CARBONATE SEDIMENTATION DURING THE ARCHEAN[*]

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ABSTRACT

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Archean ($>$ 2400 m.y.) sediments of the Canadian Shield are principally composed of greywacke and shale of flysch facies that are preserved within slightly metamorphosed "greenstone" belts. These Archean sedimentary sequences contain only trivial proportions of carbonate rocks compared to those of Proterozoic and Phanerozoic age. Archean sediments from other parts of the world appear to have a similarly low proportion of limestone and dolomite.

One possible explanation for this scarcity of carbonate rocks is that calcium (and magnesium) did not readily pass into solution upon weathering of primary rocks during the Archean. Another possible explanation is that calcium carbonate (or dolomite) was deposited as a minor component of Archean shales and greywackes rather than as discrete beds of carbonate minerals. Both of these explanations are discounted by chemical analyses of some 406 widely scattered samples of Archean shale from the Superior province of the Canadian Shield. These analyses indicate that mobile elements were removed by weathering during the Archean in approximately the same relative proportion as during later periods; and that the calcium thus liberated has not been redeposited with the shales. Explanations based on deposition of carbonates as shelf sediments and subsequent removal by erosion, or on an increased solubility of Ca^{2+} in the Archean oceans, are also discounted.

It appears that the thin crust of Archean time produced no extensive stable shelf or miogeosynclinal environments, which were important sites for carbonate deposition during the Proterozoic and Phanerozoic. It is suggested that carbonate deposition during the Archean took place largely in deep ocean basins, and that the mechanism for precipitation may have been photosynthetic reactions by algae living near the surface of the oceans. It seems likely that there were extensive oceanfloor deposits of carbonates during the Archean which were later resorbed into the mantle during ocean-floor spreading.

THE GEOCHEMICAL CYCLE OF CALCIUM

The behaviour of calcium in the exogenic cycle is characterized by the ease of weathering of its principal host minerals in igneous rocks and the ready separation of calcium, in solution, from the silicate products of rock decomposition. Calcium is, on average, the most abundant cation of modern river waters and is present in the ocean at close to its saturation concentration. Within seas of normal oceanic composition it is precipitated,

mainly organically, as calcium carbonate or as dolomite. The immediate control on the precipitation is the CO_2 content of the ocean, although over the long term it is governed by the buffering effect of silicate reactions on ocean water (Pytkowicz, 1967; Sillen, 1967a).

There have been various attempts to estimate the distribution of the elements between the different types and facies of sedimentary rocks. One of the latest is that of Horn and Adams (1966); these data provide the basis for Fig.1, which shows that carbonate rocks account for about half of the calcium budget of sediments. Most of the remainder is contained in argillaceous or arenaceous sediments where it may be present in detrital or authigenic silicates, carbonate minerals, and phosphates.
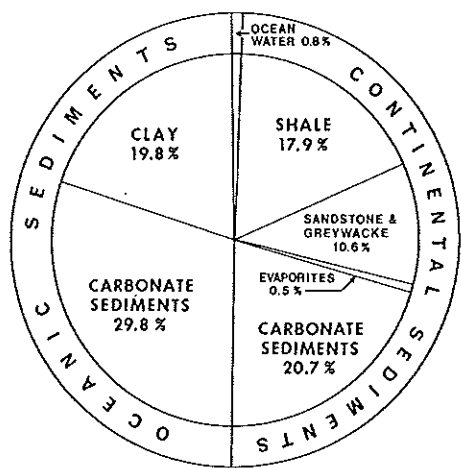

Fig.1. Distribution of calcium between continental and oceanic sedimentary lithologies and ocean water.

Estimates of the relative abundance of carbonate sediments vary widely depending on the method used. Ronov and Yaroshevsky (1967) give the proportions of different sediments from *measurement* of lithological maps of the world. They estimate 21% carbonate rocks in platform (shelf) sequences; 16.3% for geosynclinal sediments; and 41.5% for oceanic sediments. Computation based on the amounts of different elements *available* in igneous rocks for forming sediments are quite different, giving much lower carbonate abundances (7%; Brotzen, 1966). This apparent excess of calcium in the sedimentary environment has been a matter of some puzzlement. The computations made by Horn and Adams assumed 5.5% carbonates within continental sediments and 13.6% within oceanic sediments.

CARBONATE SEDIMENTS IN THE ARCHEAN

The relative abundance of limestone and dolomite noted above for Ronov and Yaroshevsky's compilation of sedimentary sequences from the Middle Proterozoic to the Neogene is in sharp contrast to their virtual absence among Archean sediments (following Stockwell, 1964, the Archean/Proterozoic boundary is considered to be 2.4 b.y.). Numerous workers have commented upon the rarity of beds of carbonate rock in the Archean.

Pettijohn (1943) in his classic study of the Archean sediments of the Canadian Shield summarizes some of the earlier observations on this topic and he notes that the absence of limestones is paralleled by a similar absence of quartzites. The paucity of limestones in the Canadian Shield appears to be characteristic of the Archean of the rest of the world (Ronov, 1964). An informal census of a number of our colleagues at the Geological Survey of Canada, who collectively have examined much of the Archean terrane of Canada, leads us to believe that discrete beds of carbonate account for a good deal less than 1% of Archean sediments of the Shield, and probably less than 0.1%.

Within the Archean Superior and Slave provinces of the Canadian Shield there are a number of elongate volcanic—sedimentary or "greenstone" belts of low metamorphic grade enclosed within a matrix of high grade metamorphic and plutonic rocks. The volcanic rocks, which may average 30,000—40,000 ft. in thickness (Goodwin, 1968), have been extruded in a crude sequence of mafic to felsic types. They are generally succeeded by sediments, up to 10,000 ft. thick, which are in large part derived from the underlying volcanics. Other sediments appear to be derived, in part at least, from pre-existing sialic material (Donaldson and Jackson, 1965; Goodwin, 1968) which on the average was of granodioritic composition. Most Archean sediments show features characteristic of rapid physical erosion, and deposition in an environment which may be likened to the flysch facies of younger geosynclinal belts. Current thought points to these greenstone belts having formed on a thin, very unstable crust (Anhaesser et al., 1969). Greywacke—shale are the typical rock types of the sedimentary sequences, with lesser amounts of arkose, impure quartzite, and iron formation. The rocks of the greenstone belts have usually been metamorphosed to no higher than lower greenschist facies and are as readily studied as many sediments of much younger age.

Whereas Archean sediments were probably deposited on a thin, unstable crust, this crust was thickened and stabilized at the end of the Archean by the injection of vast amounts of granitic material. Ronov (1968) notes that 50—60% of the granitic rocks of the world bear an apparent age of 2.6—2.7 b.y. One of the results of this thickening of parts of the crust was that in Proterozoic time extensive, stable shelf seas marginal to the continents developed. Within these seas chemically and physically mature sedimentary sequences, including carbonate rocks, were deposited.

Although there are but few sedimentary carbonates in the Archean, those that do exist have attracted a fair degree of interest because of their rarity. Armstrong (1960) brought together much of this information for the southern part of the Canadian Shield, comprising parts of the Superior and Churchill provinces. He classified the occurrences into the following types:

(1a) Limestone—orthoquartzite in a dominantly sedimentary succession: 25 definite, 8 possible occurrences.

(1b) Limestone—orthoquartzite in a dominantly volcanic succession: 9 definite, 3 possible.

(2) Carbonate rocks with ferruginous cherts and/or black shales: 10 definite, 3 possible.

(3) Carbonate—volcanic association: 6 definite, 3 possible.

(4) Limy—clastic sediments: 10 definite, 5 possible.

Ten feet of carbonate rock would be a typical measurement at these occurrences, although at a few the thickness may range up to hundreds of feet.

From the dominance of the limestone—orthoquartzite association in Armstrong's compilation it would appear that the carbonate rocks of the Archean were mainly formed during periods of temporary stability that quite locally simulated the miogeosynclinal environments of later geological periods. Another important mechanism was the precipitation of volcanic exhalative material.

Most authors who have discussed causes for the scarcity of carbonates in the Archean favour a more acid ocean in which the solubility of calcium was a good deal higher than the present ocean. This allowed the element to accumulate in ocean water, rather than precipitate. A high partial pressure of CO_2 in the atmosphere prior to extensive photosynthesis has been proposed as a mechanism for lowering the pH (Strakhov, 1964; Jolliffe, 1966; Cloud, 1968). The presence of HCl in the ocean has also been suggested (Hills, 1947). A quite different explanation is that limestones and quartzites were deposited on stable shelves, where they were more subject to erosion than the deeply downfolded rocks of the greenstone belts (Pettijohn, 1943).

EVIDENCE FOR THE SEPARATION OF CALCIUM FROM SILICATES IN THE EXOGENE ENVIRONMENT OF THE ARCHEAN

In previous discussions of Archean sedimentation, one of the topics that has been inadequately considered is the question whether the processes of weathering and sedimentation taking place during the Archean were as effective in separating calcium from silicates as they were in subsequent geological periods. If the rapid physical erosion and deposition of Archean time allowed only limited chemical attack of igneous rock detritus, this could provide a ready explanation for the paucity of carbonate rock during this period. Further, any calcium that was liberated during weathering could have precipitated with the greywacke-type sediments, its presence being obscured by dilution with rapidly sedimenting detrital material.

Shales of Archean age provide an appropriate medium to test whether calcium was separated from the silicate components of weathering. Chemical data for these shales may be compared with the composition of contemporaneous igneous source rocks or with data from younger shales. The authors had available a suite of 406 samples of shale (shale is used here as the collective term for argillaceous sediments and their metamorphic equivalents) taken from 153 localities within a number of greenstone belts of the Superior province of the Shield. The principal areas from which samples were taken are shown in Fig.2. Samples were taken from outcrops, and from drill cores provided by exploration companies. The sampling programme was of a rapid reconnaissance nature; no attempt was made to sample shale units in proportion to their total thickness or area of outcrop. Further, the dark, carbonaceous, shales probably were sampled in greater amount than their true proportion, because of their possible economic interest — although this is not reflected in their average composition compared to other shales (Table I). Because of the
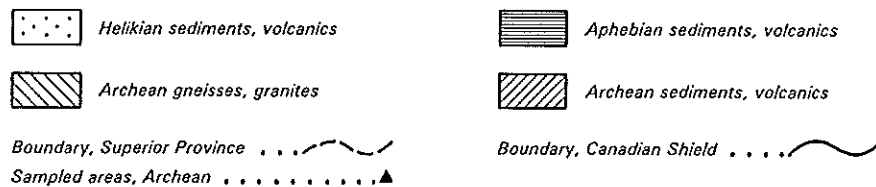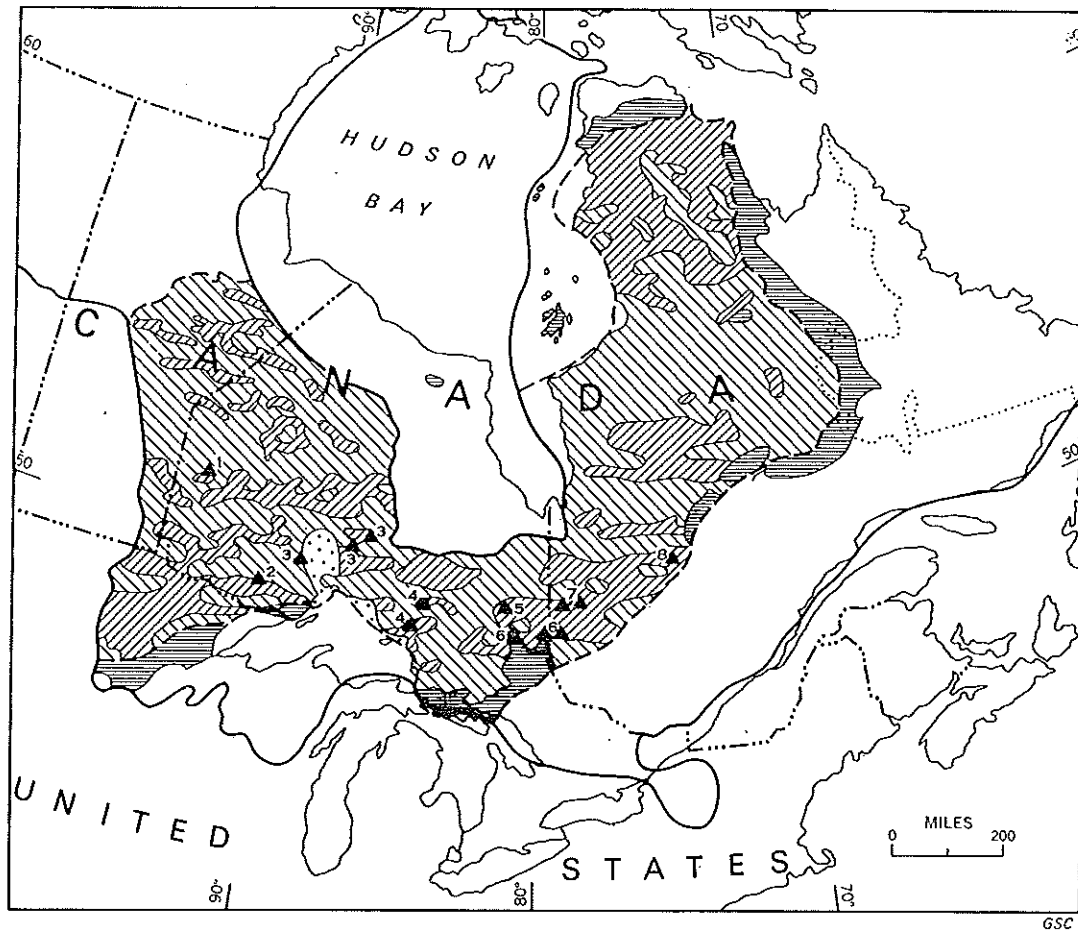
Fig.2. Superior Province of the Canadian Shield: Areas sampled for Archean shales. 1, Red Lake; 2, Atikokan; 3, Lac des Iles—Beardmore—Geralton; 4, Michipicoten—Oba; 5, Timmins; 6, Matachewan—Larder Lake—Kenojevis River; 7, Desmeloizes—Amos—Barrante; 8, Chapais.

reconnaissance nature of the sampling programme, the data cannot be considered to be an unbiased or "average" sampling of Archean shales of the region.

For the elements described below, Si, Al, Ti, Ca, Mg, and Mn were analyzed by a direct-reading emission spectrometric method involving sparking on a tape machine of a finely powdered solid solution of the sample dissolved in a borate flux (Danielsson, 1967). Analytical precision is similar to that reported by Cameron and Horton (1967) for major element analysis with fusion. Na and K determinations were made by atomic absorption analysis of the fused material used above, dissolved in dilute HNO_3. S was measured by X-ray fluorescence excitation of the ground, but unfused, powder. C was determined by subtracting the CO_2 liberated by hot HCl attack from the total CO_2 generated by combustion of the sample in oxygen.

TABLE I

Comparison of chemical composition of 406 Archean shales with average shale composition and comparison of high Ca shales with basalts

	A	B	C	D	E	F
SiO_2	58.0	55.76	55.09	58.9	48.9	49.7
TiO_2	0.73	0.71	0.86	0.78	0.94	1.00
Al_2O_3	16.9	17.56	16.30	16.7	13.5	14.9
ΣFe as Fe_2O_3	7.58	7.33	6.25	6.9	10.8	12.2
MnO	0.091	0.08	0.05	0.09	0.21	0.19
MgO	3.33	2.52	2.46	2.6	5.04	6.31
CaO	2.07	4.08	4.75	2.2	8.60	9.39
Na_2O	2.51	1.27	0.75	1.6	2.14	2.11
K_2O	2.73	2.76	3.01	3.6	0.95	0.32
C	0.74	0.78	0.99	0.6	1.45	−
S	1.25	−	−	0.24	2.36	−
CO_2	−	2.80	3.92	1.3	−	0.97

A: Arithmetic mean composition 406 Archean shales.
B: Geosynclinal clays and shales, Ronov and Yaroshevsky (1967). 455 analyses representing 11,151 specimens.
C: Platform clays, Ronov and Yaroshevsky (1967). 695 analyses of 10,746 specimens.
D: Shales mainly from geosynclines, Wedepohl (1969). 277 samples.
E: 28 of 406 Archean shales with 5.0% CaO or greater.
F: Average Archean basalt, Canadian Shield. Baragar and Goodwin (1969).

The interpretations of the chemical data presented here assume, as do most geochemical studies of the rocks of the greenstone belts, that the rocks have acted as a closed system for the nonvolatile components during the relatively low grade of metamorphism of most samples. For the volcanic rocks of the greenstone belts, there is little to contradict this general assumption, and some supporting evidence has been presented (Hart et al., 1970). For argillaceous rocks this assumption has been largely confirmed by the studies of Shaw (1956) and Zwart (1958), although Shaw's data for calcium was difficult to interpret because of sampling bias.

A histogram of the frequency distribution of CaO for the 406 samples of shale (Fig.3) shows that values in the range of 1—2% CaO are most common. The midpoint of this class is close to both the geometric mean of 1.43% CaO and to the median of 1.51% CaO (Table II). The arithmetic mean, at 2.07% CaO, is somewhat higher because of the influence of a number of samples with a high content of calcium. For these samples the high calcium does not seem to be caused by carbonates; rather the composition of 28 samples with 5.0% CaO or greater (Table I) approximates that of a basic igneous rock. It is presumed that these samples are basic volcanic tuffs.

If data for the Archean shales are compared with published averages for various post-Archean shales (Table I) it may be seen that the Archean samples are similar to, or are lower in calcium, than the younger shales. Yet the Archean shales were not derived from low-calcium igneous rocks. Geological evidence indicates that for most of the areas sampled,
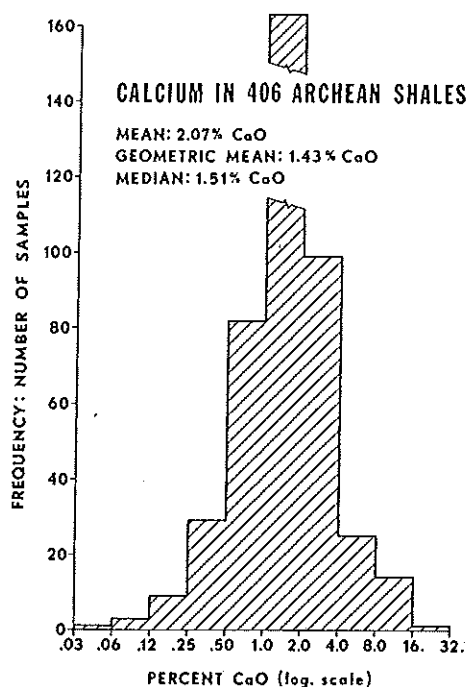
Fig.3. Frequency distribution of calcium in 406 Archean shales.

TABLE II

Statistical data on the major element composition of 406 samples of Archean shale from the Superior province of the Canadian Shield

	Arithmetic mean	Geometric mean	Standard deviation	Median
SiO_2	58.0	57.7	6.0	58.3
TiO_2	0.73	0.68	0.26	0.71
Al_2O_3	16.9	16.6	2.8	17.0
ΣFe as Fe_2O_3	7.58	6.81	3.6	7.20
MnO	0.091	0.075	0.070	0.080
MgO	3.33	2.75	1.98	3.10
CaO	2.07	1.43	2.20	1.51
Na_2O	2.51	2.12	1.10	2.50
K_2O	2.73	2.22	1.36	2.60
C	0.74	0.26	2.13	0.20
S	1.25	0.29	3.40	<0.10

the dominant source of sediments was contemporaneous volcanic rocks within the same greenstone belt. These volcanics have a relatively high calcium content (Table III). A lesser number of the sections sampled may have been derived from pre-existing sialic material of average granodioritic composition. A possible example is the Pontiac Group (Goodwin and Ridler, 1970). The sialic source material may be represented (Table III) by Fahrig and Eade's (1968) average Archean rock, which is largely composed of samples from high grade metamorphic and plutonic terrane of the craton. Again, this material is higher in

TABLE III

Comparison of Archean shales with possible source rock

	A	B	C	D	E	F	G
SiO_2	53.9	52.6	66.8	65.1	59.3	58.0	− 2%
TiO_2	0.97	1.05	0.50	0.50	0.77	0.73	− 5%
Al_2O_3	15.0	15.1	14.8	16.0	15.3	16.9	+10%
ΣFe as Fe_2O_3	10.5	11.0	4.43	4.83	7.81	7.58	− 3%
MnO	0.18	0.18	0.10	0.08	0.14	0.091	−35%
MgO	5.03	5.23	1.78	2.3	3.64	3.33	− 9%
CaO	7.45	7.94	2.55	3.4	5.46	2.07	−62%
Na_2O	2.88	2.80	4.06	4.1	3.44	2.51	−27%
K_2O	0.65	0.55	1.78	2.7	1.40	2.73	+95%

A: Average Archean volcanic rock, Baragar and Goodwin (1969).
B: Average Archean mafic volcanic rock, Baragar and Goodwin (1969).
C: Average Archean salic volcanic rock, Baragar and Goodwin (1969).
D: Archean, sialic material, Canadian shield, Fahrig and Eade (1968).
E: 50% B, 25% C, 25% D, representing hypothetic source rock for 406 Archean shales, F.
G: Percent difference of F compared to E.

calcium than the sampled shales. There is thus no evidence that the shales were derived from a calcium-poor source rock; indeed it seems likely that the Archean crust was more mafic than that of today (Engel, 1963).

We may assess the composition of a hypothetical source rock for the sampled shales (Table III). This is based on two very approximate estimates. Firstly, that the source areas were 25% sialic material and 75% volcanic. Secondly, that the volcanic material was two parts mafic to one part salic. Although Baragar and Goodwin (1969) found that 11.7% of the volume of volcanic rocks in the greenstone belts that they examined were salic, these rocks are likely to have contributed in greater proportion than that to the sediments. This is because the sediments of the greenstone belts generally lie above a mafic to salic volcanic sequence. The estimated ratio of sialic to volcanic material is based on the widespread impression, among field geologists who have studied this part of the shield, that volcanic source rocks dominated. For other areas, such as the sediments of the Slave province, a quite different estimate may be more appropriate.

Comparing the average mean composition of the Archean shales with this hypothetical source rock, the composition is quite similar for the less mobile components: Si, Al, Fe, Ti. The shales are depleted in those elements — Na and particularly Ca — that usually pass into solution upon weathering and are enriched in K which is normally enriched in argillaceous rocks. Mg, which shows a more limited tendency towards mobility in the sedimentary environment than either Na or Ca is slightly depleted. It is not certain to what degree analytical bias may be responsible for the observed differences in Mn at the low concentrations of this element. Conway (1942) has estimated that 67% of the Ca, 44% of the Na, and 20% of the Mg is dissolved from igneous rocks during one weathering cycle. The corresponding loss for the Archean shales compared to the source rock given

above is 62% Ca, 27% Na, 8% Mg. On this basis, weathering during Archean time produced results not dissimilar to that of younger geological periods. These values and the conclusion are based on a speculative source rock composition, which time and increased geological knowledge will see revised.

From the above evidence it appears that calcium was removed from igneous rocks during weathering in Archean time and was not later returned to the shale component of the sediments of the greenstone belts. It would seem reasonable to extrapolate the latter conclusion to the rest of the sedimentary sequences, principally the greywackes. In most belts the shales and greywackes are intimately associated. Data collected by Eade and Fahrig (1971) on the average composition of the total Archean sedimentary sequences of the New Quebec (2.7% CaO) and the Fort Enterprise (3.7% CaO) areas supports this extrapolation.

THE PROBLEM OF CARBONATE DEPOSITION DURING THE ARCHEAN

Because calcium passed into solution on weathering and was not reprecipitated within the sediments of the greenstone belts, it must have been precipitated elsewhere or was held in solution in the oceans. As was pointed out above, the latter has been the favoured choice of most workers. This concept appears to be supported by considerations which indicate that the CO_2 content of the atmosphere during Archean time was higher than that of today. The long term equilibrium level of CO_2 in the atmosphere is maintained by the rate of weathering. An increase in the CO_2 partial pressure of the atmosphere (say by volcanic activity) stimulates a greater growth of land plants, which in turn increases the level of CO_2 and organic acids in the underlying soil. Greater quantities of soluble cations are therefore produced by weathering and are carried to the sea. There calcium and magnesium carbonates are precipitated and, at least temporarily, remove CO_2 from the atmosphere—ocean system. Prior to the development of land plants the partial pressure of CO_2 must have been greater to maintain the same rates of weathering. On the basis of an estimate that the partial pressure of CO_2 in soils supporting higher land plants is 10—100 times that of the atmosphere, Holland (1965) has estimated that the CO_2 level of the pre-Silurian atmosphere was 10—100 times that of the present atmosphere. More recently, Cawley et al. (1969) have suggested a level of no more than 5 times present atmospheric level on the basis of studies of weathering processes in barren areas of Iceland.

If the pH level of the ocean was solely determined by the level of CO_2 in the atmosphere, the increased concentration of CO_2 in the Archean atmosphere might account for a build up of Ca^{2+} in the oceans of that time. The relatively short residence time of calcium (1.2 m.y. on the basis of recent river discharge; 4.5 m.y. on the average over the last 1.5 b.y.; Ronov, 1968) indicates that there would have been a massive build-up of this element over the long time span of the Archean if little had precipitated. However, it is unlikely that such a build-up could have occurred. Sillen (1961) first suggested that the oceans are buffered by reaction with silicate minerals, as well as by the CO_2—CO_3^{2-} system. This idea has since been amplified and largely confirmed by the work of Sillen (1967a, b), Holland

(1965), Garrels (1965), Mackenzie and Garrels (1965, 1966a, b), Mackenzie et al. (1967), and Siever (1968). Pytkowicz (1967) has suggested that over the short term (<1000 years) the CO_2–CO_3^{2-} system regulates oceanic pH, but silicates have long-term control. In an ocean held at a more or less constant pH by silicate reactions, even if this be a lower pH than that of today's oceans, the solubility of Ca^{2+} actually decreases as the CO_2 pressure increases (Holland, 1965). Thus higher atmospheric pressure of CO_2 cannot be appealed to as a valid explanation for the absence of carbonate rock.

The remaining explanation is that carbonate rocks were deposited in parts of the crust where they have since been destroyed or buried. Mention has already been made of the suggestion by Pettijohn (1943) that carbonate rocks could have been removed by erosion; yet another possibility is that they could have been metamorphosed beyond recognition. However, in those provinces of the Canadian Shield that are somewhat younger than the Superior and Slave provinces, considerable volumes of Aphebian miogeosynclinal rocks, including thick carbonates, have been deposited — often in association with Archean rocks — then folded and metamorphosed. Yet these rocks are easily recognised today. If similarly extensive sequences were deposited during the Archean why were they not preserved within the Superior and Slave provinces?

Could it be that carbonates were deposited in the deep ocean basins during the Archean and have since become resorbed into the mantle or hidden below younger oceanic sediments? Through the geological record carbonate rocks are generally found in shelf environments. From the Proterozoic on, with the beginning of stable conditions in parts of the crust, epicontinental shelf deposits contain thick sequences of carbonate rock. In the present ocean, however, relatively little carbonate is being deposited in epicontinental shelf environments; most instead is accumulating in the ocean basins. This change has been attributed by Twenhofel (1939), Kuenen (1950), and others to the development of *Globigerina* and other planktonic foraminifera during the Cretaceous. They argue that since this time the ocean-wide precipitation of carbonates as foraminiferal tests has fundamentally altered the locus of deposition of carbonate rocks.

Berger (1970) has given sound reasons to doubt this hypothesis. Within the present oceans, the rate of organic precipitation of $CaCO_3$ is greatly in excess of the supply of Ca^{2+} to the oceans. Thus the rate by which precipitation exceeds dissolution of carbonate on the sea floor is the critical factor for determining areas of carbonate accumulation, rather than the precipitation rate alone. In terms of this control, Berger has distinguished two broad types of marginal sea or ocean basin, these being determined by water circulation patterns. The lagoonal type has deep water outflow; their waters are of high salinity, low nutrient content and are aerated. Estuarine basins have deep water inflow; their waters have high nutrient contents and low salinity. They tend to be anaerobic, their sediments are rich in organic matter, and their bottom waters contain higher levels of CO_2. Although their high nutrient content stimulates greater growth and greater biological precipitation of $CaCO_3$, dissolution of $CaCO_3$ is also greater in the CO_2-rich bottom waters. Thus $CaCO_3$ accumulates faster in lagoonal basins. The present Atlantic is lagoonal relative to the Pacific and accumulates carbonate sediments to a greater extent than the latter.

Berger attributes the large-scale transfer of carbonate sedimentation from shelves to ocean that occurred at the end of the Mesozoic, to a shift from a pattern of basin—shelf fractionation of $CaCO_3$ to one of basin—basin fractionation; these changes being determined by an increasing exchange of water between the major ocean basins and by a reduction in the volume of the continental marginal seas.

During much of the Archean it appears that the crust was so thin and unstable that conditions resembling the epicontinental seas of the Proterozoic and Phanerozoic were quite local, ephemeral events. It does not seem unreasonable to suggest that at this time carbonate sedimentation was largely confined to parts of the ocean basins. This earlier appealed to Kuenen (1950) as a logical explanation for the absence of carbonates in the Precambrian. Precipitation of carbonate could have been world-wide in the Archean seas and oceans with accumulation taking place preferentially in those areas of the ocean bottom where depth and CO_2 content did not encourage a high rate of dissolution. The agency for precipitation could well have been photosynthetic algae floating near the surface of the oceans. Schopf and Barghoorn (1967) believe that organic spheroids found in the 3.1 b.y. old Fig Tree Series of South Africa are the remnants of unicellular, non-colonial algae, possibly related to the modern coccoid blue—green algae and which had a photosynthetic ability.

Although chiefly confined to parts of the deep ocean basins, carbonate sediments would also have accumulated in local areas of the unstable continents, where temporary conditions favoured stability. The black carbonaceous muds typical of the greenstone belts may have been deposited in an environment of high CO_2 content generated by the decomposition of organic material: an environment unfavourable for carbonate deposition. There is some evidence within the Canadian Shield that the carbonate content of Archean sediments may be broadly correlated with the stability of the region during sedimentation. Reilly and Shaw (1967) have estimated the calcium content of the metasedimentary rocks of the Red Lake—Lansdowne House area of northwestern Ontario as 4.62% CaO. This is rather higher than the Archean shale average given earlier and the data for other areas of the shield quoted from Eade and Fahrig (1971). In part of the area evaluated by Reilly and Shaw, Donaldson and Jackson (1965) have identified the Archean sediments as being more mature than most other Archean sediments of the shield, being derived from a sialic source area. In South Africa the Archean Moodies Series, which appears in part at least to have been deposited on a low-lying stable land surface, contains calcareous quartzites. These rocks have been classed as molasse facies by Anhaeusser et al. (1967).

CONCLUSIONS

The data presented in this paper on the composition of Archean shales from the Canadian Shield demonstrate that during the Archean much of the calcium in igneous rocks was effectively taken into solution during weathering. The thin, unstable crust of the period did not allow the development of extensive, stable seas marginal to the continents within which carbonate sediments could be precipitated and accumulate, although thin

carbonates did accumulate in places of local, temporary stability. Instead, carbonate material that was precipitated rather widely through the earth's oceans and seas (possibly by photosynthetic algae) accumulated extensively only in parts of the deep ocean of favourable depth and CO_2 content. These pelagic carbonate deposits have almost certainly since been moved into submarine trenches or into the mantle by the movement of the crustal plates on which they rest. Here these masses of carbonate rocks may have played an important part in Archean or post-Archean tectonics and magmatism along the plate margins. The thickening and stabilization of many parts of the continental crust that occurred at the end of the Archean allowed the development of stable epicontinental seas during the Proterozoic and most subsequent geological periods, which providing sites for the deposition of great thicknesses of carbonate rocks. Thus the crustal evolution at the close of the Archean produced a major shift in the locus of deposition of carbonate rocks from the oceans to the continents, which has lasted for most of post-Archean time. Calcium has presented a puzzling anomaly in geochemical balance calculations. In computing the proportion of limestones and dolomites relative to other sediments, it is important to consider the migration of carbonate sedimentation between the ocean basins and epicontinental seas throughout geological history.

ACKNOWLEDGEMENTS

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