.244	.240	.237	.233	.229	.226	.222
28		.235	.231	.228	.224	.220	.217	.213

Salinity calculated from

$$S = 0.03 + 1.805 \, Cl$$

Table 17

Solubility of Argon in Sea Water by Various Workers

Worker	Cl	0	5	10	15	20	25	30
(a) König	19.12%	-	0.329	0.306	0.282	0.245	-	-
(b) Fox + Benson &Parker	20%	0.375	.335	.306	.282	.262	.245	.230
(c) Rakestraw & Emmel + Benson & Parker	20%	.382	.337	.304	.276	.254	.235	(.219)
(d) Rakestraw & Emmel	20%	(0.405)	.352	.314	.283	.259	.238	(.217)

References:

(a) König (1963

(b), (c) Benson & Parker (1961a)

(d) Rakestraw & Emmel (1938b)

Table 18

Dissolved Argon in Atlantic Waters (after Rakestraw & Emmel, 1938a)

Station A2893 **35° 30'N, 67° 17'W** **12 July 1937**

Depth (m)	Temp. (°C)	Cl ‰	S (‰)	Ar (ml/l)
0	26.5	20.07	36.26	0.250
50	24.0	20.25	36.58	.260
100	19.0	20.2	36.49	.270
150	18.5	20.2	36.49	.280
200	18.2	20.2	36.49	.290
300	17.8	20.2	36.49	.320
400	17.5	20.15	36.40	.290
500	16.7	20.1	36.31	.295
600	15.5	19.95	36.04	.290
800	11.5	19.57	35.35	.315
1000	7.5	19.42	35.08	.335
1500	4.2	19.37	34.99	.340
2000	3.5	19.35	34.96	.345
2500	3.3	19.35	34.96	.350
3000	3.0	19.32	34.90	.350
3500	2.8	19.32	34.90	.355
4000	2.5	19.32	34.90	.355
4500	2.3	19.30	34.87	.360

con't

Station A 2899   36° 01'N   69° 57'W   8 August 1937

Depth (m)	Temp. (° C)	Cl‰	S‰	Ar (ml/l)
1	27.37	19.99	36.11	0.226
23	27.06	20.05	36.22	.275
46	25.54	20.14	36.38	.274
93	20.97	20.21	36.51	.254
139	19.64	20.24	36.56	-
185	18.84	20.20	36.49	.261
278	18.25	20.20	36.49	.266
371	17.89	19.43	35.10	.267
464	-	20.17	36.44	.271
556	16.87	20.11	36.33	.272
861	12.36	19.70	35.59	.279
1076	7.78	20.19	36.47	.315
1291	4.98	19.37	34.99	.356
1722	3.96	19.36	34.97	.358
2690	3.31	19.36	34.97	.353
3773	2.55	19.36	34.97	.362

Station A 2901   39° 40'N,   71° 43'W   11 August 1937

1	25.05	17.78	32.12	-
25	14.62	18.46	33.35	0.314
50	8.50	19.47	35.17	.329
87	8.42	18.79	33.94	.326
131	9.49	19.24	34.76	.314
176	9.22	19.38	35.01	.299
268	6.40	19.33	34.92	.332
363	5.40	19.33	34.92	.336
460	4.87	19.34	34.94	.352
560	4.48	19.39	35.03	.348
768	4.22	19.35	34.96	.340
977	3.98	19.36	34.97	.343

Table 19

Rare Gas Concentrations in Pacific Waters (cc STP/liter)
Samples Collected at Lat. 31° 24'N; Long. 120° 04'W
(from Goldberg, unpublished data)

Depth (m)	He x 10^5	Ne x 10^4	Ar x 10	Kr x 10^5	Xe x 10^6
46	4.4	1.74	3.10	7.0	7.7
93	3.6	1.23	2.15	4.8	10.0
189	3.7	1.24	2.25	5.1	7.9
462	3.1	1.06	1.78	3.7	4.4
1039	3.2	1.04	1.50	2.6	3.7
1930	4.6	1.54	3.28	7.9	12.5
3065	4.5	1.54	2.91	6.0	7.4
3437	5.0	1.62	3.28	7.4	11.0

Table 20

Dissolved Argon in Pacific and Indian Waters
(after König, et al., 1964)

Location	Depth (m)	Temp. (°C)	Ar (cm³/1000g sea water)
		Pacific Ocean	
27° -22'-27° -27 'N	10	25.05	0.218
150° -08'-150° -37'W	36	24.09	0.225
	60	20.40	0.242
	2235	1.86	0.336
	3125	1.52	0.348
	4274	1.48	0.346
		Indian Ocean	
32° -05'S, 98° -53'E	581	8.69	0.297
32° -05'S, 98° -53'E	1355	3.19	0.338
31° -30'S, 61° -53'E	3300	1.50	0.357
51° -00'S, 66° -00'E	3200	0.75	0.350
51° -00'S, 66° -00'E	1800	1.90	0.337

Note: All salinities between 34.5°/oo and 35.5°/oo

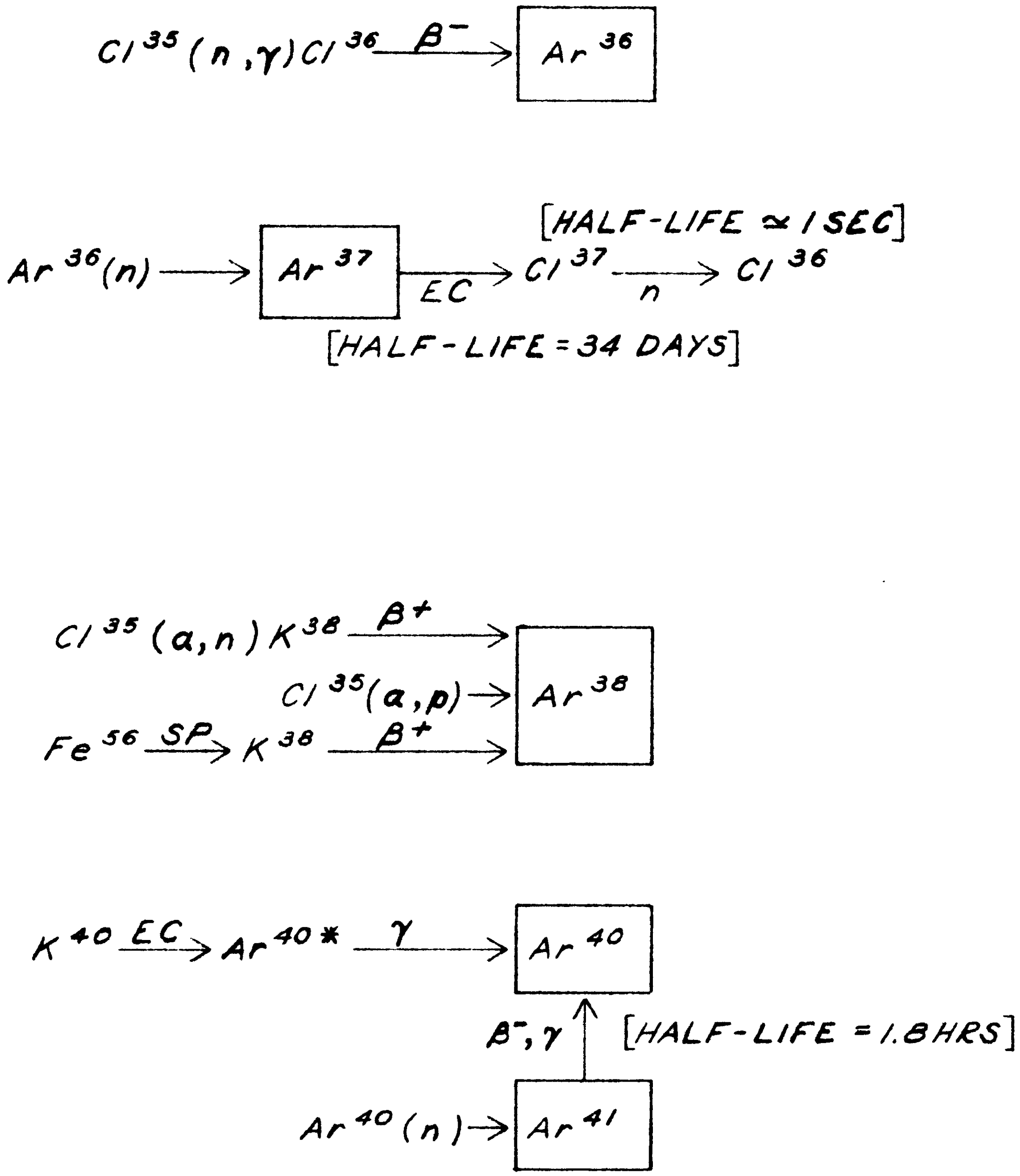


Fig. 1 Formation of Argon Isotopes

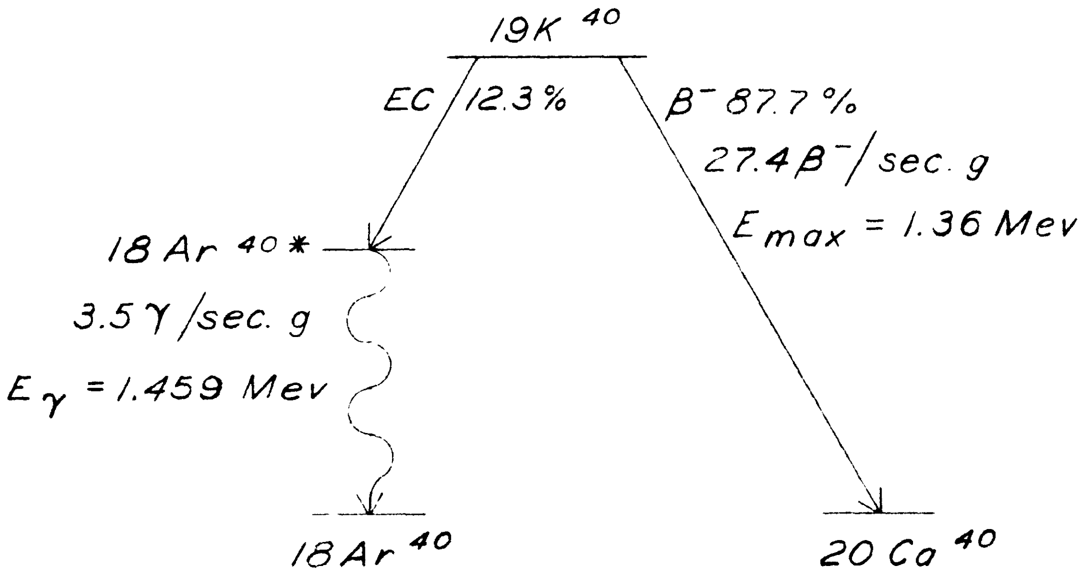


Fig. 2 Decay Scheme of Potassium-40

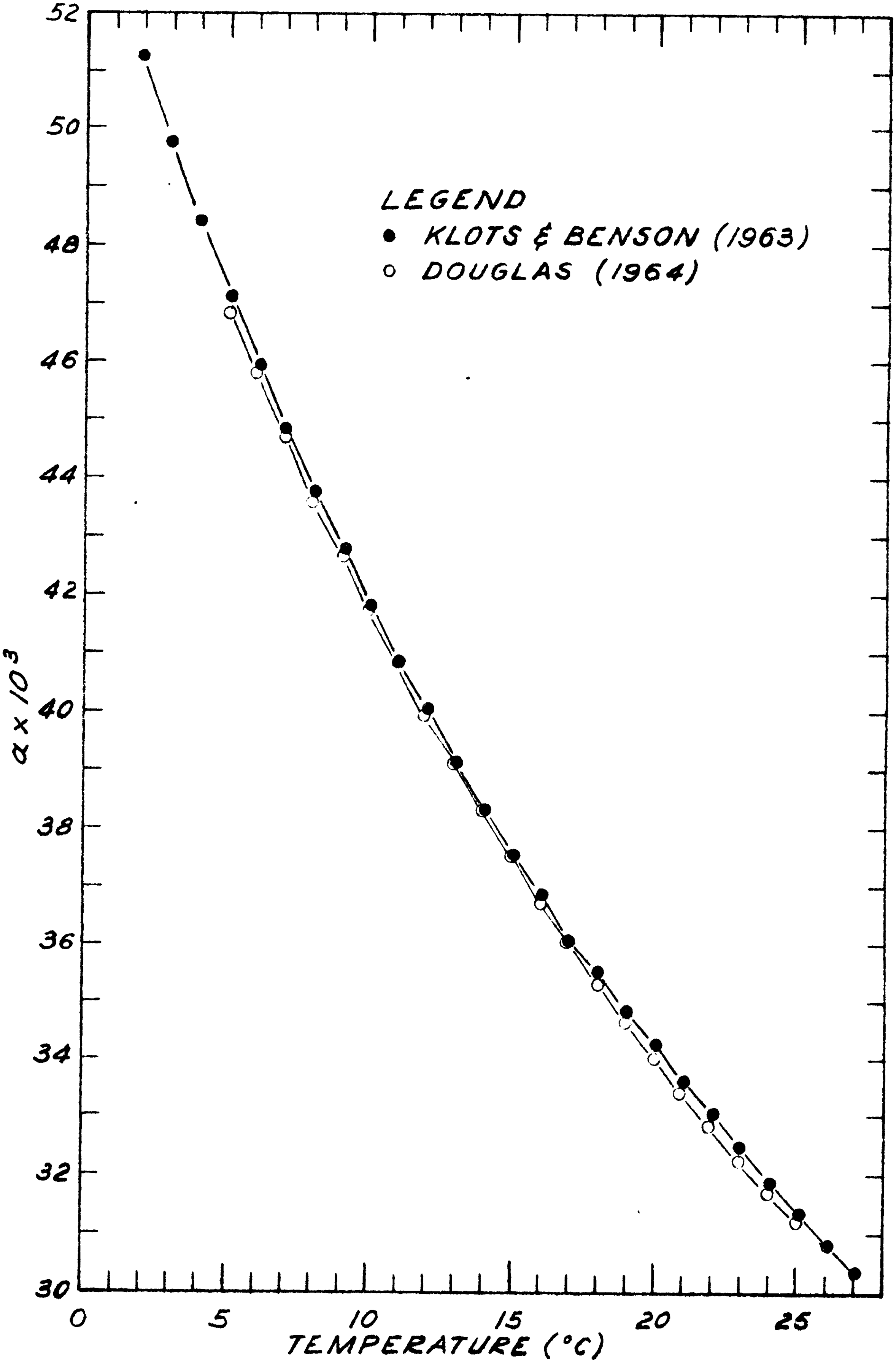


Fig. 3 Solubility of Argon in Distilled Water

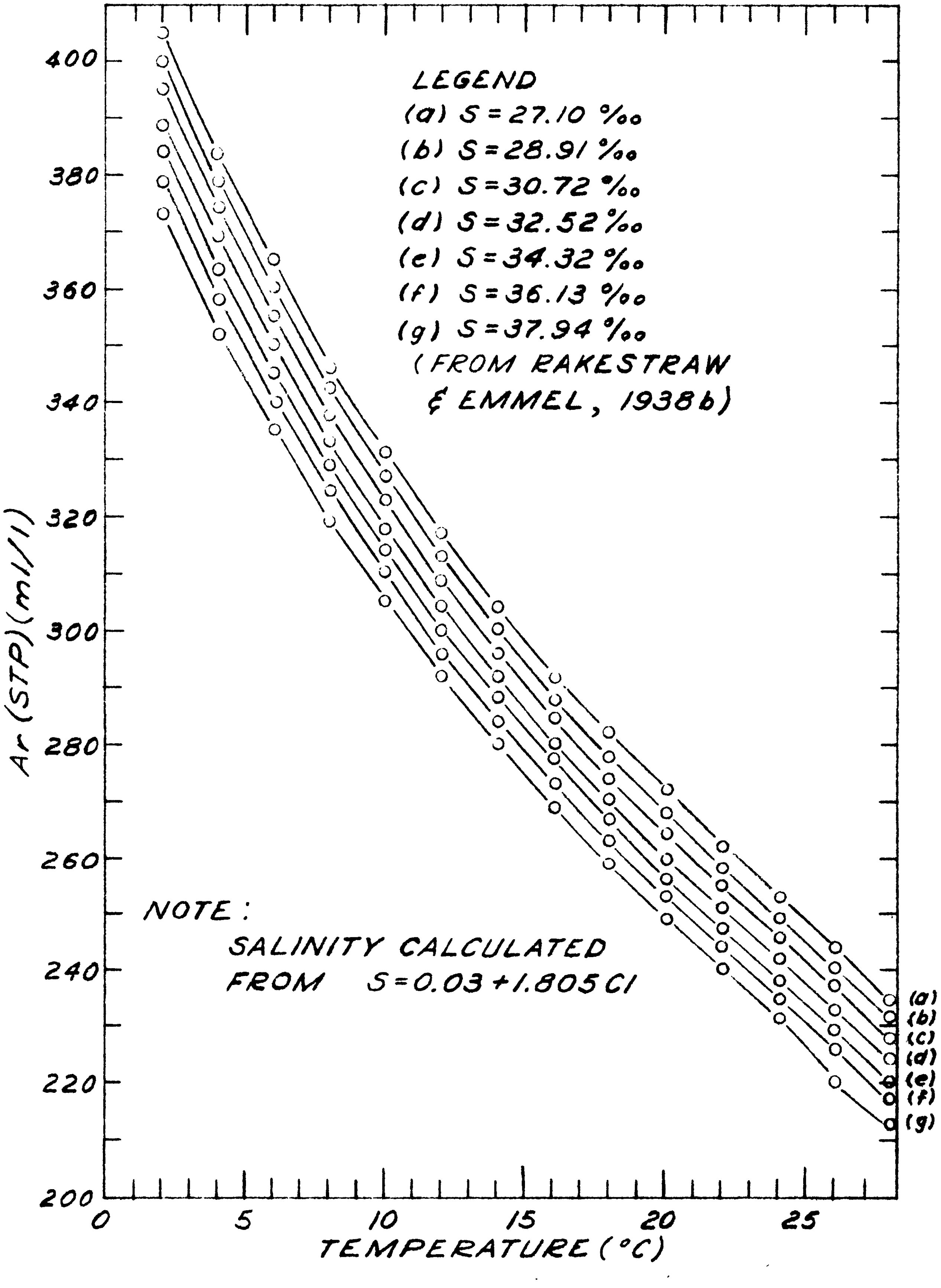


Fig. 4 Solubility of Argon in Sea Water

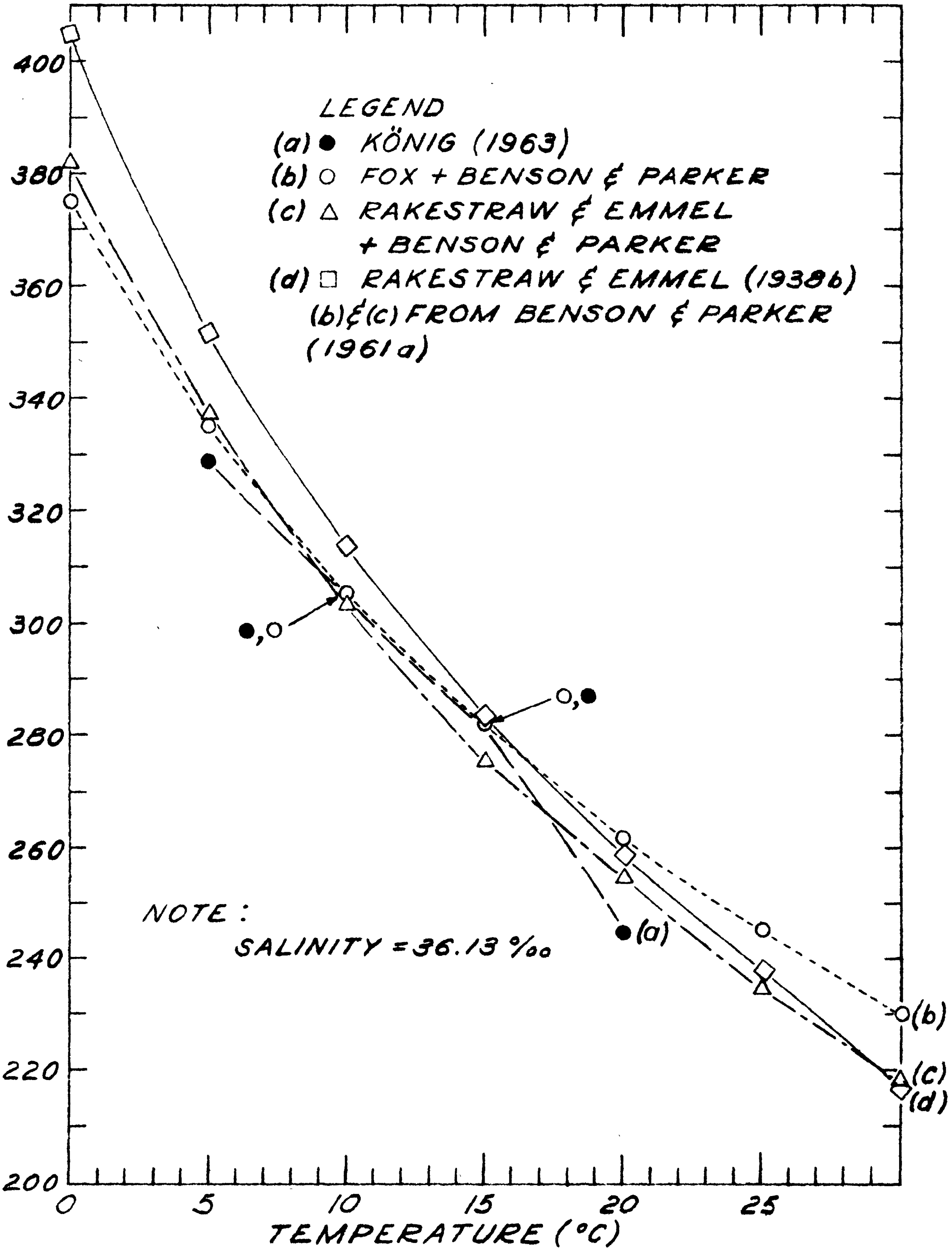


Fig. 5 Solubility of Argon in Sea Water after Various Workers

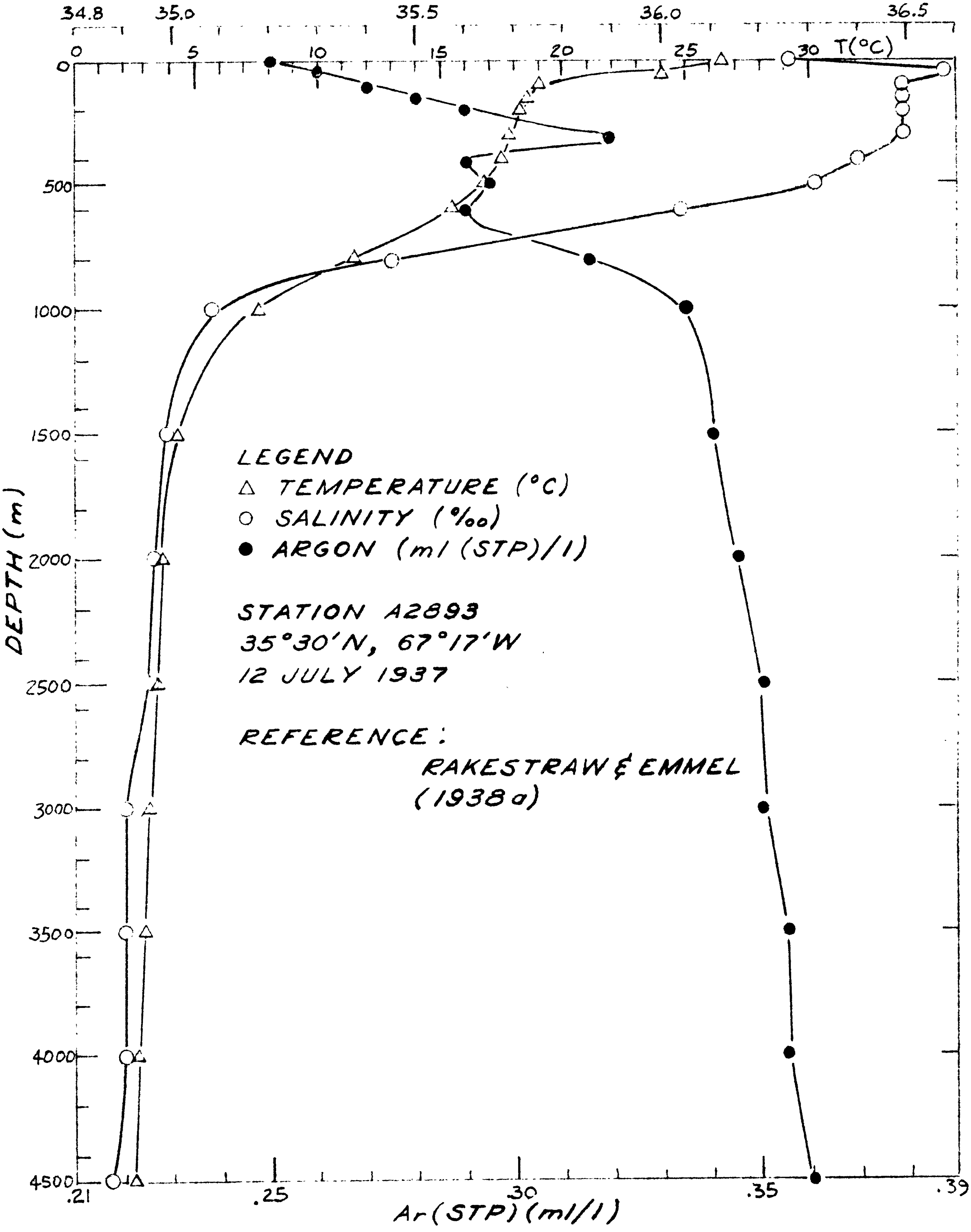


Fig. 6 Dissolved Argon in Atlantic Waters - I, Station A2901

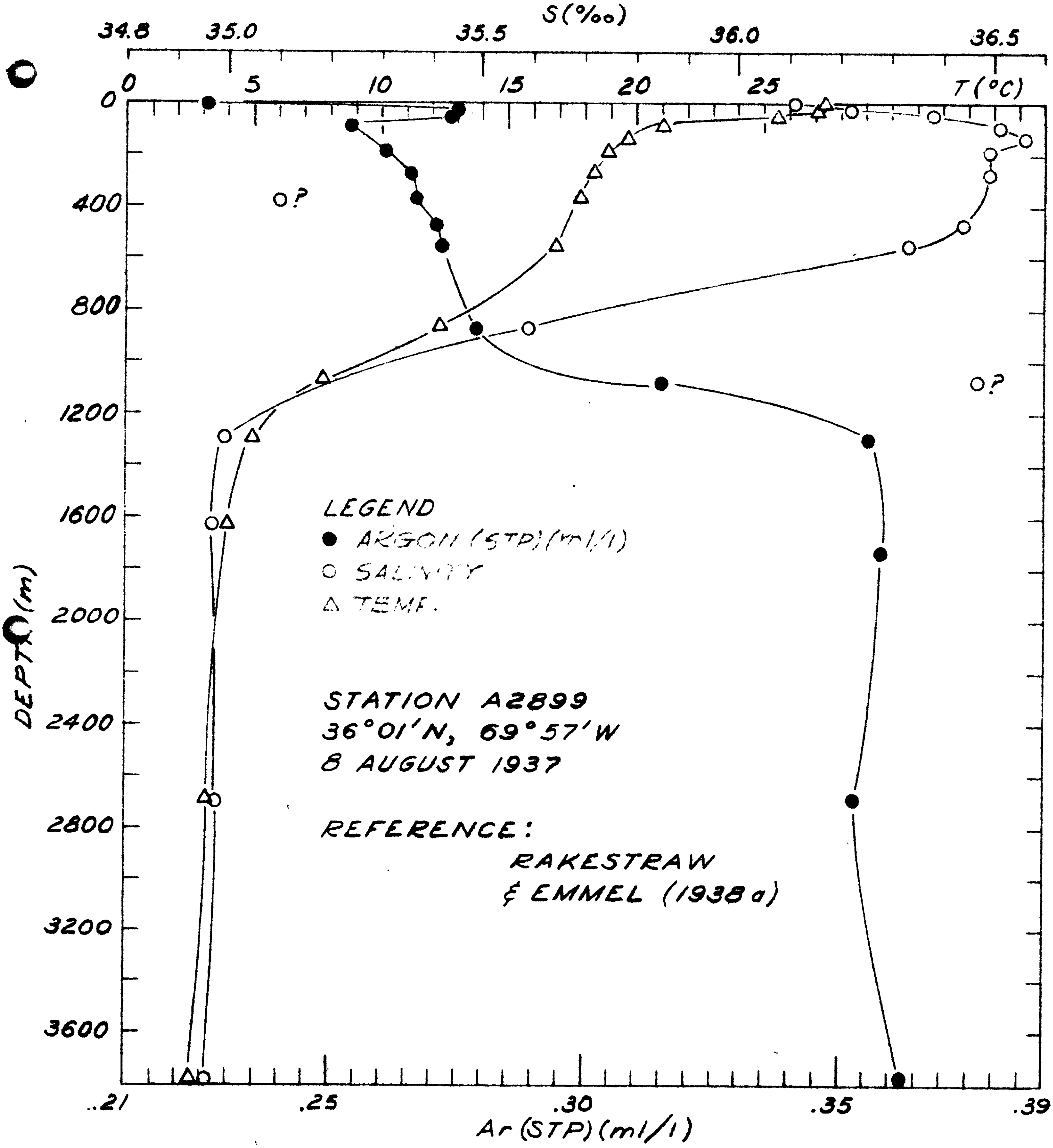
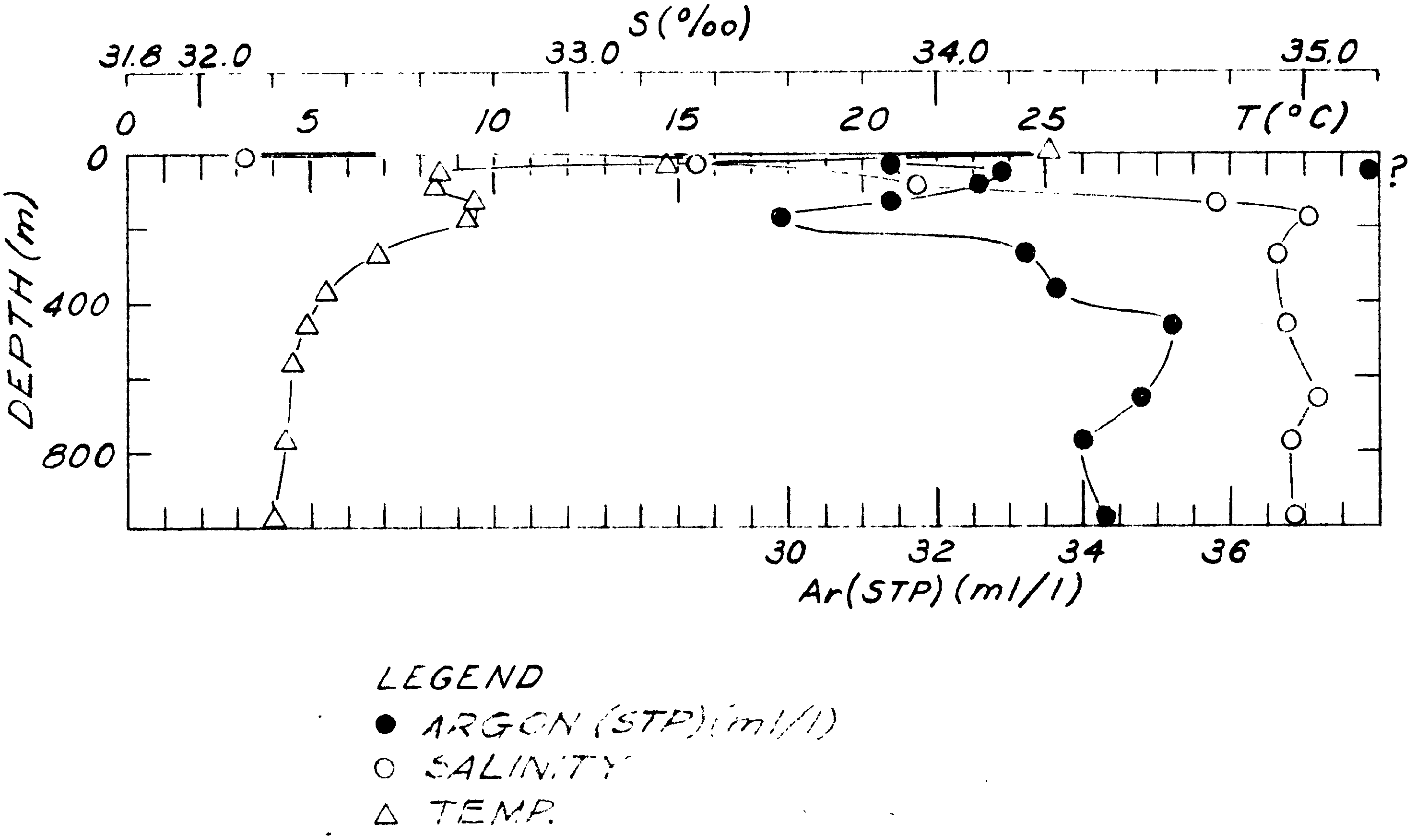


Fig. 7 Dissolved Argon in Atlantic Waters - II, Station A2899



STATION A2901
39° 40′ N, 71° 43′ W
11 AUGUST 1937

REFERENCE:
RAKESTRAW & EMMEL
(1938a)

Fig. 8 Dissolved Argon in Atlantic Waters - III. Station A2901

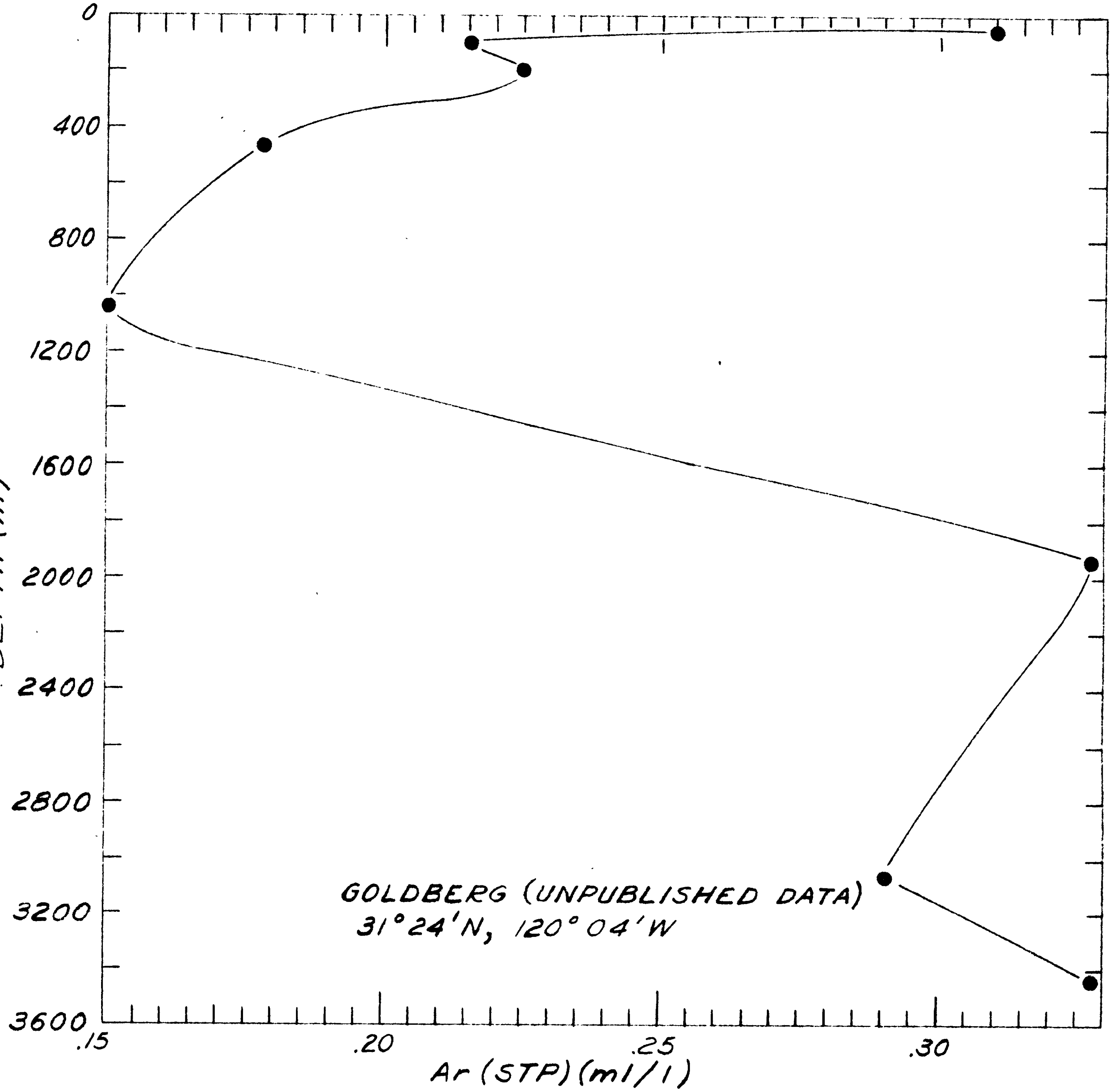


Fig. 9 Dissolved Argon in Pacific Waters