NBS 18 and 19 for which there are no accepted values but our preliminary determinations give −5.15‰ PDB and +1.87‰ PDB respectively.

The results presented in Table 1 show that the phosphorites from the Agulhas Bank, Blake Plateau, Californian Borderland and Chatham Rise, which are all considered to be phosphatized carbonates from petrographic[6] and carbon isotope studies[4–6], all have $\delta^{34}S$ values similar to sulphate evaporites of the same age. This suggests that the phosphatizing medium was open seawater. The phosphatized carbonates from the Moroccan Shelf are slightly enriched in ^{34}S relative to the seawater at the time of formation. This is the result of bacterial sulphate reduction. One of these samples (1022(1)) contains an appreciable amount of light organically derived carbon and is associated with pyrite which is also a by-product of this process. It is impossible to tell whether the upper boundary of the sulphate reduction zone was within the sediment or above as in an anaerobic basin.

The sample from the Phosphoria Formation is also enriched in ^{34}S compared with the supposed seawater value at the time of formation. Our value (+15.3‰) compares well with that of previous workers (+15.0‰)[8] who have analysed a suite of samples from this deposit and interpreted their data as evidence for genesis in an early diagenetic reducing environment. This is consistent with the light carbon isotopic composition of these phosphorites[5,6].

The francolite samples from the Peru/Chile Shelf, Namibian Shelf (pelletal) and onshore South Africa all contain structural sulphur which is isotopically much lighter than that of the seawater during formation. This implies that oxidation of H_2S occurred before the sulphate was incorporated into the francolite structure. This can only occur at the interface of the sulphate reduction zone and the overlying suboxic or oxic zone but below open access to oxic seawater. This may account for the fact that some of the Peru/Chile phosphorites have been reported to form at the periphery of the zone where the sediments are anoxic[19]. The $\delta^{13}C$ data for the offshore deposits of Peru/Chile and Namibia (pelletal) suggest that they are phosphatized carbonates[4–6]. Dissolution of these carbonates may have been aided by the local increase in acidity on oxidation of the H_2S. There is a possibility that the onshore South African samples have light sulphur isotopic compositions due to weathering[8]. If this were the case one would expect sample SA/V3(C)/79 to have a lighter $\delta^{34}S$ value than sample SA/V7(B)/79 which has been less weathered. Since it is the other way round, these $\delta^{34}S$ values are thought to be essentially unaltered.

The Recent concretion from the Namibian Shelf has a slightly lighter $^{34}S/^{32}S$ composition than present-day seawater. This may also be the result of oxidation of H_2S which is known to be present in these sediments[12]. This sample contains a substantial amount of isotopically light carbon ($\delta^{13}C = -8.9$‰) derived from the bacterial sulphate reduction process but only a small depletion of ^{34}S relative to seawater. This probably reflects the varying sizes of the seawater reservoirs; the bicarbonate reservoir being small ($140\ \mathrm{mg\ l^{-1}}$)[10] and thus isotopically sensitive to small inputs whereas the sulphate reservoir is larger ($2{,}712\ \mathrm{mg\ l^{-1}}$)[10] and therefore isotopically less sensitive to inputs.

The sulphur composition of sedimentary francolite has great potential in unravelling past environments of formation, especially when used in conjunction with its structural carbon isotopic composition. This study alone suggests that both authigenic francolite and phosphatized carbonate can form in both sulphate reducing conditions and more oxic conditions. It has also pin-pointed the depth of formation in the sediment column for the francolite samples from Namibia, onshore South Africa and offshore Peru/Chile to the sulphate reducing–oxic porewater interface. It is interesting to speculate that the oxidation of H_2S, referred to above, would produce a slight increase in acidity which may favour precipitation of phosphate relative to carbonate[20] and be a pertinent environmental control.

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Possible limits on the composition of the Archaean ocean

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It has been suggested that the partial pressure of carbon dioxide in the terrestrial atmosphere was larger in the past than it is at present[1–4]. In particular, partial pressures of 100–1,000 times those of the present have been invoked for the early Earth as a means of insuring equable climates at a time when the Sun was significantly less luminous[5–7]. While the climatic argument is not conclusive[8], it is worth considering whether the geological record is in any way inconsistent with the proposed high partial pressures of carbon dioxide. I now examine the potential impact of high carbon dioxide partial pressure on ocean chemistry and ask what constraints are imposed by the known record of chemical sedimentation through time. The evidence consists of the persistence throughout almost the entire sedimentary rock record of calcium carbonate and sulphate precipitation. I adopt a uniformitarian point of view that assumes no very great change in the conditions for the deposition of these chemical sediments. The methods of Holland[9] are used to set limits on the composition of the water from which precipitation occurred. I find no inconsistencies between the sedimentary rock record and presumed higher partial pressure of carbon dioxide early in Earth history, provided that high partial pressure was accompanied by a generally lower *p*H for seawater, higher concentrations of calcium and bicarbonate ions, and lower concentrations of carbonate and sulphate ions.

For specified values of the *p*H and carbon dioxide partial pressure the concentrations of carbonate ions and bicarbonate ions in solution are determined by equilibrium relationships among the carbon-bearing species[10]. At a temperature of 25 °C and pressure of a few atmospheres the relationships are

$$[\mathrm{H^+}][\mathrm{HCO_3^-}] = 10^{-7.5}P \qquad (1)$$

$$[\mathrm{H^+}]^2[\mathrm{CO_3^{2-}}] = 10^{-16.6}P \qquad (2)$$

where [X] denotes the concentration of dissolved species X in $\mathrm{mol\ l^{-1}}$ and P denotes the partial pressure of carbon dioxide in

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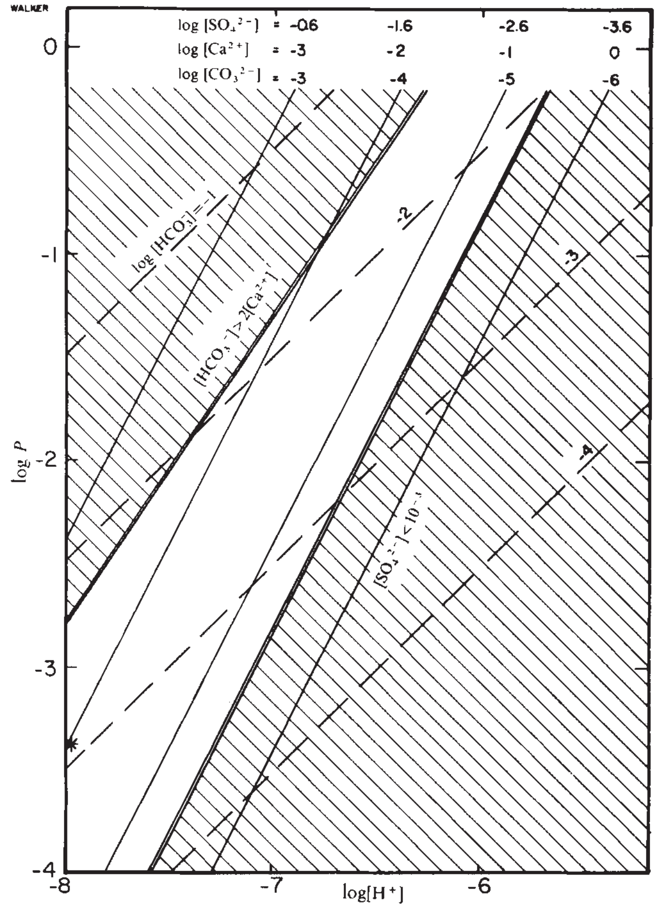

Fig. 1 Concentrations of dissolved species in seawater as functions of the carbon dioxide partial pressure and the concentration of H^+ ions. Concentrations are expressed in mol l^{-1} and the partial pressure in atmospheres. Equilibrium in the carbonate system yields the dashed lines for bicarbonate concentration and the solid lines for carbonate concentration. The values for calcium and sulphate concentrations are derived by assuming a constant product of calcium and carbonate concentrations and of calcium and sulphate concentrations. The star indicates the composition of present day seawater. The cross-hatched regions correspond to compositions that are not consistent with the sedimentary rock record.

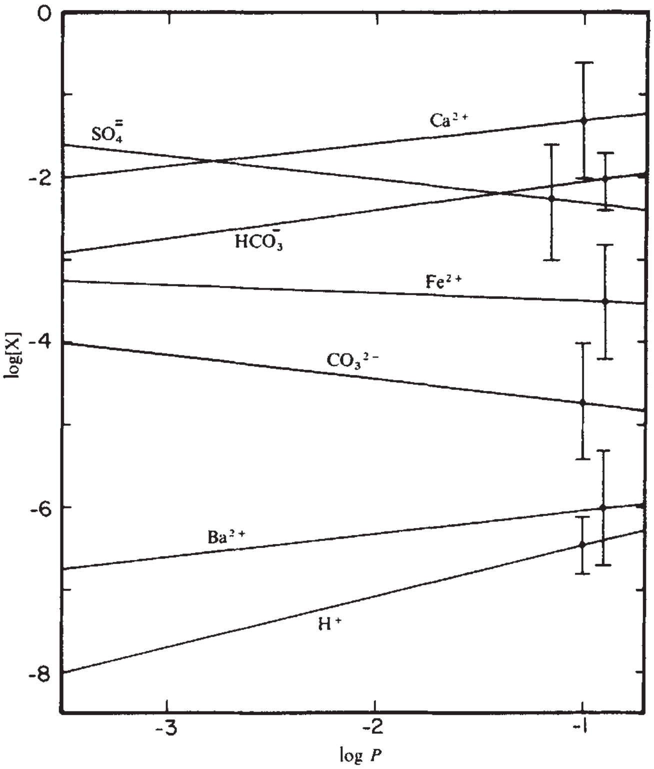

Fig. 2 Seawater composition consistent with the rock record as a function of carbon dioxide partial pressure. The lines correspond to the middle of the allowed region of Fig. 1. The bars represent the range of allowed concentrations. The barium ion concentration corresponds to the assumption of constant product of barium and sulphate concentrations. The iron concentration corresponds to an ocean saturated with respect to siderite.

atmospheres[11]. I ignore the weak dependence of the equilibrium constants on pressure and temperature. Constant carbonate and bicarbonate ion concentrations are shown as solid and dashed lines in Fig. 1.

Deposits of calcium carbonate are present in sedimentary rocks of all ages extending back to the oldest yet discovered[12]. From the persistence of calcium carbonate precipitation in the sedimentary rock record I estimate that the ocean has always been close to saturation with respect to calcium carbonate, as it is today. With the assumption that the product of calcium and carbonate ion concentration has not changed markedly with time, then,

$$[Ca^{2+}][CO_3^{2-}] = 10^{-6} \tag{3}$$

where values for the present day oceanic average are as quoted by Broecker[13]. In Fig. 1, therefore, the lines of constant carbonate ion concentration apply also to the calcium ion concentration, with the values shown.

Sedimentary sulphate evaporites are known from rocks on all the contents except Antarctica and of all ages extending back to 3,500 Myr ago[14]. These sulphate evaporites include massive deposits tens of metres thick and covering thousands of square kilometres in horizontal extent. Many of them contain evidence of having been initially precipitated as gypsum ($GaSO_4.2H_2O$). With allowance for the ease with which evaporite deposits may have been destroyed by weathering processes, the record suggests that the mineralogy of the initial stages of evaporite formation has not changed significantly with time. The record is at least consistent with the uniformitarian assumption that gypsum was the first abundant mineral, after carbonate, to precipitate from evaporating seawater in the Precambrian as in the Phanerozoic[15]. The record is not sufficiently good to determine whether the proportions of carbonate and gypsum have changed with time. It is therefore conservative to assume that the product of calcium and sulphate ion concentrations has not changed with time. Then

$$[Ca^{2+}][SO_4^{2-}] = 10^{-3.6} \tag{4}$$

and the lines of constant carbonate concentration in Fig. 1 apply also to sulphate, with values as shown. The oxidation state of sulphur in the Archaean ocean and atmosphere has been discussed by Brimblecombe and Walker[16,17]. Even in the absence of free oxygen it seems likely that photochemical reactions in the atmosphere and surface ocean would have yielded abundant sulphate from volcanic emanations of hydrogen sulphide and sulphur dioxide. The banded iron-formations of the Archaean and early Proterozoic provide evidence for abundant ferrous ions in solution[18–21], which argues against high sulphide concentrations because of the low solubility of iron sulphides[22].

Some constraints on the composition of seawater follow from the occurrence of massive deposits of evaporitic sulphate minerals some tens of metres thick. An approximate lower limit on the sulphate concentration can be derived from the requirement that such a deposit accumulate in a reasonable period of time. A generous upper limit on the evaporation rate in arid terrestrial environments is 10 m yr^{-1} (ref. 23). At this rate and at a sulphate concentration of 10^{-3} mol l^{-1} it would take 13,500 yr to accumulate a layer of gypsum 1 m thick. The stability of evaporitic environments for times longer than 100,000 yr seems unlikely, so sulphate concentrations $<10^{-3}$ mol l^{-1} are probably not consistent with the geological record. The excluded compositions are indicated by shading on the right of Fig. 1. A lower limit on carbonate ion concentration and upper limit on calcium ion concentration correspond to the lower limit on sulphate ion concentration.

If evaporating seawater is to precipitate first calcium carbonate and then calcium sulphate then the calcium ion concentration must exceed one half the bicarbonate ion concentration[9]. If this were not the case, precipitation of calcium carbonate would exhaust the calcium ions in seawater leaving none to enter gypsum. The persistence of calcium sulphate evaporites in the sedimentary rock record therefore sets an upper limit on the bicarbonate ion concentration indicated by the shaded area on the left of Fig. 1. The clear band in the middle of Fig. 1 depicts compositions of seawater that are consistent with the sedimentary rock record in the sense that they would have yielded no obvious secular changes in the minerals deposited during the initial stages of evaporite formation. The allowed concentrations are summarized as functions of carbon dioxide partial pressure in Fig. 2. Higher carbon dioxide partial pressure on the early Earth would have corresponded to generally higher concentrations of calcium, bicarbonate and hydrogen ions and generally lower concentrations of carbonate and sulphate ions. Cameron[24] has argued from sulphur isotope data that sulphate concentrations were $<10^{-3}$ mol l^{-1} in the Archaean ocean.

Modern seawater is close to saturation with respect to the mineral barite ($BaSO_4$) (ref. 10). The concentrations of barium ions shown in Fig. 2 are derived assuming that the product of barium and sulphate ion concentrations has not changed with time. The generally higher barium concentrations that correspond to higher carbon dioxide partial pressures are consistent with the deduction of Veizer *et al.*[25] that the concentration of barium ions was enhanced by about a factor of 10 in the Archaean ocean. The concentrations of iron ions are those that yield saturation with respect to the mineral siderite ($FeCO_3$), calculated in accordance with the factors described by Holland[19]. High concentrations (exceeding 10^{-4} mol l^{-1}) of dissolved ferrous iron in Archaean and early Proterozoic seawater[26] are favoured as a source of the chemically precipitated iron in banded iron formations[18–21].

In the absence of silica-precipitating organisms, the oceans were presumably approximately saturated with respect to amorphous silica. Holland[9] estimates a concentration of dissolved silica of about 100 p.p.m. This high concentration of dissolved silica is presumably responsible for the abundance of chemically precipitated siliceous sediments in formations of Archaean and early Proterozoic age. In the absence of extensive continental land masses[27] there were presumably few large deposits of evaporitic halite (NaCl). Enhanced concentrations of sodium and chloride ions in Archaean seawater are a possibility. The oceans would be far from saturation with respect to halite even if all known evaporite deposits were dissolved[15].

I have not discussed possible reasons for the postulated high pressures of carbon dioxide on the early Earth. Mechanisms that relate to the rate of weathering of continental rocks[6,28,29] cannot be invoked for the Archaean era, when oceanic composition was dominated by interactions with the mantle rather than with continental rocks[25]. In general terms, the carbon dioxide partial pressure would have been determined by the partitioning of carbon between the fluid (ocean plus atmosphere) and solid (rock) phases. Higher internal temperatures and more tectonic activity on the early Earth may have promoted the remobilization of carbon from the solid to the fluid phases[1,30]. In the conditions described here, the fraction of total terrestrial carbon in the fluid phase is still small. A more precise understanding of the controls on the composition of the Archaean ocean and atmosphere undoubtedly involves the details of the interaction of seawater with mantle rocks[25,27,31].

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Seasonal sedimentation of phytoplankton to the deep-sea benthos

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Until recently the deep sea was considered to be a particularly stable environment[1], free from seasonal variations. However, atmospheric storms may cause periodicity in deep-ocean currents[2] and nepheloid layers[3] while seasonality in the particulate flux to the deep sea is known to occur in the Sargasso Sea[4,5] and Panama Basin[6]. Evidence is presented here of a similar seasonal pulse of detrital material to bathyal and abyssal depths in temperate latitudes; this material seems to be derived directly from the surface primary production and to sink rapidly to the deep-sea benthos. Considerable sedimentation occurs soon after the spring bloom and continues throughout the early summer. This process acts as a pathway for the descent of carbon from the euphotic zone, providing a periodic food source for the deep pelagic and benthic communities.

Since 1979, routine photo-transects obtained with the Institute of Oceanographic Sciences' epibenthic sledge[7–9], and time-lapse photography using the Bathysnap system[10], have revealed a patchy, detrital layer on the sea floor in the Porcupine Seabight in the north-east Atlantic (50° N, 13° W), at depths between 1,370 and 4,100 m, during the 4 months from April to July. Six cruises conducted at other times of the year have failed to detect the presence of the material. On 1 April 1982, Bathysnap was deployed at 2,000 m to take hourly photographs over a 33-day period. Detrital particles began to accumulate on the sediment surface from 24 April, but there was no appreciable sedimentation until 30 April, when the detrital layer increased rapidly over a 38-h period (Fig. 1). No substantial increase occurred during the remaining 2 days of observation, but considerably more of the sediment surface was covered in the same locality by the end of May in both 1981 and 1982. A further deployment at the end of July 1982 for 30 days at