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Factors Influencing the Degree of Saturation of the Surface and Intermediate Waters of the North Pacific Ocean With Respect to Aragonite

RICHARD A. FEELY,¹ ROBERT H. BYRNE,² PETER R. BETZER,² JAMES F. GENDRON,¹ AND JAMES G. ACKER²

New carbonate chemistry data obtained during a 1982 cruise have been combined with earlier GEOSECS and INDOPAC data to determine the degree of aragonite saturation of surface and intermediate waters of the North Pacific. Large gradients in saturation state occur in the region of the Subarctic Front in the north-south direction and across the Subtropical Gyre in the east-west direction. These gradients are primarily due to the extensive mixing that occurs in the intermediate waters of the western North Pacific. The major variations in saturation state were primarily related to the carbonate ion concentration, which, in turn, is primarily a function of mixing and biological processes. The present aragonite saturation depth at our northernmost station in the western North Pacific was calculated to be within 120 m of the surface. This result was directly corroborated by observations of aragonite dissolution under *in vitro* conditions. Our calculations show that one possible effect of fossil fuel-derived CO₂ on the surface of the North Pacific will be a steady progression of undersaturation from the northern to southern and western areas, with the first sign of undersaturation possibly occurring as early as the second half of the next century.

INTRODUCTION

In recent years, concern about the progressive increase in the levels of fossil fuel-derived CO₂ in the atmosphere has prompted several investigators to examine the potential impacts of increased levels of total CO₂ on the degree of calcite and aragonite saturation in the oceanic mixed layer [Broecker *et al.*, 1971; Fairhall, 1973; Zimen and Altenhein, 1973; Whitfield, 1974; Skirrow and Whitfield, 1975; Broecker *et al.*, 1979]. The results of these investigations vary widely in their predictions of the fossil fuel CO₂ inputs required to induce calcite and aragonite undersaturation. This is due partly to a lack of agreement about the exchange of fossil fuel CO₂ across the air-sea interface and its subsequent penetration into the deeper layers of the ocean, and partly due to a lack of agreement about the salinity, temperature, and pressure effects on the stoichiometric solubility products for calcite and aragonite. Solubility product discrepancies are particularly important for aragonite because some of the earlier solubility measurements did not take into account the long times required for equilibration [Morse *et al.*, 1980]. To provide a comprehensive picture of aragonite saturation in the surface and intermediate waters of the North Pacific, we have combined the most recent aragonite solubility data for seawater temperatures and salinities [Mucci, 1983] with the GEOSECS, INDOPAC, and new National Oceanic and Atmospheric Administration (NOAA) total CO₂ and alkalinity data (Figure 1). We have examined the major factors influencing the spatial variations in the degree of saturation and have used this information to discuss potential impacts of elevated levels of CO₂ in surface waters. The North Pacific was chosen for this study because of the extensive data base that exists for this region and also because, with respect to aragonite, the North Pacific is known to have the most highly undersaturated intermediate

waters of all the oceans [Takahashi *et al.*, 1981]. On this account, it might be one of the first regions where the surface waters become undersaturated as fossil fuel CO₂ is progressively elevated over the next several decades.

BACKGROUND

The degree of saturation of aragonite in seawater is defined as the ratio of the ion product of the concentrations of calcium and carbonate, at the *in situ* temperature, salinity, and pressure, divided by the stoichiometric solubility product for these conditions:

$$\Omega_a = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] / K'_{spa} \quad (1)$$

When $\Omega_a > 1$, seawater is supersaturated with respect to aragonite, and conversely, when $\Omega_a < 1$, seawater is undersaturated with respect to aragonite. Since the calcium to salinity ratio in seawater does not vary by more than 1.5% [Culkin and Cox, 1966], variations in the degree of saturation of aragonite in seawater are primarily governed by variations in the ratio of the ion concentration of carbonate to the stoichiometric solubility product. These variables are independent under natural conditions, and consequently, a study of the factors influencing the degree of saturation of aragonite in seawater must necessarily consider simultaneous variations in both. Since the concentration of carbonate ions in seawater cannot be directly determined, it is calculated from measurable variables such as total carbon dioxide TCO₂, total alkalinity A_T, and pH, assuming the dissociation constants for carbonic acid in seawater are well defined. Takahashi *et al.* [1976] reviewed the internal consistency of five sets of apparent dissociation constants of carbonic acid and boric acid in seawater using the GEOSECS Atlantic TCO₂, A_T, and partial pressure of carbon dioxide, pCO₂, data. By comparing the measured values of pCO₂ with those calculated from A_T and TCO₂, they found that the apparent dissociation constants determined by Mehrbach *et al.* [1973] and by Lyman [1956] provided the most consistent data. These conclusions were verified by the comprehensive study by Millero [1979], wherein the effects of temperature pressure and salinity on dissociation constants are described. We have used the equations of Millero [1979] in the present work

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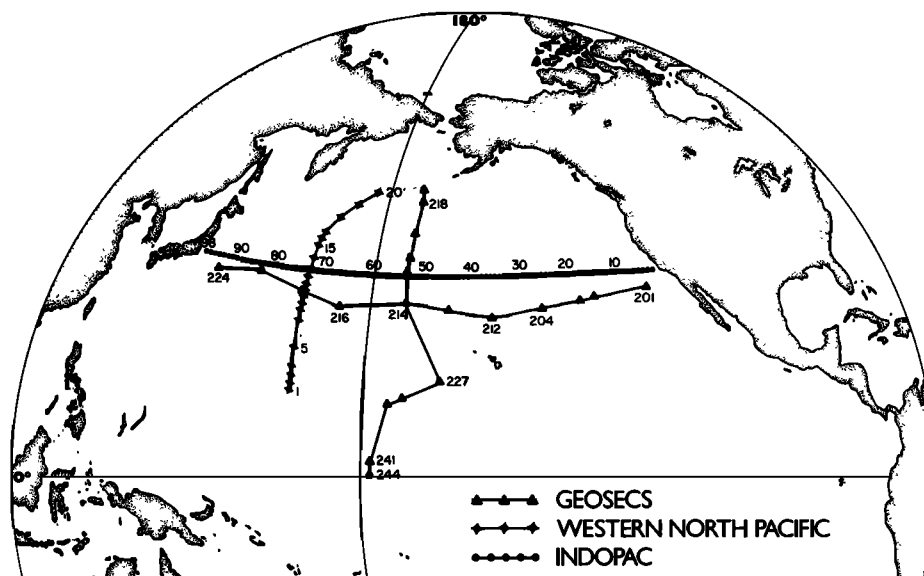


Fig. 1. Locations of stations used for this study. The GEOSECS stations were occupied in 1973, the INDOPAC stations in 1976, and the NOAA western North Pacific stations in 1982.

The stoichiometric solubility product of aragonite in seawater under various conditions has been studied by a number of investigators, and the subject has been extensively reviewed by *Morse et al.* [1980]. As has been pointed out by these authors, some of the earlier estimates by *MacIntyre* [1965], *Berner* [1976], and *Plath and Pytkowicz* [1980] were high because the investigators did not take into account the long times required for equilibration. Using equilibration times in excess of 60 days, *Morse et al.* [1980] found the stoichiometric solubility product for aragonite to be $6.65 \times 10^{-7} \text{ mol}^2 \text{ kg}^{-2}$ at 25°C, 35‰ salinity, and 1 atmosphere total pressure. This value ranges from as little as 7% to as much as 42% lower than previous values for similar conditions. The long-duration solubility studies for aragonite and calcite were recently expanded by *Mucci* [1983] to include a temperature range between 5°C and 40°C and a salinity range between 5‰ and 44‰.

On the basis of free energy differences between the two polymorphs (i.e., -230 cal/mol at 25°C and 1 atmosphere pressure), *Berner* [1976] showed that the theoretical ratio of the solubility products for aragonite and calcite is 1.48. The ratio of K'_{spa}/K'_{spc} should therefore be close to this value. Since the calcite solubility measurements of *Ingle et al.* [1973] have been verified by a number of field studies [*Broecker and Takahashi*, 1978; *Sayles*, 1980], a comparison of the ratio of the aragonite solubility data at 25°C, 35‰ salinity, and 1 atmosphere total pressure with the 25°C, 35‰ salinity calcite solubility data of *Ingle et al.* [1973] should provide further confirmation of the importance of equilibration time for accu-

rate aragonite solubility data. Table 1 gives the ratio of K'_{spa}/K'_{spc} versus equilibration time using the calcite solubility data of *Ingle et al.* [1973] and the aragonite solubility data obtained by various investigators in seawater at 25°C, 1 atmosphere pressure, and 35‰ salinity. The data show that as the equilibration time increases, the ratio of K'_{spa}/K'_{spc} approaches the theoretical value, indicating that the stoichiometric solubility products for aragonite, based on the longer equilibration times [*Mucci*, 1983], are probably more correct.

SAMPLING AND ANALYTICAL METHODS

The analytical methods and complete data for the GEOSECS and INDOPAC TCO_2 and A_T sections are given by *Takahashi et al.* [1980a] and *Scripps Institution of Oceanography* [1978], respectively. The details of the potentiometric titrations used in these studies are described by *Bos and Williams* [1982]. The method is based upon techniques developed by *Gran* [1952] and later modified by *Dyrssen and Sillen* [1967] and *Edmond* [1970]. The titrations were performed with 0.25 N Baker analytical grade HCl standardized against gravimetrically prepared sodium borate decahydrate solutions adjusted to an ionic strength of 0.7 using NaCl. The GEOSECS titration data were processed using a Gran plot computer program. As was pointed out by *Takahashi et al.* [1980a], the program contained a systematic error in the TCO_2 calculation. On the basis of independent measurements of pCO_2 and TCO_2 , they applied a correction of $-15 \mu\text{M/kg}$ to the calculated TCO_2 data.

TABLE 1. Aragonite Solubility, Equilibration Times, and Ratio of K'_{spa}/K'_{spc} for 25°C, 35‰ Salinity, and 1 Atmosphere Total Pressure

K'_{spa} , $\text{mol}^2 \text{ kg}^{-2} \times 10^{-7}$	Equilibration Time, days	$\frac{K'_{spa}}{K'_{spc}}$	Reference
8.69 (± 0.49)	2	1.89	<i>Plath and Pytkowicz</i> [1980]
8.11 (± 0.25)	4	1.76	<i>Berner</i> [1976]
7.33 (± 0.31)	10	1.59	<i>MacIntyre</i> [1965]
6.65 (± 0.12)	7–102	1.54	<i>Morse et al.</i> [1980]
6.65 (± 0.12)	7–102	1.54	<i>Mucci</i> [1983]

Ratio of K'_{spa}/K'_{spc} after the data by *Ingle et al.* [1973].

TABLE 2. Station Data for the NOAA Western North Pacific Cruise

Depth, Temperature, Salinity, DO, A _T , TCO ₂ , TCO ₂	DO, A _T , TCO ₂ , TCO ₂
m °C ‰ Sigma t μM/kg meq/kg mM/kg A _T	m °C ‰ Sigma t μM/kg meq/kg mM/kg A _T
<i>WNP 3: 16°00.1'N, 165°03.4'E, May 29, 1982</i>	
1	27.270 34.854 22.527 204.4 2.296 1.965 0.856
26	27.230 34.868 22.550 204.4 2.299 1.958 0.852
96	26.030 35.026 23.049 209.5 2.311 1.961 0.849
196	21.050 35.093 24.554 184.4 2.309 2.030 0.879
305	15.590 34.548 25.495 178.1 2.318 2.116 0.913
396	9.800 34.231 26.378 161.4 2.277 2.144 0.942
495	7.610 34.240 26.737 80.9 2.299 2.245 0.977
595	6.380 34.368 27.007 48.7 2.324 2.294 0.987
792	5.340 34.488 27.232 59.6 2.352 2.311 0.983
994	4.420 34.516 27.359 60.9 2.371 2.332 0.984
1244	3.560 34.551 27.476 72.1 2.384 2.364 0.992
1471	3.030 34.580 27.549 84.3 2.400 2.352 0.980
1957	2.150 34.622 27.658 101.2 2.422 2.361 0.975
2437	1.830 34.647 27.704 119.9 2.429 2.361 0.972
2934	1.590 34.664 27.735 134.3 2.436 2.355 0.967
<i>WNP 5: 21°05.5'N, 165°08.7'E, June 1, 1982</i>	
1	26.490 35.149 22.997 220.9 ... 2.006 ...
30	25.666 35.223 22.311 220.8 2.310 1.949 0.844
100	21.866 35.186 24.400 209.2 2.314 1.991 0.860
200	16.896 34.804 25.390 210.4 2.285 2.019 0.884
300	15.006 34.643 25.697 217.3 2.285 2.043 0.894
400	12.896 34.347 25.910 195.4 2.272 2.091 0.920
500	9.256 34.182 26.439 157.5 2.278 2.157 0.947
600	6.616 34.119 26.779 101.8 2.303 2.238 0.972
800	5.156 34.321 27.121 70.4 2.344 2.316 0.988
1000	4.316 34.471 27.334 34.3 2.377 2.333 0.981
1250	3.286 34.536 27.490 84.8 2.389 2.342 0.980
1500	2.796 34.559 27.553 86.5 2.402 2.347 0.977
2000	2.087 34.609 27.653 102.6 2.418 2.351 0.972
<i>WNP 6: 26°11.2'N, 165°11.5'E, June 4, 1982</i>	
1	25.120 35.247 23.496 236.9 2.324 1.981 0.852
43	19.980 35.119 24.861 236.6 2.309 1.977 0.856
112	17.480 34.837 25.276 224.7 2.293 2.005 0.874
211	15.980 34.735 25.550 215.1 2.289 2.032 0.888
310	15.670 34.615 25.528 215.5 2.288 2.050 0.896
407	12.340 34.429 26.082 207.6 2.280 2.077 0.911
508	9.790 34.214 26.376 174.0 2.280 2.121 0.930
609	6.710 34.025 26.693 200.5 2.287 2.182 0.954
805	4.300 34.145 27.077 70.4 2.334 2.303 0.987
1006	3.550 34.326 27.297 34.3 2.367 2.357 0.996
1251	2.890 34.474 27.477 48.2 2.390 2.371 0.992
1497	2.480 34.545 27.570 68.7 2.394 2.358 0.985
1977	1.910 34.616 27.673 102.6 2.410 2.350 0.975
2469	1.700 34.644 27.711 206.8 2.420 2.344 0.969
2962	1.580 34.664 27.736 234.2 2.422 2.337 0.965
<i>WNP 8: 30°02.5'N, 165°07.0'E, June 7, 1982</i>	
1	24.200 35.053 23.626 247.4 2.305 1.983 0.860
40	18.190 34.893 25.145 247.0 2.293 1.981 0.864
109	16.420 34.761 25.469 223.4 2.287 2.002 0.875
208	15.550 34.723 25.638 218.1 2.293 2.032 0.886
307	14.070 34.591 25.858 212.4 2.281 2.046 0.897
406	12.300 34.395 26.064 209.3 2.280 2.082 0.913
505	10.040 34.265 26.373 204.9 2.282 2.113 0.926
604	8.060 34.104 26.564 186.2 2.284 2.153 0.943
704	6.120 33.996 26.747 159.6 2.299 2.210 0.961
802	4.880 34.053 26.941 102.2 2.320 2.272 0.979
1000	3.800 34.238 27.203 51.3 2.358 2.343 0.994
1248	3.030 34.400 27.405 32.2 2.387 2.377 0.996
1496	2.560 34.494 27.522 41.3 2.409 2.389 0.992
1997	1.950 34.586 27.645 73.4 2.421 2.380 0.983
2480	1.680 34.636 27.706 108.6 2.420 2.358 0.974
2964	1.540 34.660 27.736 132.1 2.424 2.346 0.968
<i>WNP 9: 32°02.6'N, 165°02.7'E, June 8, 1982</i>	
1	23.990 34.860 23.542 244.3 2.286 1.973 0.863
38	19.663 34.875 24.757 249.3 2.294 1.976 0.861
107	17.043 34.796 25.349 234.3 2.291 2.004 0.875
207	16.430 34.778 25.480 234.3 2.288 2.010 0.878

TABLE 2. (continued)

Depth, Temperature, Salinity, DO, A _T , TCO ₂ , TCO ₂	DO, A _T , TCO ₂ , TCO ₂
m °C ‰ Sigma t μM/kg meq/kg mM/kg A _T	m °C ‰ Sigma t μM/kg meq/kg mM/kg A _T
407	14.334 34.556 25.775 209.4 2.283 2.053 0.899
605	9.314 34.205 26.447 189.3 2.286 2.134 0.934
804	5.018 34.233 27.068 119.6 2.299 2.240 0.974
1004	4.017 34.375 27.289 57.4 2.346 2.322 0.990
1252	3.085 34.376 27.381 42.2 2.378 2.362 0.993
1501	2.614 34.468 27.497 42.6 2.397 2.377 0.992
2000	2.015 34.579 27.635 68.2 2.412 2.372 0.983
2497	1.694 34.634 27.703 104.3 2.427 2.365 0.974
2995	1.564 34.653 27.728 130.8 2.422 2.345 0.968
<i>WNP 12: 34°57.3'N, 164°58.7'E, June 10, 1982</i>	
1	20.140 34.648 24.459 244.1 2.277 1.970 0.865
48	16.010 34.722 25.533 249.1 2.285 1.999 0.875
118	13.090 34.545 26.024 223.3 2.282 2.049 0.898
218	12.470 34.450 26.073 248.5 2.272 2.040 0.898
318	10.820 34.287 26.225 235.8 2.270 2.063 0.909
416	8.860 34.140 26.469 224.5 2.269 2.101 0.926
518	6.650 33.993 26.675 200.5 2.275 2.155 0.947
619	5.330 33.987 26.836 137.9 2.292 2.219 0.968
717	4.710 34.090 26.989 92.6 2.310 2.266 0.981
818	4.320 34.177 27.100 72.6 2.331 2.301 0.987
1017	3.480 34.295 27.279 46.9 2.363 2.346 0.993
1266	2.920 34.408 27.422 35.2 2.391 2.379 0.995
1548	2.420 34.493 27.533 43.5 2.396 2.377 0.992
2040	1.930 34.584 27.645 68.7 2.409 2.372 0.985
2538	1.670 34.635 27.706 103.9 2.412 2.352 0.975
3032	1.540 34.657 27.733 127.3 2.420 2.345 0.969
3526	1.480 34.672 27.750 142.5 2.419 2.334 0.965
4012	1.450 34.679 27.757 152.1 2.418 2.327 0.962
4515	1.470 34.684 27.760 159.0 2.417 2.323 0.961
5000	1.500 34.683 27.757 165.5 2.412 2.315 0.960
<i>WNP 14: 37°58.4'N, 164°59.8'E, June 12, 1982</i>	
1	16.480 34.012 24.879 252.7 2.265 1.976 0.872
67	10.650 34.257 26.261 253.3 2.273 2.063 0.908
136	7.890 33.900 26.429 272.4 2.258 2.086 0.924
234	7.220 33.968 26.578 223.6 2.270 2.133 0.940
333	5.770 33.969 26.769 163.5 2.289 2.197 0.960
432	4.890 34.008 26.904 118.3 2.302 2.244 0.975
530	4.480 34.089 27.013 87.0 2.312 2.275 0.984
628	4.150 34.176 27.117 65.2 2.335 2.308 0.988
727	3.710 34.244 27.216 50.9 2.350 2.329 0.991
825	3.420 34.298 27.288 44.3 2.362 2.347 0.994
1021	2.940 34.386 27.402 40.9 2.381 2.364 0.993
1268	2.500 34.459 27.499 40.9 2.396 2.379 0.993
1514	2.220 34.518 27.569 49.5 2.405 2.380 0.990
2007	1.870 34.590 27.655 78.7 2.414 2.373 0.983
<i>WNP 16: 41°58.1'N, 165°02.6'E, June 15, 1982</i>	
1	9.920 33.415 25.730 296.0 2.242 2.033 0.907
45	7.290 33.647 26.316 296.8 2.243 2.058 0.918
114	5.610 33.824 26.674 284.5 2.258 2.094 0.927
214	6.100 33.904 26.677 211.8 2.283 2.169 0.950
316	4.340 33.897 26.876 160.5 2.292 2.232 0.974
412	4.320 34.040 26.991 94.4 2.305 2.272 0.986
512	3.740 34.138 27.129 57.0 2.329 2.316 0.994
612	3.810 34.249 27.210 50.4 2.336 2.320 0.993
710	3.450 34.303 27.289 46.1 2.354 2.339 0.994
810	3.250 34.376 27.366 40.4 2.360 2.345 0.994
1005	2.820 34.419 27.439 36.1 2.384 2.374 0.996
1256	2.460 34.492 27.529 39.1 2.396 2.381 0.994
1505	2.190 34.545 27.594 49.5 2.405 2.379 0.989
1997	1.870 34.623 27.681 78.7 2.416 2.376 0.983
2498	1.620 34.664 27.733 110.8 2.423 2.359 0.974
2998	1.530 34.687 27.758 130.4 2.419 2.341 0.968
<i>WNP 18: 45°17.4'N, 167°15.9'E, June 17, 1982</i>	
1	5.620 32.903 25.944 335.2 2.226 2.064 0.927
73	2.130 33.108 26.447 336.7 2.243 2.118 0.944
143	2.580 33.403 26.648 265.3 2.258 2.151 0.943
243	3.110 33.698 26.838 136.1 2.286 2.255 0.986
344	3.760 33.968 26.992 87.0 2.312 2.288 0.990
443	3.150 34.000 27.075 53.5 2.324 2.327 1.001

TABLE 2. (continued)

Depth, m	Temperature, °C	Salinity, ‰	DO, Sigma t μM/kg	A_T , meq/kg	TCO_2 , mM/kg	$\frac{TCO_2}{A_T}$
542	3.320	34.149	27.178	42.2	2.342	2.336
642	3.330	34.229	27.241	37.8	2.344	2.340
742	3.080	34.274	27.300	34.8	2.362	2.356
842	2.900	34.322	27.355	27.8	2.371	2.370
1040	2.690	34.410	27.444	36.5	2.388	2.378
1291	2.350	34.476	27.525	39.5	2.402	2.374
1540	2.150	34.535	27.589	48.7	2.395	2.374
2040	1.850	34.613	27.675	77.8	2.411	2.368
2209	1.760	34.617	27.685	89.5	2.413	2.363
2538	1.620	34.639	27.713	109.9	2.412	2.347
3038	1.510	34.664	27.741	132.1	2.412	2.338
WNP 20: 49°59.5'N, 175°01.0'E, June 19, 1982						
1	5.840	32.678	25.740	315.6	2.224	2.046
54	5.120	32.680	25.825	315.6	2.216	2.037
123	3.640	33.597	26.708	115.3	2.272	2.252
172	3.620	33.889	26.942	77.4	2.300	2.319
222	3.590	33.966	27.007	39.1	2.312	2.337
271	3.550	34.020	27.053	23.0	2.320	2.344
320	3.510	34.077	27.103	19.1	2.327	2.346
418	3.420	34.156	27.174	19.6	2.342	2.356
517	3.210	34.225	27.249	20.4	2.356	2.366
615	3.080	34.278	27.303	19.6	2.362	2.370
713	2.940	34.326	27.354	18.7	2.370	2.374
812	2.810	34.366	27.398	21.3	2.379	2.382
1015	2.580	34.423	27.463	25.2	2.361	2.370
1261	2.310	34.488	27.538	34.3	2.377	2.383
1512	2.060	34.542	27.602	53.0	2.409	2.392
2007	1.770	34.628	27.693	81.7	2.412	2.392
2505	1.640	34.633	27.707	103.4	2.418	2.385
3002	1.550	34.656	27.732	126.0	2.421	2.371

DO, dissolved oxygen.

For the NOAA data, water samples were collected in 30-L Niskin bottles and immediately transferred into 1-L glass-stoppered bottles containing 1.0 mL of a saturated solution of $HgCl_2$ to decrease bacterial oxidation of organic matter prior to analysis. The samples were stored in a dark cold storage room at 4°C for as much as 12 hours. The samples were analyzed by the potentiometric method described above using a Brinkman E636 titroprocessor linked to a Hewlett-Packard 85 computer. The data from the titroprocessor were automatically fed into the computer and processed using the modified Gran equations described by Bradshaw *et al.* [1981]. Alka-

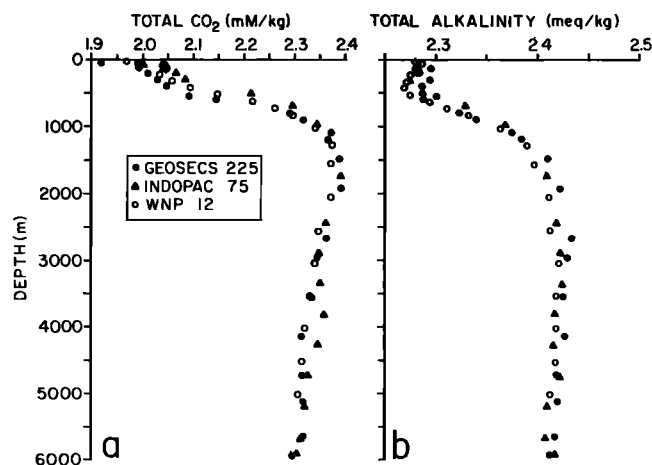


Fig. 2. Vertical profiles of (a) total CO_2 and (b) total alkalinity from GEOSECS 225 (32°37.0'N, 161°55.0'E), INDOPAC 75 (35°03.3'N, 164°65.7'E), and WNP 12 (34°57.3'N, 164°58.7'E).

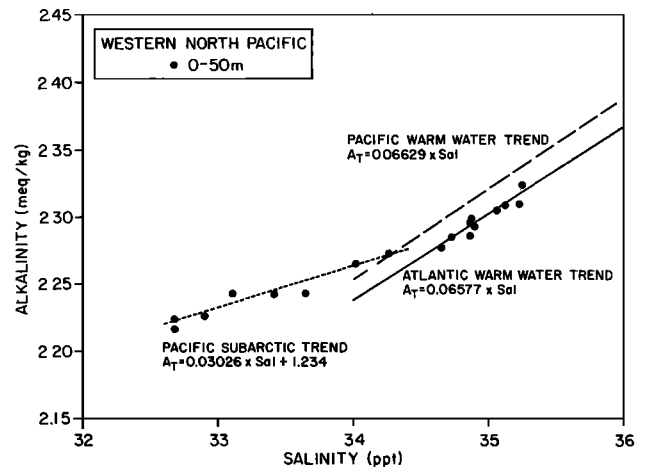


Fig. 3. Plot of A_T versus salinity for the NOAA western North Pacific near-surface (0–50 m) data. The GEOSECS Pacific Subarctic Trend (short-dashed curve), the Pacific Warm Water Trend (long-dashed curve), and the Atlantic Warm Water Trend (solid curve) are also given.

linity contributions from boric, silicic, and phosphoric acid were computed from equations similar to those presented by Takahashi *et al.* [1982] in the GEOSECS Pacific Expedition report. Total borate concentration was computed using the relation given by Culkin [1965]. The dissociation constants of carbonic acid and boric acid are from the work by Almgren *et al.* [1977]. Potassium chloride was used to adjust the ionic strength of the sodium tetraborate decahydrate standards to 0.7. At each station a blank was determined by titrating aliquots of a KCl solution containing no borate. The average blank was 4 $\mu eq/L$. Figure 1 gives the station locations, and Table 2 provides listings of the station number, depth, salinity, temperature, A_T , and TCO_2 for *Discoverer* cruise RP-14-DI-82 in the northwest Pacific.

The equations for aragonite saturation are based on the work by Mucci [1983] in which the degree of in situ saturation is the product of the concentrations of calcium and carbonate ions, at the in situ temperature, salinity, and pressure, divided by the stoichiometric solubility product for those conditions (equation (1)). Calcium concentration is estimated from the salinity [after Takahashi *et al.*, 1980a, b], while the carbonate ion concentration is calculated from the TCO_2 and A_T data using the dissociation constants of Mehrbach *et al.* [1973] as revised by Millero [1979]. The stoichiometric solubility product for aragonite is expressed by

$$\log K'_{spa} - \log K'_{spa}^{\circ} = (b_0 + b_1 T + b_2/T) S^{0.5} + C_0 S + d_0 S^{1.5} \quad (2)$$

where K'_{spa} is the stoichiometric solubility product for ambient conditions; K'_{spa}° is the stoichiometric solubility product for 298°K, 35‰ salinity, and 1 atmosphere total pressure; $b_0 = -0.06839$, $b_1 = 1.728 \times 10^{-3}$, $b_2 = 88.14$, $C_0 = -0.1002$, and $d_0 = 5.942 \times 10^{-3}$; T is temperature in degrees Kelvin; and S is salinity in parts per thousand. The pressure effect on solubility is estimated from the equation [Mucci *et al.*, 1982]

$$\ln (K'_{spa}/K'_{spa}^{\circ}) = (-\Delta V/RT)(P) \quad (3)$$

where P is the gauge pressure and the molar volume for aragonite is determined from the data presented by Millero [1979]. A maximum uncertainty of $\pm 12 \mu M/kg$ in TCO_2 and

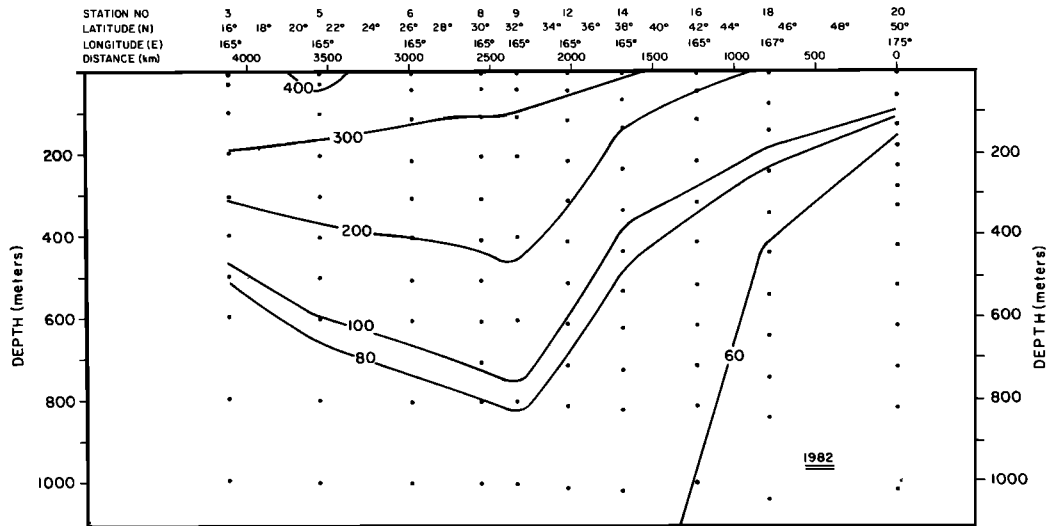


Fig. 4. Percent aragonite saturation in the northwest Pacific roughly along 165°E longitude. The data are based upon the NOAA TCO_2 and A_T data which were collected during May–June 1982.

$\pm 5 \mu\text{eq/kg}$ in A_T leads to an uncertainty of $\pm 5\%$ in the calculated Ω_a .

RESULTS AND DISCUSSION

Relative Consistency of the Data Sets

Since there are no stations from all three data sets that exactly overlap in location or time of sampling, the relative consistency of the individual data sets is difficult to define. However, three stations, GEOSECS 225 (32°37.0'N, 161°55.0'E), INDOPAC 75 (35°03.3'N, 164°05.7'E), and western North Pacific (WNP) 12 (34°57.3'N, 164°58.7'E), are within 389 km of each other and may be used to compare TCO_2 and A_T data in the deeper portions of the water column where other water mass properties (i.e., temperature and salinity) are virtually the same. Figure 2 shows vertical profiles of TCO_2 and A_T for the three stations. In the upper 1000 m of the water column, distinct differences in concentrations of TCO_2 and A_T exist between the stations. These variations are probably real, because there are distinct variations in temperature and salinity in the upper region of the water column. According to the studies by Shiller and Gieskes [1980] and Kenyon [1983], small-scale variability of water properties in this region of the Pacific is often the result of migrations of the Kuroshio Extension. Below about 3000 the temperature and salinity are virtually the same for the three data sets, and the TCO_2 data show reasonably good agreement, with the data from WNP 12 being similar to those from GEOSECS 225 and slightly lower than those from INDOPAC 75. With the possible exception of two INDOPAC 75

samples at 3807 and 4268 m, the deep-water data are all within about $10 \mu\text{M/kg}$ of each other for any given depth.

Most of the GEOSECS 225 A_T data appear to be about 2–10 μeq higher for a given depth than either the INDOPAC 75 or the WNP 12 data. These differences are probably primarily a function of the blanks in the different data sets [Takahashi *et al.*, 1980a; Bos and Williams, 1982], which can be illustrated by comparing the A_T -salinity relationship for near-surface data (Figure 3). The trend lines are reproduced from the GEOSECS data, as discussed by Takahashi *et al.* [1980a, b]. The GEOSECS Warm Water Trend ($> 8^\circ\text{C}$) indicates a possible systematic difference between the Pacific and Atlantic Warm Water Trends. In contrast, the NOAA data for the northwest Pacific appear more consistent with the Atlantic Warm Water Trend than the Pacific Warm Water Trend, which suggests that the small differences between the NOAA and the GEOSECS data are probably due to calibration errors in the Pacific GEOSECS data. Nevertheless, it should be noted that a systematic difference of 2–10 $\mu\text{eq/kg}$ in A_T leads to a difference of about $3 \mu\text{M/kg}$ in the carbonate ion concentration or about a 4% difference in the computed value of Ω_a . Because these differences are relatively small, we have not made an attempt to correct data sets for these potential errors.

North-South Trends in the Degree of Saturation With Respect to Aragonite

Figure 4 shows north-south profiles of the degree of aragonite saturation in surface and intermediate waters of the North Pacific along 165°E longitude from 16°N to 45°N, and obliquely northeast to 50°N, 175°E. Figure 5 shows saturation profiles along 177°W from the equator to 53°N. The profiles show that the 100% saturation horizons are shallowest in the cold-water region north of the Subarctic Front, located near 40°N. In the northwest Pacific (Figure 4) the 100% saturation horizon reaches its shallowest depth (≈ 100 m) at about 50°N, whereas in the north central Pacific (Figure 5) the 100% saturation horizon is slightly deeper (≈ 170 m). At both these locations the water is relatively colder ($< 4^\circ\text{C}$) and has a higher TCO_2/A_T ratio (see Table 2) than corresponding waters farther to the south. These factors are indicative of a decreasing carbonate ion concentration and an increasing solubility

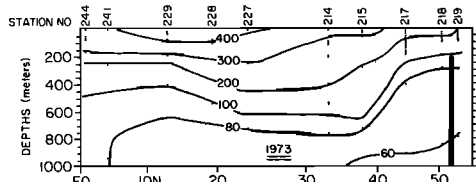


Fig. 5. Percent aragonite saturation in the north central Pacific roughly along 177°W longitude. The data are based upon the GEOSECS TCO_2 and A_T data which were collected during October–December 1973.

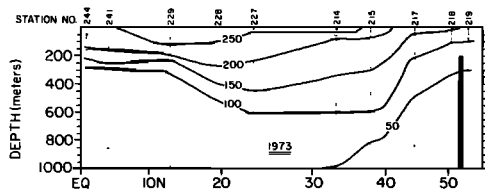


Fig. 6. Carbonate ion concentration in the north central Pacific roughly along 177°W longitude.

product such that there is a substantial shoaling of saturation horizons toward the north. These trends are consistent with the aragonite saturation data presented by Feely and Chen [1982] for a similar transect along 150°W longitude in the northeast Pacific and also with the calcite saturation data presented by Takahashi [1975] for the GEOSECS north-south transect.

Between about 45°N and 32°N in the northwest Pacific and 45°N and 25°N in the north central Pacific the 100% saturation horizon increases in depth with decreasing latitude. The maximum depth of the 100% saturation horizon occurs at about 750 m at 32°N in the northwest Pacific and at about 650 m in the region between 37°N and 25°N in the north central Pacific. The downward slopes of these isopleths are greatest near and immediately south of the Subarctic Front. As indicated by the oxygen distributions of Reid [1965] and the ^{14}C and tritium data of Ostlund *et al.* [1979], mixing and lateral transport of the North Pacific Intermediate Water south of the Subarctic Front induce greater vertical exchange with upper water (probably below the mixed layer) than the subsarctic water farther to the north. The shallow level of the horizons north of the Subarctic Front also seems to be a result of the general cyclonic circulation within the Subarctic Gyre where upward vertical mixing produces a doming of property isopleths [Dodimead *et al.*, 1963]. As a result of the increased vertical exchange, the TCO_2/A_T ratio decreases rapidly across the front, and the corresponding carbonate ion concentrations increase significantly (Figure 6), producing most of the observed increases in the degree of saturation of these waters with respect to aragonite. For example, the northwest Pacific data (Figure 4) indicate that between 214 m at station WNP 16 (41°58.1'N, 165°2.6'E) and 234 m at station WNP 14 (37°58.4'N, 164°59.8'E) the degree of saturation of the water with respect to aragonite increases from about 125% of saturation to about 142%. Approximately 5% of this change is due to temperature and salinity effects on the carbonate ion concentration and the stoichiometric solubility product for aragonite. The remaining 95% of the change is due to the increase in the carbonate ion concentration from 90 to 102

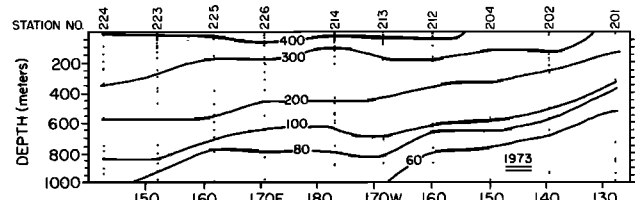


Fig. 7. Percent aragonite saturation roughly along 32°N latitude. The data are based upon the GEOSECS TCO_2 and A_T data which were collected during August–November 1973.

$\mu\text{M}/\text{kg}$, resulting from a change in the TCO_2/A_T ratio from 0.950 to 0.940 (see Table 2). Thus the increase in carbonate ion concentration due to the decrease in the TCO_2/A_T ratio is about 10 times more important to aragonite solubility than changes due to temperature and salinity.

South of 30°N in the northwest Pacific and about 24°N in the north central Pacific the 100% saturation horizon for aragonite decreases in depth by about 150–300 m. The slopes of the isopleths follow the general upward sloping trends of the isopycnal surfaces in these regions [J. Cline, unpublished data, 1983; Craig *et al.*, 1981]. This trend in the slope of the 100% horizon appears to be mainly associated with circulation around the center of the Subtropical Gyre [Reed, 1973]. Furthermore, there is a suggestion in Figures 5 and 6 that the maximum depth of the saturation isopleths tends to shift poleward with increasing depth. This also is in agreement with the distributions of thermohaline properties in the work by Reed [1973] and with the conclusions of Reid and Arthur [1975] that the Subtropical Gyre shifts northward with increasing depth.

Evaluation of the 100% Saturation Horizon at 50°N, 175°E

Although the degree of aragonitic saturation, Ω_a , appears to be reasonably well defined according to our method of calculation, in one instance we felt it worthwhile to compare our results with ancillary measurements. Our calculations at station WNP 20 (49°59.5'N, 175°01.0'W) indicate an unusually shallow aragonite saturation depth (≈ 100 m) and an intense vertical Ω_a gradient. The substantial aragonite undersaturation at depths of 123 m and greater ($\Omega_a \leq 0.72$) indicates that aragonite dissolution will proceed at a substantial rate under in situ conditions. In an attempt to directly verify the existence of undersaturation at shallow depths at this station, the saturation states at 123 and 418 m were directly examined through aragonite dissolution experiments on freshly collected materials under in situ conditions.

TABLE 3. In Vitro Examination of Aragonite Saturation at 49°59.5'N, 175°01.0'E

Seawater Source Depth, m	Aragonitic Materials and Mass, mg	Temperature, °C	Pressure, atm	Initial Percent Ω_a	ΔpH^*
123	aragonite fragments, 3.96	3.6	≤ 24	69.7	0.06 ± 0.01
123	Cuvierina columnella (2), 9.42	3.6	≤ 14	71.1	0.09 ± 0.01
418	Diacria trispinosa, 13.97	3.6	39	55.0	0.07 ± 0.02
418	Limacina helicina (3), 1.24	3.6	41	54.8	0.05 ± 0.02

*The ΔpH shows pH increase in 9-mL sample vials relative to controls which contained no solid aragonite. The uncertainties provided with each ΔpH reflect the pH variability observed in three control vials (containing no solid carbonate) for each seawater source. The duration of each experiment was 27.0 ± 1.5 hours.

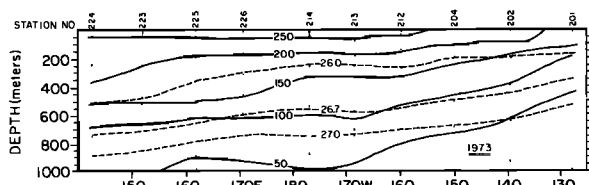
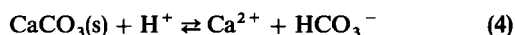


Fig. 8. Carbonate ion concentration roughly along 32°N latitude. The 26.0, 26.7, and 27.0 sigma t surfaces are presented as dashed curves.

Our experiments were performed on aragonite fragments and whole pteropod tests collected in the western North Pacific using free-floating sediment traps (P. R. Betzer et al., unpublished manuscript, 1984). Aragonite materials were housed in 9-mL glass vials containing seawater collected at depths of 123 and 418 m. To retard respiration of microorganisms, each seawater sample contained 2×10^{-5} M Hg^(II). Each reaction vial, sealed with a plastic cap, was housed in a high-pressure cell thermostated at 3.6°C. The pressure of each of four sample cells was maintained near the appropriate in situ values (~ 12 and ~ 40 atm). Additional reference cells, containing unfiltered seawater from each depth but no added carbonates, were used for comparison with the carbonate-containing sample cells. The pH of the seawater samples were measured before and after a 27-hour period, during which all samples were gently oscillated through a 90° angle at approximately seven repetitions per minute. Dissolution of calcium carbonate in these experiments is revealed as an increase in pH:



The results of these experiments on aragonite fragments and three pteropod species are shown in Table 3. The final column provides the pH increase which occurred in each aragonite-containing sample cell relative to the reference cells.

The substantial pH increase in each of our sample vials compared to the reference vials indicates that substantial aragonite dissolution occurred for each of our four samples. These results support our conclusion that the saturation horizon at this station occurs at a depth less than 123 m. Furthermore, we note that the substantial calculated undersaturation at 123 m and the reasonably direct interpretation of our dissolution experiments make alteration of this conclusion unlikely.

East-West Trends in the Degree of Saturation With Respect to Aragonite

The east-west profiles of the degree of aragonite saturation in surface and intermediate waters are given in Figures 7 and 10. Figure 7 shows the results based upon the GEOSECS

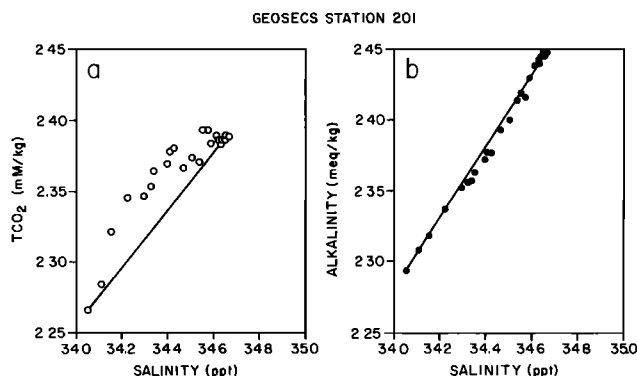


Fig. 9. Plot of (a) total CO_2 versus salinity and (b) total alkalinity versus salinity from GEOSECS 201 (34°11.0'N, 127°54.0'W) for the intermediate water depths where the temperature-salinity relationship is linear. The positive excess of TCO_2 is due to oxidation of organic matter.

TCO_2 and A_T data for measurements made roughly along 32°N latitude (range: 30°00.0'N to 34°58.0'N), and Figure 10 shows the results based upon the more detailed INDOPAC data from observations taken along 35°N latitude (range: 34°56.5'N to 35°03.3'N). Both profiles indicate a general trend of increasing depth of the 100% saturation horizon from about 140 to 280 m in the northeast Pacific (GEOSECS station 201 and INDOPAC station 01) to a little more than 750 m in the northwest Pacific (GEOSECS station 224 and INDOPAC station 98). This increase in the depth of the 100% saturation horizon is, in large part, due to a general increase in the carbonate ion concentration along the transect (Figure 8). Only a small part of the shift can be ascribed to the influence of temperature and salinity on carbonate ion equilibria and aragonite solubility. For example, the last three columns in Table 4 show the changes in the degree of saturation that would occur if a parcel of water having the same TCO_2 and A_T concentrations as that from 444 m at GEOSECS station 201 were placed at the same temperature, pressure, and salinity conditions as those found at GEOSECS station 224. The increase in temperature from 6.00°C to 15.06°C and an increase in the salinity from 34.108‰ to 34.635‰ (at constant TCO_2/A_T ratio) cause approximately a 10% increase in the degree of saturation. The actual increase in the degree of saturation between the two stations ($\approx 300\%$) is primarily due to the decrease in the TCO_2/A_T ratio from 0.994 to 0.889 and a concomitant increase in the carbonate ion concentration from 51 to 174 $\mu\text{M}/\text{kg}$. Thus the degree of saturation of these intermediate waters primarily depends upon the extent to which they are enriched in TCO_2 in relation to A_T . The concentration variations of these two parameters are governed by

TABLE 4. Example of the Effects of Changes in Temperature, Salinity, and the Ratio of TCO_2/A_T on the Degree of Saturation With Respect to Aragonite for a Parcel of Water at 444 m From GEOSECS Station 201

	Physical-Chemical Alterations (Final Conditions), GEOSECS 224 (445 m)			
	Initial Conditions, GEOSECS 201 (444 m)	Temperature	Temperature and Salinity	Temperature and Salinity and TCO_2/A_T
Temperature, °C	6.00	15.06	15.06	15.06
Salinity, ‰	34.108	34.108	34.635	34.635
TCO_2/A_T	0.994	0.994	0.994	0.889
CO_3^{2-} , $\mu\text{M}/\text{kg}$	51.1	55.1	55.1	179
Ω_a , %	61.5	68.4	68.1	240

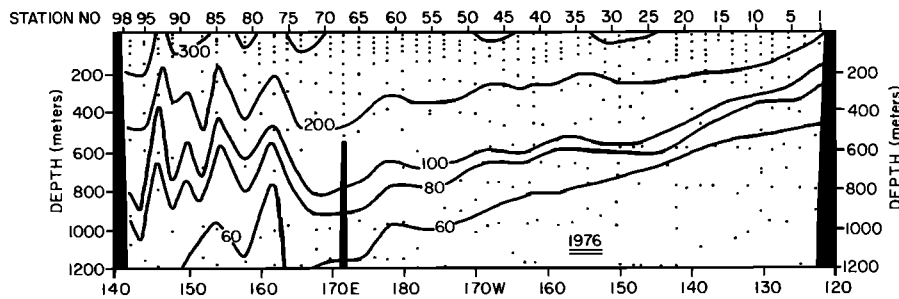


Fig. 10. Percent aragonite saturation along 35°N latitude. The data are based upon the INDOPAC TCO_2 and A_T data which were collected during April 1976.

mixing and biogeochemical processes such that in most cases, TCO_2 increases more rapidly with depth than does the alkalinity. The reason for this is that whereas the TCO_2 is increased in subsurface waters as a result of a relatively rapid process of microbiological oxidation of organic matter falling from the euphotic zone, the increase in alkalinity is due to the dissolution of calcareous tests, a process which proceeds much more slowly. The buildup of TCO_2 relative to A_T significantly decreases the carbonate ion concentration and the degree of aragonite saturation. Both ^{14}C and tritium data indicate that the intermediate waters of the northeast Pacific are not as well ventilated as those intermediate waters of the northwest Pacific [Ostlund *et al.*, 1979], and consequently, there is a relative enhancement of CO_2 from oxidation and respiration processes (Figure 9) and from upwelling near the continental margin [Bryden, 1978]. This effect is evidenced by the upward sloping isopleths of the carbonate ion concentrations which intersect the isopleths of sigma t at about 200–500 m near GEOSECS stations 202 and 201 in Figure 8. The increased acidity resulting from these processes decreases the carbonate ion concentration, with the result that the waters are undersaturated much closer to the surface. This effect is significantly enhanced in productive upwelling areas such as those along the continental margin of North America and those in the subarctic waters north of the Subarctic Front. In the oligotrophic waters of the central and western Pacific the excess of TCO_2 over A_T is diminished significantly, and mixing processes predominate.

Another interesting feature evident in the east-west saturation profiles from the INDOPAC transect is the high degree of lateral variability in the northwest Pacific. Such variability is much less evident in the data from the northeast Pacific. Zonal variability in the northwest Pacific has also been observed for temperature and salinity data [Kenyon, 1983] and for normalized TCO_2 and A_T data [Shiller and Gieskes, 1980]. In both cases the authors ascribed this feature to the complexity of the excursions and eddies associated with the Kuroshio Extension. The highly saturated waters are apparently associated with the warm saline waters of Kuroshio Extension origin. However, from the TCO_2 and A_T observations presented by Shiller and Gieskes [1980], most of the lateral variability appears to be limited to the upper 1500 of the water column. Thus local differences in circulation and water mass characteristics can have a profound effect on the local saturation state with respect to aragonite in this region of the North Pacific.

Possible Effects of Fossil CO_2 on the Degree of Saturation in Surface Waters

As stated in the introduction of this paper, in recent years there has been some concern about the possible effects of fossil

fuel-derived CO_2 on the saturation state of the surface oceans with respect to calcite and aragonite. The subject was recently reviewed in a general way by Broecker *et al.* [1979], who stated that in a typical warm tropical ocean the mixed-layer water will not become undersaturated with respect to aragonite until the partial pressure of CO_2 in the atmosphere is increased to a level of about 1760 μatm , a condition the authors stated would not occur during the next several decades. The underlying assumption of their model is that the surface ocean pCO_2 would be in equilibrium with pCO_2 in the atmosphere. In the North Pacific the recent data of Takahashi *et al.* [1983] indicate that this assumption is basically true, except for regions near the equator (10°N to 10°S), where the surface waters are supersaturated with respect to pCO_2 , and in the northwest Pacific along the Subarctic Front, where the surface waters are undersaturated with respect to pCO_2 . Thus there are large regions of the North Pacific where the model should be generally applicable.

Figure 11 shows a plot of the relationship between carbonate ion concentration and the partial pressure of CO_2 for three representative surface water samples from our northwest Pacific data set. The solid line shows the equilibrium carbonate ion concentration for aragonite saturation based upon the equations discussed earlier. The dashed curve, representing warm water conditions, shows that undersaturation will occur at a pCO_2 value of approximately 2085 μatm , which is similar to the value predicted by Broecker *et al.* [1979] for tropical surface waters. However, the curves representing progressively colder, less saline conditions indicate much lower values of pCO_2 are sufficient to initiate undersaturation. In the coldest waters, representative of northern subarctic surface waters, undersaturation will occur at pCO_2 values as low as 650 μatm . Thus for those surface waters that maintain equilibrium with the atmosphere, a consequence of increasing atmospheric pCO_2 should be the onset of undersaturation of northern sub-

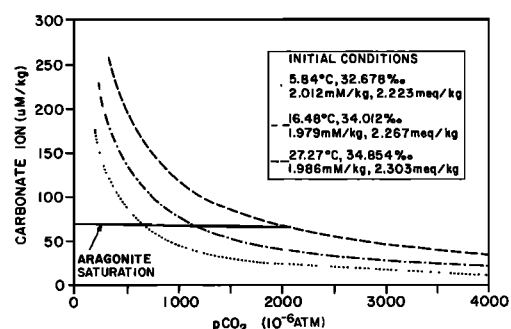


Fig. 11. Plots of the concentration of carbonate ion as a function of pCO_2 at constant salinity and alkalinity for three surface water samples from the northwest Pacific spanning the range of conditions usually observed in surface waters of the North Pacific.

arctic surface waters (at $p\text{CO}_2 > 650 \mu\text{atm}$) followed by a steady progression of undersaturation to the south and west. On the basis of recent projections [Keeling, 1980], estimated $p\text{CO}_2$ values for the middle of the next century will probably range between 650 and 1240 μatm . Consequently, undersaturation of some regions of the northern subarctic waters could occur during the second half of the next century.

CONCLUSIONS

The saturation state of the surface and intermediate waters of the North Pacific with respect to aragonite is largely dependent upon the carbonate ion concentration, variations of which are principally due to mixing and biological processes. Large gradients in saturation state occur in the vicinity of the Subarctic Front, particularly in the northwest Pacific. This is because of the extensive mixing which is a result of the formation and lateral transport of the North Pacific Intermediate Water. Our calculations indicate that one possible effect of fossil CO_2 on the degree of aragonite saturation in surface waters will be a steady progression of undersaturation starting in the northern North Pacific and moving steadily to the southern and western North Pacific, with the first sign of undersaturation possibly occurring as early as the second half of the next century.

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