Major Ions

Major ions are defined as those elements whose concentration is greater than 1 ppm. The main reason this definition is used is because salinity is reported to \pm 0.001 or 1 ppm. Thus, the major ions are those ions that contribute significantly to the salinity. According to this definition there are **11 major ions**. At a salinity of S = 35.000 seawater has the following composition. Using the concentrations units of g kg⁻¹ allows us to determine the contribution to salinity. Chemists prefer to use moles for units. mmol kg⁻¹ are preferred (e.g. rather than mmol Γ^1) because one kg of seawater is the same at all values of T and P.

Table 4.1 Concentrations of the major constituents in surface seawater

		At salinity (PSS 1978): $S = 35.000\%$				
	$mg \ kg^{-1} \ S^{-1}$	g/kg	mmol/kg	mM		
Na ⁺	308.0	10.781	468.96	480.57		
K+	11.40	0.399	10.21	10.46		
Mg ⁺⁺	36.69	1.284	52.83	54.14		
*Ca++	11.77	0.4119	10.28	10.53		
*Sr++	0.227	0.00794	0.0906	0.0928		
CI-	552.94	19.353	545.88	559.40		
SO ₄	77.49	2.712	28.23	28.93		
*HCO ₃	3.60	0.126	2.06	2.11		
Br ⁻	1.923	0.0673	0.844	0.865		
$B(OH)_3$	0.735	0.0257	0.416	0.426		
F-	0.037	0.00130	0.068	0.070		
Totals	1004.81	35.169	1119.87	1147.59		
*Alkalinity			2.32	2.38		
Everything else		~0.03	—.—			
Water		~964.80	~53,555.	~54,881.		

All authorities recommend the mole (abbreviation: mol) as the unit for amount of substance (including the series: mmol, μ mol, nmol, pmol, etc.). In marine studies, the most common convention for expressing concentration is the mol per kg of solution, sometimes called the "molinity" scale, by analogy with "salinity." This scale has the advantage of being conservative with changes in temperature and pressure, and with mixing. Many analysts, whose laboratory measurements are based on volume, use the "molarity" or "molar" scale (mol/L, = M), but for maximum accuracy this requires that the density of the solution be specified. Here the millimolar concentrations are calculated for t = 20°C, density = 1.024763 kg/liter. Another important scale is "molality": mol per kg of H₂O, used mostly by physical chemists.

Additional dissolved solids, not listed above, include many micro-constituents that in sum are barely significant in the above totals, as well as organic matter, commonly about 1 to 2 mg/kg, and dissolved silica, which varies from <0.001 to (in some deep seawater) about 0.21 mmol/kg (=20 mg/kg, expressed as Si(OH)₄). There is, in addition, about 20 mg of dissolved gases.

At salinity S = 35.000%, the chlorinity Cl = 19.374%.

The data above were derived as follows: the best averages for various ions were taken from the papers by Culkin and Cox 1966, Riley and Tongudai 1967, Morris and Riley 1966, Culkin 1965, Wilson 1975, Carpenter and Manella 1973 and Uppström 1974. The total CO_2 , at a common value for surface seawater in equilibrium with the atmosphere, is expressed as HCO_3^- . In order to make a charge balance, however, the total alkalinity concentration was substituted for the HCO_3^- and the sodium ion adjusted accordingly. The constituents with an (*) are known to increase slightly with depth (relative to S) due to downward biological transport.

Table 4-1 Concentrations of the Major Ions (from Pilson, 1998)

Na and Cl account for >86% of the salt content by mass. The order of the other cations is $Mg^{2+} > Ca^{2+} > K^+ > Sr^{2+}$. The anion Cl⁻ is approximately equal to the sum of the cations. The other anions are barely significant in the charge balance of seawater.

An element is conservative in seawater if its ratio to salinity is constant. The ratio of one conservative element to another will also be constant. One way to establish if an element of unknown reactivity is conservative is to plot it versus another conservative element or potential temperature or salinity. This is referred to as **The Law of Constant Proportions.** Conservative elements have very low chemical reactivity in the ocean and their distributions in the ocean interior are determined only by currents and mixing. The list of elements considered conservative has changed over time as analytical techniques have improved.

The **Law of Constant proportions** breaks down some places where water sources have different ionic ratios or where extensive chemical eactions modify the composition. Examples are:

- 1. estuaries: The average composition of **river water** is given in Table 4-2 (from Langmuir, 1997). The concentrations are given in mg l⁻¹ and can be compared with seawater concentrations. The main differences are that in river water HCO₃ has a much higher concentration than Cl⁻ (which is now the lowest of the major anions in river water). Calcium is the main cation in river water, followed by Mg and Na, then K.
- 2. evaporitic brines from isolated seawater embayments where solid precipitates form, thus changing the relative concentrations.
- 3. anoxic waters in restricted marine basins and pore (interstitial) waters in sediments where dissolution/precipitation and oxidation/reduction reactions can change the relative composition.
- 4. hydrothermal vents (see attached table 4-3 from Von Damm et al (1985). These high-temperature waters differ from seawater in that Mg, SO₄ and alkalinity have all been quantitatively removed.
- Q. If the Law of Constant Proportions breaks down what does this imply for the salinity determination by conductivity approaches?
- a) Na, K, SO₄, Br, B and F have constant ratios to Cl and each other, everywhere in the ocean. These elements are conservative. There are reasons to think that SO₄ may be non-conservative in anoxic marine basins like the Black Sea but conclusive results have not been published. Boron is partly present as the neutral species (B(OH)₃°) and

it has been hypothesized that B may be distilled from the tropics and transported to high latitudes through the atmosphere. Rain is enriched in B but non-conservative distributions in the ocean have not been identified.

Table 4-2 River water versus Seawater (from Langmuir, 1997)

FABLE 4.2 Chemical analyses of mean river water and seawater, along with residence times of he species and a comparison of relative concentrations in mean river water and the ocean

Species	Mean river water [†] (mg/L)	Seawater ⁴ (mg/L)	Residence time in seawater (my)	Concentration in seawater relative to river water
Ca	15	410	1.2	27 times
Mg	4.1	1,350	15	330 times
	6.3	10,500	190	1670 times
Na K	2.3	390	8	170 times
HCO ₃	. 60	142	.—	2.4 times
Cl	7.8	19,000	300	2,400 times
SO ₄	11	2,700	22	245 times
	13.1	6.4	0.016	0.49 times
SiO ₂ .	0.67	0.003	(0.003?)	0.004 times
Fe	0.07	0.001	(0.003?)	0.014 times
Al TDS	120	34,500		288 times

lource: [†]Livingstone (1963). [‡]Hem (1985).

Table 4-3 Composition of Hydrothermal vent solutions. Four high temperature (~350°C) sites from 21°N on the East Pacific Rise and the average value from the low temperature Galapagos Spreading Center (GSC). Concentrations in mmol kg⁻¹. From Von Damm et al, 1985).

	NG	21° 5 OBS	NORTH SW	HG	GSC ¹	SEAWATE
The Alk	Ka.					•
	101	3 891	200	1322	689-1142	26
Na m	81		439	448	++	484
K ma	- 25.		23.2	23.9	18.7→18.8	9.70
Rb 🗯	31		27	23	13.4→21.3	1.3
NH4 m	<0.	01 <0.01	<0.01	<0.01	23.0.	<0.01
	line Earths					
Be m	81		10	18	11→37 0	0.02 52.7
Mg m Ca m			16.6	0 11.7	24.6-40.3	10.3
Sr #		61	83	6.5	87	87
			>0	>10	17.2→42.6	0.14
Ba B	. >1		>10	>11		
87Sr/80S	r .703			.703026	B.A	.7001
	±6	8 ±32	±103	±120		
pH	8.1		3.6	8.8		7.8
Alk me			-0.30	-0.50	0	2.3
Cl m	87		496	496	21.9	541 0.16
SiO ₂ m	19.		17.3	15.6	B.a.	0.008
AI #						
Trace Me					***	<0.0017
Mn #	100		499 750	878 2429	\$60→1140 +	< 0.001
Fe/Mn	0.1		1.0	2.0		(0.001
Co a	2:		66	227	B.a.	0.03
Cu #	<0.		9.7	44	0	0.007
Zn #	40	108	89	104	D.S.	0.01
Ag m	<		26	87	n.a.	0.02
Cd m	12		144	180 359	D.S.	0.01
	TABLE	5: SULFUR.	ARSENIC	AND SEL	ENIUM	
•		5: SULFUR,	NOI	TH		GSC ¹ S
imember Co	TABLE NGS oncentrations	<u> </u>		TH	ENIUM HG	GSC ¹ S
	NGS	21° OBS	NOF SY	RTH W	нG	W
, m²	NGS oncentrations	21.	NOI	RTH W		W
m²	NGS oncentrations	21° OBS	NOE ST	RTH W	HG 0.4	W
m ²	NGS oncentrations 0 6.57	21° OBS	NOF S1	RTH W	HG 0.4 8.37	0 2 +4
m ²	NGS oncentrations 0 6.57	21° OBS	NOF S1	RTH W	HG 0.4 8.37	0 2 +4
m 2 m m	NGS oncentrations 0 6.57	21° OBS	NOF S1	6 15	HG 0.4 8.37	0 2 +4
m ² m n n n n n n n n n n n n	NGS oncentrations 0 6.57 <30	21° OBS 0.5 ³ 7.30 247	NOF SY 0. 7.4 21	6 6 6 4 -11 1	HG 0.4 8.37 452 1160-6 1.03	0 2 +4
m ² m n n n n n n n n n n n n	NGS oncentrations 0 6.57 <30	21° OBS 0.5 ³ 7.30 247	NOF S1 0. 7.4 21	6 6 6 4 -11 1	HG 0.4 8.37 452 1160-6 1.03 9.22	0 2 + n.s.4
m ² m n	NGS oncentrations 0 6.57 <30 1155-18 2.13) m 7.33	21° OBS 0.5 ³ 7.30 247	NOF SY 0. 7.4 21	6 15 4	HG 0.4 8.37 452 1160-6 1.03	0 2 + 4 B.s. 4
m ² m m miffur mple m (SO ₄ + H ₂ S	NGS oncentrations 0 6.57 <30 1155-18 2.13) m 7.33	21° OBS 0.5 ³ 7.30 247 1158-11 1.44 8.18	NOF SY 0. 7.4 21 1150 1.1 8.3	6 15 4	HG 0.4 8.37 452 1160-6 1.03 9.22	0 2 + 4 B.s. 4
m m m m m m m m m m m m m m m m m m m	NGS oncentrations 0 6.57 <30 1155-18 2.13) m 7.33 m 6.25	21° OBS 0.5 ³ 7.30 247 1158-11 1.44 8.18 7.59	NOF 51 0. 7.4 21 1150 1.1 8.5	0 15 4 	HG 0.4 8.37 452 1160-6 1.03 9.22 9.35	0 2 + 4 B.s. 4
i m ² i m iliur inple m (SO ₄ + H ₂ S (Ampoule)	NGS oncentrations 0 6.57 <30 1155-18 2.13) m 7.33	21° OBS 0.5 ³ 7.30 247 1158-11 1.44 8.18	NOF 51 0. 7.4 21 1150 1.1 8.5	6 15 4 -11 1 1 4 6 -	HG 0.4 8.37 452 1160-6 1.03 9.22	0 2 + 4 B.s. 4

b) Ca has small (± 0.5%) but systematic variations within the ocean. When the Ca increase was first discovered by Dittmar it was supposed to be due to dissolution of CaCO₃ particles. New data for de Villiers (in press) shows that Ca increases systematically from the surface to the deep water and from the North Atlantic to North Pacific (Fig 4-1a). The corresponding Si values are given in Fig 4-1b and the increase with depth reflects dissolution of opal (SiO₂) shells. CaCO₃ dissolution may not be the only source of disolved Ca.

Brewer et al. (1975) showed that the change in alkalinity (Alkalinity \approx HCO₃⁻ + 2 CO₃²-) was less than that expected for the change in Ca. Actually according to the CaCO₃ solubility reaction (e.g. CaCO₃(s) = Ca²⁺ + CO₃²⁻), the change should be Δ Alkalinity = 2 Δ Ca. Ca increases by 100-130 μ M as deep water flows from the Atlantic to the Pacific (Fig. 4-1) but alkalinity only increases by 120-130 μ M. Brewer et al.(1975) suggested that this was because the alkalinity was low due to titration by HNO₃ produced by respiration of organic matter in the deep sea. The correct comparison should be with potential alkalinity which is the total alkalinity corrected for the NO₃ produced according to:

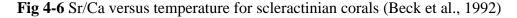
Δ Potential Alkalinity = Δ alkalinity + Δ NO₃

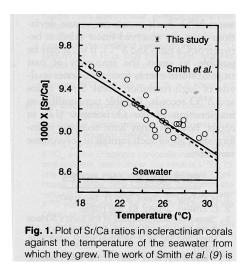
The increase in NO_3 from the deep Atlantic to Pacific is about 30 μ M, which should decrease alkalinity by the same amount. This is an important correction to make but there is still a "calcium problem". deVilliers (in press) showed that variations in Ca and potential alkalinity were in good agreement from 0-1000 m and in the deep water (>3500 m), but that there was additional excess Ca in the mid-water column centered at about 2000 to 2500 m (Fig. 4-2). She argued that this was primarily due to diffuse source low-temperature hydrothermal input from mid-ocean ridges. For support the xsCa correlates well with other hydrothermal tracers like 3 He and Si (Fig. 4-3), and low Mg (Fig. 4-7).

c) Sr also increases from the surface to the deep water and from the north Atlantic to the north Pacific (Fig. 4-4)(de Villiers, 1999). The deep water is about 2% enriched relative to the surface water. The nutrient element PO₄ has a similar pattern and there is an excellent correlation of Sr with PO₄ in both surface waters and with depth (Fig. 4-5) confirming that Sr shows a nutrient like pattern. The biogenic mineral phase Celestite (SrSO₄) has been proposed to be the transported phase (Bernstein et al., 1987; 1992). The microzooplankton, Acantharia, make their shells out of Celestite.

Sr has been attractive as a proxy in paleoceanographic studies because of its long residence time in the ocean (5Ma), which implies a uniform distribution and conservative nature. Sr is taken up by corals and the coral Sr/Ca ratios have been used to infer variability in sea surface temperature. An example SST - Sr/Ca correlation is shown in Fig. 4-6 (from Becks et al., 1992). Beck et al (1992) and Guilderson et al (1994) used coral Sr/Ca results to suggest that the tropical western Pacific and

western Atlantic were 4°C and 6°C cooler during the last glacial maximum (LGM) than today.





This approach has to be used with care as interspecies differences and effects of growth rate can also affect the Sr/Ca ratio (de Villiers et al., 1995). Sr turns out to be difficult to use as a proxy as its partitioning has multiple controls.

Stoll et al (1999) analyzed the Sr/Ca ratio in planktonic foraminifera for the past 150 ka and found variations of up to 12% on glacial / interglacial timescales. At least some of this variability was interpreted in terms of sea level changes, together with large changes in river input and carbonate sediment accumulation.

d) Until recently Mg was thought to be conservative. Its residence time in seawater (13 Ma) is much longer than that of Sr (5Ma) or Ca (1 Ma). Again, de Villiers (in press) has recently found relatively large Mg anomalies in deep waters located over midocean ridges. An example of vertical profiles of Ca and Mg above the East Pacific Rise at 17°S 113°W show that depletions in Mg mirror increases in Ca (Fig. 4-7). Mg is known to be totally removed in high temperature hydrothermal vent solutions. However, diffuse low-temperature hydrothermal solutions are thought to be 10x to 100x more important for chemical fluxes. Unfortunately these end member concentrations have not been well defined.

Mg is also taken up by foraminifera shells. The tropical planktonic foraminifera *Globigerinoides sacculifer* is a popular sample for such studies. Experimental studies by Lea et al (1999) demonstrate the potential of Mg/Ca as a paleothermometer. The response of Mg/Ca to temperature is stronger than that for Sr/Ca. Lea et al (2000) used the historical Mg/Ca record from equatorial sediments to postulate that sea surface temperature was lower by about 3°C in that region during the last glacial period and that the increase in tropical SST led Greenland warming during the Bolling Transition at the end of the last glacial period (about 14.6 thousand years ago). The time lags in such records remains controversial as other paleo-SST records (e.g. from

the South China Sea by Kienast et al., 2001) suggest close synchronous SST change between tropical ocean regions in the Pacific and Greenland.

The deep-sea temperature record for the past 50 million years has been produced from the Mg/Ca ratio in benthic foraminifera calcite (Lear et al., 2000). This record suggests a cooling of ~12°C over the past 50 My in the deep-sea. When combined with the simultaneous measurement of benthic δ^{18} O, the Mg record provides estimates of global ice volume. The data suggest that the first major continental-scale ice accumulation occurred in the earliest Oligicene (34 Ma) (**Fig 4-8**).

e) DIC (H₂CO₃ + HCO₃ + CO₃) varies by ≤ 20% with depth in the ocean due to vertical transport and remineralization of both CaCO₃ and organic matter. This will be discussed more in a later chapter.

Fig. 4-8 Mg/Ca as a Temperature tracer. When used with δ^{18} O can be used to estimate variations in ice volume.

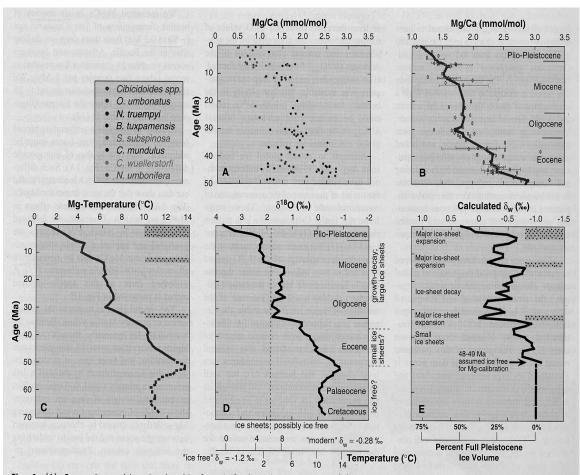


Fig. 1. (A) Composite multispecies benthic foraminiferal Mg/Ca records from three deep-sea sites: DSDP Site 573, ODP Site 926, and ODP Site 689. (B) Species-adjusted Mg/Ca data. Error bars represent standard deviations of the means where more than one species was present in a sample. The smoothed curve through the data represents a 15% weighted average. (C) Mg temperature record obtained by applying a Mg calibration to the record in (B). Broken line indicates temperatures calculated from the $\delta^{18}{\rm O}$ record assuming an ice-free world. Blue areas indicate periods of substantial ice-sheet growth determined from the $\delta^{18}{\rm O}$ record in conjunction with the Mg tem-

perature. (D) Cenozoic composite benthic foraminiferal δ^{18} O record based on Atlantic cores and normalized to *Cibicidoides spp.* from Miller et al. (2). Vertical dashed line indicates probable existence of ice sheets as estimated by (2). ‰, per mil; δ_{w} , seawater δ^{18} O. (E) Estimated variation in δ^{18} O composition of seawater, a measure of global ice volume, calculated by substituting Mg temperatures and benthic δ^{18} O data into the δ^{18} O paleotemperature equation (Eq. 2). The volume of "full Pleistocene glacial ice volume" is from Dwyer et al. (7). All records are plotted to the time scale of Berggren et al. (34)

Fig. 4-1

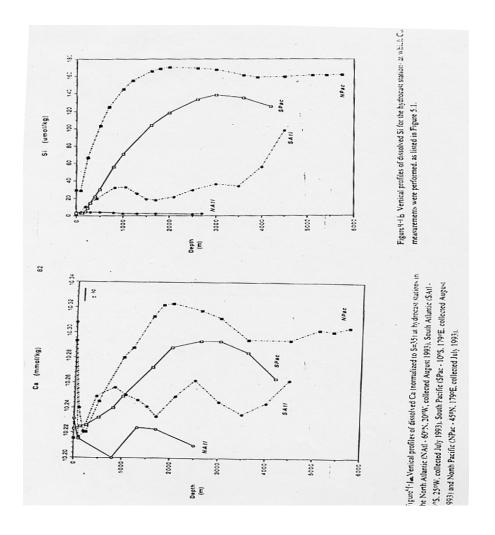


Fig. 4-2 Ca, alkalinity and potential alkalinity from GEOSECS Stn 222 in the North Pacific (de Villiers, 1994)

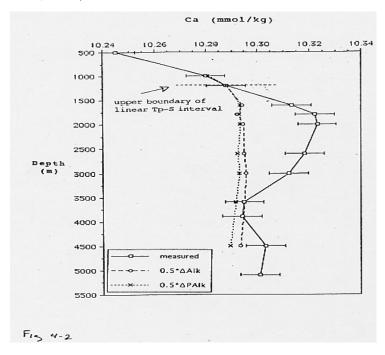


Fig. 4-3 Ca, He, Si and ¹⁴C at GEOSECS 222 in the North Pacific (de Villiers, 1994)

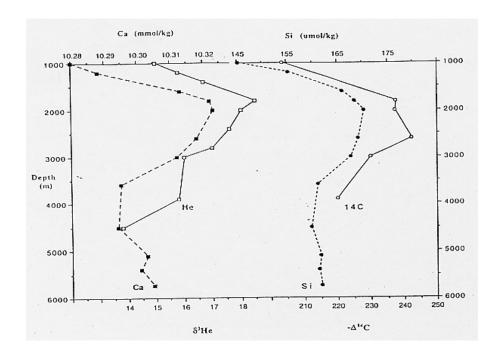


Fig. 4-4

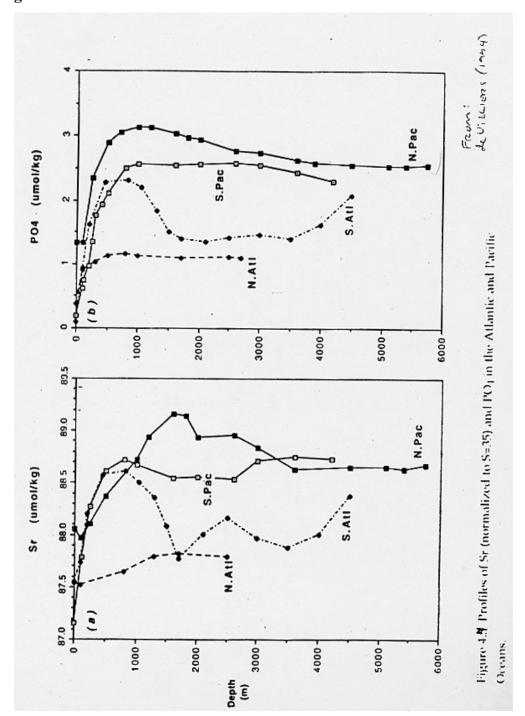
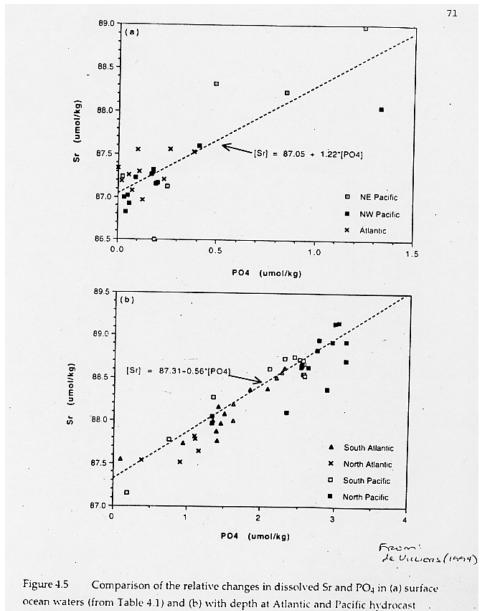
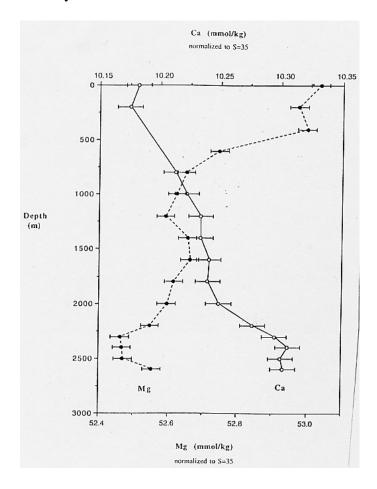


Fig. 4-5 Correlations of Sr and PO₄ (de Villiers, 1994)



ocean waters (from Table 4.1) and (b) with depth at Atlantic and Pacific hydrocast ... stations (from Table 4.2).

Fig 4-7 Seawater Ca and Mg vertical profiles above the East Pacific Rise at 17°S, 113°W, all normalized to Salinity = 35.



Variations in Salinity

Salinity in the ocean varies by 5 - 10%. Its value is determined by the net evaporation at the seasurface.

What controls the salinity of surface seawater?

Surface seawater salinity is determined by the balance between evaporation and precipitation, which in turn is controlled by solar heating. The variation in **evaporation** and **precipitation** with latitude is shown in Fig 4-7 as well as the difference between evaporation and precipitation as a function of latitude. Insolation decreases with latitude and thus temperatures are highest in the tropics and decrease towards the poles. Evaporation is highest near the equator but this is not the location with highest salinity because rainfall is also high.

Attached are Maps of the annual average sea-surface temperature (Fig 4-9) and salinity (Fig 4-9). The highest surface salinities for the open ocean are located at about 25° N and S in the center of the subtropical gyres. Salinities can reach higher values in relatively isolated waters like the Red Sea (S = 39).

Fig. 4-11 shows the N - S sections for temperature and salinity in the Atlantic (Fig 4-11a) and Pacific (Fig 4-11b). Temperature and salinity vary in the interior of the ocean but all the variability is acquired at the sea surface.

Q Why is there a plume of relatively salty water extending from high to low latitude in the Atlantic?

Q Why does the Atlantic tend to be saltier than the Pacific. Thus no deep water forms, under present day conditions, in the North Pacific.

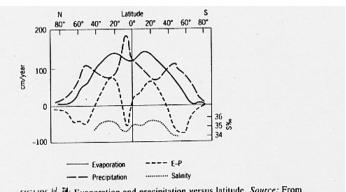


FIGURE 4. 4 Evaporation and precipitation versus latitude. Source: From Oceanography: An Introduction, 4th ed., D. E. Ingmanson and W. J. Wallace, copyright © 1989 by Wadsworth, Inc., Belmont, CA, p. 94. Reprinted by permission.

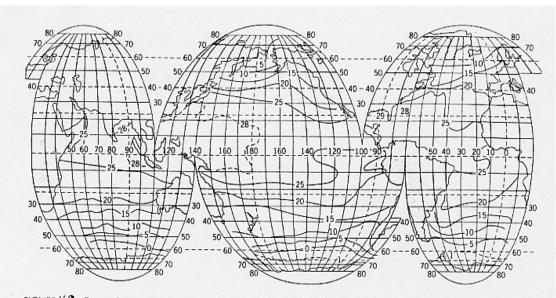


FIGURE 4.8 Sea-surface temperatures (°C) during the Northern Hemisphere summer. Source: From Introductory Oceanography, 5th ed., H. V. Thurman, copyright © 1988 by Merrill Publishing Company, Columbus, OH, p. 200. Based on data from The Oceans, H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, copyright © 1941 by Prentice Hall, Inc., Englewood Cliffs, NJ, p. 230. Reprinted by permission.

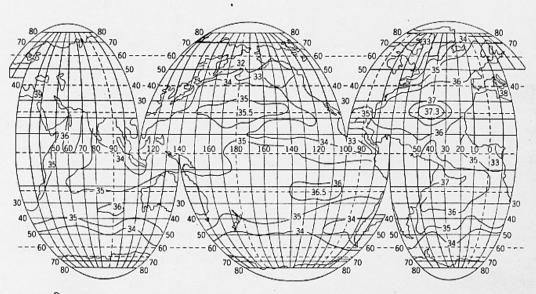
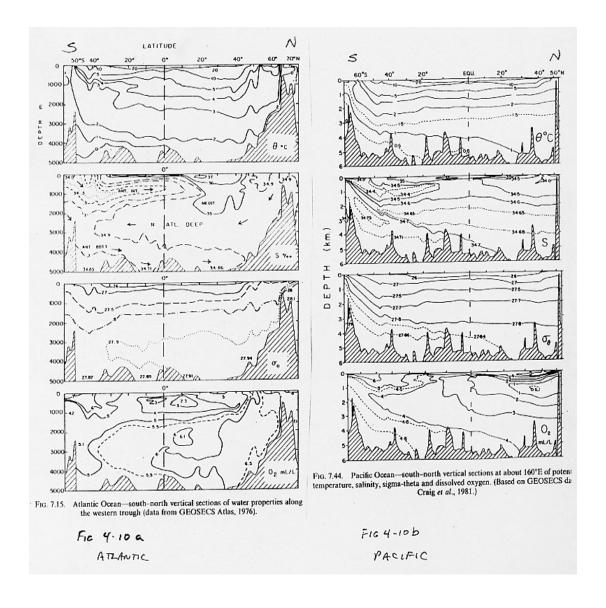


FIGURE 4.2 Salinity of surface seawater in the world's oceans. Source: From Introductory Oceanography, 5th ed., H. V. Thurman, copyright © 1988 by Merrill Publishing Company, Columbus, OH, p. 201. Based on data from The Oceans, H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, copyright © 1941 by Prentice Hall, Inc., Englewood Cliffs, NJ, p. 230. Reprinted by permission.

Fig 4-11



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