Distributions of dissolved calcium and alkalinity in the Weddell Sea in winter

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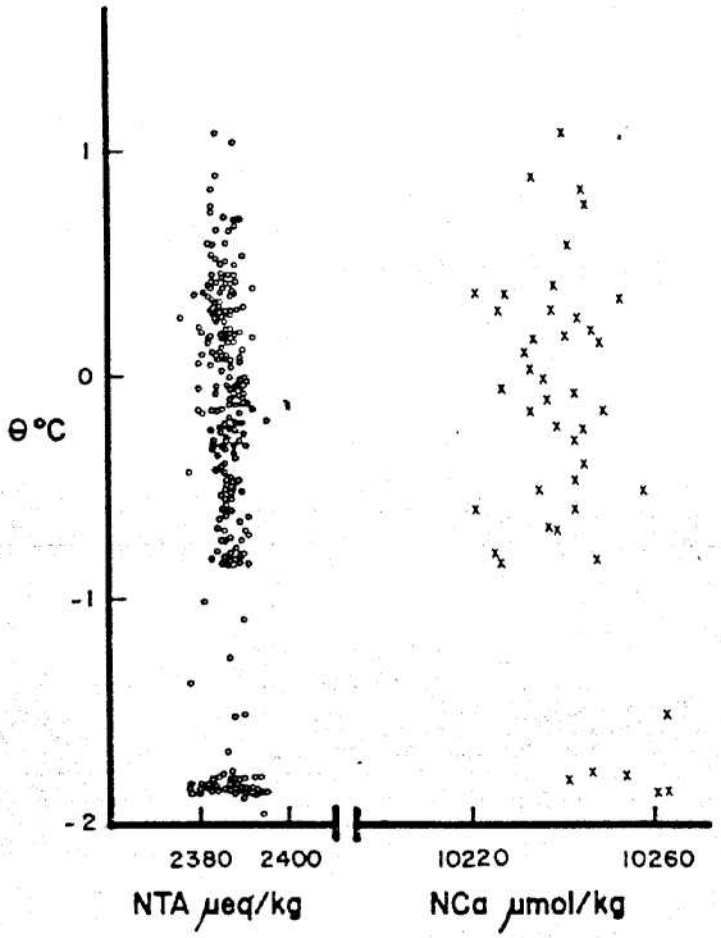
In the late austral winter of 1981, from 9 October to 25 November, as part of the U.S.-U.S.S.R. Weddell Polynya Expedition (Gordon 1982; Chen 1982a) we measured dissolved calcium and titration alkalinity (TA) in the Weddell Sea. Our values were the first winter data collected in the Weddell Sea and probably represent the initial calcium and TA concentrations of the deep Pacific waters. With this information we can now calculate more accurately the *in situ* calcium carbonate ($CaCO_3$) dissolution rate in the Pacific.

Previous attempts for evaluating the *in situ* $CaCO_3$ dissolution, based on the measurements of dissolved calcium or TA in seawater (Almgren, Dryssen, and Strandberg 1977; Brewer et al. 1975; Chen 1978; Horibe, Endo, and Tsubota 1974; Tsunogai and Watanabe 1981; Tsunogai, Yamahata, and Saito 1973; Tsunogai, Yamazaki, and Nishimura 1971), frequently used local surface calcium and TA values as references. This approach leaves the erroneous impression that the differences between the deep values and the references represent the vertical inorganic carbon flux, whereas deep waters may simply have higher calcicum and TA concentrations than the surface waters when formed (Chen and Millero 1979; Chen, Pytkowicz, and Olson 1982; Edmond 1974; Tsunogai and Watanabe 1981; Tsunogai et al. 1973). The observed deep values, therefore, should be higher even without the *in situ* $CaCO_3$ dissolution.

Chen, Pytkowicz, and Olson (1982) believe that a large portion of the apparent calcium concentration increase reported previously for the Pacific Ocean is probably not due to the *in situ* $CaCO_3$ dissolution in the water column but rather due to the transport by the water itself. This conclusion, however, was reached from using data collected by various investigators [calcium data of Tsunogai *et al.* 1973 and Horibe et al. 1974; TA data from Horibe et al. 1974 and Geochemical Ocean Sections Study (GEOSECS), Takahashi et al. 1980]. No comprehensive data including both calcium and TA in the Weddell Sea, the source of the antarctic bottom water (AABW), were available. As a result, large arbitrary systematic adjustments of the different data sets had to be made to make them comparable.

With the winter Weddell Sea data collected on the U.S.-U.S.S.R. Weddell Polynya Expedition, we have now calculated the *in situ* $CaCO_3$ dissolution rate in the Pacific. Both TA and calcium seem to behave conservatively in the Weddell Sea, as expected (Weiss, Ostlund, and Craig 1979), because the marine organisms are mainly siliceous, and little production or dissolution of $CaCO_3$ occurs in this region. The normalized TA (NTA) ($NTA = TA \times \frac{35.0}{\text{Salinity}}$) and normalized calcium (NCa) ($NCa = \text{calcium} \times \frac{35.0}{\text{Salinity}}$) concentrations remain essentially constant (average NTA = 2,386±10 microequivalents per kilogram; NCa = 10,240 ± 15 micromoles per kilogram) and show little variation with depth or temperature (figure 1). These values compare well with the average deep NTA values of GEOSECS (2,386 microe-

quivalents per kilogram and NCa values of 10,234 micromoles per kilogram of Tsunogai et al. (1971).



The potential temperature vs. normalized titration alkalinity (NTA), measured in microequivalents per kilogram, and normalized calcium (NCa), measured in micromoles per kilogram, in the Weddell Sea.

Our data in the northeast Pacific show an average NCa value of 10,276 micromoles per kilogram below 2,000 meters, only 36 micromoles per kilogram higher than the Weddell Sea value. On the other hand, the deep Pacific NCa values are 80 micromoles per kilogram higher than the local surface values. The difference of 36 micromoles per kilogram reflects the true flux of $CaCo_3$ relative to the source of the water. Dividing 36 micromoles per kilogram by the average replacement time (500 years) of the deep Pacific water, also referenced to the southern ocean (Stuiver, Quay, and Ostlund 1983), we obtain an inorganic carbon flux of 0.072 micromoles per kilogram per year, in good agreement with the latest literature value of 0.09 micromoles per kilogram per year (Tsunogai and Watanabe 1981).

It has been a common practice to estimate the $CaCO_3$ flux using TA data. Our NTA values in the deep northeast Pacific (largely unpublished but partially shown in Chen 1982b and Chen et al. 1982) are, on the average, 55 microequivalents per kilogram higher than the Weddell Sea values. We used the relationship Δ Ca = 0.5 Δ TA 0.63 Δ NO_3 (Brewer et al. 1975; Chen 1978) where Δ denotes the difference between the measured values and the references (in this case, the Weddell Sea values) and NO_3 is, of course, nitrate. The coefficient 0.63, instead of 0.53, is used to take into consideration the effect of sulfur on TA. For the NO_3 data, we used the Weddell Sea average of 39 micromoles per kilogram and the deep northeast pacific average of 32 micromoles per kilogram. We obtained a calcium enrichment of 32 micromoles per kilogram in the deep northeast Pacific Ocean, in good agreement with our direct calcium results. This is also in good agreement with the value of 35 micromoles per kilogram obtained both by Fiadeiro (1980) based on an elaborate three-dimensional modeling of the GEOSECS TA data and by Chen et al. (1982) based on the calcium (Tsunogai et al. 1973) and the GEOSECS TA data.

This work was supported by the Department of Energy grant 81EV10611 A001 and by National Science Foundation grant OCE 82–15053.

Acknowledgment. We thank Louis I. Gordon for use of the nutrient data in the Weddell Sea and R. A. Feely for use of the nutrient data in the northeast pacific.

References

Almgren, T., D. Dryssen, and M. Strandberg. 1977. Computerized highprecision titrations of some major constituents of seawater on board the RV *Dmitry Mendeleev*. *Deep-Sea Research*, 24, 345–364.

Brewer, P. G., G. T. F. Wong, M. P. Bacon, and D. W. Spencer. 1975. An oceanic calcium problem? *Earth and Planetary Science Letters*, 26, 81–87

Chen, C. T. 1978. Decomposition of calcium carbonate and organic carbon in the deep oceans. *Science*, 201, 735–736.

Chen, C. T. 1982a. Carbonate chemistry during the WEPOLEX-81. *Antarctic Journal of the U.S.*, 17(5), 102–103.

Chen, C. T. 1982b. Oceanic penetration of excess CO_2 in a cross section between Alaska and Hawaii. *Geophysical Research Letters*, 912, 117–119.

Chen, C. T., and F. J. Millero. 1979. Gradual increase of oceanic CO_2. *Nature*, 277(5693), 205–296.

Chen, C. T., R. M. Pytkowicz, and E. J. Olson. 1982. Evaluation of the calcium problem in the South Pacific. *Geochemical Journal*, 16, 1–10.

Edmond, J. M. 1974. On the dissolution of carbonate and silicate in the deep ocean. *Deep-Sea Research*, 21, 455–480.

Fiadeiro, M. 1980. The alkalinity of the deep Pacific. *Earth and Planetary Science Letters*, 49, 499–505.

Gordon, A. L. 1982. The U.S.-U.S.S.R. Weddell Polynya Expedition. *Antarctic Journal of the U.S.*, 17(5), 96–98.

Horibe, Y., K. Endo, and H. Tsubota. 1974. Calcium in the south Pacific, and its correlation with carbonate alkalinity. *Earth and Planetary Science Letters*, 23, 136–140.

Shiller, A. M., and J. M. Gieskes. 1980. Processes affecting the oceanic distributions of dissolved calcium and alkalinity. *Journal of Geophysical Research*, 85(C5), 2719–2727.

Stuiver, M., P. D. Quay, and H. G. Ostlund. 1983. Abyssal water carbon-14 distribution and the age of world oceans. *Science*, 219, 849–851.

Takahashi, T., W. S. Broecker, A. E. Bainbridge, and R. F. Weiss. 1980. *Carbonate chemistry of the Atlantic, Pacific and Indian Oceans: The results of the GEOSECS expeditions, 1972–1978.* (Lamont-Doherty Geological Observatory Technical Report No. 1. CV–1–80.) Palisades, N.Y.: Columbia University Press.

Tsunogai, S., T. Yamazaki, and M. Nishimura. 1971. Calcium in the Antarctic Ocean. *Journal of the Oceanographical Society of Japan*, 27(5), 191–196.

Tsunogai, S., H. Yamahata, and O. Saito. 1973. Calcium in the Pacific Ocean. *Deep-Sea Research*, 20, 717–726.

Tsunogai, S., and Y. Watanabe. 1981. Calcium in the north Pacific water and the effect of organic matter on the calcium-alkalinity relation. *Geochemical Journal*, 15, 95–107.

Weiss, R. F., H. G. Ostlund, and H. Craig. 1979. Geochemical studies of the Weddell Sea. *Deep-Sea Research*, 26(10A), 1093–1120.