

## Comparison of seawater carbonate parameters in the East China Sea and the Sea of Japan

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**Abstract:** During the Kuroshio Edge Exchange Processes-Marginal Sea Studies expedition (KEEP-MASS) in the summer of 1992, three parameters of the carbonate system were measured—pH, total alkalinity (TA) and total carbon dioxide (TCO<sub>2</sub>). All measurements were made by two independent methods. The pH values based on the NIST phosphate buffers were lower than those based on the Tris buffer by  $0.004 \pm 0.014$  pH unit ( $n=210$ ). The TA determined from the potentiometric Gran titration was about  $6.5 \pm 5.0 \mu\text{mol/kg}$  ( $n=154$ ) lower than that determined by the single-point indicator method. The TCO<sub>2</sub> determined from the coulometry method was about  $17.8 \pm 6.1 \mu\text{mol/kg}$  ( $n=139$ ) lower than that determined by the potentiometric Gran titration. Typical distributions of these parameters in the East China Sea and the Sea of Japan are presented.

### 1. Introduction

Recently, the fate of fossil fuel CO<sub>2</sub> and the carbon cycle in the ocean have promoted much interest in the study of carbonate chemistry in the oceans (CHEN and DRAKE, 1986; CHEN, 1993). The carbonate system can be characterized by measuring two of the four parameters, pH, TA (total alkalinity), TCO<sub>2</sub> (total carbon dioxide) and pCO<sub>2</sub>. The other parameters can then be calculated using the thermodynamic constants. However, when the measured values are compared with the calculated values, discordant results are often found (BROECKER and TAKAHASHI, 1978; BRADSHAW and BREWER, 1988; MILLERO *et al.*, 1993a).

The rate of increase of TCO<sub>2</sub> in the surface ocean is about  $1 \mu\text{mol/kg/yr}$ . In order to detect such a small change and to assure the internal consistency in the CO<sub>2</sub> system, it is necessary to make reliable and precise measurements of the parameters. The purpose of this article is to present the intercomparison results of 3 carbonate parameters during the Kuroshio Edge Exchange Processes-Marginal Sea Studies (KEEP-MASS) expedition (CHEN, 1992).

### 2. Method

In 1992, a multinational, multidisciplinary study of the West Philippine Sea (WPS), the East China Sea (ECS) and the Sea of Japan, called the KEEP-MASS, was conducted aboard the Russian R/V Academic Alexander Vinogradov. The ship departed Kaohsiung, Taiwan on 10 July, and returned to Vladivostok on 5 August. During the expedition 71 hydrographic stations were occupied: 11 in the WPS; 49 in the ECS and 11 in the Sea of Japan. The pH, TA and TCO<sub>2</sub> were measured as follows:

We used the NIST (National Institute of Standards and Technology, U.S.A.) 4.006 and 7.415 phosphate buffers to calibrate the Radiometer GK 2401C combination electrode at 25°C. The reproducibility of the pH measurements was better than  $\pm 0.001$  units for replicate samples. All measurements were performed within 30 minutes of sampling. The electrode drift (assumed to be linear) was determined at approximately 10 day intervals. The drift was approximately 0.0018 unit/day and the correction was made to the measured values. Altogether 534 samples were measured. Independent pH measurements on 210 samples were made by a Russian group using Tris (2-amino-2-hydroxymethyl-1, 3-propanediol) seawater buffer to calibrate the glass and

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reference electrodes (CHEN *et al.*, 1992). The composition of the artificial seawater buffer was the same as used by MILLERO (1986). The reproducibility of the pH measurements was  $\pm 0.009$  units for replicate samples.

We determined the alkalinity of 373 samples by the Gran titration at  $25 \pm 0.05^\circ\text{C}$  with a PC-controlled titration cell (CHEN and WANG, 1993). These measurements have a precision of  $\pm 0.05\%$  and were performed within 12 hours of sampling. The accuracy of this method shown in HUANG and CHEN (1995) is  $\pm 3 \mu\text{mol/kg}$ . The Russian team measured 154 TA samples using the single-point indicator method following Bruevich's procedure (IVANENKOV and LYAHIN, 1978). The end-point was decided by eye with an accuracy of about  $\pm 5 \mu\text{mol/kg}$  at room temperature (CHEN *et al.*, 1992).

The  $\text{TCO}_2$  measurements were conducted by us with two independent methods. The SOMMA (single-operator multiparameter metabolic analyzer) system first extracted  $\text{CO}_2$  gas from acidified seawater and subsequently the  $\text{CO}_2$  gas was measured by UIC (Coulometrics, Inc.) model 5011 coulometric detector (DICKSON and GOYET, 1991). One hundred fifty two samples were performed within 12 hours of sampling, and the precision was  $\pm 0.025\%$ . The Centre for Ocean Climate Chemistry (COCC) in the Institute of Ocean Sciences, Canada, prepared the  $\text{TCO}_2$  standard seawater for us as the running standard. The reference material could be traced to the standard material from the Scripps Institution of Oceanography, U.S.A. with the accuracy of about  $\pm 1 \mu\text{mol/kg}$ . Three hundred seventy three  $\text{TCO}_2$  samples were also determined by the Gran titration at  $25 \pm 0.05^\circ\text{C}$ . The accuracy was  $\pm 4 \mu\text{mol/kg}$ .

### 3. Results and Discussion

When all the pH values based on the Tris buffer were changed to the NIST scale (MILLERO, 1986), these two sets of data agreed to within  $0.004 \pm 0.014$  pH unit based on 210 measurements (Table 1). The Russian data were a little higher than ours, but the agreement was much better than the combined precision of  $\pm 0.01$  pH unit. A 1985 SCOR report stated that "the usual reproducibility of ocean pH measurements is not better than  $\pm 0.02$  pH units". The present results and the results of BYRNE *et al.* (1988) and CHEN (1994) clearly nullified that statement. Indeed these studies indicate that the usual reproducibility of ocean pH measurements is now about  $\pm 0.003$  pH units.

Figure 1 shows the vertical profiles of  $\theta$ , S and pH in the Sea of Japan. The vertical temperature gradient was very large in the surface water, about  $20^\circ\text{C}$  in a matter of 100m. The salinity was lower for surface water then gradually increased with depth. In the deep water the water was very homogeneous and had a salinity of about 34.07. The pH data showed a large decrease with depth in the surface water and a minimum was found at about 1800m.

The pH minimum is shown more clearly when our data from several stations are plotted with depth (Fig. 2). This minimum, an indication of the presence of older water, is shown even more dramatically when plotted vs.  $\theta$  (Fig. 3). CHEN *et al.* (1995a) also found an AOU maximum in the deep water, corresponding to the pH minimum. It should be pointed out that the magnitude of the pH signal was only 0.02 pH unit. High precision of the data is needed in order to detect it.

The comparison of TA data collected at the

Table 1. Comparison of the carbonate parameters during the KEEP-MASS Expedition

	pH	TA	$\text{TCO}_2$
ROC	NIST buffers	potentiometry	potentiometry, coulometry
Russia	Tris buffer	single-point	—
$\Delta$	$0.004 \pm 0.014$ (Russia-ROC)	$6.5 \pm 5.0$ (Russia-ROC)	$17.8 \pm 6.1^{\#}$
n	210	154	139

$\#$  potentiometry-coulometry

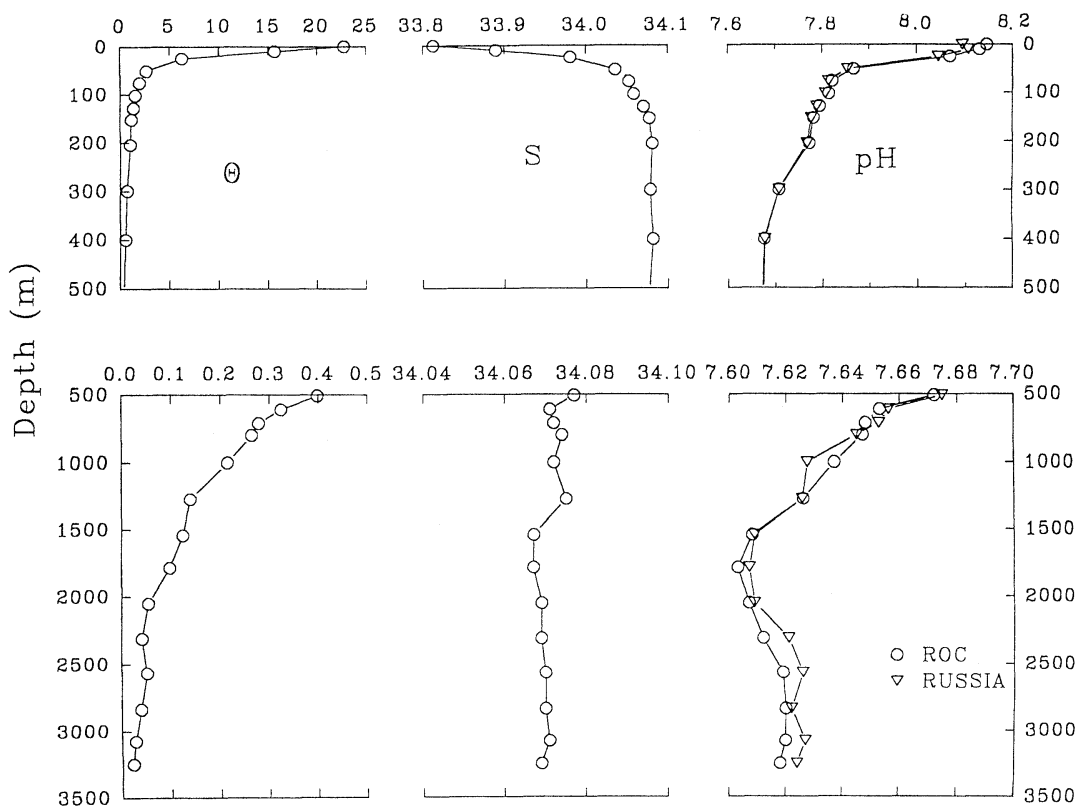


Fig. 1. The vertical profiles of  $\theta$ , S and pH (25°C) at station 10 (40°56.3'N, 133°01.2'E) in the Sea of Japan.

same locations showed that our TA values were about  $6.5 \pm 5.0 \mu\text{mol/kg}$  ( $n=154$ ) lower than that determined by the single-point indicator method. The vertical profile of the normalized alkalinity ( $\text{NTA} = \text{TA} \cdot 35/\text{S}$ ) in the Sea of Japan shown in Fig. 4 indicates that both methods gave reliable results, but the single-point method was less precise. The NTA increases steadily with depth below 500m. In the whole water column the NTA values varied less than  $40 \mu\text{mol/kg}$  in the Sea of Japan.

The NTA is an useful tool for studying the mixing processes on the shelf (CHEN, 1985). The NTA data in the ECS are plotted vs. salinity in Fig. 5. In the shelf area, the NTA-S correlation falls into a linear trend with NTA shooting up at lower salinity, reflecting the alkalinity input of the river water (CHEN *et al.*, 1995b). The bottom water of shelf area in the northern ECS falls into a different trend which indicates a different water source. The Kuroshio has a

very different correlation with salinity as compared to the ECS shelf water.

The  $\text{TCO}_2$  determined from the coulometry method was about  $17.8 \pm 6.1 \mu\text{mol/kg}$  ( $n=139$ ) lower than that determined by the potentiometric Gran titration (Table 1), similar to that reported by BRADSHAW and BREWER (1989). The vertical distributions of normalized total  $\text{CO}_2$  ( $\text{NTCO}_2 = \text{TCO}_2 \cdot 35/\text{S}$ ) is shown in Fig. 6. The difference between these two methods has been attributed to the presence of unknown protolytes in seawater (BRADSHAW and BREWER, 1988) but MILLERO *et al.* (1993b) suggested that the offset in the  $\text{TCO}_2$  is due to deviations in the slope of the electrode from the Nernstian behavior. It suggests that the  $\text{TCO}_2$  measured by the potentiometric method needs more attention vis-a-vis the condition of the electrode. Fig. 7 shows the pH- $\text{NTCO}_2$  correlation and clearly indicates the pH minimum but the quality of the  $\text{NTCO}_2$  data is not sufficient

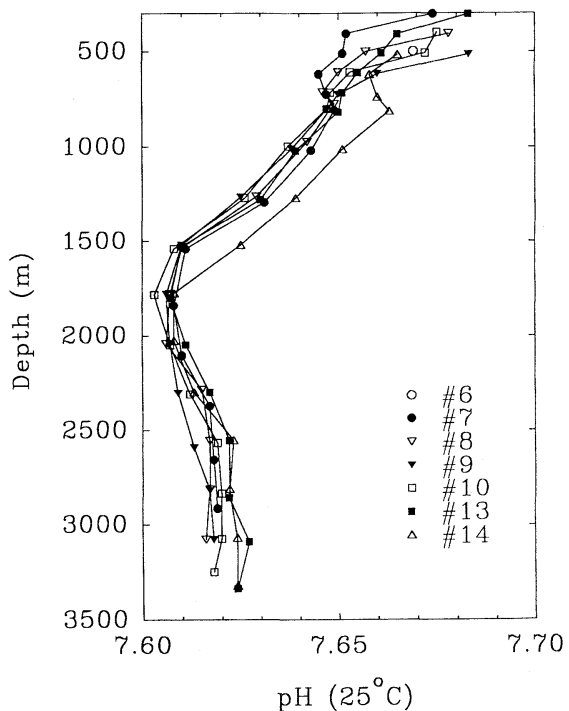


Fig. 2. The vertical profiles of pH (25°C) below 300m in the Sea of Japan.

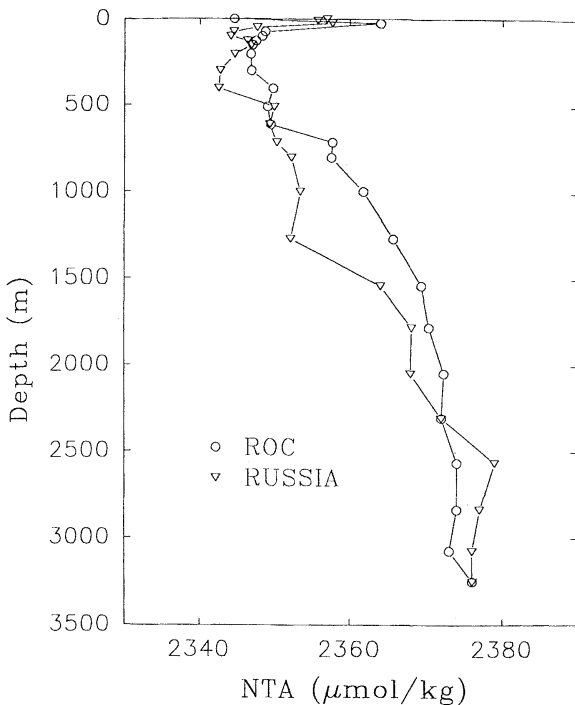


Fig. 4. The vertical profiles of NTA at station 10 (40°56.3'N, 133°01.2'E) in the Sea of Japan.

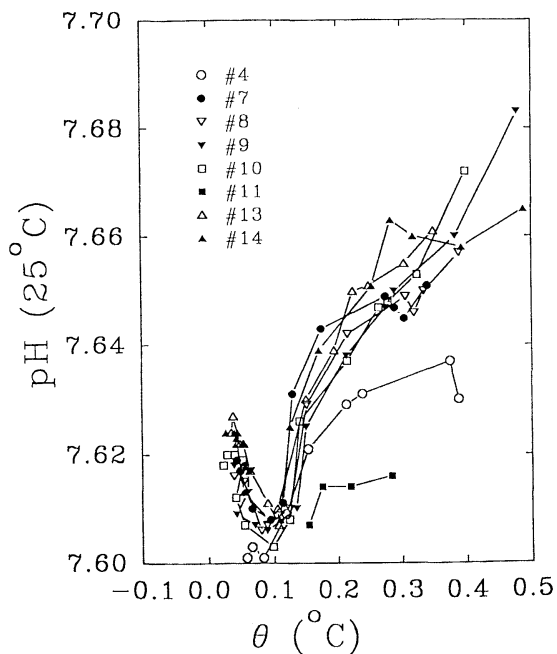


Fig. 3. The correlation of pH (25°C) with  $\theta$  in the Sea of Japan.

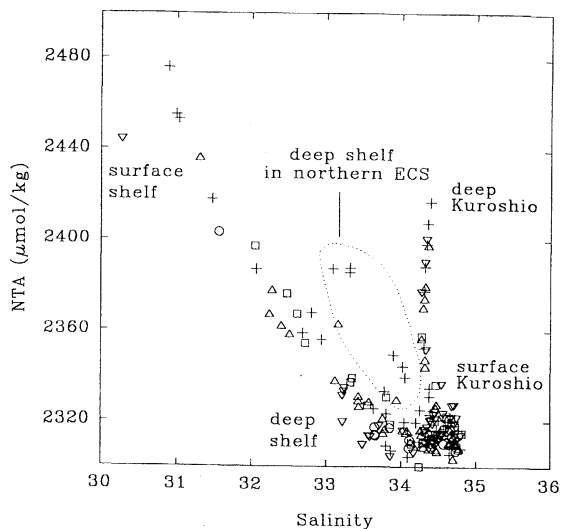


Fig. 5. The NTA vs. S diagram in the East China Sea. Enclosed area with dotted line indicates the deep shelf water in the northern ECS.

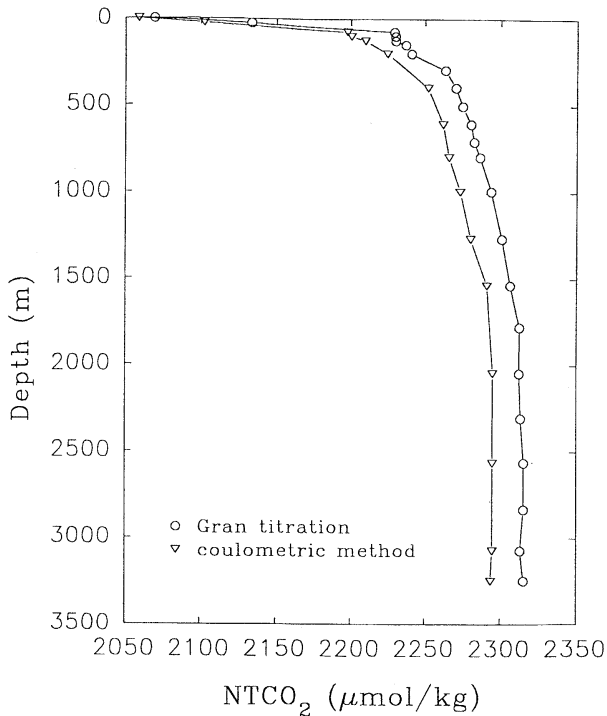


Fig. 6. The vertical profiles of  $\text{NTCO}_2$  at station 10 ( $40^\circ 56.3' \text{N}$ ,  $133^\circ 01.2' \text{E}$ ) in the Sea of Japan.

to tell whether there is a  $\text{NTCO}_2$  maximum.

#### 4. Conclusion

The pH measurements based on the NIST and Tris buffers agreed to within  $0.004 \pm 0.014$  pH unit during the KEEP-MASS expedition. The TA measurements showed that both of the potentiometric Gran titration and the single point method could give reliable results but the potentiometric Gran titration is more precise. The  $\text{TCO}_2$  values determined by the potentiometric Gran titration apparently had a systematic shift compared with those determined by the coulometry method.

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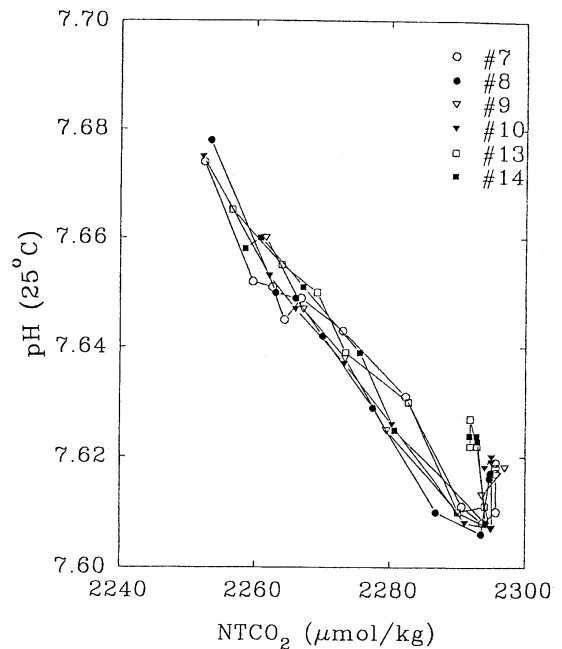


Fig. 7. The correlation of pH ( $25^\circ \text{C}$ ) with  $\text{NTCO}_2$  in the Sea of Japan.

#### References

- BRADSHAW, A. L. and P. G. BREWER (1988): High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration-1. Presence of unknown protolyte(s) ? *Mar. Chem.*, **23**, 69-86.
- BRADSHAW, A. L. and P. G. BREWER (1989): High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration-2. Measurements on standard solutions, *Mar. Chem.*, **24**, 155-162.
- BROECKER, W. S. and T. TAKAHASHI (1978): The relationship between lysocline depth and in situ carbonate ion concentrations, *Deep-Sea Res.*, **25**, 65-95.
- BYRNE, R. H., G. ROBERT-BALDO, S. W. THOMPSON and C. T. CHEN (1988): Seawater pH measurements: an at-sea comparison of spectrophotometric and potentiometric methods, *Deep-Sea Res.*, **35**, 1405-1410.
- CHEN, C. T. (1985): Preliminary observations of oxygen and carbon dioxide of the wintertime Bering Sea marginal ice zone, *Cont. Shelf Res.*, **4**, 465-483.
- CHEN, C. T. A. (1992): A preliminary multination

- multidisciplinary study of the western marginal seas in the North Pacific, *Bull. Mar. Sci. Tech.*, **11**, 4-33.
- CHEN, C. T. A. (1993): The oceanic anthropogenic CO<sub>2</sub> sink, *Chemosphere*, **27**, 1041-1064.
- CHEN, C. T. A. (1994): Vertical distributions of pH and fluorescence in the western tropical Indian ocean-the INDIGO 2 expedition, *TAO*, **5** (1), 77-90.
- CHEN, C. T. and E. T. DRAKE (1986): Carbon dioxide increase in the atmosphere and oceans and possible effects on climate, *Annu. Rev. Earth Planet. Sci.*, **14**, 201-235.
- CHEN, C. T. A. and S. L. Wang (1993): International intercalibration of the CO<sub>2</sub> parameters, *Acta Oceanol. Sin.*, **15**(6), 60-67. (in Chinese)
- CHEN, C. T. A., S. L. WANG and A. S. BYCHKOV (1995a): Carbonate chemistry of the Sea of Japan, *J. Geophys. Res.*, **100**, C7, 13737-13745.
- CHEN, C. T. A., R. RUO, S. C. PAI, C. T. LIU and G. T. F. WONG (1995b): Exchange of water masses between the East China Sea and the Kuroshio off northeastern Taiwan, *Cont. Shelf Res.*, **15**, 19-39.
- CHEN, M. P., C. C. HUANG, F. L. LIN C. C. LIU, H. W. LI, G. C. GONG, J. J. HUNG and Y. L. LEE (1992): The KEEP-MASS data report, 728pp., NSC R. V. Ocean Researcher 1, Reg. Instrum. Cent., Taipei, Taiwan.
- DICKSON A. and C. GOYET (eds) (1991): DOE Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water, 104pp., U. S. Department of Energy, Washington, D. C.
- HUANG, M. H. and C. T. A. CHEN (1995): Carbonate chemistry in northeast South China Sea, *J. Oceano. in Taiwan Strait*, **14**, 2, 124-134. (in Chinese).
- IVANENKOV, V. and Y. LYAHIN (1978): The determination of the seawater alkalinity. Methods of hydrochemical investigation of seawater, *Science, Moscow*, 110-114. (in Russian)
- MILLERO, F. J. (1986): The pH of estuarine waters, *Limnol. Oceanogr.*, **31**, 839-847.
- MILLERO, F. J., J. Z. ZHANG, S. FIOLE, S. SOTOLONGO, R. N. ROY, K. LEE and S. MANE (1993a): The use of buffers to measure the pH of seawater, *Mar. Chem.*, **44**, 143-152.
- MILLERO, F. J., J. Z. ZHANG, K. LEE and D. M. CAMPBELL (1993b): Titration alkalinity of seawater, *Mar. Chem.*, **44**, 153-165.
- SCOR (1985): Oceanic CO<sub>2</sub> measurements. Rep. 3rd Meet. Working Group 75, Les Houches, France, October 1985.

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