High Pressure Solubility of Calcium Carbonate in Seawater

Abstract. *The saturation concentration of calcium carbonate, equilibrated with aragonitic oolites, is about 2.7 times larger after exposure to 1000 atmospheres than it is when saturation is achieved at 1 atmosphere. This suggests that deep ocean waters may be undersaturated with calcium carbonate, in which case the alkalinity of the oceans would increase as sinking calcareous organisms dissolve.*

It has been known since the work of Wattenberg and Timmerman (*1*) that near surface ocean waters are supersaturated with calcium carbonate (*2*). Members of many expeditions measured the *p*H and alkalinity and calculated the ion product $(Ca^{++}) \cdot (CO_3^{--})$ of deep waters brought to the surface and analyzed on shipboard. However, nothing could be said about the saturation of these samples in their original location because the ion product at saturation had been measured only for equilibration at 1 atm. Revelle and Fairbridge estimated the effect of pressure on this product from scarce thermodynamic data but stated that measurements were needed (*2*). Another estimate of this effect was made by Zen (*3*); however, his estimate is a first approximation because the partial molal compressibility was not available and the partial molal volume was assumed constant with pressure.

We measured the saturation ion product in a narrow-necked tube (Fig. 1), using artificial seawater (*4*) and 40- to 60-mesh Bahama oolites, which are spherules of aragonite deposited in marine environments. The tube was placed in a pressure cell (*5*) which was inverted several times until the *p*H of the supernatant water was unaffected by further inversions. The *p*H was read after pressure release, to simulate conditions when a sample is raised to the surface. The narrow section of the tube improved mixing during inversions and separated the bulk of the supernatant water from the oolites during pressure release.

As the pressure decreased, the water became supersaturated, but no precipitation occurred because nucleation in seawater requires long periods of time. We increased the supersaturation of unfiltered sea-water samples by adding sodium carbonate to surface waters collected off the Oregon Coast. The time intervals between addition of sodium carbonate and the onset of precipitation varied from two hours to several weeks in the tenfold to fivefold supersaturation range (*6*). Thus the only effect of pressure release is the readjustment of the carbonate species because the dissociation constants of carbonic acid change with pressure (*7*). This readjustment does not need to be calculated because water samples for comparative purposes are not measured *in situ* but are brought to the surface, and also undergo a rearrangement of the carbonate and bicarbonate concentrations. If approximate values of the ion products *in situ* are desired, they can be estimated by the methods outlined in a previous paper (*8*).

The samples of artificial seawater were equilibrated with atmospheric carbon dioxide before each run. Although this initial carbon dioxide content was not carefully controlled, any variations were compensated for because the initial carbonate concentrations were calculated from the alkalinites and *p*H of the samples. The change in ion product at saturation was determined from the change in *p*H. We calculated the ion products from the initial and final values of *p*H and the apparent dissociation constants of carbonic acid in seawater (*9*). The term "apparent" is used because the concentrations of the carbonate species were used. The changes in ion product at saturation after exposure to pressure are presented in Table 1. The precision of the present equipment does not permit a study of the effect of temperature and chlorinity on the pressure coefficient. Results listed are for measurements made at temperatures between 4° and 24°C with chlorinities from 17.6 per mil to 20.2 per mil. Within these ranges of temperature and chlorinity the pressure coefficient is $(1.65 \pm 0.3) \times 10^{-3}$ or 0.17 percent per atmosphere. This coefficient was measured after pressure release. The corresponding coefficient at the pressure *in situ*, calculated from the dissociation constants of carbonic acid at high pressures (*7*) is 0.11 percent per atmosphere.

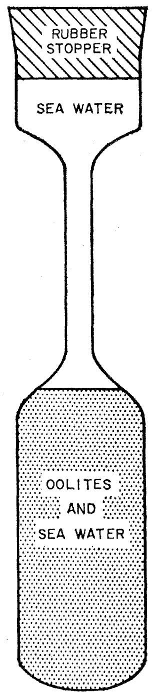

Fig. 1. The pressure tube.

Table 1. Change in the solubility of calcium carbonate in seawater after exposure to pressure. Results expressed as the ion product at saturation after exposure to pressure divided by the ion product at saturation at 1 atm.

Runs	Temperature (°C)	Chlorinity (per mil)	Ion product at 1 atm (mole^{2}Kg^{-2}) × 10^7	Pressure			
				1	400	700	1000
1	21 ± 3	20.5	8.0	1	1.66	2.24	2.95
2	21 ± 3	20.5	8.4	1	1.51	1.95	2.35
3	21 ± 3	17.6	6.8	1	1.74	2.19	2.88
4	6 ± 3	20.2	8.7	1	1.51	1.90	2.57
Average				1	1.65 ± 0.11	2.12 ± 0.15	2.69 ± 0.24

Weyl has shown that the solubility of calcium carbonate depends on the history and surface conditioning of the solid phase (*10*). This may account for part of the scattering shown in Table 1.

The concentration of carbon dioxide in the oceans increases with depth. This increase is small in comparison to the ionic strength of seawater and its effect on the apparent solubility product of calcium carbonate can be neglected. Therefore, if oceanic data is reported as ion products $(Ca^{++}) \cdot (CO_3^{--})$, these products can be compared to our laboratory values even though the samples have different carbon dioxide contents. However, the carbon dioxide content must be taken into consideration if it is desired to determine how many moles of calcium carbonate must dissolve or precipitate to saturate a sample of seawater. This can be done by an acid titration of the sample and the calculation procedures of Weyl (*10*).

From the data obtained during the Meteor expedition and the solubility of calcium carbonate at 1 atm, Wattenberg concluded that the deep waters of the Atlantic Ocean are nearly saturated with respect to calcite (*11*). Because calcite rather than aragonite is present in most sinking calcareous organisms and our results apply only to aragonite, we are limited to a tentative evaluation of Wattenberg's conclusion.

Revelle and Fairbridge estimated that the pressure coefficients of the apparent solubility products of calcite and aragonite differ by 12 percent at 1000 atm. If this is the case, the difference is within the precision of our results and the data in Table 1 represent the effect of pressure on the solubility of calcite. Because Wattenberg used the solubility at 1 atm and this increases with depth, our results suggest that the deep Atlantic waters are undersaturated rather than saturated. In this case sinking calcareous organisms should partly dissolve and the alkalinity of deep oceanic waters would increase with time. If, on the other hand, future data on the solubility of calcite at high pressures should indicate saturation at great depths, the solution of aragonitic shells would be accompanied by precipitation of calcite. Then a steady-state alkalinity is possible.

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Uranium Contents of Ancient Man-Made Glass

Abstract. *The concentrations of uranium impurities in a variety of ancient man-made glasses have been determined by counting the sites of neutron-induced fissions. There appears to be a chronological trend from low to high and back to low uranium contents over the past three millennia. Crude estimates of ages by fission-track counting should be possible with considerable labor for the group of glasses which was found to have the highest concentration of uranium.*

Sayre and Smith (*1*) suggested that the grouping of ancient glasses according to their composition might be useful for indicating their times and places of origin. By sorting approximately 200 glasses from Europe, Africa, and eastern Asia according to their major constituents, they proposed five major compositional categories, each of which they found to be prevalent over a wide geographical area for a period of several centuries or more. In this report we consider the questions of whether the quantity of a trace impurity such as uranium follows any similar, systematic regional or chronological pattern and whether knowledge of the uranium content will make possible further subdivision of the larger groups proposed by Sayre and Smith.

Uranium is of special interest because very minute quantities ($< 10^{-13}$ weight fraction) may be readily detected by means of neutron-induced fission (*2*). The sites of fissions are then displayed as conical pits (such as are shown in Fig. 1) (*3*). The concentration, *c*, of uranium by weight may be found from the relation

$$c = \rho_i \, u/(\sigma \, \phi R \, \delta \, N_o \cos^2\theta)$$

Where ρ_i is the number of fission track etch pits per square centimeter, *u* is the molecular weight of uranium, σ is the cross section for thermal neutron-induced fission, ϕ is the total flux of thermal neutrons, *R* is the range over which a fission fragment creates a track that may be etched, δ is the glass density, N_o is Avogadro's number, and the factor $\cos^2\theta$ results from the fact (*4*) that tracks are not revealed if their inclination to the etched surface is less than an angle θ. To find *c*, ρ_i was measured, θ was specified by the irradiation, and $\cos^2\theta$ was interpolated from the following experimental results: $\cos^2\theta = 0.915$, 0.75, and 0.50 for $Na_2O + K_2O$ contents of 0 percent, 4 percent, and 14 percent. The values $R = 10^{-3}$ cm and $\delta = 2.4$ g/cm^3 were assumed. Although both these quantities depend on the composition of the glass, one increases while the other decreases, so that little error is introduced by assuming their product to be constant. Although absolute values found by this procedure are probably good to no better than ± 40 percent, the relative values are considerably more precise; and our estimated error (±15 percent) is primarily the statistical standard deviation on the fission track count (at least 100 tracks usually being counted).

A group of 34 ancient glasses was selected by Sayre and Smith from samples whose major constituents they had analyzed earlier (*1, 5*). Our results for uranium content as a function of age and compositional category are presented in Fig. 2 and Table 1. A list giving descriptions of the glasses and their uranium contents as measured by counts of the fission tracks is available on request. No results are given for four of the glasses, three because of the presence of crystalline phases, and one because of an excessive bubble content,

Table 1. Uranium content of ancient glasses from various categories.

Glass group*	No. of samples	Uranium (ppm by wt.)	
		Av.	Range
2nd millennium B.C.	3	0.46	0.42–0.50
High antimony	7	3.0	1.5–6.6
Roman	6	1.3	1.0–1.7
Early Islamic	10	0.7	0.2–1.7
High lead content	1	0.4	
Others	3	1.1	0.5–1.8

* Classifications are those of Sayre and Smith (see *1*).