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THE GEOCHEMICAL BEHAVIOUR
OF SODIUM

with special reference to post-Algonkian sedimentation

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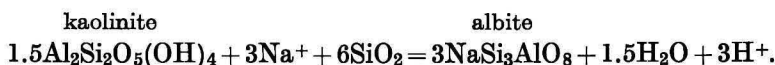
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SUMMARY

The sodium carried in rivers is commonly held to be derived by the conversion of "primitive" igneous rocks to sediments. This "classical hypothesis" has difficulty in accounting for the large volume of sedimentary rocks now existing, and tallies badly with the high radio-metrically determined age of the lithosphere. Recent evidence suggests that the salinity of the ocean has remained constant since Proterozoic times, and an independent estimate of the quantities involved shows that sodium may well be incorporated in marine sediments at the same rate at which it is released to the ocean by denudation.

The rock salt deposits are far more extensive than has hitherto been supposed, and may contain one-third as much sodium as the ocean. The concentration of sodium in the sediments, taking into account the pore solutions, adsorbed sodium and salt deposits, is 1.8 percent, i.e. much the same as in metamorphic and igneous rocks. Hence no "juvenile" sodium is needed for gneissification, which amounts essentially to the fixation in silicate structures (feldspars) of alkalis already present in more mobile form:



Anatectic melts (magmas) may form and dissolve the supercritical gas phase derived from the original pore water; such systems become unstable at low temperatures, and autopenumatolysis (kaolinization) sets in with consequent remobilization of some of the "fixed" sodium.

The predominantly andesitic and rhyolitic lavas of late geosynclinal volcanism are richer in water, chlorine and other volatiles than are the basalts associated with crustal tension. This is as we should expect on the assumption that the former are derived from marine sediments and their pore solutions and the latter by melting of mantle material in which possibly some deep sea sediments have been incorporated.

As far as our data go the geochemical behaviour of sodium is in accordance with a steady state model of the ocean where the elements gained through denudation are for the most part lost to the sediments laid down on the continental margins. Material lost to the deep sea sediments may be incorporated in the mantle, compensating for that gained by the continents in basalts of subcrustal origin. The fixation of sodium from solution, a key process in the regeneration of tectosilicates from clay minerals, can begin at temperatures well below the conventional limits of metamorphism. Albite has been synthesised from illite and quartz using a 4-M solution of NaCl at 150° and pH 10.

1. THE CLASSICAL HYPOTHESIS

Although the distribution of sodium in the outer parts of the earth (continents and ocean) is fairly well known, disagreement still exists as to the paths followed by this common element in geochemical processes. The traditional view can be traced to EDMUND HALLEY (1646–1742). Realizing that the salinity of the ocean was due to accumulation of sodium brought there from the continents by rivers, HALLEY (1715) proposed that “the duration of all things” might be estimated by observing the increment in salinity over a given time interval. Supposing the age of the earth to be of the order indicated “by the evidence of sacred writ”, he not unnaturally expected the sea to have become measurably saltier since classical times, and wished “that the ancient Greek and Latin authors had delivered down to us the saltiness of the sea, as it was about 2000 years ago”. He urged the Royal Society to arrange for measurements to be made forthwith, “that they might stand upon the record for the benefit of future ages.” Nearly two centuries later DITTMAR’S (1884) analyses of ocean water were published in the *Challenger* Reports and Sir JOHN MURRAY (1887) made an estimate of the amount and composition of salts discharged annually by rivers into the sea. JOLY (1899), apparently unaware of Halley’s paper, used these data, together with an estimate of the volume of the ocean based on data from MURRAY (1888) and WAGNER (1895), to calculate the time necessary for the total quantity of sodium now in the ocean to accumulate there.¹⁾

Joly did not assume that the ocean had originally contained no sodium: he appears to have believed (in common with others of his generation) in something like the “constant chloride” hypothesis discussed by CONWAY (1943), and supposed that the chlorine present (as hydrochloric acid) in the primitive ocean would have been neutralized by bases from the rocks of the ocean floor. Taking an analysis by Clarke “which may fairly represent the composition of the older crust of the earth,” he concludes that 14 percent of this chlorine must have been accounted for by sodium. He next assumes what he is in fact trying to discover, *viz.* “that . . . the duration of denudation will not be far from 86×10^6 years,” and calculates the amount of chloride supplied by the rivers during that time. Subtracting the result from the amount now present, he arrives at the original chlorine content of the ocean and thence (by attributing 14 percent of this to sodium chloride) at the original sodium content. Subtracting

¹⁾ Joly’s principle was anticipated by T. M. READE (1879), who tried to use the accumulation of calcium sulphate. But as Joly observed, this substance “does not possess the requisite qualifications to enter into such a calculation.”

this last from the present sodium content, he divides the difference by the net amount of sodium annually contributed by the rivers (after allowing for atmospheric recycling of sea salt), and concludes that the process has been going on for about 90 million years. This argument, though criticized at the time (FISHER, 1900), is logically (if not geologically) quite sound: if we put t for time and y for the amount of chlorine in the primitive ocean we can write:

$$y + t \cdot (\text{rate of supply of Cl by rivers}) = \text{Cl now in sea};$$

$$0.14y + t \cdot (\text{rate of supply of Na by rivers}) = \text{Na now in sea};$$

i.e. two simultaneous equations with two unknowns, which Joly solved by inspection.

Joly's result, in no way disturbing to a society already conditioned by Lord Kelvin to think in tens of millions of years, was accepted by most geologists without serious criticism; ¹⁾ SOLLAS (1909) and later JOLY himself (1925), applying further corrections for recycling of salt by the atmosphere, eventually admitted maximum ages of 175 and 141 m.y. respectively. Sollas was worried lest geological time get out of hand, but he decided to set up his defences far ahead of the enemy instead of wasting them on hand-to-hand fighting. Halving Joly's value for the net rate of sodium transport, he said of the result (175 m.y.): "I think we may admit that this . . . approaches a superior limit." But in the very next paragraph he becomes uneasy again and makes a complicated manoeuvre involving silica which takes him back to "a maximum limit of 421 million years." "Although excessive," says Sollas, "this result has one merit at least, it sets bounds which cannot be overstepped to those extravagant speculations demanding thousands of millions of years, which have sometimes been put forward even by distinguished investigators." More recently LIVINGSTONE (1963b), after evaluating possible sources of error in the light of modern geochemical data, has shown that the age of the ocean as given by Joly's method cannot be extended beyond about 280 m.y. The absurdity of this, by no means obvious in Joly's time, is plain enough in terms of our modern radiometric time scale, implying as it does that the ocean originated at some time in the late Permian. Marine formations ten times as old as this are known: for example, the Bulawayo Dolomite Series in Southern Rhodesia is cut by dykes of a radiometrically dated granite 2700 m.y. old.

This model of the ocean as a receptacle in which sodium constantly accumulates by the working of the hydrologic cycle was adopted by CLARKE (1908 and subsequent editions of *The Data of Geochemistry*) in an attempt to calculate the volume of sedimentary rocks produced

¹⁾ T. M. READE (1893) had recently concluded from a calculation based on estimates of the average rate of denudation and the total bulk of the sediments that 95 m.y. had elapsed since the beginning of the Cambrian.

throughout geologic time. The average igneous rock contained 2.8 percent of sodium, the average sedimentary rock 1 percent. Assuming that the 14×10^{15} tons of sodium in the ocean had been derived by the conversion of "primitive" (i.e. igneous) rocks to sediments, the latter should form a layer 1700 m thick spread over the surface of the continents and their shelves. We may now visualize this as having accumulated over a space of something like 3.5×10^9 years, i.e. at an average rate of 24×10^{13} g or (at a density of 2.5) less than 0.1 km^3 per year. The yearly output of volcanic rocks must be at least five times this, yet we should be very surprised to find that five-sixths of the stratigraphic column consisted of volcanics. If in the 1908 edition of *The Data* (where he first hits on the idea and gingerly tries it out) CLARKE has a twinge of misgiving about the meagreness of his result, by 1911 he is quite confident and stays so throughout the remaining three editions of the book. In 1893 T. M. READE, trying to estimate geological time by the rate of sedimentation, had written: "... few geologists will cavil if we take the average thickness of the earth's sedimentary crust down to the Cambrian base at one mile." And he did not include in this the sediments of the ocean floor, for which he allowed an equal amount. It is amusing to observe the shifts by which JOLY (1899, p. 45) argues Reade's two miles back to one again so as to get a better fit with his oceanic sodium. In this connexion it must be admitted that the difference in "fixed" sodium content¹⁾ between igneous and sedimentary rocks has in the past been exaggerated. SEDERHOLM (1925) considered CLARKE and WASHINGTON'S (1924) average for sodium in igneous rocks too high; POLDERVAART (1955, Table 21A) has collected 25 means representing over 3900 analyses of "igneous" rocks (including granites), all made later than 1930, and has added to these the averages of KNOFF (1916), CLARKE (1924) and VOGT (1931). The arithmetic mean for the sodium content in these 28 groups is 2.04 percent. Poldervaart's average sediment contains 1.07 percent Na, giving in round figures a difference between igneous and sedimentary sodium of 1 percent. BROTZEN (1966), using different sources, finds a difference of 1.2 percent. Repeated on this basis, Clarke's calculation produces a layer of sediments about 3 km thick instead of 1.7, or a total volume of about $600 \times 10^6 \text{ km}^3$. This does not fall far short of the probable volume of post-Algonkian sediments on the continents and shelves (see Table XVI): but the deep sea sediments remain unaccounted for; also the metasediments, which, as NIEUWENKAMP (1948) has pointed out, must have contributed their share of sodium to the ocean when originally laid down.

Considering the waste products of his "average igneous rock" in relation

¹⁾ By "fixed sodium content" is meant the sodium more or less firmly held in the silicate minerals, as opposed to that adsorbed on mineral surfaces and held in pore solutions.

to analyses of compound samples of shale, sandstone and limestone, Clarke concluded that these sediments ought to be formed in the relative proportions of:

16 shale : 3 sandstone : 1 limestone.

This does not correspond with the ratio observed in the post-Algonkian sediments now found on the continents, where limestone makes up something like 30 percent of the total bulk (KUENEN, 1941; RONOV, 1959). NIEUWENKAMP (1956) has pointed out that the discrepancy disappears if we take into account the Precambrian metasediments, where limestones (marble) make up only 0.1 percent of the total. Thus a layer of Precambrian schist and paragneiss 9 km thick added to Clarke's 1.7 km of sediments would have brought the proportion of limestone into agreement with his prediction: though only at the cost of invalidating his supposition about the relation of oceanic sodium to the accumulation of the sediments. As will be shown below on the basis of measurements by RONOV (1959), the average thickness of post-Algonkian sediments on the continents and shelves is about 4 km. To restore the proportion of limestone to the value predicted by Clarke a layer of Precambrian metasediments 21 km thick is now needed, making a total thickness of 25 km. This begins to approach the 35 km normally adopted as the average thickness of the continents: an ominous hint to those who still hope to find "primitive" rocks somewhere in the continental crust.

GOLDSCHMIDT (1933), KUENEN (1941), CONWAY (1943) and WICKMAN (1954) have all tried to calculate the volume of the sediments by using modified versions of Clarke's principle. Kuenen questions Clarke's "source rock": volcanic products, being more exposed than plutonic rocks and less resistant to weathering, account for a larger proportion of the sediments than would follow merely on the basis of the area covered by them. The source rock has to be corrected by adding basalt; which, with its relatively high calcium content, brings a slight easing of the limestone problem. By assuming the presence on the ocean floor of huge masses of red clay free from calcium carbonate (the pelagic foraminifera being of recent origin in terms of geologic time), Kuenen is able to bring the proportion of limestone into agreement with Clarke's prediction without upsetting the sodium balance: the extra sodium going into the pore water of the oceanic sediments.

The underlying idea is always the same: a secular evolution of the continents and oceans, the latter becoming steadily saltier as a result of the irreversible conversion on the former of igneous rocks to sediments. The igneous rocks intruded from time to time into the crust or expelled at the surface are supposed to be "juvenile," i.e. to consist of matter stored since the foundation of the world deep down in or beneath the lithosphere and now reaching the periphery for the first time; moreover the elements (mainly sodium) added to the sediments during metamorphism are likewise believed to come "from below" in migrating fluids or by

ionic diffusion along intergranular boundaries and even right through the lattices of the rock forming minerals. The weakness of this concept shows most plainly in its inability to account for more than a fraction of the real (radiometric) age of the ocean. Sodium reaches the continents from a hidden source and is removed by weathering to the ocean, whence (unless the geological time scale is wrong by an order of magnitude) it disappears into a hidden sink. (See Fig. 1.)

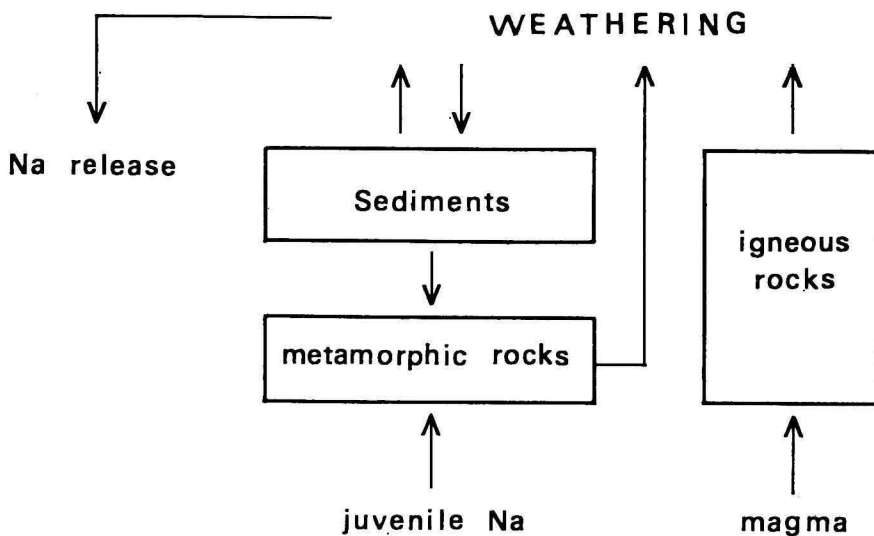


Fig. 1. Geochemistry of sodium: the traditional concept.

We may be forgiven for wondering that so many eminent geochemists did not give even a moment's thought to the alternative cyclic view, the original concept of JAMES HUTTON (1785) assiduously advocated by Playfair and Lyell: The world has seen countless cycles of denudation and rebuilding. Today's rocks are formed from the waste of yesterday's; tomorrow they will have been remade into others. We can find no vestige of a beginning, no prospect of an end. BARTH (1961) tells in a few evocative words of Sederholm's vain search for the basement on which the first sediments were laid down: the oldest rocks he could find were sediments.

Reade and Joly and all their followers replaced what in Hutton's and Lyell's view is a cyclic process by a secular one. When the same materials are going round and round of course the volume of existing sediments has nothing to do with time; nor has the amount of salt in the sea. Both are approximately constant; the relationship between them is simple but meaningless.

2. THE SEDIMENTARY CYCLE

That one of the main sources of the sodium in river water is the sediments themselves seems to have dawned very gradually on twentieth century geologists. It is curious that so little attention should have been paid to LYELL, who (1871) was aware that the sediments are by no means as poor in alkalis as analyses of leached material from outcrops are apt to suggest. SOLLAS (1909, p. xcvi), considering the effect of atmospheric recycling, studied an early rain isochlor map of the northeastern United States by JACKSON (1905, Plate I) and realized that, whereas west of the Ohio River the atmosphere was virtually free of chloride, the chloride in river water actually began increasing as the western tributaries of the Mississippi were followed headwards towards exposures of the Triassic, whose saltiness however he attributed to juvenile sources. CLARKE (1911, p. 139) realized that "the sedimentary rocks of marine origin must contain, in the aggregate, vast amounts of saline matter, widely distributed, but rarely determined by analysis. These sediments, laid down from the sea, can not have been completely freed from adherent salts, which, insignificant in a single ton of rock, must be quite appreciable when cubic miles are considered. The fact that their presence is not shown in ordinary analyses merely means that they were not sought for." Clarke however saw these "adherent salts" only as a portion withheld from the ocean, in comparison with whose salt content he judged them to be insignificant, and not as a form of cyclic sodium withdrawn from the sea and returned again with each successive cycle of uplift and denudation.

FISHER (1900) and BECKER (1910) grasped the importance of recycled sedimentary sodium in relation to the age of the ocean as obtained by the sodium method. STERRY HUNT (1875) had already alluded to the "fossil sea water still to be found imprisoned in the pores of the older stratified rocks," and Fisher in his review of Joly's paper reasoned that the weathering of igneous rocks ought to produce carbonate rather than chloride, and that the latter, when found in river waters, was probably traceable to connate brines in sedimentary formations. Impressed by reports of the United States Geological Survey on saline waters in the Silurian of Ohio, Fisher concluded "that some of the sodium found in river waters may probably be derived from the 'fossil waters' of old sea muds, and if that is the case, it is in circulation from the ocean to the stratified rocks and back again. No doubt much sodium may find its way into rivers immediately from the felspar of rocks, but we are not justified in crediting all the sodium conveyed to the ocean as having been supplied *de novo* in that manner. This consideration would lengthen Professor Joly's estimate of the world's age by an unknown period."

With characteristic energy and shrewdness, Fisher collected samples of Silurian and Devonian shale from deep boreholes and took them to the Chemical Laboratory at Cambridge for comparison as to their soluble salts with marine muds taken from Southampton Water and the Fleet. He writes (*op. cit.* p. 130): "... the amount of salts in the ancient rocks being so near that in the rocks now being deposited, shows that the ocean was about as salt then as it is now, and consequently not much additional sodium can have accumulated in it during the long ages since Silurian times."

SALINITY OF THE OCEAN IN GEOLOGIC TIME

Fisher's suggestion that the sea might not be getting any saltier fell on deaf ears. His data were scanty; moreover he offered no explanation as to where the sodium being brought by the rivers was disappearing to. In the last decades two lines of evidence have been uncovered which suggest that the salinity of the ocean may have remained substantially unchanged since the Precambrian.

Boron in marine clays

The boron content of sea water is about 5 ppm and bears a constant ratio to total salinity (FREDERICKSON and REYNOLDS, 1960). Oceanic boron is incorporated in marine clays, mainly illite, where it appears to substitute for silicon in the $\text{Si}_2\text{O}_5^{2-}$ layers (STUBICAN and ROY, 1962). Given sufficient time an equilibrium distribution is established between the sea water and the illite; moreover, once fixed, the boron seems not to be readily removable. Frederickson and Reynolds' studies of illites from sediments of geologically recognizable facies indicate a strong correlation between salinity and boron content, the latter varying from about 100 ppm for fresh water deposits to 2000 ppm for evaporite beds. Consequently the boron content of illites can, with appropriate reservations ¹⁾, be used as an index of the salinity of ancient sedimentary environments.

LANDERGREN (1945) concluded from his studies of boron in marine sediments that the concentration of boron in sea water had not changed since at least the Cambrian. REYNOLDS (1965) has determined the boron content of illites from 31 Precambrian sediments (25 carbonate rocks and 6 shales). The results are summarized in Table I, together with those from 70 post-Algonkian rocks previously studied by FREDERICKSON and REYNOLDS (1960) and by WALKER and PRICE (1963), and judged by petrographic and paleontological criteria to be normal marine sediments. Fig. 2 shows the Precambrian data plotted on a stratigraphic time table;

¹⁾ See HARDER (1963); WALKER and PRICE (1963); REYNOLDS (1965).

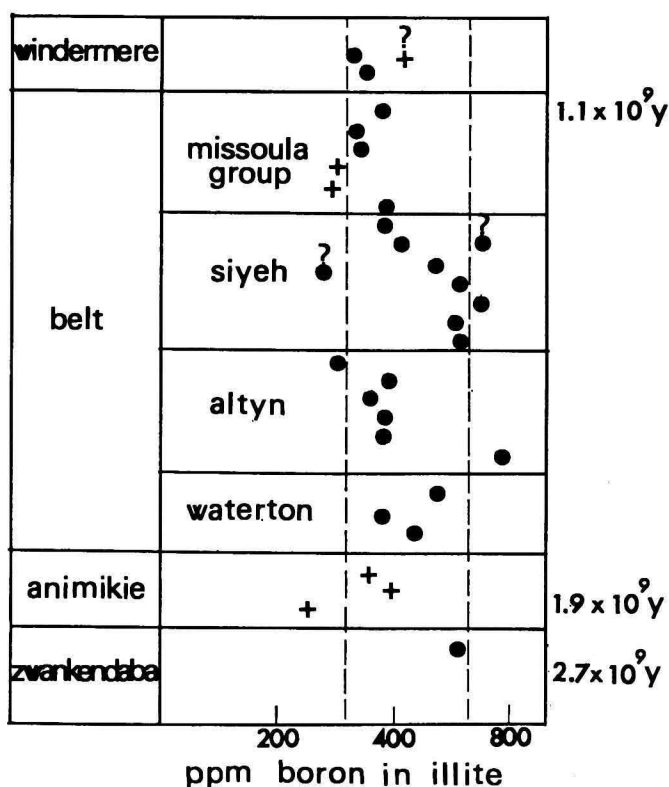
the two vertical dashed lines represent the 95 percent confidence limits for the post-Algonkian group. It can be seen that:

1. The distribution of the Precambrian data shows no particular correlation with age over the interval represented, some 2×10^9 years;
2. Practically all the Precambrian values lie within the 95 percent confidence limits for the post-Algonkian group;
3. The difference between the two means is small in comparison with the standard deviation.

If the relationship observed between boron content and salinity in present-day sea water has held good over geological time, these data suggest that the salinity of the ocean has been essentially constant for the last two or three thousand million years.

The chloride-alkali ratio in sediment pore waters

SCHOELLER (1956) has pointed out the importance of ion exchange reactions in determining the composition of pore solutions in sediments.



The equilibrium distribution of several cations M_1, M_2, M_3 , etc. between a pore solution and the ion exchangers (generally clay minerals) of the sediment can be represented by partition equations of the type

$$\frac{[M_i]_{\text{solution}}}{[M_j]_{\text{solution}}} = k \cdot \left\{ \frac{[M_i]_{\text{clay}}}{[M_j]_{\text{clay}}} \right\}^{1/p},$$

$[M]$ standing for molar concentration and the values of k and p depending on the nature of the cations and the exchanger. Thus a sediment in equilibrium with a pore solution having given cation ratios will itself have acquired cation ratios defined by suchlike equations. If now the pore solution is replaced by another of different composition, ions will be exchanged until the new solution in turn reaches equilibrium with the rock. A marine mud, for example, will initially be in equilibrium with a pore solution near enough in composition to sea water. If later the concentration of alkalis in the pore solution increases, either through endogenous enrichment or replacement of the original pore solution by a stronger one, Na^+ and K^+ will be adsorbed by the clay minerals in exchange for Ca^{2+} and Mg^{2+} released into the pore water: the ratio in the latter of anions to alkali cations will increase. The most important anion in sea water is Cl^- , and it is present in slightly greater equivalent concentration than the alkalis. Consequently if at equilibrium the concentration of Cl^- in the new brine exceeds that of the alkalis in the old one, the ratio $[\text{Cl}^-] : [\text{Na}^+ + \text{K}^+]$ will be greater than unity.¹⁾

SCHOELLER (1951, 1956), in a rather extended study of ground water analyses, has observed that the high-chloride interstitial brines always have a chloride-alkali ratio greater than unity for chloride concentrations exceeding the concentration of alkalis in modern sea water (i.e. about 500 milliequivalents per kg). For chloride concentrations below this value the ratio may be greater or less than 1. When a series of progressively more concentrated brines can be obtained from a single formation, the transition can sometimes be strikingly demonstrated by a logarithmic plot of the concentrations of chloride and alkalis (see Fig. 3). The implication here is that the maximum value of $[\text{Cl}^-]$ in pore waters of normal marine sediments for which $[\text{Cl}^-] : [\text{Na}^+ + \text{K}^+]$ can be less than unity should be the same as the value of $[\text{Na}^+ + \text{K}^+]$ in the sea water in which deposition took place.

Although Schoeller has made no claim for his principle as a means of studying paleosalinities, it seems not without possibilities in this

¹⁾ Schoeller expresses this by saying that the base exchange index will be positive. He defines the base exchange index (when positive) as

$$\frac{[\text{Cl}^-] - [\text{Na}^+ + \text{K}^+]}{[\text{Cl}^-]} \text{ or (when negative) } \frac{[\text{Cl}^-] - [\text{Na}^+ + \text{K}^+]}{2[\text{SO}_4^{2-}] + 2[\text{CO}_3^{2-}] + [\text{NO}_3^-]}$$

(SCHOELLER, 1956, p. 128). For the present purpose it is simpler to consider merely the ratio of chloride to alkalis.

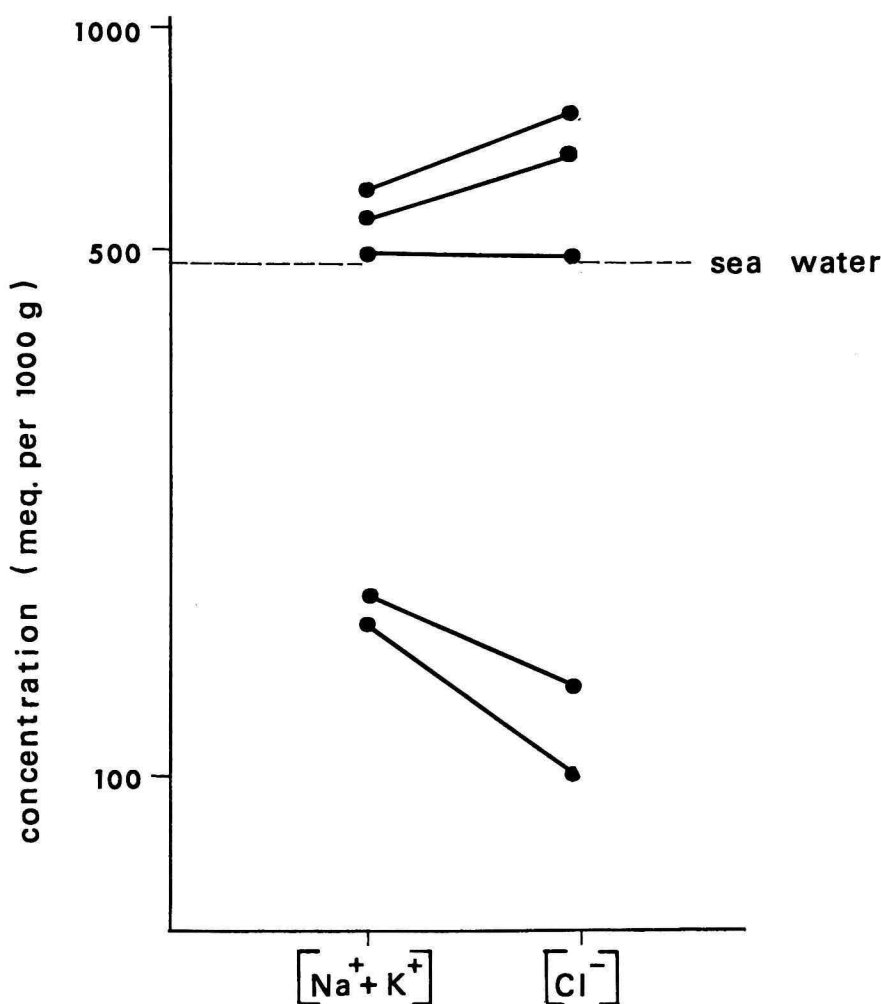


Fig. 3. Concentration of chloride and alkalis in pore water from Tertiary sediments in the Midway-Sunset area, California. Dashed line represents concentration of alkalis in present-day sea water. (Modified after SCHOELLER, 1956; data from JENSEN, 1934).

direction. There are however a number of difficulties to be overcome. Many groundwater series from reputed marine horizons have chloride-alkali ratios greater than unity for chloride concentrations far below that of sea water: a fresh water sediment invaded by dilute alkali-chloride brine will adsorb alkalis from the brine in exchange for alkaline earths, thus raising the chloride-alkali ratio of the brine above unity. The same could apply to a regressive marine formation flushed by meteoric water before being again invaded by sea water in a new transgression; the dilute brines surviving in such formations in the neighbourhood of fresh-salt water transition zones might be expected to have chloride in excess over

alkalis, as seems to be the case in a large number of dilute brines in the Appalachian oil field, where the sedimentary environment appears to have been rather changeable in Upper Devonian and Mississippian times (see TORREY, 1934). Again, diagenetic changes in the sediments must have a strong effect on the exchange of ions by modifying the partition coefficients k and p . Finally, although Schoeller's study includes a large number (646) of analyses, relatively few of these cover the important range of chloride concentration immediately bracketing the 500 meq./kg level, say from 300 to 700 meq./kg. The amount of published and unpublished data on sediment pore waters must by now be very large, and a painstaking study of these in relation to Schoeller's idea might yield valuable indications as to the history of the ocean.¹⁾ For the present it can be said that Schoeller's observations, though they do not offer any proof of the hypothesis that the salinity of the ocean has remained constant in post-Algonkian time, are so far as they go consistent with it.

SODIUM BALANCE SHEETS

NIEUWENKAMP (1948, 1956), BARTH (1961a, b) and LIVINGSTONE (1963b) have emphasized the importance of sedimentary recycling in relation to the sodium balance of the ocean. The "sodium age" of the ocean is of no significance nowadays; for these authors it merely underlines the failure of the traditional hypothesis to account for the sodium removed from the continents by chemical denudation. Livingstone has expressed this imbalance by showing that (allowing for atmospheric but not for sedimentary recycling) the rivers have in post-Algonkian time brought to the ocean 64×10^{15} tons of sodium, of which (allowing for the pore solutions and adsorbed sodium in both deep sea and shelf sediments) only 25×10^{15} tons are now to be found there. We shall here follow Livingstone and try to draw up a balance sheet showing the net amounts of sodium supplied to and removed from the ocean during post-Algonkian time. This will be based on a consideration of the following quantities:

- a. The average content of "mobile" ²⁾ sodium in sedimentary rocks;
- b. The total volume of sediments formed in post-Algonkian time;
- c. The volume of unmetamorphosed sediments surviving from post-Algonkian time;
- d. The volume of metamorphosed post-Algonkian sediments still surviving;
- e. The total mass of sodium discharged annually in solution from the continents via the rivers ($= 20.5 \times 10^7$ tons: LIVINGSTONE, 1963b);

¹⁾ Some of the brines from the Permian of West Texas reveal by their composition the highly saline depositional environment of the rocks in which they are now found. (See SCHOELLER, 1956.)

²⁾ As opposed to "fixed" sodium; see footnote, p. 4 above.

- f. The fraction of (e) contributed by post-Algonkian rocks, not derived from the mantle, $= \frac{a(b-c-d)}{6 \times 10^8}$;
- g. The fraction of (e) derived from the ocean via the atmosphere;
- h. The fraction of (e) contributed by human agency;
- i. The fraction of (e) contributed by Precambrian rocks and by continental rocks derived from the mantle, $= e - (f + g + h)$;
- j. Net gain of sodium by ocean from continents in post-Algonkian time, $= i(6 \times 10^8)$;
- k. Mass of "mobile" sodium withdrawn from the ocean and now held in surviving post-Algonkian sediments and metasediments, $= a(c + d)$;
- l. The average content of "mobile" sodium in deep-sea sediments;
- m. The volume of deep-sea sediments formed in post-Algonkian time;
- n. Mass of "mobile" sodium withdrawn from the ocean in deep-sea sediments in post-Algonkian time, $= l.m.$;
- o. Net loss of sodium from ocean in post-Algonkian time, $= k + n$.

"MOBILE" SODIUM IN SEDIMENTARY ROCKS

1. *Pore solutions*

The existence in sedimentary formations of saline interstitial pore solutions has been common knowledge since the late 19th century, when oil drillings first penetrated to levels which had not been extensively flushed by meteoric water. These solutions are generally dominated by chloride and either sodium or sodium and calcium, and their salinities range up to ten times that of sea water, showing an indistinct correlation with depth below the surface and age of the host rocks (see Fig. 4). Representative analyses can be found in WRATHER and LAHEE (1934) and WHITE, HEM and WARING (1963), as well as in the volumes of the Bulletin of the American Association of Petroleum Geologists. That these concentrated pore solutions are not merely derived by leaching of nearby salt deposits is suggested by their Br : Cl ratios, which are often greater than that for sea water (0.003 parts by weight). Br does not readily enter the NaCl structure; brines derived by leaching of rock salt should have much lower Br : Cl ratios (WHITE, HEM and WARING, 1963).

STERRY HUNT (1875) and LANE (1906) thought the oil field brines were unchanged connate waters from an earlier, saltier ocean. The first serious attempt to explain them came from MILLS and WELLS (1919), who noted that gas wells in the Appalachian oil field rapidly became clogged with salt and reasoned that pore waters could be concentrated by evaporation into a gas phase separating from petroleum and expanding on its way to regions of low pressure. (Water in a static system can also be transferred down a temperature gradient: such as the geothermal gradient: by evaporation through gas bubbles, leaving a more concentrated solution behind it. See Fig. 5). Mildly euxinic conditions are probably

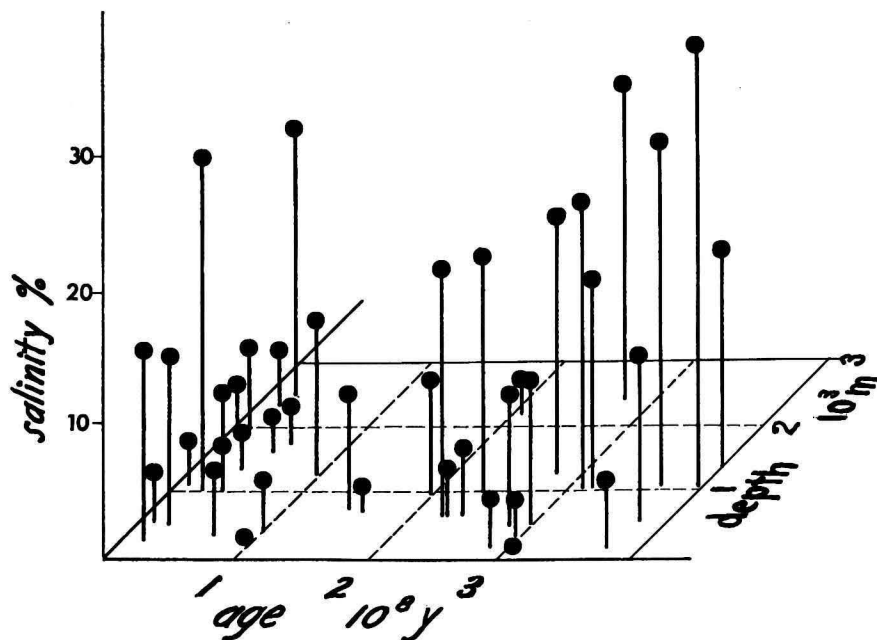


Fig. 4. Salinity of 40 sedimentary pore solutions in relation to depth of burial and age of the host rocks. (Data from WHITE, HEM and WARING, 1963, and WRATHER and LAHEE, 1934).

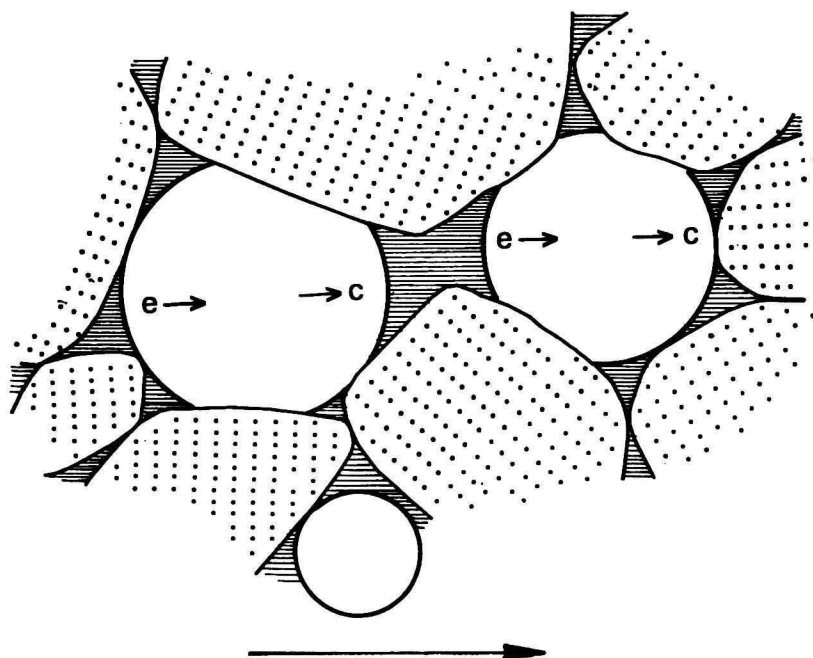


Fig. 5. Transfer of water down a temperature gradient by evaporation through gas bubbles in the pores of a rock. Mineral grains stippled; hatched areas: pore solution. e: evaporation; c: condensation.

common in marine muds, and considerable volumes of gas (mainly methane) might seep out of these during compaction, carrying water vapour from the pore solutions which would in consequence become enriched in dissolved salts.

DE SITTER (1947), by showing how the composition of waters taken from progressively younger formations approaches that of the ocean, has argued that the oil field brines are originally developed from sea water. He considers that they become concentrated by "sieving", the water molecules escaping through the intergranular channels during compaction while the (hydrated) ions are held back. Of the common cations in these brines (Na^+ , Ca^{++} , Mg^{++} , K^+), all except K^+ are hydrated and are consequently larger than water molecules. K^+ , because of its low ionic potential, is unhydrated; it has a radius in solution of 1.24 Å (SUTRA, 1946), i.e. about the same as a water molecule. If mechanical filtration were involved to an important degree, the concentration of potassium ions in the residual solution should be relatively low, since they ought to escape through the meshes of the "sieve" as easily as the water molecules. The ratio $\frac{[\text{K}^+]}{[\text{Na}^+]}$ in sea water is 0.022; the mean value of 0.009 for 11 oil field brines (see Table II) is therefore in accordance with De Sitter's theory.

McKELVEY, SPIEGLER and WYLLIE (1957) showed that synthetic ion-exchangers can act as ionic filters. A solution of an ionized salt when forced through a membrane of such a material tends to become more concentrated on the high-pressure side; the solution which flows on through is correspondingly diluted. McKELVEY and MILNE (1962) have demonstrated the same effect with plugs of bentonite and disaggregated shale. When a porous cation exchanger such as a clay is in contact with a solution of an ionized salt, the negative charges of the exchanger are balanced by cations located within its pores. Anions are discouraged from entering the pores, which therefore contain fewer anions than cations. If now a pressure gradient is set up across the exchanger, water and ions will begin to flow down it; but the anions being impeded, an electric potential (the so-called "streaming potential") develops and makes the cations "wait" for their partners. Thus the neutral water molecules, being relatively unhindered, flow through the exchanger faster than the ions. The result is that the solution leaving the exchanger is rarefied, whilst that remaining inside becomes correspondingly concentrated. For their experiments McKelvey and Milne used samples 0.5 cm thick under a confining pressure (supported by the solid mineral grains) of about 650 bars and forced a 1-N sodium chloride solution through them at a pressure of about 330 bars. In these conditions the bentonite gave a maximum concentration ratio ¹⁾ of 8.0 and the shale one of 1.7. The respective porosities were 39

¹⁾ $\frac{\text{Normality of concentrate}}{\text{Normality of filtrate}}.$

and 24 percent. Other observations (*ibid.*) suggest that the concentration ratio rises steeply with decreasing porosity, other things being equal. (The efficiency of the filter is greatest for dilute solutions.)

The interstitial pore waters of recent marine muds often show an enrichment in salts relative to the water in which these are deposited. Hecht (*in* KREJCI GRAF, 1934) found 35 parts per thousand in the muds of the Jade embayment (Heligoland Bight) as against 27 in the water there; TAKAHASI (*ibid.*) records 32.7 ppt in water extracted from diatomaceous ooze on the sea floor, compared with 52.2 at a depth of 5 m. Boeuf (cited by SCHOELLER, 1956) reports salinities ranging from 32.76 to 40.36 in the pore water of marine muds. SIEVER and GARRELS (1962) found a general tendency towards concentration of Na and Cl in the pore waters of Atlantic and Pacific bottom sediments; MANHEIM (1966) has observed a downward increase in the chlorinity of interstitial waters of Recent and Tertiary sediments on the Atlantic shelf off Florida to 28.6 ppt at a depth of 275 m below the sea floor. SIEVER, BECK and BERNER (1965) have reviewed the ultrafiltration properties of clays, and have pointed out that inhomogeneities in the sediments are likely to upset locally the correlation between salinity and depth of burial which might ideally be expected. The impoverished solutions expelled from the clay during compaction will tend to follow a more or less devious course and may be sampled at greater depths than the uppermost few centimetres where we should otherwise expect to find them. This is no doubt the reason why the chlorinity measured in ocean cores, though generally slightly higher than in sea water, may locally be lower (BRUJEWICZ, 1955; SIEVER, BECK and BERNER, 1965).

BREDEHOEFT and others (1963) have developed a model to explain the concentration of salts in a permeable aquifer bounded by semipermeable formations and recharged by rain water. This state of affairs lies beyond the scope of our present interest, and the model is not without drawbacks (RITTENHOUSE, 1964); but the idea evokes the possibility of concentrating connate water in a permeable marine formation by compaction under a semipermeable overburden.

The concentrated pore solutions reported in the literature are mostly from drillings in formations more or less liable to invasion by meteoric water. Some may be derived from rock salt formations, but here the bromine content is probably a reliable guide except in rare cases of evaporite sequences culminating in bromide deposits. The mean sodium concentration of the 24 examples given by WHITE, HEM and WARING (1963), viz. 3.2 percent, is probably as good a value for the average concentration in sedimentary pore solutions as any other we might adopt. It is the same as that used by LIVINGSTONE (1963b), who assumed a sodium content equal to that of three times concentrated sea water.

2. *Adsorbed sodium*

Many natural substances, including clays, zeolites and organic matter (to which soils no doubt owe a substantial part of their exchange capacity), act as ion exchangers. Most carry negative charges and adsorb cations; the hydroxides of iron and aluminium can act as cation or anion exchangers depending on the oxidation potential and pH of the environment. As explained elsewhere (p. 10), the equilibrium distribution of bases between an exchanger and a solution in contact with it is determined by partition equations whose coefficients depend on the nature of the exchanger and the bases. The most widespread cation exchangers in nature are the clay minerals, whose capacity varies according to the distribution of charges on their surfaces. Some base exchange properties of common clay minerals are summarized in Table III. The exchange capacity, being a surface property, is dependent on the size of the particles: a given mineral in a finely divided state will have a greater capacity per unit weight or volume than when coarsely crystalline. This factor is more important in "edge-fixers" than in "surface fixers." The usual order of affinity of the main cations (when of equal normality in solution) for clay particles is H^+ , Ca^{2+} , Mg^{2+} , K^+ , Na^+ .

Most sediments are argillaceous, and consequently have a greater or less tendency to adsorb bases from the aqueous environment of deposition and consolidation. Revelle (*in* SVERDRUP, JOHNSON and FLEMING, 1942, p. 990) determined the exchangeable bases in marine clay and obtained a value of 40 milliequivalents per 100 g. KELLEY and LIEBIG (1934) treated clays and soils with sea water and found that their preference for bases was in the order Mg^{2+} , Na^+ , Ca^{2+} , K^+ . This is confirmed by BRUJEWICZ (1955) in studies of marine clays from the Sea of Okhotsk and adjacent Pacific Ocean. Some of Kelley and Liebig's results are summarized in Table IV.

Livingstone took Revelle's figure of 40 meq. per 100 g as representative of the sediments as a whole and supposed one-third of this capacity to be taken up by sodium, giving an average adsorbed sodium content of 13 meq. per 100 g of rock. This estimate agrees in order of magnitude with Kelley and Liebig's data; it may even be on the high side for rocks in equilibrium with sea water, especially when limestones and sandstones are taken into account. But we are concerned with pore solutions several times richer than sea water in sodium, and should be guided by data on rocks in equilibrium, not with sea water, but with their own interstitial brines. Table V gives figures for exchangeable sodium and calcium found in 54 samples of oil field shales from 8 countries. The Oklahoma samples contain roughly twice as much adsorbed sodium as the same material equilibrated with sea water (Table IV); the mean for the sodium content of the 54 samples is 24 meq. per 100 g. This suggests that Livingstone's estimate of 13 meq. per 100 g, so far from being over-liberal (as he thought

it was), may well be erring in the other direction. Allowing for the inferior exchange capacity of the sandstones and carbonate rocks in the sedimentary column, an overall estimate of 15 meq. per 100 g seems reasonable.

Ion-exchange equilibria are temperature-dependent; according to ANDREWS and MALDONADO (1940) Mg^{2+} and Na^{+} show an increasing tendency with rising temperature to replace K^{+} , Ca^{2+} and H^{+} . It would be interesting to know whether this effect contributes to the formation of high-calcium brines in deep-seated formations: comparison of Tables IV and V shows that Na : Ca ratios are in general higher for the oil field shales than for the materials equilibrated with sea water at (presumably) room temperature. So far as the bulk composition of the sediments is concerned the temperature effect is probably of little importance, since by the time any appreciable rise in temperature occurs the formation will be too deeply buried for any noticeable exchange of material to take place except between the rock and its own pore solution, the bulk composition remaining the same.

3. *Rock salt*

It has long been common to neglect the rock salt deposits in studies of the sodium cycle. The earlier data on them led to bulk estimates corresponding to about 0.4×10^{15} tons of sodium: an insignificant quantity in relation to the 15×10^{15} tons in the ocean and to the wide margins of uncertainty between which geochemical calculations have often to be carried out. However recent results of geophysical investigations and drillings in salt provinces suggest that we should take a closer look at the world's rock salt deposits before dismissing them as negligible.

RONOV (1959) estimates the surviving salt deposits for the Devonian-Jurassic interval at 2.2×10^6 km³, equivalent to 2.1×10^{15} tons of sodium. His estimate for the Permian alone, a million km³, is equivalent to more than twice the earlier estimates for the whole of post-Algonkian time (see for example KUENEN, 1941). Still more recently HOLMES (1965) has discussed data from the Gulf Coast salt province (Permian of Louisiana and Texas and the neighbouring offshore region) which indicate that this alone may contain a million km³ of salt, and suggesting, as Holmes puts it, "the existence of salt deposits on a scale that would have been considered incredible only a few years ago." Seventeen diapiric salt provinces are shown on the new 1 : 5,000,000 tectonic map of Eurasia edited by YANSHIN (1966). Rough estimates of their areas (Table VI) total over a million km², more than one-half percent of the total area of the continents and their shelves; the North Sea extension of the Zechstein province is not included. The Cambrian salt of the Persian Gulf area (170,000 km²) has formed diapiric mountains in Laristan rising to 1200 m above sea level through a thick cover of Mesozoic and Tertiary rocks. The average diameter of the salt plugs in this province is about 6.5 km, suggesting

that the underlying source bed must have been at least 5 km thick.¹⁾ On this basis the Persian Gulf province should contain about 850,000 km³ of salt: an amount comparable with that estimated for the Gulf Coast province of North America.

Other important salt deposits, not mentioned in Table VI, are: Europe: the North Sea, England (Cheshire and Shropshire), the Calcareous Alps, Portugal (Estremadura), Bulgaria (Morovo); Asia: India (Salt Range, Hyderabad), the Near East (N Iraq, the Dead Sea area), China (Szechuan, Yunnan); N.W. Australia (Canning Basin), Africa: Nigeria (Ogoja and Benue Provinces), Gabon (under the continental shelf), Morocco and Algeria (Atlas); South America: Peru (N.E. Cordillera), Colombia, Brazil, Argentina (Tucuman), Chile (Atacama); North America: Michigan, New York State, Kansas, Oklahoma.

The available data are too fragmentary for any accurate estimate of the total volume of the rock salt deposits. The Permian seems to have been an exceptional period so far as salt formation is concerned: according to Ronov it accounts for nearly half of the rock salt now surviving from the Devonian-Jurassic interval. Even though Ronov's estimates are far too low, the estimated content of the Gulf Coast province and the area of the enormous Permian province of Kirghiz (at the northern end of the Caspian) seem to confirm the preeminence of the Permian as a salt-producing period. This may simply be due to a lucky combination of climatic and tectonic factors in the late stages of the Hercynian orogeny: for example, according to paleomagnetic evidence the Permian provinces of Texas, northwestern Europe and Kirghiz all lay between 10 and 25 degrees from the equator at the time of their formation (see VAN HILTEN, 1962, p. 409). If the Zechstein and Kirghiz deposits contain between them one and a half times as much salt as the Texan province (a conservative estimate, for their combined area is nearly four times as great), then these three Permian provinces alone must contain something like 2.5 million km³ of salt. At this rate 5 million km³ for the aggregate volume of all post-Algonkian salt deposits, roughly equivalent to 5×10^{15} tons of sodium, can hardly be called an extravagant estimate.

As will be shown later (p. 25), the total volume of unmetamorphosed post-Algonkian sediments now surviving on the continents and shelves is about 700×10^6 km³. Their average porosity and density are 16 percent and 2.4 g per cm³ respectively (see Table X). On the basis of the estimates just made, the total amount of "mobile" sodium held in these rocks,

¹⁾ PARKER and McDOWELL (1955) have made experiments from which they conclude that where salt plugs are formed their average diameter should be roughly equal to the thickness of the source bed, and the diameter of the peripheral sink about 6 or 8 times that of the plug. These predictions have been partially verified by studies of actual salt structures, so they may be used with some degree of confidence in estimating the thickness of source beds in diapiric provinces where the diameter of the plugs is known.

including the salt deposits, is about 14.5×10^{15} tons (see Table VII). Expressed in other terms, 100 g of average sedimentary rock contain 0.85 g of mobile sodium (Table VIII).

SEDIMENTARY DIFFERENTIATION

The foregoing discussion concerns a hypothetical "average" sediment, and raises the question whether any such generalisation is in fact permissible. The main obstacles to deciding the "average" composition and properties of the sediments are the wide range of variability within each of the three main groups and uncertainty as to their relative abundances. NIEUWENKAMP (1956) avoided these difficulties by introducing his ingenious "alumina ratio" and showing that the proportion of fixed sodium relative to Al_2O_3 is in all sediments roughly the same. But we are here concerned with "mobile" sodium, which (in at least two of the three forms considered) is not amenable to this kind of treatment.

Thanks to the work of RONOY and KHAIMOV (see RONOY, 1959), the relative amounts of the three principal kinds of sediment are now reasonably well known for a fairly large part of the sedimentary column. If we take Ronov's marine clastics as mainly shale and his continental clastics as mainly sandstone,¹⁾ we arrive at the ratio 45 shale: 30 carbonate: 25 sandstone (Table IX). Some data on the porosities and densities of these three classes of sediment (after DALY, MANGER and CLARK, 1966) are given in Table X.

1. *Shale*

Keeping to the same assumption as before about the concentration of the pore solution, we can refine our previous estimate by allowing for this fraction of the sediments 25 percent pore space, a density of 2.3 g per cm^3 , and an exchangeable sodium content of 24 meq. per 100 g (see p. 17 above).

2. *Carbonate rocks*

The porosity of the carbonate rocks is very variable, ranging from zero in compact limestones and dolomites to 25 percent or more in chalk or oolitic material. 4 percent may be a fair overall average, although the porous limestones are probably underrepresented among the determinations reported in Table X. (The extensive fissures characteristic of many limestones are largely developed by meteoric water and will not be considered here.) So far as concentration of the pore solution is concerned, the few waters from limestone horizons reported by WHITE,

¹⁾ It may be objected that this neglects the grauwackes; but many of these (e.g. the Silurian of the Southern Uplands in Scotland) are more akin to shales than to sandstones.

HEM and WARING (1963) seem to cover roughly the same range as the whole group: these solutions may be acquired at second hand from adjacent non-carbonate formations. Marly limestones may contain 30 percent or more of clay minerals: thus exchangeable sodium, though low, will not be negligible. Perhaps 4 meq. per 100 g is a reasonable guess. The average density is near 2.7.

3. *Sandstones*

Most of the horizons represented in White, Hem and Waring's tables are sandstones. Though no doubt partly continental in origin these seem to acquire concentrated pore solutions, probably either during marine transgressions (they are often intercalated with marine shales) or through deposition in saline basins of internal drainage (as at present in many of the world's deserts). The clay content of sandstones rises gradually as they merge into shales; an allowance of 7 meq. exchangeable sodium per 100 g is reasonable. Density and pore space may be taken as 2.4 and 15 percent respectively.

A new calculation for the "average" sediment taking into account the relative abundances of shale, carbonates and sandstones and the above estimates of their respective pore space and exchangeable sodium, is shown in Table XI; from which it can be seen that the content of "mobile" sodium, after addition of the allowance for rock salt deposits, becomes 0.83 g per 100 g of rock instead of 0.85. The most uncertain quantity is the allowance for rock salt, and until the total volume of rock salt deposits can be gauged with greater reliability it does not seem useful to try to refine our estimates of adsorbed and pore-water sodium by drawing a distinction between the different kinds of sediment.

SEDIMENTARY RECYCLING IN POST-ALGONKIAN TIME

The gross annual rate of sedimentation

KUENEN (1950, p. 391) estimates the present rate of marine sedimentation at 13.5 km³ per year, of which 12 km³ are contributed by rivers and the remaining 1.5 km³ by marine erosion, dust and "dissolved silica and lime." (It is not clear whether all carbonates and radiolarites are included in the last category, but this is of little moment for our present purpose.) We should subtract 0.4 km³ per year for the pelagic deposits, which are probably not recycled in the sense understood by Livingstone. Kuenen does not explicitly state how compact these sediments are supposed to be; LIVINGSTONE allows a reduction of one-third for compaction and thus arrives at a corrected rate of 8 km³ per year as a basis for his (1963b) estimate of the rate at which the sediments are recycled.

HOLMES (1965), using data from rivers draining a large area (100 million km²) of the continental surface, obtains an average rate of

denudation of 8×10^9 tons per year,¹⁾ sufficient to produce about 3.2 km^3 of sediments of average density 2.4: a significantly smaller estimate than that adopted by Livingstone. Data for a selection of 48 river basins (from RUTTEN, 1938), mostly in Europe and North America, are given in Table XII. The mean (0.04 mm per year) is undoubtedly too high for a world average, being unduly influenced by 4 basins with unusually high rates; the mode (0.02), on the other hand, may be slightly too low, since the basins with this value all drain to the Atlantic coast of North America and do not include a fair share of tropical and mountainous areas. In view of this we are probably justified in adopting a rate of 0.03 mm per year, which corresponds to a volume of $3 \times 10^{-8} \times 10^6 \times 150 \text{ km}^3$ ²⁾, or 4.5 km^3 .

GILLULY, WATERS and WOODFORD (1951) estimate the overall rate of denudation in the United States of America at 1 foot in 9000 years, or 0.03 mm per year; LEOPOLD, WOLMAN and MILLER (1964) assume an average world rate of 0.027 mm per year. These correspond respectively to 4.5 and 4.1 km^3 per year. The new atlas of physical geography edited by GERASIMOV and others (1964) contains abundant data on denudation in the U.S.S.R., which, with an area of 20 million km^2 , makes up more than one-eighth of the exposed continental surface. Two features make this region untypical of the continents as a whole: a vast, flat-lying tract including Siberia and part of Europe drains to the Arctic Sea by rivers whose mouths are frozen for the greater part of the year; and a relatively smaller but still enormous area comprising the Volga basin, Armenia, Turkestan and southern Kirghiz drains internally to the Caspian Basin, the Aral Sea and the territory lying to the east of these. The difference in activity between the Siberian rivers and this internal drainage system may be appreciated from the fact that in the latter one river alone (the Amu Daria) carries annually as much detritus as the fourteen principal rivers discharging into the Baltic, the Arctic Sea and the Sea of Okhotsk. Despite these enormous variations the overall denudation rate for the U.S.S.R. (detritus and dissolved salts, including the internally-drained area) is not very exceptional, being just short of 10^9 tons per year: corresponding if extrapolated to a world rate of just less than 3 km^3 .

It should be possible to estimate the rate of sedimentation by considering the sodium discharged from the continents in river water, making allowances for atmospheric recycling and sodium of industrial origin. Our assumptions about rock salt deposits, pore solutions and adsorbed sodium imply that (neglecting any weathering of sodium fixed in sedimentary silicates) 100 g sedimentary rock will yield about 0.8 g of

¹⁾ Holmes does not state whether this includes material transported from basins draining to the interior of the continents, as it should do in order to give a correct estimate of the overall rate of sedimentation (marine and continental) for comparison with the volume of sediments now surviving (see below).

²⁾ Exposed area of the continents = $150 \times 10^6 \text{ km}^2$.

sodium (see above, p. 20). 100 g of metamorphic rock should yield 0.7 g sodium on weathering (1.7 less 1.0; see POLDERVAART, 1955 for analyses of metamorphic rocks), and 100 g igneous rock 1.1 g (see p. 4 above). Without considering the proportions of sedimentary, metamorphic and igneous rocks exposed on the continents or their relative susceptibilities to chemical denudation, we shall probably not be far wrong in assuming that for every 100 g of rock weathered 0.9 g sodium are released to the hydrosphere. From Livingstone's figure of 20.5×10^7 tons per year for the gross rate of sodium discharge from the continents we should deduct 8.1×10^7 tons for sodium recycled through the atmosphere and 1.3×10^7 tonr for sodium contributed by human activity (see below, p. 26), giving a net rate of discharge due to chemical denudation of 11.1×10^7 tons per year. This corresponds to a denudation rate of 4.8 km^3 per year, to which a correction of about one-ninth should be added for sediments formed in the interior of the continents, giving an overall figure of about 5.3 km^3 per year (see Table XIII).

Finally, a rough correlation between the maximum known thicknesses of a number of systems and estimates of their respective volumes (see below, p. 24) suggests that the 6000 or so m of Pleistocene and Recent sediments should correspond to a volume of about $9.5 \times 10^6 \text{ km}^3$. Spread over 2 million years this gives a rate of 4.8 km^3 per year (see Table XVI).

These various estimates of the gross annual rate of sedimentation are summarized in Table XIV. They suggest that Kuenen's and Livingstone's values are too high; Holmes's may be a little too low. For the purpose of the present study we shall assume a rate of 5 km^3 per year. An allowance of 1 km^3 per year for material lost to the ocean floor (see below, p. 31) gives an annual rate for the continents and shelves of about 4 km^3 .

The net annual rate of sedimentation

No sooner is a generation of sediments uplifted than it begins to be eroded, yielding waste which is carried away to form a still younger generation. This concept is familiar in the phenomenon of unconformity, where it is clear that the surviving volume of the lower series is less than the volume originally deposited. We may therefore speak of the average rate of survival of the sediments formed during a given time interval: or, if we divide the surviving volume of a system by the number of years in the period during which it was laid down, the "net annual rate of sedimentation," which we may compare with the gross rate just estimated above in order to judge the rate at which the recycling process goes on.

According to RONOV (1959) $268 \times 10^6 \text{ km}^3$ of sedimentary rocks have survived on the continents from the interval of 265 m.y. extending from the Devonian through the Jurassic (see Table XV). This corresponds to an average net rate of accumulation of 1 km^3 per year, from which the individual rates for the five separate periods do not seem to differ very significantly. LIVINGSTONE (1963b) has remarked on the apparent lack

of correlation between volume and age, and thinks it may mean that the sedimentary rocks are only exposed to the risk of uplift and erosion for a limited period following deposition. Ronov's data on the Cretaceous and Tertiary sediments, when they are published, will no doubt throw some light on this question; in the meantime an idea of the trend over post-Algonkian time may be had by considering the maximum known thicknesses of the different systems as given by HOLMES (1965; see Table XVI).

The thicknesses for the Devonian-Jurassic interval show a rough correlation with Ronov's estimates of the corresponding volumes, with a mean of $1.59 \times 10^6 \text{ km}^3$ per thousand feet. Using this to convert the rest of Holmes's data from linear to cubic measure, we can make an estimate of the net rate of sedimentation for each period. The results are shown in Fig. 6, where the rates are plotted in a histogram against the corresponding time intervals. Despite the crudeness of the method, a general downward tendency can be observed as the age increases, with a pronounced break in the Devonian. The average rate for post-Algonkian

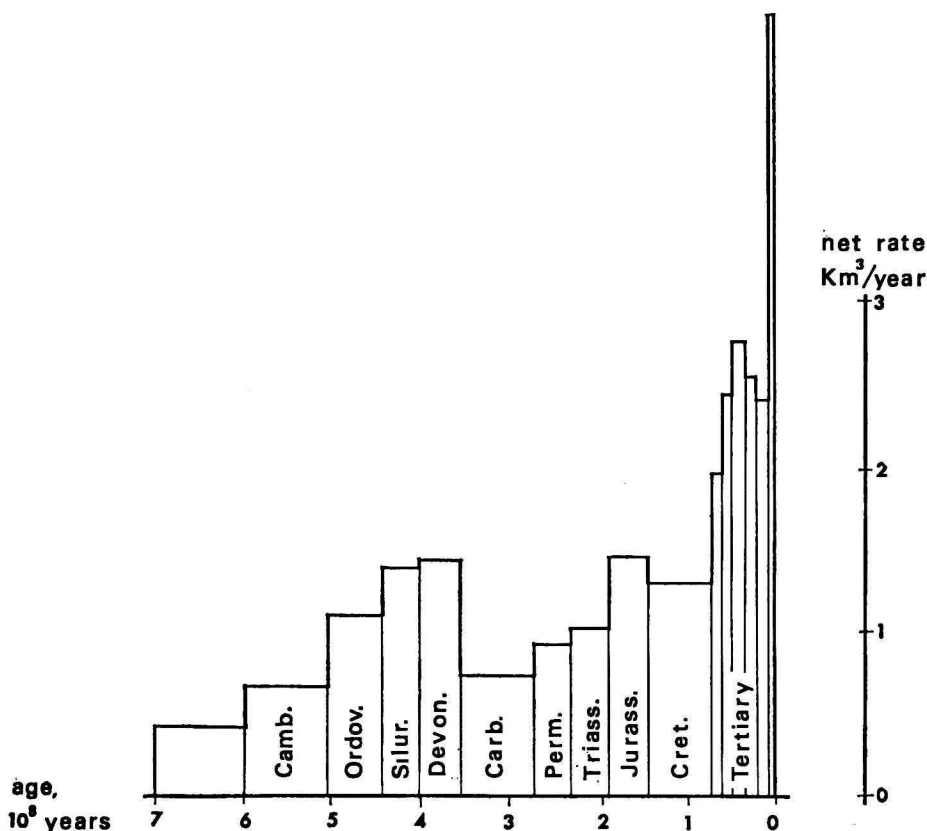


Fig. 6. Survival rate of sediments in relation to their age. Areas of columns represent surviving volumes of the different geological systems. Ordinates represent the average survival rate in km^3 per year.

time (1.2 km^3 per year) is not materially different from that obtained from Ronov's data for the Devonian-Jurassic interval, but this more extended picture of sedimentation in geologic time has in it a suggestion that the volume of sediments surviving from a given period should dwindle gradually with the passage of time until finally swallowed up in the endless cycle of geologic change.

The total volume of the post-Algonkian sediments on the continents

Livingstone's figure of $178 \times 10^6 \text{ km}^3$ (from POLDERVAART, 1955) for the volume of post-Algonkian sediments on the continents seems much too small when compared with Ronov's of 268×10^6 for less than half of post-Algonkian time. Even with $120 \times 10^6 \text{ km}^3$ added for the shelf sediments (POLDERVAART, *ibid.*), it corresponds to a layer only 1.7 km thick on the continents and shelves. Table XVI suggests that $700 \times 10^6 \text{ km}^3$ would be nearer the mark. This is equivalent to a layer 4 km thick, about which there seems nothing unreasonable when we remember the thicknesses in the mountain systems and the great sedimentary basins of the world. Examination of the 1 : 5,000,000 tectonic map of Eurasia by YANSHIN and his collaborators (1966) confirms this impression.

The post-Algonkian metasediments

In ascribing all of the difference between gross and net rates of accumulation of the sediments to sedimentary recycling, Livingstone neglected the formation of the post-Algonkian metasediments. The surviving volume of these is difficult to estimate: the younger metamorphic rocks are confined to geosynclinal regions, but where they exist they are generally thick. A provisional estimate of $350 \times 10^6 \text{ km}^3$ (i.e. half the volume of the surviving post-Algonkian sediments) will be made here for the purpose of calculating the average rate of recycling; this volume will be taken as including igneous rocks formed by the melting of continental and shelf sediments of post-Algonkian age. When originally laid down as sediments these rocks must have removed from the ocean some 7×10^{15} tons of sodium (Cp. Table VII).

The rate of sedimentary recycling

We have now enough estimates to consider the effect of sedimentary recycling on the discharge of soluble sodium from the continents. The gross rate of sedimentation appears to be about four times the net rate (or rate of survival) for post-Algonkian time as a whole. 1 volume ($700 \times 10^6 \text{ km}^3$) of post-Algonkian sediments still survives on the continents, and one-half volume more ($350 \times 10^6 \text{ km}^3$) survives as metasediments. 2.5 volumes, or $1750 \times 10^6 \text{ km}^3$, must therefore have been recycled in the 600 m.y. of post-Algonkian time. The recycled material should have contained $2.5 \times 15 \times 10^{15}$ tons of sodium derived from the ocean in post-Algonkian time (see above, p. 20), and the annual portion of river sodium

derived from it will be $\frac{2.5 \times 15 \times 10^{15}}{6 \times 10^8}$ or 6.3×10^7 tons. That some of the recycled rocks have been metamorphosed or melted before disintegration does not alter the fact that they must have given up to the rivers the portions of "mobile" Na and of Cl they originally held when sediments. This amount of 6.3×10^7 tons is thus the annual discharge of sodium from the post-Algonkian sediments and their metamorphic and igneous derivatives.

THE RATE OF ATMOSPHERIC RECYCLING

LIVINGSTONE (1963b) gives a good summary of the considerations involved in estimating the rate at which salt is carried inland in sea spray and deposited on the continents as dust particles or in rain. Such salt contributes an important fraction of the sodium in river water, and a deduction must be made for it before we can arrive at the rate of discharge of sodium released by chemical denudation. Livingstone's allowance for this atmospherically-recycled sodium is intentionally generous: he is seeking a lower limit for the rate of denudation, and adopts for this purpose a concentration of 3 ppm for atmospherically recycled sodium in river water, whose total sodium content averages 6.3 ppm. (LIVINGSTONE, 1963a). His calculations, however, suggest that the real concentration is probably nearer 2.5 ppm, and this latter value will be adopted here.

It has been suggested (by SUGAWARA and others, 1949; CAUER, 1949; FOURNIER D'ALBE, 1959) that meteoric sodium is not accompanied by chlorine in the ratio found in sea water; but insufficient data are available for any reliable generalization to be made. TWOMEY (1957), using material collected on sampling flights over southeastern Australia as far as 900 km inland, could detect no evidence of any change in the Na : Cl ratio.

THE EFFECT OF HUMAN ACTIVITY

Sodium produced by human activity now constitutes a more important fraction of river sodium than the 3 percent allowed by LIVINGSTONE (1963b). Industrial extraction of common salt rose from 14.5 million tons a year in Clarke's time to 85 million in 1960 (see Fig. 7). Round about 1950, when a rate of about 40 million tons had been reached, there began a marked increase in the rate of production, which by 1955 had settled to a more or less steady increment of 4 million tons per year. This period corresponds roughly with the blossoming of the "plastics" industry, for which common salt is a source of chlorine. The resistance of plastic articles to destruction is a matter of common observation and has begun to cause embarrassment among municipal authorities: an increasing proportion of the sodium discharged by industry is thus accompanied back to the

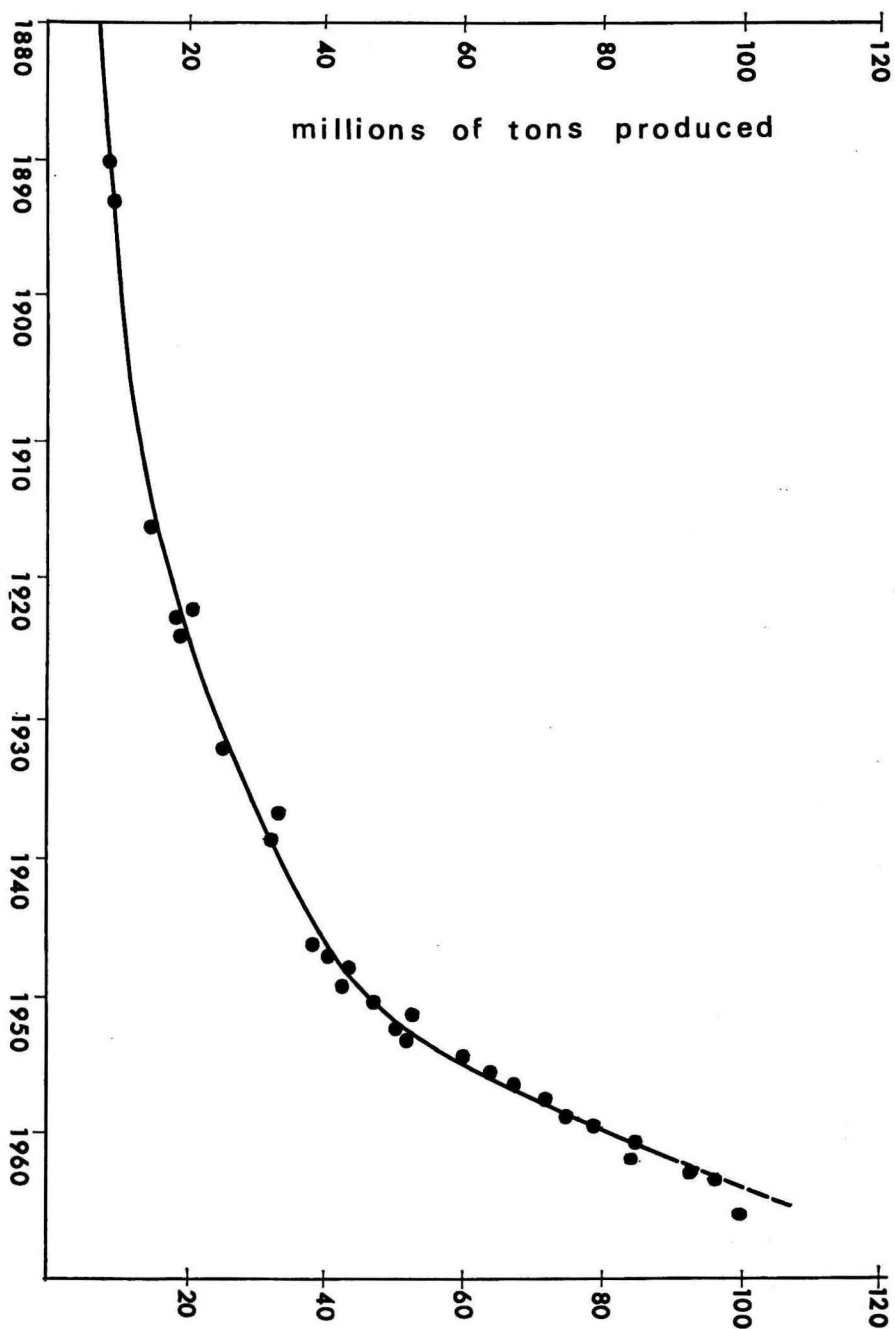


Fig. 7. World production of common salt, 1890–1964. (Data mainly from *Minerals Yearbook* and *The Mineral Industry*).

sea by other anions than chloride. Apart from glass manufacture (which indirectly absorbs but a small fraction of the world production of NaCl), industrial uses of salt probably do not result in the fixation of any appreciable amount of sodium: so that at the present time some 4×10^7 tons of sodium (corresponding to 100 million tons of common salt, six-sevenths of it extracted from the continents) must be contributed to the ocean each year by human agency. A certain proportion of this industrial sodium must be released direct to the sea in the larger coastal cities such as New York, San Francisco, Rio de Janeiro, Buenos Aires, Liverpool, Naples, Bombay Hong Kong, etc. Notwithstanding, most of it is probably discharged into rivers: the St. Lawrence, the Mississippi, the Rhine, the Elbe, the Seine, the Rhone, the Po, the Danube, the Nile, the Ganges, the Yang-tse-Kiang and the Huang Ho, to mention only a few, all drain industrialized or densely populated areas. Perhaps five-sixths of all the sodium liberated by human activities, i.e. 3.3×10^7 tons per year, finds its way into the rivers.

Strictly speaking, we should correct river analyses individually for industrial sodium, according to the years in which they were carried out, using a curve like that of Fig. 7. But it would then be necessary to take into account the extent to which the individual river basins were industrialized, etc. and it is doubtful whether any overall gain in accuracy would result. For our present purpose it is probably sufficient to take the year 1950 as representative for the analyses averaged by LIVINGSTONE (1963a); this has the advantage that there was probably as yet no marked stoichiometric imbalance between sodium and chloride in industrial waste. The 40 million tons of common salt extracted in 1950 correspond to 1.6×10^7 tons of sodium; allowing that one-sixth of this was discharged direct into the sea, we obtain a correction for river water of 1.3×10^7 tons.

GROSS AND NET RATES OF SODIUM DISCHARGE FROM THE CONTINENTS

The corrections for sedimentary recycling, atmospheric recycling and human activity together account for 15.7×10^7 tons Na per year, or more than three-quarters of the gross amount (20.5×10^7 tons) transported yearly by the rivers. The difference, 4.8×10^7 tons, representing the annual quantity of sodium released by weathering of rocks not recycled in post-Algonkian time, might be considered too small in relation to the quantities from which it is derived to be of much significance. It can be tested approximately, however, by considering the average chlorine content of river water, which is 7.8 ppm (LIVINGSTONE, 1963a).

The sodium released from interstitial brines in sediments will be accompanied by an excess of chlorine, since in these brines chlorine often accompanies calcium as well as sodium; but this will be more than offset by release of sodium adsorbed on the clay minerals. The sodium contributed by rock salt and by industry (pre 1950) will probably be accompanied

by chlorine in roughly stoichiometric proportion; for the atmospheric fraction the proportions should be as in sea water, i.e. 11 : 19. By making estimates of the amount of chlorine accompanying each of these different fractions, we can see how much of the river chlorine is accounted for in this way. Such a calculation is given in Table XVII, using estimates already derived concerning the distribution of sodium in the sediments (pp. 4-12) and using the mean Cl : Na ratio for the 24 analyses of interstitial brines reported by WHITE, HEM and WARING (1963). It appears that about 7 of the 8 ppm chloride in river water accompany cyclic and industrial sodium, leaving 1 ppm over to balance sodium and other bases leached from Precambrian sediments: which does not seem unreasonable. Consequently, although it should be regarded with the reserve due to a small number derived by difference from two large and uncertain ones, the figure of 4.8×10^7 tons representing the net annual rate of discharge of sodium from the continents in post-Algonkian time is not without interest. Gross and net rates, together with the corrections for recycling and industrial waste, are summarized for convenience in Table XVIII.

The rate of denudation in geologic time

It has thus far been tacitly assumed that the present rate of denudation is characteristic of geological time as a whole, and it is worth noting that the early treatments of the subject summarized on pp. 2-7 were uniformitarian to this extent. This assumption has been criticized, notably by BECKER (1910) and CONWAY (1943). Becker thought that in early times the sodium must have been leached more rapidly from the continents than now because the waters had fresh rocks to work on. He reasoned that the rate ought to dwindle as the once naked "primitive" rocks became coated and buried in their own waste, and developed an asymptotic equation to describe the accumulation of sodium in the ocean. Conway attaches considerable importance to human activity, in particular deforestation, as a factor likely to augment the rate of denudation. He cites the dilute waters of the Amazon as an example of sodium transportation from a large area relatively undisturbed by agriculture; but as LIVINGSTONE (1963b) points out, he neglects the high rate of discharge relative to the area of the drainage basin, which in this case more than compensates for the low concentration. As has been shown above, the salt industry now has an appreciable effect on the sodium content of rivers, but this can be determined with reasonably good precision and allowed for.

It is commonly held that as we are now living at the culmination of a great orogeny the present rate of denudation must be higher than the average for geological time. On the other hand, as suggested by Th. Raven (personal communication) the addition to the sea in recent times of water from the Pleistocene ice has raised the base level of the rivers and should have had a compensating effect. The development of

land plants since the Devonian must have had a progressively inhibitory effect at least on mechanical denudation; it would be interesting in this connexion to try to evaluate the effects of the rapid development of tropical forests in the Carboniferous and of grasses in the Tertiary. The solvent effect of land plants might be expected to accelerate chemical denudation. This effect can be appreciated from the fact that in the Amazon basin (equatorial rain forest) the rate of chemical denudation is 8 percent higher than the world average (LIVINGSTONE, 1963b); but if the development of the atmosphere has been influenced to an important degree by green plants, the withdrawal of carbon from it and consequent reduction in the partial pressure of CO_2 may have offset this. These various factors being difficult if not impossible to evaluate quantitatively, it does not seem useful to attempt to apply any correction for them. We shall therefore follow Livingstone who, after a careful examination of the same question, taking many additional factors into account, concluded that an extrapolation of the present rate of denudation is likely to be as near the truth as any corrected rate could be.

SODIUM BALANCE OF THE OCEAN: GAINS AND LOSSES IN POST-ALGONKIAN TIME

The net rate of transfer of sodium to the sea, 4.8×10^7 tons per year, represents the contribution of weathered Precambrian rocks and any post-Algonkian igneous (or metamorphic) rocks not formed from post-Algonkian continental or shelf sediments. It is the quantity Joly thought he needed to determine the age of the ocean: which, if sodium were really accumulating there, would be about 310 million years; or, making the fullest possible allowance for sodium held in sediments under the deep sea,¹⁾ 520 million.

These "ages" cannot be taken seriously; nor is there any evidence that the sea has become saltier since the early Precambrian. We may therefore explore the alternative: that sodium is leaving the ocean at about the same rate as it enters. Considering post-Algonkian time only, we have to account for a total of $4.8 \times 10^7 \times 6 \times 10^8$ or about 29×10^{15} tons of sodium. According to our earlier calculations (p. 25) the post-Algonkian sediments and metasediments contain 22×10^{15} tons; about 7×10^{15} tons have therefore still to be accounted for.

The floor of the ocean

Interest in the ocean floor has grown apace in the present century, and the last decades have seen this vast and little-known domain become

¹⁾ Using in the first case the sodium content of sea water, 15×10^{15} tons; in the second, LIVINGSTONE's (1963b) estimate of 25×10^{15} tons, which includes adsorbed and pore-water sodium in the deep sea and shelf sediments, and assumes the former to be 5 km thick.

the object of intensive study. Here geophysics is in its element, and more is known about the structure of the ocean floor than about its composition or history. Work in the Atlantic by BROEKER, TUREKIAN and HEEZEN (1958) indicates that the present rate of pelagic sedimentation is a few mm per thousand years, i.e. of the order of a km^3 per year. The thickness of the accumulated sediments varies rather widely from place to place, but seems usually to be a few hundred metres¹⁾: this corresponds to an age of the order of 100 m.y., which is in agreement with the apparent absence of pre-Cretaceous sediments.

The well-known mid-ocean ridges are characterized by deep median valleys, copious basaltic volcanism and shallow focus earthquakes. Along and under the continental margins where these form mountain ranges or island arcs, earthquakes occur at depths down to 700 km. The migration of some strings of volcanic islands away from the East Pacific Rise in either direction suggests that the ocean floor creeps steadily away from the ridges where it is constantly renewed by outpourings of basalt, and turns downwards under the continents. Irrespective of whether or not we make conjectures about how the system "works," we are led to picture the ocean floor not as becoming ever more deeply buried under accumulating pelagic sediments, but rather as continually carrying these away and possibly downwards to be assimilated in the mantle of the earth.

The "mobile" sodium content of these deep sea sediments can only be guessed at. Supposing it to be the same as that of the shelf sediments less salt deposits, i.e. $0.21 + 0.35$ or 0.6 percent (see Table VIII), and taking the total rate of sedimentation in the deep sea, including material carried out to the ocean floor from the shelves of the continents, at 1 km^3 per year, we can account for the transfer to the ocean floor of about 1.5×10^7 tons sodium per year, or 9×10^{15} tons over the whole of post-Algonkian time.

The lavas poured out on the ridges and elsewhere under the ocean are more or less altered by sea water; so much we may judge from the condition of samples dredged up from the floor of the Pacific (BONATTI, 1966). But the alteration seems to consist for a large part in the formation of zeolites, and it is doubtful whether on balance any sodium will be released to the ocean by this process.

It is not known what becomes of the deep sea sediments: they might be rubbed off onto the continents like luggage carried on a conveyor belt; but it is equally likely that they travel down to the mantle to be incorporated there, a small addition to this vast body of supposedly ultrabasic rock. If they become incorporated in the mantle, the sodium

¹⁾ The enigmatic "second seismic layer," about 1–3 km thick, has been interpreted by some workers as sedimentary. In the preliminary "Mohole" exercise off Guadeloupe I. it was found to be basalt (T. F. Gaskell, personal communication); but its composition in non-volcanic regions has yet to be directly ascertained. In the present study it is assumed that the second seismic layer is basaltic.

they take with them has to be accounted for. Nieuwenkamp has suggested that it might be balanced by the weathering of basalts erupted from the mantle onto the continents. These contain some 2.3 percent Na, so will yield 1.3 percent soluble sodium on weathering. 1.5×10^7 tons of sodium would be produced by 1.2×10^9 tons of basalt; at a density of 2.9 this amounts to something less than half a cubic kilometre of basalt per year: perhaps less than the volume of basalt annually erupted on dry land, but anyhow of the right order of magnitude. Far too few facts are available for any conclusive discussion of the balance between the ocean and its floor; but of needs such a balance has to be accepted if one envisages an ocean of constant salinity and volume, and it seems quite legitimate to speculate on how this balance might be maintained. May we picture the ocean floor as being on loan from the mantle, constantly taken in for reconditioning and reissued? Material lost from the mantle by the eruption of basalts on land is made good by incorporation of the deep sea sediments. In this way the mantle is conceived of as not progressively differentiating but as having reached a steady state: as evidence of which we might appeal to the apparent absence of any age-correlated trend in the composition of basalts.

We have thus accounted for all the sodium transported by the rivers (see Table XIX). Considering the errors likely to be inherent in some of our assumptions, and the speculative nature of our discussion of oceanic sedimentation, the excess of 2×10^{15} tons on the "discharge" side may probably be dismissed as meaningless.

The "steady state" ocean

RUBEY (1951) has proposed a growing ocean of constant composition, whose main components have escaped during geological time from the earth's interior in constant proportion to one another. This model has been adopted by REYNOLDS (1965) as best fitting his observations on the boron content of ancient illites. But (apart from the difficulty that the ocean does not contain anything like the amount of salt we should expect to find in it on this assumption), it is difficult to believe that the rates of release of the elements accumulating in the ocean would be likely to remain in constant proportion to one another. We might intuitively expect the rate of escape of each element to diminish as its concentration within the earth fell, in accordance with some law such as:

$$r_t = k \cdot e^{-v \cdot t},$$

k expressing the original concentration of the element, v its "volatility" or propensity for escaping and r_t the rate of escape at time t . Rubey's theory implies that such elements as sodium and chlorine should have the same value of v : a supposition which appears highly improbable when we consider the widely different affinities of these two elements for fixation in silicate structures.

So we are left with what seems to be the only reasonable alternative: the ocean, instead of accumulating sodium progressively withdrawn from the earth, merely acts as an exchanger supplying it to the new rocks as these are formed from the waste of the old. This is essentially the model proposed by CARSTENS (1949), who supposed that the rate of removal of sodium at any time would be proportional to the amount then present, and that the gains and losses had been in equilibrium since quite early in the history of the earth (see Fig. 8). MACKENZIE and

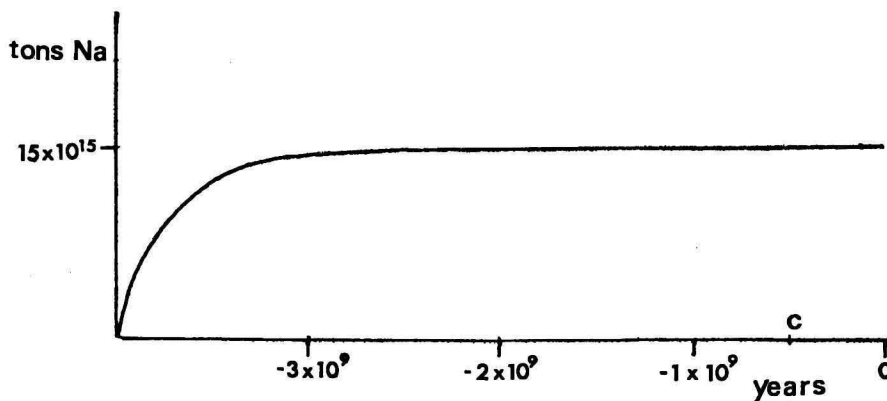


Fig. 8. Sodium content of the ocean in geologic time according to CARSTENS (1949).
C: Cambrian.

GARRELS (1966), in a paper which should have a far-reaching influence on geochemical ideas, have seized a fact whose full import has somehow escaped us ever since river water was first analysed: the evaporation of inland waters produces alkaline lakes, and never anything approaching sea water in composition. The composition of the sea must be regulated by selective removal of ions through their incorporation in the sediments. In the case of sodium this takes place by concentration of the pore water, by ion exchange reactions with detrital minerals in which sodium replaces the calcium previously adsorbed from river water, by the formation of salt deposits and by the incorporation of some sodium in authigenic aluminosilicates.

3. METAMORPHIC AND IGNEOUS PROCESSES

NINETEENTH CENTURY MAGMATISM

Hutton's posthumous victory over Werner at the beginning of the nineteenth century led to a general acceptance of the magmatic origin of volcanic and intrusive rocks. A strong defence of the cyclic aspect of Hutton's theory by PLAYFAIR (1802) and later by LYELL (1830, and in succeeding editions of *The Principles*), however, could not prevail against the contentions of physics about a primeval molten beginning and a still surviving molten interior of the globe; which latter, naturally, was taken as the source of eruptive magmas. Thus Hutton's idea of the generation of magma by melting of sediment became a mere historical curiosity.

The doctrine here for convenience called classical magmatism established itself in the latter part of the nineteenth century; by 1900 it was already widely believed that the continents were continuously added to by magma from the earth's molten interior.

The later work of N. L. BOWEN (1928) lent added force to the magmatist concept; Bowen developed a mechanism of magmatic differentiation on sound theoretical and experimental lines and succeeded in convincing petrologists of its wide applicability.

The increasing difficulties which beset the magmatist school in defending the juvenile nature of the rocks it had annexed as its legitimate concern lie outside the scope of this study. It is enough to recall the problem of finding room for the by-products of the formation of granites on the scale on which these are found in nature, and nature's perverse refusal to acknowledge using the ingenious differentiation mechanisms the magmatists had worked out for her. Notwithstanding these and other serious weaknesses, the magmatist school has left a profound and lasting impression on modern geological thought which has tended to obscure our view of petrogenesis and make us overcautious in evaluating new or heterodox ideas. Such, briefly, is the background against which we should see the still widespread belief that the "fixed" sodium gained by the continents as a result of metamorphic and igneous processes is of juvenile origin.

METAMORPHIC ROCKS

We were led to assume that 4 km³ of sediments are formed each year, of which on an average 2.5 km³ are disintegrated again in a period of 600 m.y., some after having undergone metamorphism or anatexis. 1 km³ survive as unmetamorphosed sediments, to which are added 0.5 km³

of metasediments: slate, schist, gneiss and eventually granite and other anatectic igneous rocks. These are distinguished from the sediments above all by an increase in "fixed" and a decrease in "mobile" sodium due on the one hand to the formation of alkali tectosilicates from the clay minerals, and to release of adsorbed sodium formerly held by these and the disappearance of the pore solutions on the other. The questions "where does metamorphic sodium come from?" and "what happens to the sodium of the sediments?" are natural if insinuating. SHAND (1943) considered them and wrote: "To throw all responsibility for the worldwide granitization of sediments upon a hypothetical ichor is not a satisfactory solution of the problem . . . Perhaps some of the phenomena that are attributed to the ichor are capable of a more prosaic solution, namely the redistribution of alkalis by connate water contained in the pores of the sediments." Seventy years earlier LYELL (1871, p. 571) had already realized that the sediments were richer in alkalis than was commonly believed; rich enough, he held, to permit the formation of metamorphic rocks without any additional supply of potash or soda.

Lyell's and Shand's prediction has been amply borne out by the now famous experiments of Winkler and Von Platen (WINKLER, 1958; WINKLER and VON PLATEN, 1960, 1961). Starting with a natural clay from Heppenheim consisting of illite, kaolinite and quartz, WINKLER (1958) added small quantities (1.8 and 5 percent) of sodium chloride to represent the "mobile" sodium of an unleached marine sediment and heated the mixture under a water pressure of 2000 bars. In this way he was able to demonstrate the formation, at different temperatures, of mineral assemblages corresponding to the known natural metamorphic facies. He ultimately obtained at temperatures slightly above 670° C an anatectic melt of about two-thirds the bulk of the starting material and having the mineralogical composition of a calc-alkali granite. Next, using calcitic illite-bearing clays, WINKLER and VON PLATEN (1960) produced at 740° C (again under 2000 bars water pressure) an anatectic melt of aplitic composition which with rising temperature increased in volume and changed through granitic through granodioritic composition. The total volume of the final melt reached about 80 percent that of the starting material, leaving a residue of anorthite-rich plagioclase with mafic minerals.

In another series of experiments, this time on grauwackes (which are relatively rich in fixed sodium) without any addition of salt, WINKLER and VON PLATEN (1961) were able to produce a melt whose composition changed with rising temperature from aplitic through granitic to give a granodiorite and finally a tonalite occupying from 70 to nearly 100 percent of the volume of the starting material.

The experiments of Winkler and Von Platen are summarized in Table XX; a good review of their petrological significance can be found in WINKLER (1960). They prove beyond any reasonable doubt that argillaceous sediments maintained in the presence of water and sodium

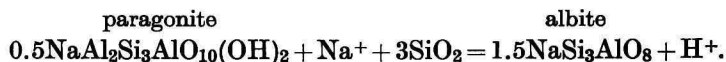
chloride at temperatures in the higher metamorphic range will produce gneiss and eventually anatectic granite magmas, and incidentally provide an answer to the puzzling question why ordinary pelitic sandstones are mysteriously replaced by "orthogneiss" in regionally metamorphosed terrains. So far as the sodium cycle is concerned, they imply that the weathering of metamorphic rocks and their anatectic derivatives does not release to the ocean any sodium other than that taken out in the sediments from which these rocks were formed.¹⁾ This is not surprising; for otherwise the oceanic gains would be well in excess of the losses: granted the post-Algonkian metasediments are less exposed on the whole and less easily weathered than the sediments, they may be weathered more slowly than our guess at their relative volume (0.5 vol. metasediments to 1 vol. sediments) suggests. Supposing only one volume of metasediments to be degraded for every 4 volumes of sediments, this still corresponds over post-Algonkian time to one-fifth of $2.5 \times 15 \times 10^{15}$ tons of sodium (see p. 25), or 7.5×10^{15} tons: one-half the present sodium content of the ocean.

THE MECHANISM OF SODIUM FIXATION

HEMLEY (1959) made the first reliable determinations of the stability fields of minerals in the system $K_2O-Al_2O_3-SiO_2-H_2O$, using potassium chloride solutions at 1000 bars in the temperature range 200-550° C. HEMLEY, MEYER and RICHTER (1961) followed this with a similar exploration of the system $Na_2O-Al_2O_3-SiO_2-H_2O$, and HEMLEY and JONES (1964) have summarized the results of these experimental studies and discussed their geological implications. As might be expected, the two systems behave in essentially the same way, the principal phases being kaolinite, mica and feldspar and succeeding one another in that order with increasing temperature. Kaolinite alters to paragonite by losing some water and exchanging hydrogen ions for sodium ions from the solution:



Paragonite changes in turn to albite by a similar mechanism, with addition of quartz:



¹⁾ 100 g of sedimentary rock contain 1 g "fixed" and 0.8 g "mobile" sodium. 100 g metasediments contain on an average 1.7 g fixed sodium (gneiss more, schists less), and 100 g of their anatectic derivatives (whose volume is small relative to that of the metasediments) about 2.5 g fixed sodium. That there is sodium and to spare may be inferred from the presence of NaCl in the fluid inclusions of minerals in intrusive igneous rocks and in springs associated with terminal magmatic activity.

The other two phases involved, pyrophyllite and montmorillonite, behave respectively like kaolinite and paragonite to the extent that they participate in the comparable reactions



and



by exchanging hydrogen ions for sodium.

The equilibria are controlled by temperature and the relative concentrations of NaCl and HCl in the solution. Fig. 9, taken from HEMLEY and JONES (1964), shows the stability fields of the different minerals in relation to temperature and the molar concentration ratio $m_{\text{NaCl}} : m_{\text{HCl}}$. With rising temperature the albite field progressively extends towards lower $m_{\text{NaCl}} : m_{\text{HCl}}$ ratios. At low temperatures Al^{3+} , considerably larger than Si^{4+} , fits less comfortably into the 4-coordinated lattice positions;

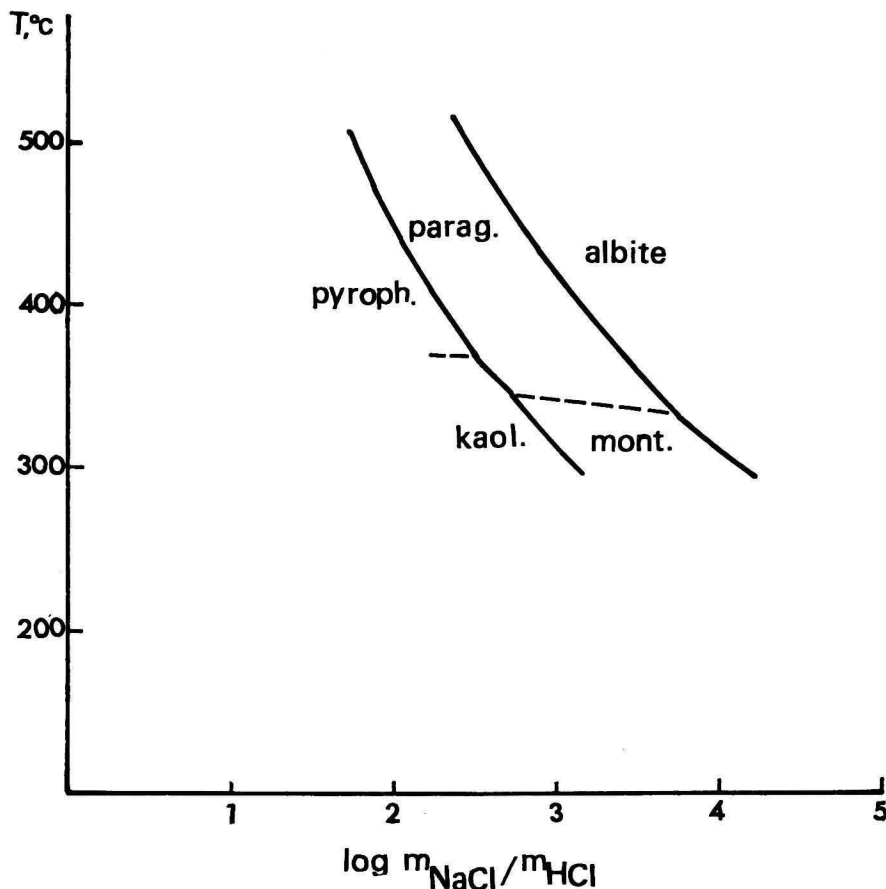


Fig. 9. Equilibria in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ in relation to temperature and molar concentration ratio NaCl : HCl. 1000 bars water pressure, excess quartz present. (After HEMLEY and JONES, 1964).

however it is encouraged to enter them by increased activity of alkalis, essential constituents of the feldspar structure. H^+ is too small to occupy satisfactorily the positions of the alkalis; increased hydrogen activity therefore favours the kaolinite structure. In relation to this it is worth while to consider not only the molar concentrations of NaCl and HCl, but also their degree of ionization, which gives a better idea of the relative activities of Na^+ and H^+ . Fig. 10, based on data from FRANCK (1956, 1961), shows approximately the ionization constants of NaCl and HCl in the P, T range with which we are here concerned.

At 1000 bars water pressure and 600° C the albite-paragonite boundary will be reached at a molar concentration ratio $\left(\frac{m_{NaCl}}{m_{HCl}}\right)$ of about 10^2 , i.e. 100 (Fig. 9). At this temperature and pressure the dissociation constants of NaCl and HCl are respectively 10^{-5} and $10^{-5.5}$ (Fig. 10); we may therefore take $\frac{m_{NaCl}}{m_{HCl}}$ as approximately equal to $\frac{[NaCl]}{[HCl]}$.

$$\text{Now } \frac{[Na^+]}{[H^+]} = \frac{[HCl]}{[H^+][Cl^-]} \times \frac{[Na^+][Cl^-]}{[NaCl]} \times \frac{[NaCl]}{[HCl]};$$

$$\text{so that } \log \frac{[Na^+]}{[H^+]} = 5.5 - 5.0 + 2.0 = 2.5,$$

$$\text{or } \frac{[Na^+]}{[H^+]} = 320.$$

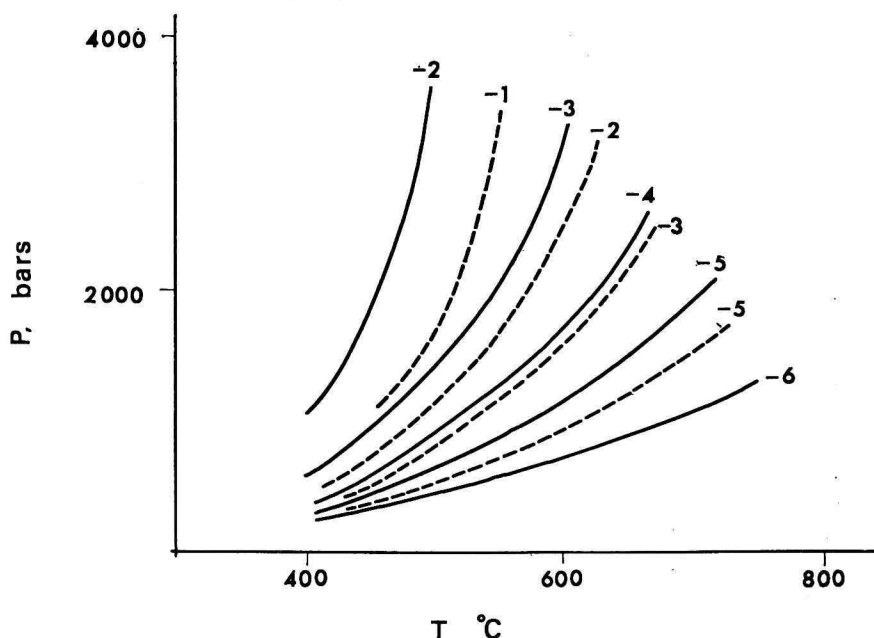


Fig. 10. Dissociation constants of HCl and NaCl as functions of temperature and water pressure. Full lines: $\log K_{HCl}$; broken lines $\log K_{NaCl}$. Data from FRANCK (1956, 1961).

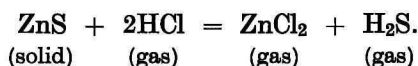
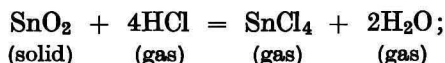
At the same pressure and 500° C, we have at equilibrium $\frac{m_{\text{NaCl}}}{m_{\text{HCl}}} = 10^{2.5}$ (Fig. 9). The dissociation constants (Fig. 10) are now $K_{\text{NaCl}} = 10^{-2.5}$ and $K_{\text{HCl}} = 10^{-4}$. $\text{Log } \frac{[\text{Na}^+]}{[\text{H}^+]}$ is now equal to

$$4.0 - 2.5 + 2.5 = 4.0,$$

$$\text{or } \frac{[\text{Na}^+]}{[\text{H}^+]} = 10,000.$$

In other words a relatively small drop in temperature is accompanied by a large increase in the equilibrium value of $\frac{[\text{Na}^+]}{[\text{H}^+]}$. Gneissification must involve the expulsion of the fluid phase, since gneiss contains no pore space worth mentioning. Sodium having been fixed in the feldspar, the volatile phase will be correspondingly enriched in hydrogen chloride. So long as the temperature remains high, this will exist almost exclusively as the unionized complex HCl: at 1000 bars and 500°, for instance, it is only 0.01 percent dissociated; but as the temperature drops, K_{HCl} rises sharply: already at 400° something like 0.1 percent is ionized. If the gas phase accompanies an anatectic melt (granitic magma) there will come a point at which, the system having cooled sufficiently, autopenumatolysis will set in giving rise to the familiar phenomena of greisenizing and kaolinization.

The well known experiment of DAUBREE (1879), who succeeded in transporting tin by passing steam over stannic chloride in a heated tube, laid a practical foundation for the "acid" theory of ore transportation and emplacement: at high temperatures and pressures those trace elements disseminated through the sediments whose ionic radii unsuit them to incorporation in the silicates form halogen complexes which are gathered up and carried away in the supercritical pore fluid.



If an anatectic melt (magma) forms, this fluid will dissolve in it. When the magma erupts and cools the fluid will come out of solution again with falling temperature and pressure and travel along tectonically-controlled channels (joints and faults). At the same time the HCl will begin to dissociate and attack the granite (kaolinization) and the country rock into which it is intruded. The resulting fall in partial pressure of HCl causes the equilibria to move to the left, with consequent redeposition of the solid phases (ores) in the passages as lodes.

The characteristic enrichment in calcium and sodium chloride of mine

waters in crystalline rocks themselves practically devoid of pore water completes this rough picture of ore transport: the considerable amounts of sulphate and bicarbonate generally found in at least the higher levels can be ascribed to oxidation of sulphides by oxygen in circulating meteoric water and alteration of carbonate country rock by the ascending fluids. The relative insolubility of topaz and fluorite and their consequent abundance among the gangue minerals has directed much attention to hydrogen fluoride as a transporting agent. Chlorine, far more important but easily flushed away by meteoric water, is apt to be overlooked. The association of metalliferous deposits with eruptive rather than metasomatic rocks is readily understood: the anatectic melt gathers up the "impurities" (rare metals) formerly dispersed in the sediments, to deposit them again later in narrowly localized channels where the composition of the residual volatile phase carrying them is sharply sensitive to changing temperature and pressure. Unless a magma forms in which the volatiles can dissolve and be carried bodily along, these will merely migrate away from the granitized sediments in all directions, too diffuse to leave any concentrated deposits in the surrounding country rock.

VOLCANOES AND VOLCANIC EMANATIONS

We may distinguish volcanoes according to whether they are associated with geosynclines or with rift systems and other manifestations of crustal tension. Those of the first group produce mainly andesitic and rhyolitic lavas, doubtless anatectic melts derived from metamorphosed sediments; those of the second produce basalt, and are evidently fed from the subcrustal regions (mantle) of the earth.

Apart from the obvious petrographic differences between the rocks produced by these two classes of volcanoes, we might reasonably expect to find other chemical differences between them having regard to the materials from which we suppose their respective magmas to have originated. Those of the geosynclinal group, supplied by the melting of sediments with relatively abundant saline pore water, should produce more steam and chloride emanations than those of the rifts, which derive their magma from compact basaltic material in the upper mantle with perhaps a small admixture of deep sea sediments. This expectation is borne out by observation: the geosynclinal group are well known for their violent behaviour, as exemplified by the famous explosions of Krakatao and Mont Pelée. The viscous character of the more siliceous magmas predisposes these to violent eruption, but this would not occur were it not for the tremendous quantities of pent-up steam which provide the driving force. Violent eruptions of basalt are far less common: the great laminar flows of Ethiopia, the Deccan traps and the Columbia Plateau all bear witness to vast, quiet outpourings; present-day examples can be seen in Hawaii and Iceland.

The association of chloride with the geosynclinal group can be demonstrated from the data presented by WHITE and WARING (1963) on volcanic emanations. A summary of these is given in Table XXI, where the volcanoes concerned are grouped according to whether they are associated with geosynclinal activity or not. Numerous other examples can be cited: the Valley of Ten Thousand Smokes (Katmai) has produced chlorine and fluorine on a scale which has no counterpart among the rift volcanoes; the boron deposits at Larderello (Tuscany) have made the fortune of an immigrant family; the chlorine content of Japanese river water averages 11 ppm as opposed to 8 ppm for the world average (data from LIVINGSTONE, 1963a). The average abundance of chlorine in rhyolites and obsidians according to SHEPHERD (1940, cited by VAN GROOS, 1966) is 630 ppm, compared with 130 ppm in basalts (KURODA and SANDELL, 1953). Van Groos sums up the behaviour of chlorine in petrogenesis by writing: "... the halogens are concentrated in granitic and alkalic rocks. Chlorine shows a tendency to be concentrated in extrusive rocks." If the volcanic volatiles were really juvenile, where could we better look for them than in the basaltic volcanoes fed direct from the only possible source of "juvenile" material, the mantle?

4. THE FIXATION OF SODIUM AT LOW TEMPERATURES

AUTHIGENIC SODIUM SILICATES

An item which should have figured in our sodium balance sheet (p. 12) but has been left out for lack of quantitative data is the sodium fixed in authigenic sedimentary silicates. The assumption that the "fixed" sodium content of the sediments remains constant at 1 percent is not strictly correct. In fact sodium is weathered out of the sedimentary silicates just as from metamorphic and igneous ones, the loss being later made good by sodium fixed in authigenic silicates during sedimentation and diagenesis. A comparison of old marine sediments with river-borne detritus should indicate approximately how much sodium becomes fixed in the former during deposition and diagenesis; unfortunately the necessary data are not at present available.

The principal authigenic sodium silicates are analcime and other zeolites, and albite. The extent of some occurrences, and dependence of their mineralogy on depth (for example in the Triassic of New Zealand; see COOMBS and others 1959), is a reminder that the boundary between diagenesis and metamorphism is an arbitrary one, and has led Turner (*in* FYFE and others, 1958) to propose a zeolite facies of regional metamorphism to include the deeper zones characterized by laumontite, whose formation he considered dependent on the liberation of lime and alumina by albitization of plagioclase; COOMBS (1961) would extend the zeolite facies to include the more superficial zones where heulandite and analcime are formed, arguing that metamorphism includes "... mineralogical and textural modification . . . in response to a temperature differing appreciably from that under which a sediment has been deposited . . .," irrespective of the degree of interdependence of the reactions involved.

HAY (1966) has written an excellent review of these authigenic sodium silicates and the literature concerning them. Although they may not be quantitatively very important in the geochemical balance of sodium, their formation is of great interest because here we have unequivocal proof of the incorporation of sodium from the pore solutions of the sediments. Three main types of formational environment are known: alkaline lakes (of which Lake Natron in Tanzania is a typical example); hypersaline marine environments; and the sea floor. The process goes on most readily in tuffs, but important occurrences are known in non-volcanic pelitic formations: the Popo Agie member of the Chugwater Formation (Triassic of Wyoming) contains about 40 m of analcime-bearing rocks covering some 15,000 km², and the analcimolites of the Sahara (Cretaceous) are about equally extensive. Other important non-volcanic formations are

found in the Congo Basin (Jurassic-Cretaceous) and the Chinle Formation (Triassic) in Utah.

The alkaline lake environment, with its high $\frac{[\text{Na}^+]}{[\text{H}^+]}$ ratios, would naturally be expected to favour the substitution of sodium for hydrogen in aluminosilicates, and the occurrence of analcime in the Recent sediments of Searles Lake in California (HAY and MOIOLA, 1963) indicates that, at normal ambient temperatures and a $\frac{[\text{Na}^+]}{[\text{H}^+]}$ ratio of about 10^{10} , clay minerals can be converted to analcime in a few tens of thousands of years or less. The importance of silica activity has been stressed by some writers (e.g. COOMBS and others, 1959); this is supported by a report from HAY (1966) of analcime formation in illitic clays now being deposited in Lake Natron, where the water contains about 150 ppm silica. The abundance of analcime in analcime-bearing sediments, especially in thick marine and lacustrine tuffs, is often correlated with depth of burial, suggesting that the rate of formation, either from clay minerals or other zeolites,¹⁾ is sharply dependent on temperature. This is borne out by experimental work: substantial yields of analcime can be obtained at 120° C in two weeks, using a brine with a $\frac{[\text{Na}^+]}{[\text{H}^+]}$ ratio of 10^{10} (GREGOR, 1966).

The occurrence of zeolites and authigenic feldspars in redbeds and normal marine sequences (see HAY, 1966) indicate that these minerals are stable in the hydrosphere at $\frac{[\text{Na}^+]}{[\text{H}^+]}$ ratios down to about 10^8 . At this value the formative reactions are probably very sluggish, and reaction kinetics are probably the dominant factor in limiting the development of these minerals in marine sediments. Thus Hay reports that the amount of analcime is greater in Mesozoic than in Cenozoic rocks, and that the abundance of authigenic albite shows an overall increase from Cenozoic to Precambrian. In marine conditions the buffering action of bicarbonate and borate in sea water must play an important role in removing hydrogen ions, which would otherwise accumulate and cause the $\frac{[\text{Na}^+]}{[\text{H}^+]}$ ratio to fall below the equilibrium value. Fig. 11 shows the H^+ activity recorded while adding $\frac{\text{N}}{100}$ HCl to a 25 ml portion of sea water taken from the Scheldt Estuary; it can be seen that the addition of H^+ equivalent to 1 mg per litre, enough to reduce the pH of unbuffered water to 3, only reduces the pH of sea water from 8 to 7.

¹⁾ HAY (1966, p. 91) thinks that analcime does not form from volcanic glass as an initial product, but only through the intermediary of earlier-formed zeolites such as clinoptilolite and phillipsite.

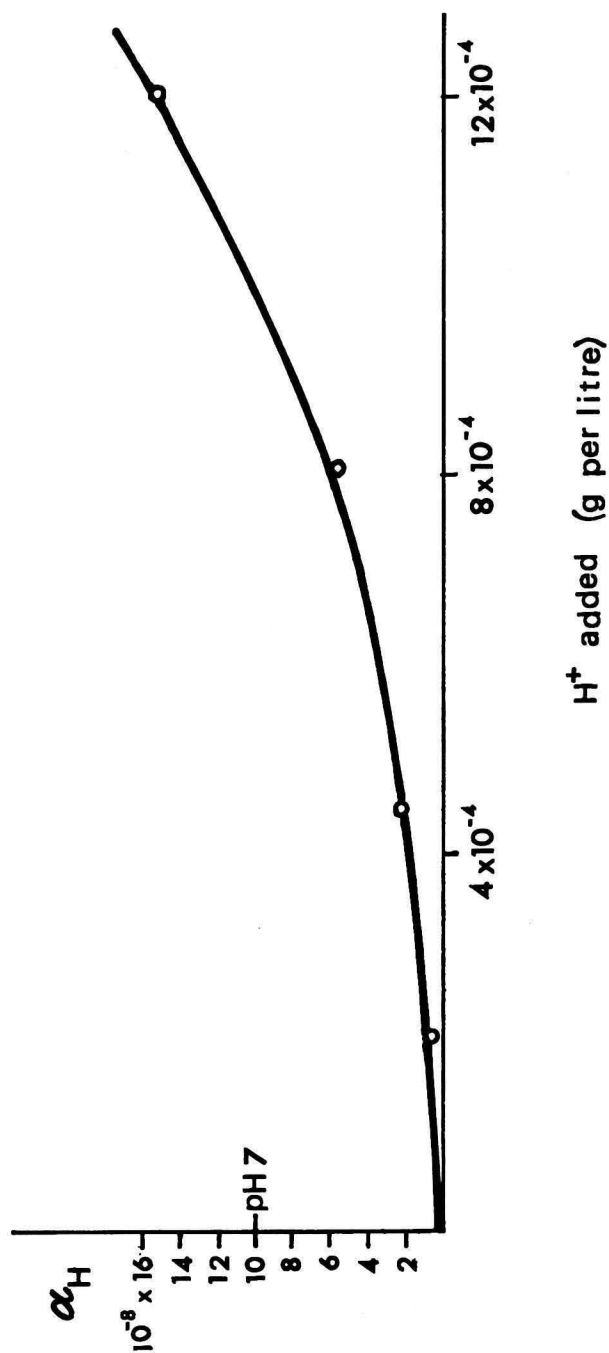
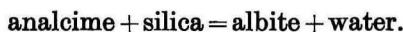


Fig. 11. Hydrogen ion activity recorded while adding N/100 HCl to sea water.

THE STABILITY OF ALBITE

Though from a quantitative and petrogenetic point of view the sodium cycle is only complete when the sediments have been regionally metamorphosed to gneiss, etc., we may look upon the neoformation of albite as representing the return of an individual sodium ion to the environment from which it started its wanderings. Epigenetic growth on detrital feldspar grains in sediments shows that albite can be precipitated directly from solution, but the rather widespread occurrence of analcime in sediments makes it convenient to discuss the formation of albite at low temperatures in terms of the reaction



This reaction is driven to the right by increased silica activity such as occurs in solutions in contact with metastable forms of silica. The diminished activity of water in very concentrated solutions will tend to reinforce this effect, although it is generally believed that alkaline solutions favour the reversion of unstable forms of silica to quartz. This is borne out by the ease with which quartz crystals can be grown commercially in dilute solutions of sodium carbonate or hydroxide, but it should be remembered that a natural alkaline environment in which quartz is crystallizing might be recharged by water rich in silica (e.g. from hot springs) at a rate sufficient to keep the silica activity high notwithstanding. Something of this sort might explain the high silica concentration in Lake Natron, where the pH is about 9.8 (HAY, 1966).

Experimental determination of the stability field of albite at low temperatures is hindered by the sluggishness of the reactions taking place at its boundaries, and in particular by the reluctance of quartz to crystallize in these conditions. Experimentally-determined reaction curves for the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ reviewed by CAMPBELL and FYFE (1965) indicate equilibrium temperatures above 260°C for the reaction $\text{analcime} + \text{quartz} = \text{albite} + \text{water}$ at 1 atmosphere. Campbell and Fyfe consider analcime to be metastable at these temperatures, and by using weighed crystals of albite suspended in presaturated quartz-analcime solutions have determined an equilibrium temperature of 190°C .

HESS (1966) concludes from a study of data on naturally occurring mineral assemblages that albite is metastable at temperatures below 100°C , and attributes its formation below this temperature to pore solutions supersaturated in silica or having diminished water activity because of high concentrations of salts.

THE ACTION OF BRINES ON ILLITE-QUARTZ MIXTURES

In an attempt to study the formation of albite at low temperatures, 15 small (50 mg) samples of illite from Fithian, Illinois, were mixed with excess quartz and kept for 6 months in 4-M NaCl brines at temperatures

in the range 100–200° C. The brines were buffered¹⁾ to stabilize them at different $\frac{[\text{Na}^+]}{[\text{H}^+]}$ ratios between 10^5 and 10^{12} , and the experiments were carried out in sealed gold capsules placed in electrically heated autoclaves connected through variable transformers and a voltage stabilizer to the laboratory mains. Temperatures were monitored by chromel-alumel thermocouples in the autoclaves, and remained constant to within $\pm 2^\circ \text{C}$.

At the end of the 6 months quartz, analcime and low albite were found in 6 of the capsules and analcime and quartz in the remaining 9. (Data on the products are given in Table XXIII). Although the presence of analcime and quartz together with the albite shows that equilibrium was not reached, these results, which are presented in Table XXII and Fig. 12, suggest that albite may be stable at temperatures lower than that (190° C)

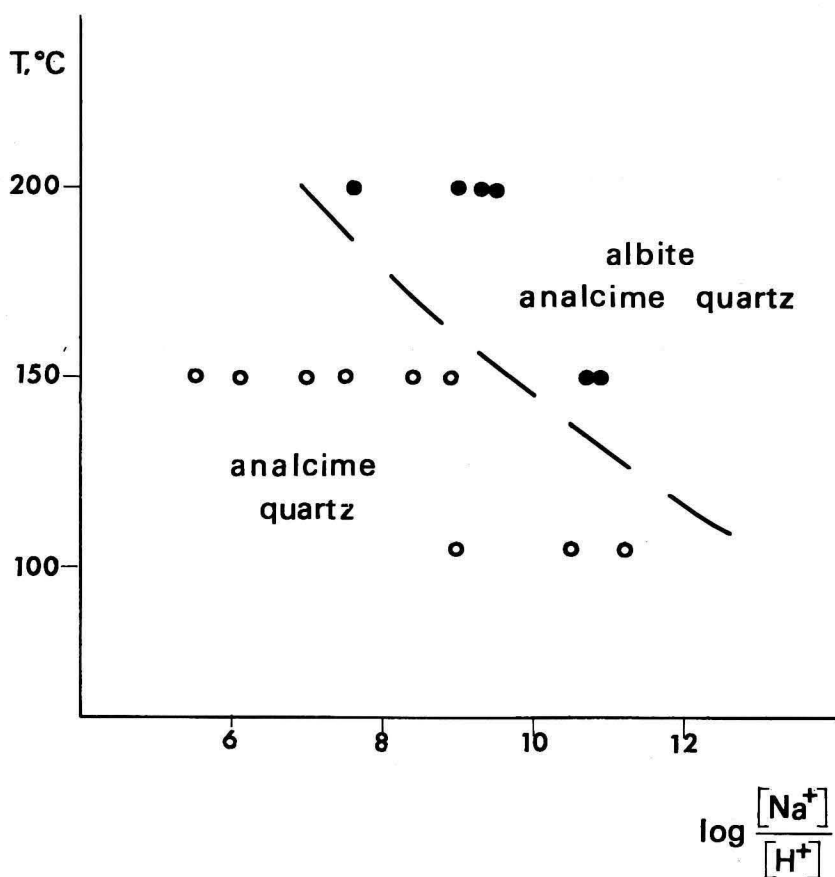


Fig. 12. Products formed by the action of 4-M NaCl on illite between 100 and 200 °C at Na-H activity ratios between 10^5 and 10^{12} . Excess quartz present; duration of experiments 6 months.

¹⁾ Prideaux and Ward's universal buffer, essentially a phosphate-borate buffer with some phenylacetic acid.

found by Campbell and Fyfe. The reaction curve is roughly continuous with the albite-montmorillonite boundary found by Hemley, Meyer and Richter (see Fig. 9); this should not be expected of the equilibrium between analcime and albite, which ought to be comparatively unaffected by Na^+ and H^+ activities. We may therefore conclude that the boundary indicated here is determined by kinetic factors, presumably the rate of formation of analcime. In relation to this it is worth mentioning that in earlier experiments with kaolinite using the same brine, the analcime-forming reaction was accelerated by increased $\frac{[\text{Na}^+]}{[\text{H}^+]}$ ratios, but was still not complete after 76 days.

No evidence was found of conversion of the quartz to metastable forms, and the alkaline environment at the low-temperature end of the curve practically rules out the possibility so far as this region is concerned. In the present state of uncertainty about the true equilibrium curve for analcime + quartz = albite + water the reduced activity of water in a 4-M sodium chloride solution can be neglected. These experiments therefore indicate that albite can grow stably at 150° C, and suggest that the limit of its stability field may lie considerably below this temperature at pressures of a few atmospheres. Reaction kinetics are all-important in determining the products of low-temperature experiments of short duration on aluminosilicate systems, and experiments similar to those outlined here, carried out over periods of years instead of months, might prove interesting in relation to the behaviour of such systems in sedimentary environments.

5. CONCLUSION

Much remains to be discovered about the geochemistry of sodium: in particular, the volume of the salt deposits; the amount and the fate of sodium removed from the ocean in deep-sea sediments; and the extent to which sodium silicates are formed in sedimentary environments. But though far from exhaustive, the facts available justify a re-examination of some of the important and controversial aspects of geology on which the migration of sodium touches.

Some difficulties beset the traditional hypothesis of an ocean of constant volume in which salt accumulates through the ages as well as the *ad hoc* concept of a growing ocean of constant composition. The available evidence points rather to the circulation of sodium in closed cycles, the more important of which (apart from the atmospheric cycle) are suggested in Fig. 13. "Mobile" sodium from the ocean is incorporated in the sediments, which, if uplifted and weathered without being metamorphosed, return their quota via rivers in a "short" (sedimentary) cycle. In regional metamorphism mobile sodium is fixed in silicates (feldspars), whence it is more slowly released by chemical weathering. That the continents consist

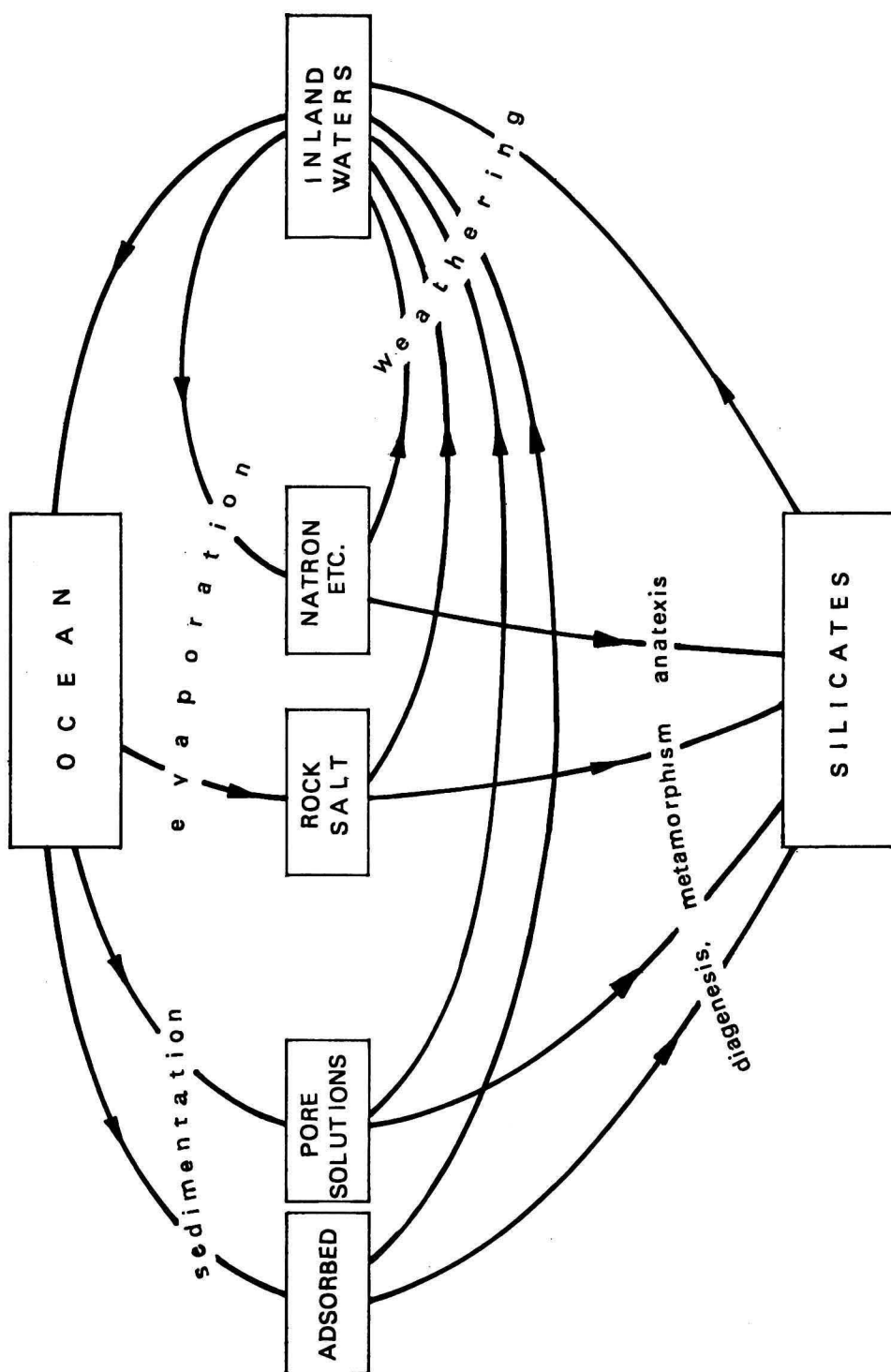


Fig. 13. The sodium cycle.

mainly of "crystalline" rocks merely reflects the superior durability of these, and we are in no way forced to believe that eruptive rocks constitute the source out of which all other rocks came forth. The proportion of sediments to metamorphic and eruptive rocks on the continents (something like 1 : 8) represents a balance between the respective rates of erosion of sedimentary and metamorphic rocks and the rate of formation of the latter from the former. There is no particular reason for supposing that the mantle differentiates to any appreciable extent; nor, *a fortiori*, that the continents are growing.

That this cyclic principle cannot serve as a guide to the primitive state of the earth need not deter us. Lyell thought that the geologist had no more business with such cosmological riddles than the historian with the origin of man. Perhaps, freed from preconceptions about what has happened in the very remote past, we may hope to make more progress in understanding that part of the earth's history that is the proper domain of geology, going back in time no farther than our documents, the really existing and accessible rocks. Barth (1961b), referring to Goldschmidt's assumptions about the history of the ocean, writes: "... I preferred to look at the problem in a different way and have assumed a balance between input and output of all elements in the sea ..."

Geology generally might greatly benefit from a growing awareness of the importance of cyclic processes. Perhaps one day the problem of priority among eruptive and sedimentary rocks will be looked upon with the same equanimity as that of the chicken and the egg.

TABLE I of p. 8

Boron content of illites in Precambrian and post-Algonkian sediments. (Data from REYNOLDS, 1965).

Age	No. of samples	Mean boron content of illite ppm	Standard deviation
Post-Algonkian	70	459	81
Precambrian	31	422	136

TABLE II of p. 15

$\frac{[K]}{[Na]}$ ratios in sea water and in oil field brines (equivalents)

							Mean	Median
A. Sea water							.022	—
B. Oil field brines ¹⁾								
	1.	2.	3.	4.	5.	6.		
	.008	.006	.028	.001	.019	.002		
	7.	8.	9.	10.	11.			
	.010	.002	.020	.002	.002		.009	.006

¹⁾ Data from WHITE, HEM and WARING (1963). Two exceptional analyses ($[K]:[Na] = 0.1$ and 0.2) have been excluded; these may represent brines enriched in potassium through ion exchange reactions with potassium-rich clays.

TABLE III of p. 17

Base exchange properties of common clay minerals. (After SCHOELLER, 1956).

Exchanger	Principal mechanism	Rate of saturation	Exchange capacity (milliequiv. per 100 g)
Kaolinite	broken bonds on edges of flakes	rapid	3-15
Chlorite	ditto	rapid	10-40
Illite	ditto	rapid	10-40
Montmorillonite	flat surfaces	slow	80-150
Vermiculite	flat surfaces	slow	100-150

TABLE IV of pp. 17, 18

Exchangeable bases adsorbed from sea water by soil, clay and shale. (Data from KELLEY and LIEBIG, 1934).

Material	Exchangeable bases adsorbed (milliequivalents per 100 g)					Na as per- centage of total	Na : Ca (meq)
	Mg	Na	Ca	K	Total		
Soil	11.04	10.72	6.05	1.98	29.8	36	1.58
Bentonitic clay .	48.35	39.13	10.85	6.90	105.2	37	3.6
Oklahoma oil field shale . .	6.24	5.74	2.69	—	14	39	2.1

TABLE V of pp. 17, 18

Replaceable calcium and sodium in oil field shales. Data from KELLEY and LIEBIG (1934) after TAYLOR (1928, 1929, 1930) and CASE (1933).

Locality	No. of samples	Ca (meq. per 100 g)	Na (meq. per 100 g)	Na : Ca (meq)
Roumania	4	3.6	32.7	9.1
W. Indies.	6	3.7	12.9	3.5
Trinidad	4	2.4	28.6	12.0
Mexico	12	3.7	46.1	12.5
Alsace	6	1.7	22.1	13.0
Texas	4	5.1	17.6	3.5
California	9	4.8	13.4	2.8
Oklahoma	9	3.8	11.2	3.0
Means for 54 samples .		3.7	24.1	

TABLE VI of p. 18

Estimated areas of diapiric salt provinces in Europe and Asia. Based on YANSHIN (1966).

Province	Area (km ²)
1. Northwestern Europe (Zechstein, excluding North Sea) . .	200,000
2. Aquitaine (SW France)	4,500
3. Valencia (Spain)	2,000
4. S Pyrenees (Spain)	2,000
5. Carpathians (Roumania).	9,000
6. Ukraine	60,000
7. Kirghiz Steppe (U.S.S.R.)	500,000
8. Yakutsk, N Siberia	3,000
9. Chatanga Bay, N Siberia	44,000
10. Kaaptschanka, Siberia	60,000
11. Merv, SE Turkestan	3,000
12. Persian Gulf (including Trucial Coast, Laristan and Bakhtiari)	170,000
13. Teheran (Persia)	25,000
14. Kashan (Persia)	10,000
15. Yezd (Persia)	1,500
16. Oman (Interior)	10,000
17. Kamaran (Red Sea)	2,000
Total	1,106,000

TABLE VII of pp. 20, 25

"Mobile" sodium content of the post-Algonkian sediments (continents and shelves).

1. <i>Held in pore solutions</i> 700 × 10 ⁶ km ³ sediments contain 112 × 10 ¹⁵ m ³ pore space. Pore solution contains 32 kg Na per m ³ , or in all	3.6 × 10 ¹⁵ tons
2. <i>Adsorbed</i> 700 × 10 ⁶ km ³ sediments weigh 1700 × 10 ¹⁵ tons. 0.15 meq. per gram = 0.15 × 23 × 10 ³ g Na per ton, or in all	5.9 × 10 ¹⁵ tons
3. <i>Rock salt</i> Estimated total quantity on continents and shelves . . .	5.0 × 10 ¹⁵ tons
Total	14.5 × 10 ¹⁵ tons

TABLE VIII of pp. 20, 31
Sodium content of 100 g average sedimentary rock.

1. <i>Held in pore solutions</i>	
$\frac{100}{2.4} \times \frac{16}{100} \times \frac{32}{1000}$, or	0.21 g Na
2. <i>Adsorbed</i>	
$\frac{15 \times 23}{1000}$, or	0.35 g Na
3. <i>Rock salt</i>	
5×10^{15} tons in 700×10^6 km ³ , or $\frac{5}{7 \times 2.4}$, i.e.	0.29 g Na
Total	0.85 g Na

TABLE IX of p. 20
Relative proportions of marine clastics, continental clastics and carbonates surviving from the Devonian-Jurassic interval (inclusive). After RONOV (1959).

System	Total surviving volume (km ³)	Percentage composition			
		Marine clastics	Carbonates	Continental clastics	Salt
Devonian	68×10^6	56	29	16	—
Carboniferous	53×10^6	33	43	23	—
Permian	40×10^6	32	33	32	2
Triassic	45×10^6	43	20	36	—
Jurassic	62×10^6	52	25	23	—
Averages		45	29	25	0.3

TABLE X of p. 20
Porosities and densities of sedimentary rocks. Compiled from data in DALY, MANGER
and CLARK (1966).

Rock	Percentage of sed. column ¹⁾	Porosity percent	Density g per cm ³
1. <i>Shale</i> Means of 36, resp. 38 samples from borings down to 2400 m deep	45	24.5	2.25
2. <i>Carbonate</i> Means of 342 samples incl. 18 of porous limestones (chalk and oolite)	30	4.1	2.70
3. <i>Sandstones</i> Means of 637 samples	25	15.0	2.40
Weighted means		16	2.4

¹⁾ See Table IX.

TABLE XI of p. 21
"Mobile" sodium in 100 g average sediment made up of 45 shale, 30 carbonate,
25 sandstone and 0.27 rock salt.

1. <i>Shale</i> Density 2.3; porosity 25 percent; exchangeable Na 24 milliequivalents per 100 g. 45 g contain: in pore solution: $\frac{45}{2.3} \times \frac{25}{100} \times \frac{32}{1000}$, or	0.16 g Na
absorbed: $\frac{45 \times 0.24 \times 23}{1000}$, or	0.25 g
2. <i>Carbonate</i> Density 2.7; porosity 4 percent; exchangeable Na 4 milliequivalents per 100 g. 30 g contain: in pore solution: $\frac{30}{2.7} \times \frac{4}{100} \times \frac{32}{1000}$, or	0.01 g
absorbed: $\frac{30 \times 0.04 \times 23}{1000}$, or	0.03 g
3. <i>Sandstone</i> Density 2.4; porosity 15 percent; exchangeable Na 7 milliequivalents per 100 g. 25 g contain: in pore solution: $\frac{25}{2.4} \times \frac{15}{100} \times \frac{32}{1000}$, or	0.05 g
adsorbed: $\frac{25 \times 0.07 \times 23}{1000}$, or	0.04 g
4. <i>Rock salt.</i> (See Table VIII)	0.29 g
Total	0.83 g

TABLE XII of p. 22

Rates of denudation (in mm per year) for some river basins. (Data from RUTTEN, 1938).

Basin	Rate
1. Upper Rhine	0.45 mm/y
2. Ganges	0.28
3. Irawaddy	0.25
4. Po	0.22
5. Colorado	0.07
6. Mississippi	0.07
7. Neckar	0.05
8. Hudson.	0.03
9-19. 11 rivers in North America	0.02
20-40. 21 rivers in North America	0.02
41. Potomac	0.02
42. Nile	0.01
43. Seine	0.01
44. Thames.	0.01
45. Meuse	0.01
46. Plata	0.01
47. Lower Rhine	0.01
48. Elbe	0.01
Mode = 0.02	Mean = 0.04

TABLE XIII of p. 23

Rate of sedimentation estimated from sodium discharged in solution by rivers.

Gross annual discharge of dissolved sodium from continents (Livingstone, 1963b)	20.5 × 10 ⁷ tons
Fraction contributed by the atmosphere	8.1 × 10 ⁷ tons
Fraction contributed by human activity	<u>1.3 × 10⁷</u> <u>9.4 × 10⁷</u>
Net discharge due to chemical denudation	<u>11.1 × 10⁷</u>
100 g rock yield 0.9 soluble sodium on weathering; hence 11.1 × 10 ⁷ tons. Na correspond to $\frac{11.1}{.9} \times 10^9$ tons of weathered rock, equivalent at a density of 2.6 to 4.8 km ³ .	
Hence volume of material carried to sea	= 4.8 km ³
correction of one-ninth added for material deposited in basins of internal drainage	= 0.5 km ³
Total	5.3 km ³

TABLE XIV of p. 23

Estimates of the present rate of sedimentation on the continents and shelves.

Author	Estimated rate (km ³ per year)	Basis of estimate
1. KUENEN (1950)	13.5	—
2. Livingstone (1963b)	8.0	modification of Kuenen's estimate
3. HOLMES (1965)	3.0	denudation
4. Table XII above	4.5	denudation
5. Table XIII above	5.3	sodium method
6. Table XVI below	4.8	maximum thicknesses of Pleistocene and Recent deposits
Mean of 4, 5 and 6	4.9	
Less losses to deep sea	1	
Estimated rate of sedimentation on continents and shelves	4	

TABLE XV of p. 23

Volumes of sedimentary rocks surviving on the continents from the interval Lower Devonian through Upper Jurassic, and net rates of accumulation in km³ per year

Period	Duration, m.y. (HOLMES, 1965)	Volume, millions of km ³ (RONOV, 1959)	Net rate of accumulation, km ³ per year
Devonian	50	68.3	1.36
Carboniferous	80	53.2	0.67
Permian	45	39.7	0.88
Triassic.	45	45.0	1.00
Jurassic	45	62.1	1.38
Mean = 1.06			

TABLE XVI of pp. 4, 23, 25

Estimates relating to the surviving volumes of the post-Algonkian systems

1.	2.	3.	4.	5.	6.	7.
System	Age of base, m.y.	Duration of period, m.y.	Max. known thickness in feet ¹⁾	Estimated vol., millions of km ³	Net rate of accumulation, km ³ /y.	Vol: thickness ratio
Late Precambrian	700	100	26,000	41	0.41	—
Cambrian	600	100	40,000	64	0.64	—
Ordovician	500	60	40,000	64	1.06	—
Silurian	440	40	34,000	54	1.35	—
Devonian	400	50	38,000	68 ²⁾	1.36	1.79
Carboniferous	350	80	46,000	53 ²⁾	0.67	1.16
Permian	270	45	19,000	40 ²⁾	0.89	2.10
Triassic	225	45	30,000	45 ²⁾	1.00	1.50
Jurassic	180	45	44,000	62 ²⁾	1.38	1.41
Mean vol: thickness ratio for Devonian-Jurassic inclusive						1.59
Cretaceous	135	65	51,000	81	1.26	—
Paleocene	70	10	12,000	19	1.90	—
Eocene	60	20	30,000	48	2.40	—
Oligocene	40	15	26,000	41	2.74	—
Miocene	25	13	21,000	33	2.54	—
Pliocene	12	10	15,000	24	2.40	—
Pleistocene + Recent	2	2	6,000	9.5	4.75	—
Estimated total vol. of post-Algonk. sediments						706
Average net rate of accumulation for post-Algonk. time =						1.17 km ³ per year

¹⁾ HOLMES (1965) pp. 157 and 362.²⁾ RONOV (1959).

Note. The five volume: thickness ratios (millions of km³ per 1000 feet) in Column 7 are obtained from the data in Columns 4 and 5. The mean (1.59) is then used with the data in Column 4 to estimate the volumes (Column 5) of the systems not reported on by Ronov.

TABLE XVII of p. 29

Estimate of chloride accompanying cyclic and industrial sodium in river water

1.	Suppose the Cl : Na ratio in pore solutions is 2.2 : 1 (parts by weight)	
	Then from 100 g average sediment are leached:	
	From pore solutions : 0.21 g Na ¹⁾ accompanied by	0.46 g Cl;
	From ion exchangers: 0.35 g Na unaccompanied by Cl;	.
	From rock salt : 0.29 g Na accompanied by	0.45 g Cl:
	In all: 0.85 g Na accompanied by	0.91 g Cl.
2.	Thus for every 6.3 g Na released from sed are released	6.7 g Cl;
	For every 8.1 g Na derived from atmosphere,	14.0 g Cl;
	For every 1.3 g Na contributed by industry,	2.0 g Cl:
	i.e. the 15.7 g Na thus derived are accompanied by	22.7 g Cl.
3.	Cyclic and industrial sodium together constitute 80 percent of all river sodium, i.e. they account for 5 of the 6.3 ppm Na in average river water. According to the above calculation, these 5 ppm Na should be accompanied by	
	$\frac{5 \times 22.7}{15.7}$ or 7.2 ppm Cl.	

¹⁾ See Table VIII.

TABLE XVIII of p. 29

Gross and net rates of sodium discharge by rivers in post-Algonkian time

	metric tons
1. Average gross annual rate of Na discharge by rivers (LIVINGSTONE, 1963b).	20.5 × 10 ⁷
2. Fraction contributed by post-Algonkian sediments and metasediments.	6.3 × 10 ⁷
3. Fraction contributed by the atmosphere	8.1 × 10 ⁷
4. Correction for industrial waste	1.3 × 10 ⁷ 15.7 × 10 ⁷
5. Average net annual rate of discharge	4.8 × 10 ⁷

TABLE XIX of p. 32

Sodium balance of the ocean in post-Algonkian time

Charge	Discharge
metric tons Na	metric tons Na
Supplied by weathering of Precambrian rocks and basalts of all ages:	Lost to surviving post-Algonkian sediments on continents and shelves (Table VII)
4.8 × 10 ⁷ × 6 × 10 ⁸ tons Na, or	15 × 10 ¹⁵
29 × 10 ¹⁵	Lost to surviving post-Algonkian metasediments and their anatectic derivatives
	7 × 10 ¹⁵
	Lost to deep sea sediments formed in post-Algonkian time
	9 × 10 ¹⁵
29 × 10 ¹⁵	31 × 10 ¹⁵

TABLE XX of p. 35

Summary of experiments by Winkler and von Platen. (WINKLER, 1958; WINKLER and VON PLATEN, 1960, 1961)

1. WINKLER (1958). 2000 bars water pressure.

Starting materials	Temperature	Products	Corresponding metamorphic facies
illite quartz kaolinite water NaCl	390 °C	muscovite, chlorite, ab-rich plagioclase	greenschist
	550 °C	cordierite, biotite, muscovite, plagioclase, quartz	amphibolite
	600 °C	alkali feldspar, cordierite, biotite, sillimanite, plagioclase, quartz (= sillimanite gneiss)	pyroxene-hornfels
	670 °C	anatectic calc-alkali granite up to 67 percent vol. of pre-existing gneiss	

2. WINKLER and VON PLATEN (1960). 2000 bars water pressure.

Starting materials	Melting temperature	Anatectic melt	Residue
illite quartz kaolinite CaCO ₃ NaCl	740 °C	First K-feldspar and quartz (aplite), later joined by plagioclase, more quartz and mafic minerals (granite to granodiorite). Vol. of melt up to 80 percent vol. of starting material	An-rich plagioclase; mafic minerals

3. WINKLER and VON PLATEN (1961). 2000 bars water pressure.

Starting materials	Melting temperature	Anatectic melt
grauwacke	685–725 °C	Alkali feldspar and quartz (aplite), followed with rising temperature by plagioclase, biotite, cordierite and sillimanite (granite – granodiorite – tonalite)
	780 °C	Melting ends; 70–96 percent of starting material liquefied.

TABLE XXI of p. 41

Distribution of chloride in volcanic exhalations (summarized from WHITE and WARING, 1963)

Areas associated with orogenesis		Oceanic islands and areas associated with rifting	
Japan	Cl definitely present	Hawaii	Cl scarce or absent
Kamchatka	definitely present	Iceland	definitely present
Kuriles	definitely present	Canaries	absent
Katmai	abundant	Azores	absent
Mexico	abundant	Congo	absent
Guadeloupe I.	definitely present	Reunion	present
Martinique	definitely present		
New Zealand	definitely present		
Italy	definitely present		
Greece	definitely present		
Java	present in traces		

TABLE XXII of p. 46

Products formed by the action of 4-M NaCl on illite in presence of excess quartz

Experiment	Temperature (°C)	log (Na ⁺ /H ⁺)	Products
1	105	9.0	analcime, quartz
2	105	10.5	analcime, quartz
3	105	11.2	analcime, quartz
4	150	5.5	analcime, quartz
5	150	6.1	analcime, quartz
6	150	7.0	analcime, quartz
7	150	7.5	analcime, quartz
8	150	8.4	analcime, quartz
9	150	8.9	analcime, quartz
10	150	10.7	albite, analcime, quartz
11	150	10.9	albite, analcime, quartz
12	200	7.6	albite, analcime, quartz
13	200	9.0	albite, analcime, quartz
14	200	9.3	albite, analcime, quartz
15	200	9.5	albite, analcime, quartz

TABLE XXIII of p. 46

Data on synthetic analcime and albite prepared by the action of 4-M NaCl on illite and quartz

<i>Synthetic analcime</i>			data on analcime ASTM standard 7-340 for comparison	
X-ray powder data:				
2θ (degrees)	intensity	$d_{hkl}(\text{\AA})$	intensity	$d_{hkl}(\text{\AA})$
15.8	SS	5.60	80	5.61
18.3	MW	4.83		
26.0	SS	3.43	100	3.43
30.6	S	2.91	80	2.93
33.4	MW	2.69		

$a = 13.7 \text{ \AA}$ (de Wolff-Guinier camera, fluorite internal standard)

Microscopic: Isotropic to very weakly birefringent; $n = 1.49$. Habit: spherular aggregates and icositetrahedra. Individual crystals up to 100 microns in diameter.

<i>Synthetic albite</i>			data on low albite ASTM standard 1-0739 for comparison	
X-ray powder data:				
2θ (degrees)	intensity	$d_{hkl}(\text{\AA})$	intensity	$d_{hkl}(\text{\AA})$
13.8	M	6.44		
22.1	S	4.02	35	4.05
24.0	MS	3.69	25	3.66
24.8	M	3.58		
28.1	SS	3.16	100	3.20
28.7	MW	3.10		

(de Wolff-Guinier camera, quartz internal standard)

Microscopic: Weakly birefringent; n less than 1.55. Habit: prisms up to 40 microns long; untwinned. Max. extinction angle 20° .

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APPENDIX

Some general data, assumptions and estimates relating to the earth

Area of land	$150 \times 10^6 \text{ km}^2$
Area of continents and shelves	$180 \times 10^6 \text{ km}^2$
Area of sea	$360 \times 10^6 \text{ km}^2$
Area of ocean floor	$330 \times 10^6 \text{ km}^2$

	Mean thickness, km	Volume, km^3	Mean density, g per cm^3	Mass, metric tons
Atmosphere	—	—	—	5×10^{15}
Ocean	3.8	1370×10^6	1.03	1410×10^{15}
Ice	1.6	25×10^6	0.9	23×10^{15}
Continental crust including shelf	35	6210×10^6	2.8	17400×10^{15}
Ocean floor	8	2660×10^6	2.9	7710×10^{15}
Mantle	2880	898000×10^6	4.53	4070000×10^{15}
Post-Algonkian sediments	4	700×10^6	2.4	1700×10^{15}
Post-Algonkian metase- dime metasediments	—	350×10^6	2.8	1000×10^{15}
Post-Algonkian carbonate rocks	—	210×10^6	2.7	570×10^{15}
Salt deposits	—	5×10^6	2.4	11×10^{15}

	<i>metric tons</i>
Sodium content of the ocean	15×10^{15}
"Mobile" sodium in the sediments (other than salt deposits), in pore solutions and adsorbed	10×10^{15}
Sodium content of the salt deposits	5×10^{15}
Carbon content of the ocean (in bicarbonate and carbonate) . . .	440×10^{11}
Carbon content of the atmosphere (in CO_2)	6×10^{11}
Carbon content of the carbonate rocks	57×10^{15}
Carbon content of the biosphere (calculated on the assumption that all the oxygen of the atmosphere has been formed from CO_2 by the agency of plants)	0.44×10^{15}

Composition of Sea Water (GOLDBERG, 1957)

	ppm	epm		ppm	epm
Ca^{2+}	400	21	HCO_3^-	140	2
Mg^{2+}	1300	108	SO_4^{2-}	2650	55
Na^+	10500	457	Br^-	65	0.8
K^+	380	10	Cl^-	19000	535
		596			593

