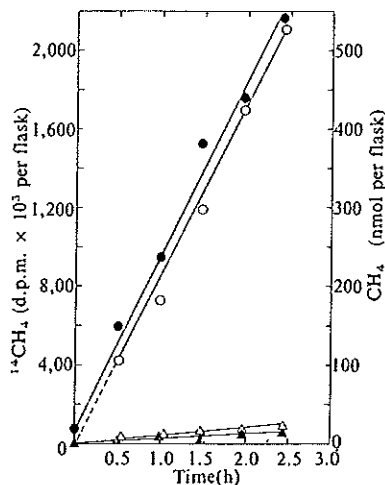Fig. 2 Formation of CH_4 and $^{14}CH_4$ by homogenates amended with ^{14}C-methanol (12.5 μCi per flask; 0.28 μmol per flask; ICN Co., initial specific activity 45 mCi mmol^{-1}). Uninhibited flasks: $^{14}CH_4$, ●; CH_4, O. Flasks inhibited with BES (1 g): $^{14}CH_4$, ▲; CH_4, △. Flasks (total volume, 263 ml) contained 145 ml of sediment homogenate (1:1 with bay water), 25 ml bay water and 65 ml of homogenized *S. foliosa* materials (1:1 with bay water). Flasks were incubated in the dark (20 °C) with constant rotary shaking (200 r.p.m.). $^{14}CH_4$ and $^{14}CO_2$ were determined by gas chromatography–gas proportional counting procedures[27] and CH_4 by gas chromatography[18].

methanogenic pathways. Therefore, the ecological niche occupied by methanogens seems broader than previously predicted[1,2]. As most studies on sediment methanogenesis used ^{14}C-acetate or ^{14}C-bicarbonate as precursors of methane[6,21], results can be misleading with regard to zones of methane production and may also underestimate carbon budgets. Future studies should be directed at determining the contribution methanol and methylated amines make to the methane formed in various aquatic sediments. Because carbon isotope enrichment factors are significantly greater in methanol-grown methanogens (~70‰)[23,26] than in hydrogen plus carbon dioxide-grown cells (~40‰)[22], such information would be of importance for the interpretation of carbon isotopic fractionations of methane during methanogenesis in anoxic sediments.

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Sulphate and sulphate reduction in early Precambrian oceans

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Sulphate reduction generally causes isotopic fractionation of sulphur[1]. Modern sedimentary sulphide is largely produced by biogenic reduction of sulphate and is typically enriched in ^{32}S (ref. 2). This is balanced by excess ^{34}S in the oceanic sulphate reservoir and evaporites[3]. High-temperature, inorganic reduction of sulphate may also cause fractionation[4,5]. Since the work of Ault and Kulp[6], there has been interest in finding the beginnings of sulphate reduction in the sedimentary record. This is important for several reasons. First, sulphate-respiring bacteria are a milestone of evolution[7,8]. Second, it established the exogenic sulphur cycle in an essentially modern form. This, with the interconnected oxygen and carbon cycles, regulates the composition of atmosphere and oceans[9-11]. Third, widespread evidence of sulphate reduction in rocks of a given age and younger indicates that sulphate was established as a major constituent of seawater. In addition to identifying a stage in the evolution of an oxygenated environment[10], this has important metallogenic implications. Schidlowski[8] has recently concluded that dissimilatory reduction commenced at 2,800–3,100 Myr in an Archaean ocean that had relatively high concentrations of sulphate. I review here the published data and present additional sulphur isotope analyses obtained from the early Precambrian of South Africa. These results indicate that sulphate was a minor component of Archaean and early Proterozoic ocean water, probably <0.001 mol l^{-1}. The concentration had increased by ~2,350 Myr to levels allowing significant biogenic and inorganic fractionation and the partitioning of $^{32}S/^{34}S$ in the exogene cycle.

Information provided by Precambrian evaporitic sediments is limited. The oldest Proterozoic evaporites for which data are published have maximum ages of only 1,300 Myr. These have $\delta^{34}S$ values of up to 30‰ (refs 12,13), indicating that sulphate reduction was well established at that time. Stratiform barites found in $>3,200$ Myr rocks on several continents have $\delta^{34}S$ of ~0‰ indicating no significant isotopic partitioning in the oceans of that time.

Figure 1 gives the means and standard deviations of $\delta^{34}S$ for groups of sedimentary sulphide of Archaean ($>2,500$ Myr) and Aphebian (2,500–1,800 Myr) age. Where geological information permits, the latter have been subdivided into 'Aphebian 1' ($>2,300$ Myr) and 'Aphebian 2' ($\geq2,300$ Myr). Data have been excluded where the rocks may have been affected by metasomatism. Care must be taken in interpreting the statistical data, as the sample collections vary greatly in size and in stratigraphical and geographical extent.

Several generalized fields have been outlined in Fig. 1, related to the genesis of the sulphides. Magmatic sulphides have $\delta^{34}S$ values close to 0‰ and low variance. Groups with more positive $\delta^{34}S$ values, but also low variance, have been identified as the product of partial reduction of ocean sulphate at high temperature, for example, the Red Sea[14] and in Homestake Mine sediments[15]. However, depending on the degree of fractionation[5] and $\delta^{34}S$ of ocean sulphate, this field can presumably extend into or across the 'magmatic' field.

Sample groups having distinctly negative $\delta^{34}S$ values and moderate to high variance are attributed to biogenic sulphate reduction in systems open to exchange with ocean sulphate[16]. Groups enriched in ^{34}S and with moderate to high variance have been imputed to closed-system sulphate reduction[17,18], that presumably may be either inorganic or biogenic.

All of the Archaean and 'Aphebian 1' groups fall into a restricted range close to 0‰ $\delta^{34}S$ and low variance, characteristic of magmatic sulphur. The possible exceptions are the 2,750 Myr Woman River and Michipicoten iron formations. The greater variation found in these two groups has been ascribed to biological reduction of low concentrations of sulphate within a restricted basin[19]. This interpretation has not been universally accepted[20-22]. As the metals of the iron formations were almost certainly derived from thermal springs[23], fractionation of sulphur at high temperature may have been involved. Indeed, sulphide formed by high-temperature reduction will tend to show the greatest variation in $\delta^{34}S$ at low sulphate concentrations, that is $\Sigma SO_4^{2-} \simeq \Sigma H_2S$, because of the sensitivity of fractionation to solution chemistry near the SO_4^{2-}/H_2S boundary[5].

While the evidence for bacterial reduction in the Archaean is debatable, there is little doubt that during this time there was no quantitatively important partitioning of $^{32}S/^{34}S$ in the exogene cycle, as shown by the data from five continents summarized in Fig. 1 that have means clustered near 0‰. Also, on the basis of the limited published evidence, this condition persisted into 'Aphebian 1' time.

Partitioning was established at the time of deposition of the Karelian schists[24] at ~2,200 Myr. Also, the Outokumpu deposit, a submarine exhalative massive sulphide body within the Karelian, dated at 2,250 Myr (ref. 25), shows a wide range of $\delta^{34}S$ from -19.2‰ to 5.8‰ (ref. 26). Unfortunately, some of the most comprehensive data on sedimentary sulphides of Aphebian age come from strata whose age is known only within broad limits, that is at the Homestake Mine[15] and the Pine Creek geosyncline[27]. The enrichment of ^{34}S in many of the early Precambrian units measured to date is intriguing and requires to be balanced by excess ^{32}S elsewhere[28].

To provide further data on sulphur isotope fractionation, I have sampled shaly sediments in the Republic of South Africa, representative of the period 3,300–2,000 Myr. This country contains some of the most complete and best exposed early Precambrian successions. Moreover, cratonic conditions were established at a relatively early date here[29,30], giving rise to Archaean sediments of different facies from the more typical 'greenstone belt' type. This is important, as the volcanogenic sulphide which dominates the greenstone belts[28] may have obscured any biogenic contribution.

Because sulphide is often difficult to separate physically from carbonaceous shale, the sulphur isotopic data were mainly obtained by burning powdered shale in O_2 at 1,300 °C to produce SO_2. Analyses of pyrite and/or pyrrhotite separated from 20 of these samples give similar $\delta^{34}S$ values to the total

burn. The organic carbon and the sulphur contents are quite variable for the samples from the Swaziland and Transvaal Supergroups, with values to 5.5% C and 3.2% S for the former and 9.6% C and 4.5% S for the latter. The West Rand Group samples have lower values for carbon, ranging to 0.4% C and 4.2% S.

Deposition of the Transvaal sediments took place mainly in a shallow, marine environment[31], while the upper part of the Onverwacht was laid down in shallow water, in part possibly evaporitic[32]. The depositional site of Witwatersrand strata has been enigmatic, either a shallow inland sea, or a lake[33]. But Watchorn[34] found tidal features in the West Rand Group and both fluvial and shallow water marine facies. Many of the West Rand shales are low grade iron formations, which has been taken as evidence of marine origin[30].
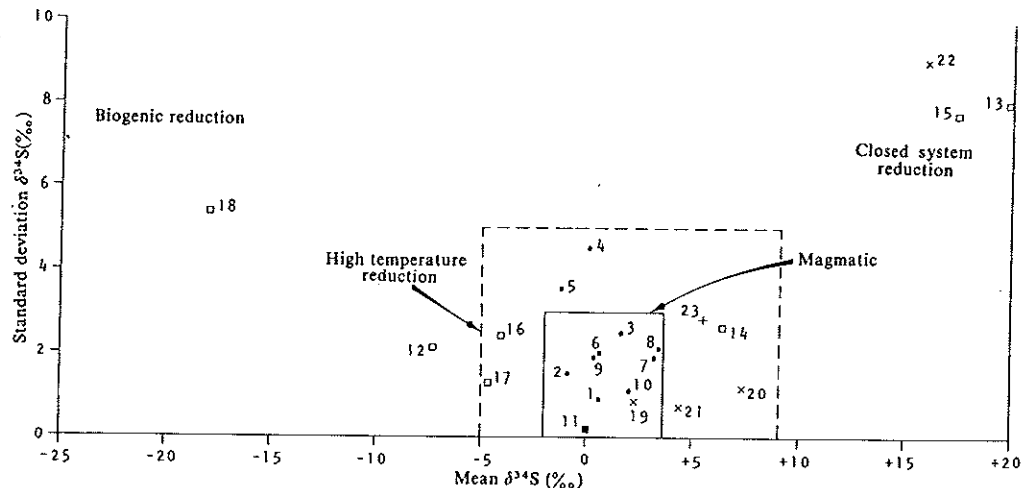
The results (Fig. 2) show $\delta^{34}S$ values close to 0‰ for all samples up to and including the lowermost part of the Malmani Subgroup. This reflects a magmatic source of the sulphide, either directly from volcanic exhalations, or from detrital sulphide that survived weathering in an O_2-poor atmosphere. Above this, the character of the isotopic distribution is entirely different, with mainly negative numbers. I suggest that the sulphides from the shales above the isotopic transition were derived from reduction of sulphate, with both biogenic and inorganic processes probably being involved.

Sulphide from carbonaceous shale of the Timeball Hill Formation is undoubtably biogenic with whole rock values to -30.6‰ (pyrite from the same sample measured -30.5‰). Two sections were sampled, one being the basal 30 m of the formation in a drill core at Mafefe, northern Transvaal and the other the basal 10 m from a core at Fochville, 400 km distant. The lowest ^{34}S values are from the most sulphidic shales.

Two 20-m sections of pyritic shale from the basal Malips Member of the Penge Iron Formation were taken: one from Mafefe, the other at Penge, 45 km away. They show very similar $\delta^{34}S$ values with means of -4.8‰ and -4.9‰ respectively and a low standard deviation for all samples of 1.3‰. These absolute values, plus the uniformity of the data, suggest derivation by high-temperature reduction, then thorough mixing before or after exhalation.

The Malmani samples are from carbonaceous shale interbeds in this carbonate unit and are taken from a 1,200-m section near Fochville, plus two samples from Mafefe immediately below the Penge Formation. In part, these data may be interpreted (Fig. 2) as hydrothermal sulphide, similar to the Malips Member. The Malmani is a chemical precursor of the great iron deposits of the Penge and Kuruman Formations, with cycles of iron enrichment in the carbonate[35]. However, caution

Fig. 1 Sulphur isotope distributions for early Precambrian sedimentary sulphides. ●, Archaean: 1, Isua, Greenland[69]; 2, North Pole, Pilbara Block, and Barberton[53]; 3, Yilgarn Block[20]; 4, Michipicoten, Ontario and 5, Woman River, Ontario[19]; 6, Rhodesia[21]; 7, Verkhnealdansk and Nimnyr Groups and 8, Fedorovka Group[48]; 9, Onverwacht and Fig Tree Groups; and 10, West Rand Group (see text). ▣, 'Aphebian 1': 11, McKim, Frood, and Snider Formations[70]. □, 'Aphebian 2': 12, Karelian schists[24]; 13, Krivoi Rog, K3[71]; 14, Hammaslahte deposit host rocks[72]; 15, Onwatin Formation[70]; 16, Malmani Formation (upper 20 samples, Fig. 2); 17 Penge Formation; 18, Timeball Hill Formation (see text). ×, Aphebian undivided: 19, Cahill Formation[27]; 20 Homestake Formation; 21, Poorman Formation and 22, Ellison Formation[15]. +, Modern: 23, Red Sea, hydrothermal (SU1 and SU2 zones)[14]. Additional geochronological data from ref. 73.

must be used in interpreting these data, as both upper intertidal and subtidal shales have been identified in the Malmani (ref. 36 and N. J. Beukes personal communication). Each shale type is likely to have a different isotopic distribution. The isotopic transition (Fig. 2) is placed between samples 45 and 77 m above the base of the Malmani. The samples above and below the transition, including those from the Black Reef, are similar, being carbonaceous to highly carbonaceous shales.

The Malmani is bracketed by age determinations of 2,640 Myr for the middle group of the Ventersdorp[37] and 2,240 Myr for the Ongeluk lavas of the Pretoria Group (D. Crampton, in ref. 38). Both of these horizons are separated from the Malmani by major unconformities. However, the base of the Malmani is probably closer in age to the Ongeluk than to the Ventersdorp. For this reason the isotopic change is estimated at ~2,350 Myr, a figure likely to be changed with more detailed geochronology.

The isotopic transition at ~2,350 Myr is indicative of one of two possible conditions, the first being an increase in the sulphate concentration of seawater to a level sufficient for reduction to cause significant isotopic fractionation. Harrison and Thode[39] showed that the fractionation by *Desulphovibrio desulphuricans* is sharply reduced at $<0.001 \, mol^{-1} \, SO_4^{2-}$, equivalent to ~4% of the concentration in present seawater. For inorganic reduction over the temperature range 200–350 °C at neutral pH, fractionation is minimal when $\Sigma SO_4^{2-} < \Sigma H_2S$ (ref. 5).

The second possible explanation is that sulphate-reducing bacteria evolved at ~2,350 Myr in a pre-existing, sulphate-rich ocean. This is less plausible if it is accepted that the Aphebian also marks the first significant appearance of sedimentary sulphide produced by high-temperature reduction of sulphate, for example, the Homestake Formation[15] and the data given here.

Further evidence of an evolutionary change from a low-sulphate Archaean ocean is the sulphur isotope composition of massive sulphide base metal deposits. Those of Proterozoic and younger age have mean $\delta^{34}S$ values that commonly differ significantly from 0‰ (refs 40,41), a fact which has been ascribed to derivation, in part at least, by reduction of seawater sulphate[40,42,43]. Late Archaean (~2,700 Myr) massive sulphides have mean values close to 0‰ (ref. 41), although seawater also had a major role in their formation[44]. Sulphate minerals are absent in these Archaean deposits[45,46], whereas they are relatively common in younger deposits.

Possibly contrary evidence is the occurrence of stratiform barite in the Archaean of southern Africa[32,47-51]; in the Pilbara Block of western Australia[52-54]; in India[55]; and in the USSR[48]. Where reliable age determinations are available, it seems that these sulphates occur in older Archaean strata, that is >3,200 Myr.

Studies carried out on the little metamorphosed Pilbara and Barberton occurrences indicate a depositional environment unusual for the Archaean. That is, a rather extensive, tectonically stable shallow-water shelf with volcanic vents but little detritus[54]. At least some sulphate was deposited in evaporitic conditions as gypsum, then replaced by silica and barite[53,54,56]. Younger Archaean strata, such as that which dominates the Canadian Shield, lack barite[50] and shallow water environments of the type described above are rare.

The Pilbara and Barberton barites probably were deposited in restricted basins where sulphate produced, for example, by bacterial oxidation of sulphide[47], could increase to higher concentration than in the ocean. Mean $\delta^{34}S$ values of 3.6–3.8‰ for these barites[53] indicates that isotopic partitioning was not established in the early ocean. The model discussed below linking global tectonics with ocean sulphate content does not, however, preclude short-term increase in sulphate within Archaean oceans in response to any temporary decline in rates of plate formation.

The data presented here indicate that during Archaean time sulphate was a minor constituent of seawater, probably $<0.001 \, mol \, l^{-1}$, except within restricted basins. This condition
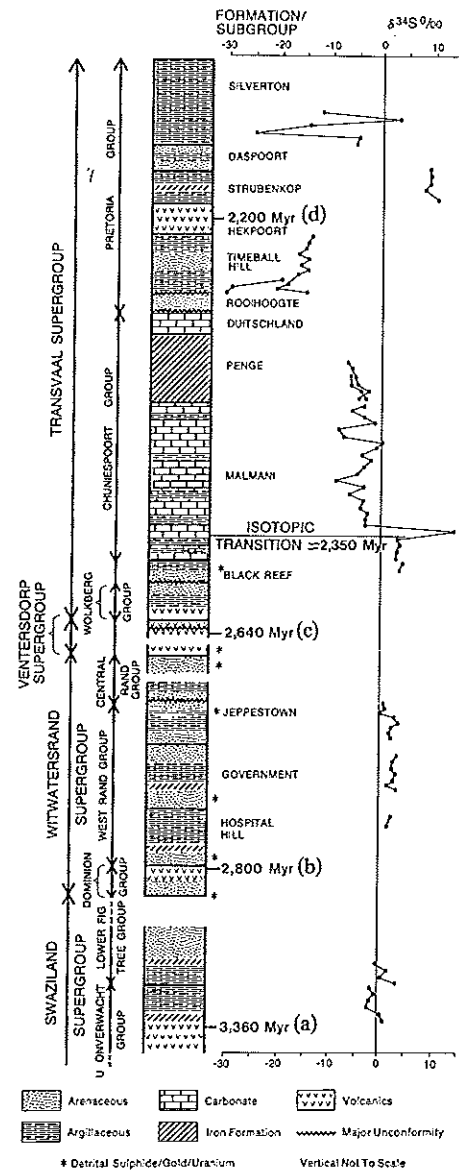

Fig. 2 Sulphur isotope results, early Precambrian argillaceous sediments, Republic of South Africa. Stratigraphical thicknesses not to scale. Isotopic data plotted in true stratigraphical order but not to represent a stratigraphical position within any given unit. Geochronological data: (a) ref. 74; (b) ref. 75; (c) ref. 37; (d) D. Crampton in ref. 38.

persisted into the Proterozoic, but by ~2,350 Myr , sulphate had reached a level sufficient for biogenic or inorganic reduction to cause significant isotopic fractionation and the partitioning of $^{32}S/^{34}S$ in the exogene cycle.

The change in the sulphate concentration of the ocean coincides with a suggested initial increase in the oxygen content of the atmosphere above the primitive level of $<(10^{-2}-10^{-6})$ PAL required for the deposition of placer uraninite[57]. The isotopic transition (Fig. 2) occurs immediately above the youngest occurrence in South Africa of detrital sulphides and uraninite in the Black Reef[58,59]. In the Huronian of Canada a change from strata hosting pyritic–uraniferous conglomerates to those with black (oxide) sands and red beds occur at ~2,300 Myr (ref. 60).

The transition, during the Lower Proterozoic, from an anoxic atmosphere to one with low levels of O_2 has been attributed to the filling of oceanic sinks for O_2, notably Fe^{2+} derived from continental weathering[61-64]. It is curious that this transition and the increase in oceanic sulphate discussed here, approximately

coincided with the greatest tectonic milestone in geological history: the change from a highly mobile Archaean crust to a Proterozoic regime of stable continental masses. Consideration must be given to alternative models, relating atmospheric and hydrospheric evolution to tectonic change.

The dominant mechanism for maintaining O_2 and SO_4^{2-} at low levels during the Archaean may have been a greater rate of exchange of reduced materials between the mantle and the ocean. Edmond *et al.*[65] estimate the flux of SO_4^{2-} into modern submarine geothermal systems as equivalent to that entering the oceans from rivers. Moreover, major amounts of Fe^{2+} and Mn^{2+} are introduced into the oceans from the ridges.

As the driving force for the exchange between mantle and ocean is heat flow, one would expect this to be greater in the Archaean. Furthermore, there is reason to believe that the exchange was even greater in the Archaean than might be predicted from a linear relationship with the Earth's heat flow. Burke and Kidd[66] suggest that during this period a greater proportion of the Earth's heat was dissipated at ocean ridges. Bickle[67] calculated that plate formation was about six times greater at 2,800 Myr than at present, compared with a factor of about three for heat flow. The Archaean/Proterozoic boundary seems to mark a change from a regime of rapid plate formation to a slower one[68] that would, in turn, produce a lower rate of exchange between reduced mantle material and the hydrosphere/atmosphere. I suggest that it is this change that allowed SO_4^{2-} to become a major component of ocean water and the entry of significant amounts of free oxygen into the atmosphere.

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Pheromones in mice: reciprocal interaction between the nose and brain

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Blockade of pregnancy by odours from strange males[1-3] has interested considerably those that adopt a sociobiological approach to reproduction[4-6]. It has been suggested that the mechanism has evolved to promote heterogeneity in the population, and that strange males in possessing the capacity to block pregnancy thereby increase their reproductive potential. However, such knowledge as we have of the territorial behaviour[7] and social organization of mice[8] makes this explanation less likely as resident males have such an advantage over intruders that access by strange males is probably an infrequent event. Another explanation relates pregnancy block to the effect that the male pheromones have on the female reproductive hormones in other contexts. Male pheromones can stimulate both early puberty[9] and induction of oestrus[10-12] in grouped females by suppressing prolactin secretion. Such a response, highly appropriate in this context, would be extremely disadvantageous following fertilization, since lowering prolactin is known to prevent implantation[13,14]. Thus, some mechanism must exist to offset the more general effect of the male's own pheromone on the endocrine function of his female at such times, and this, we suggest, is prevented by the noradrenergic mechanism which we describe here.

In the first experiment, female mice (BALB/c), which had been housed alone for part of the experiment, were taken from their home cage and placed with BALB/c stud males for 20 min to allow mating. They were then removed to cages containing F_1 male bedding while the stud male was returned to the females' home cage. The F_1 males were derived from crossing C57 females with CBA males, and produce pheromones that