

## Reply

S. BEN-YAAKOV AND I. R. KAPLAN

*Department of Geology and Institute of Geophysics and Planetary Physics  
University of California, Los Angeles, California 90024*

*Pytkowicz* [1972] is correct in assuming that we used Figure 1 given by *Hawley and Pytkowicz* [1969] when constructing Figure 4 of our paper [*Ben-Yaakov and Kaplan*, 1971]. This procedure was deemed necessary, because Table 3 given by *Hawley and Pytkowicz* corresponds to a station at a much higher latitude ( $\sim 50^\circ\text{N}$ ) than our reported carbonate saturometer stations ( $\sim 32^\circ\text{N}$ ). The degree of carbonate saturation in the Pacific is quite variable [*Lyakhin*, 1968; *Hawley and Pytkowicz*, 1969], and there is no point in comparing two profiles taken at different regions, as explained in our paper on page 727. Furthermore, owing to the uncertainty in interpolating the upper-layer points from Figure 1 in *Hawley and Pytkowicz*, we used only the points below 1000 meters in our Figure 4 and limited the comparison to the deep points. However, *Pytkowicz* is correct in describing the results published by him and his co-workers, especially in regard to the carbonate saturation minimum, which they drew attention to in an earlier paper [*Pytkowicz and Fowler*, 1967].

No comparison was made between our results and previous papers by *Pytkowicz* and his co-workers [*Pytkowicz*, 1972] for two reasons. First, they do not present data from the region of our saturometer station, and, second, the results of *Hawley and Pytkowicz* surpass the earlier results in that they are based on improved constants [*Hawley and Pytkowicz*, 1969, p. 1557].

The problem of calcite-sea-water interaction was thoroughly investigated by *Ben-Yaakov and Kaplan* [1969] and *Ben-Yaakov* [1970], and we are well aware of the problems and pitfalls. Our results generally agree with the conclusion of *Chave et al.* [1962], *Chave and Schmalz*

[1966], *Berner* [1966], *Weyl* [1967], and *Bischoff* [1968] in regard to the role of magnesium ions on the solubility of calcite in supersaturated sea water. It was found that the uncertainty due to this effect can be minimized by increasing the solid to sea-water ratio in a carbonate saturometer experiment. This ratio is maximized in the in situ carbonate saturometer as the glass electrode of the saturometer is placed in a slurry of crushed calcite [*Ben-Yaakov*, 1970; *Ben-Yaakov and Kaplan*, 1971].

It should be emphasized, in this connection, that the problem associated with the specific nature of calcite-sea-water interaction may have affected not only our results (at supersaturated layers) but also the determination of the constants used to calculate the in situ degree of saturation from analyses of sampled waters [*Edmond and Gieskes*, 1970]. Consider, for example, the experimental procedure of *Pytkowicz and Fowler* [1969] for determining the pressure coefficients of the solubility of calcite in sea water. They placed calcareous tests of pelagic foraminifera in artificial sea water and then pressurized the sample and measured the pH shift. However, by placing the foraminifera in supersaturated water (artificial sea water equilibrated with the atmosphere will be supersaturated with respect to calcite) they might have formed a coat of highly soluble magnesium-calcite [*Weyl*, 1967; *Ben-Yaakov*, 1970], which probably redissolved as the pressure was increased. One may argue then that the measured pressure coefficient is that of high magnesium-calcite and not of the original mineral composing the tests (which is low magnesium-calcite). It should also be noted that *Hawley and Pytkowicz* [1969, p. 1559] encountered difficulties when attempting to measure the pressure coefficient of calcite solubility (probably because of the same problem) and assumed,

in their saturation calculations, that the pressure effect on calcite solubility is identical to that of aragonite solubility. It appears, then, that the problem is not unique to our experimental procedure but rather to all available data on calcite solubility in sea water.

The recalculated data of *Li et al.* [1969] by the method of *Edmond and Gieskes* [1970] improves the agreement between our reported results [*Ben-Yaakov and Kaplan*, 1971] and theirs for the deep points at approximately 30°N. The degree of calcite saturation calculated from Russian measurements [*National Oceanographic Data Center*, 1958, 1959] by *Lyakhin* [1968] and *Hawley and Pytkowicz* [1969] is consistently lower. However, the important difference between the two sets of data is the shape of the calcite saturation–depth curve and not only the magnitude of degree of saturation. The Russian data suggest that at 30°N in the Pacific the degree of calcite saturation decreases rather gradually below a depth of approximately 1000 meters. However, the recalculated results of *Li et al.* [1969], for approximately the same latitude, show an interesting feature. Calcite saturation decreases approximately 6% per 1000 meters between 2000 and 4000 meters ( $IP/K'sp = 0.86$  at 3000 meters) but decreases at about twice this rate below 4000 meters. This behavior resembles the results of *Peterson* [1966] and *Berger* [1967], who reported that the rate of calcite dissolution in the central Pacific increases markedly below approximately 3700 meters. The depth of this abrupt change in dissolution was first termed 'lysocline' by *Berger* [1968, 1970] from solution of less resistant calcareous tests and is related to the carbonate compensation depth [*Ruddiman and Heezen*, 1967; *Berger*, 1968, 1970; *Heath and Culberson*, 1970].

*Pytkowicz* is correct in stating that the carbonate compensation depth is not the boundary line between supersaturated and undersaturated waters. However, as solution rates are generally considered to be diffusion dependent [*Berner*, 1971], one would expect to detect a correlation between the degree of carbonate saturation and the carbonate compensation depth. The data of *Li et al.* [1969] seem to show such a correlation. The mechanisms producing the carbonate compensation depth are still not well understood; therefore, it is wise to investigate the

problem by application of different experimental techniques.

## REFERENCES

- Ben-Yaakov*, S., and I. R. Kaplan, Determination of carbonate saturation with a carbonate saturationometer, *Limnol. Oceanogr.*, *14*, 874–882, 1969.
- Ben-Yaakov*, S., An oceanographic instrumentation system for in situ measurements, Ph.D. Dissertation, Univ. of Calif. at Los Angeles, Los Angeles, 343 pp., 1970.
- Ben-Yaakov*, S., and I. R. Kaplan, Deep sea in situ calcium carbonate saturation, *J. Geophys. Res.*, *76*, 722–731, 1971.
- Berger*, W. H., Foraminiferal ooze: Solution at depths, *Science*, *156*, 383–385, 1967.
- Berger*, W. H., Planktonic foraminifera: Selective solution and paleoclimatic interpretation, *Deep Sea Res.*, *15*, 31–43, 1968.
- Berger*, W. H., Planktonic foraminifera: Selective solution and the lysocline, *Mar. Geol.*, *8*, 111–138, 1970.
- Berner*, R. A., Diagenesis of carbonate sediments: Interaction of magnesium in sea water with mineral grains, *Science*, *153*, 188–191, 1966.
- Berner*, R. A., *Principles of Chemical Sedimentology*, 240 pp., McGraw-Hill, New York, 1971.
- Bischoff*, J. L., Kinetics of calcite nucleation: Magnesium ion inhibition and ionic strength catalysis, *J. Geophys. Res.*, *73*, 3315–3322, 1968.
- Chave*, K. E., K. S. Deffeyes, P. K. Weyl, R. M. Garrels, and M. E. Thompson, Observation on the solubility of skeletal carbonates in aqueous solution, *Science*, *137*, 33–34, 1962.
- Chave*, K. E., and R. F. Schmalz, Carbonate-seawater interactions, *Geochim. Cosmochim. Acta*, *30*, 1037–1048, 1966.
- Hawley*, J., and R. M. Pytkowicz, Solubility of calcium carbonate in seawater at high pressures and 2°C, *Geochim. Cosmochim. Acta*, *33*, 1557–1561, 1969.
- Heath*, G. R., and C. Culberson, Calcite: Degree of saturation, rate of dissolution and the compensation depth, *Geol. Soc. Amer. Bull.*, *81*, 3157–3160, 1970.
- Lyakhin*, Y. L., Calcium carbonate saturation of Pacific water, *Oceanology*, (English Trans.) *8*, 44–53, 1968.
- National Oceanographic Data Center, VITAZ Cruise 26, Physical and Chemical Data, NODC Cruise 90862, 1958.
- National Oceanographic Data Center, VITAZ Cruise 29, Physical and Chemical Data, NODC Cruise 90589, 1959.
- Peterson*, M. N. A., Calcite: Rate of dissolution in a vertical profile in the Central Pacific, *Science*, *154*, 1542–1544, 1966.
- Pytkowicz*, R. M., and G. A. Fowler, Solubility of foraminifera in sea water at high pressures, *Geochem. J.*, *1*, 169–182, 1967.

- Pytkowicz, R. M., Comments on a paper by S. Ben-Yaakov, and I. R. Kaplan 'Deep sea in situ carbonate saturometry,' *J. Geophys. Res.*, 77, this issue, 1972.
- Ruddiman, W. F., and B. C. Heezen, Differential solution of planktonic foraminifera, *Deep Sea Res.*, 14, 801-808, 1967.
- Weyl, P. K., The solution behavior of carbonate materials in sea water, *Stud. Trop. Oceanogr. Miami*, 5, 178-228, 1967.

(Received February 17, 1972.)

