

Evolution of the Atmosphere and Oceans: Evidence from Geological Records

3. Evolution of the Early Oceans

P V Sukumaran



P V Sukumaran took his M Tech degree in Applied Geology from the University of Saugar and has been with the Geological Survey of India since 1974. His interests include geochemistry, petrology and palaeo-oceanography. He is presently posted to the Marine Wing of the Department and has participated in many scientific cruises both as Chief Scientist and as a participating scientist.

The proto-ocean owes its origin to condensation of water vapour from the proto-atmosphere. Much of this ocean was lost to subsequent giant impacts. The water of the modern ocean is largely secondary, delivered by cometary impacts soon after the Moon-forming event. The early ocean had low dissolved O_2 and SO_4^{2-} but had high pH and dissolved Fe^{2+} .

Man has wondered from times immemorial about the immense volume of the seawater being saline and why the salinity does not increase. Ancient evaporite deposits offer the best clue to the composition of seawater at the time of their precipitation. But being highly soluble, the preservation of evaporite minerals in the rock record is poor. The oldest recorded halite evaporites are of late Archaean age (~ 2.7 Ga); sulphate evaporites are rare in the Archaean and early Proterozoic and they appear first in the Mesoproterozoic, ranging in age from ~ 1.5 Ga to 1.2 Ga. The rock record, therefore, does not provide us much information on the composition of the Archaean and early Proterozoic seawater. Nevertheless, we have fairly good knowledge about the source of the ocean's salinity and what keeps it unchanged, although we are still uncertain as to when the ocean acquired its salinity. Any discussion on the evolution of oceans should consider two aspects: the source of water, and how the ocean acquired its salinity.

Despite the fact that the ocean covers $\sim 71\%$ of the planet's surface, the mass of the ocean is negligible, being only 0.0002 times the mass of the Earth. This point can be driven home better by considering that if the entire mass of the ocean is distributed uniformly among the mass of the Earth, the latter will have an

Part 1. Evolution of the early atmosphere, *Resonance*, Vol. 4, No. 12, 1999.

Part 2. Enhancement of oxygen in the atmosphere, *Resonance*, Vol. 5, No. 5, p. 6, 2000.

¹ Ga means billion years (ago) and Ma, million years (ago).



average water content of < 300ppm.

Origin of Ocean Water

According to planetary formation models, the Earth is considered to have formed by the accretion of planetesimals, the composition of which can be estimated by analogy with meteorites. Though most of the meteorites are relatively dry bodies, the carbonaceous chondrites contain roughly 20% by weight of H₂O. If a few percentages of the source planetesimals have carbonaceous-chondrite-like composition the total mass of water delivered to the Earth would be 10-100 times the mass of the present oceans. The heat of accretion would have devolatilised the accreting planetesimals producing an impact-induced proto-atmosphere composed chiefly of H₂O and CO/CO₂. The water of the proto-atmosphere finally condensed to form the proto-ocean at the end of accretion. Delsemme (1996) considers that the ocean would have accumulated before 4.45 Ga.

However, much of this proto-ocean must have disappeared during the giant impact events that followed the initial accretion. The Moon is believed to have formed by a glancing impact of a Mars-sized body, shortly after the accretion of the Earth, ~4.45 Ga ago. This would have dissipated all of any ocean and atmosphere because of the extreme heat of impact. There is another reason to consider that the water of the oceans did not arrive at the beginning. According to the thermal history of the solar nebula, planetesimals at about 1AU (Astronomical Unit = the mean distance of the Earth from the Sun) from the heliocentre were at about 700°C that would eliminate any water other than water vapour. Since the Earth accreted from planetesimals at about 1 AU, the initial accumulation of the Earth was primarily from dry planetesimals.

Obviously all of the ocean water came from elsewhere, from comets. After the formation of the Earth-Moon system a rain of impactors fell on them, predominantly from residual bodies in the Oort cloud/Kuiper belt, that is huge repositories of comets. Estimates show that if 10% of these impactors were comets

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enough water would have accumulated to form the oceans. Recent quantitative estimates demonstrate that the volcanic outgassing is a grossly inadequate mechanism to explain the origin of the oceans. Water is being lost to the mantle today at rates far higher than their return rates through volcanic and hydrothermal outgassing. Mineralogical and seismic tomographic evidences indicate that this water is being stored in the upper mantle as dense hydrous magnesium silicate (DHMS). One mineral in this group of DHMS, wadsleyite, has about 3% H₂O. If wadsleyite is a significant component of the upper mantle there might be 3-4 times as much oceans in the upper mantle as on the surface (Deming, 1999), the source of which cannot be terrestrial. These data suggest that the Earth has been receiving extra-terrestrially sourced volatiles even today although their supply rates were obviously overwhelming during primordial times.

Christopher Chyba in 1990 postulated that the terrestrial planets acquired a thin veneer of ocean from comet and asteroid-impacts during the period of heavy bombardment 4.5-3.5 Ga ago. This is supported by the observation that C1 and C2 chondrites contain 20% and 13% by mass respectively of water and that comets are ~ 50% water-ice. This conclusion agrees further with evidences from lunar record that the satellite had been heavily bombarded between 4.2 and 3.8 Ga. However, many planets could not retain an H₂O-ocean either because of their closeness to the Sun or because of runaway greenhouse warming. The early impact events are believed to have initiated mantle plumes on the primitive Earth, through which volatiles escaped, setting small-scale plate movements. Geological evidences of plate movement on the early Earth are, however, rare. The oldest vestiges of plate tectonics are represented by the 3.48 Ga old Jamestown ophiolite of Barberton Mountain Land, South Africa (de Wit, 1998) and the 2.0 Ga old Pertuniqu Ophiolite of Quebec (Hoffman, 1990). It may be mentioned here that Komiya and coworkers have recently (1999) interpreted the 3.8 Ga old Isua supracrustals of Greenland, one of the oldest

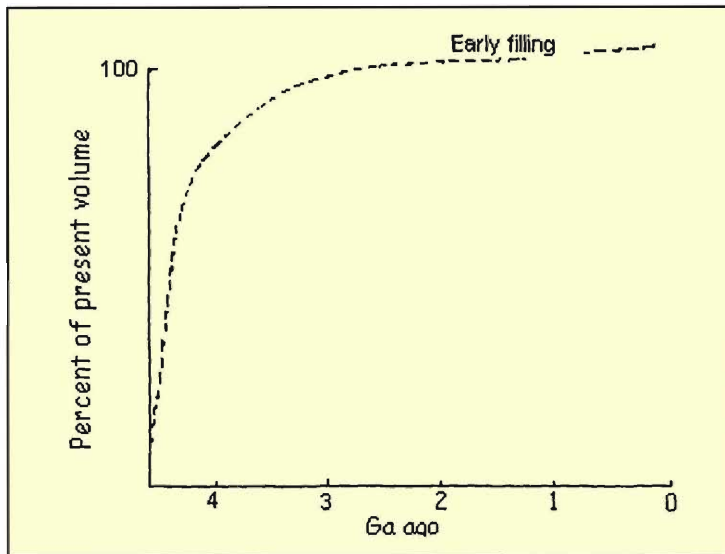


Figure 1. Growth of ocean volume (modified from van Andel, 1994).

terrains in the world, as the product of earliest plate tectonics on the Earth. The early impacts and incipient plate-tectonics-related movements must have provided the depressions into which water condensed forming the primordial ocean. As plate tectonics gained momentum, the ocean grew in size and volume. In any case the ocean had acquired its present volume by 4.0 Ga (*Figure 1*), although its composition was very different.

The Ocean in the Past

The major constituents in modern oceans, called the conservative constituents (their abundance remains largely constant), that make up 99.99% of the dissolved matter (= 34.48 ‰ salinity) are given in *Box 1*. Besides these, there are many other elements and dissolved gases whose abundances in the ocean are very low and widely variable. They are called the non-conservative constituents.

If the ocean had been in existence for hundreds of millions of years as is known today, its salinity would have doubled or tripled over the past hundred million years itself at the present rate of supply of solutes by rivers. For instance, at the present delivery rate of Na (2.05×10^8 tonnes/year) by rivers, it would

Box 1. Major Constituents of Seawater

Ion	Concentration ‰	
Cl ⁻	18.980	
SO ₄ ²⁻	2.649	
HCO ₃ ⁻	0.140	
Br ⁻	0.065	Anions total = 21.861 ‰
H ₂ BO ₃ ⁻	0.026	
F ⁻	0.001	
Na ⁺	10.556	
Mg ²⁺	1.272	
Ca ²⁺	0.400	Cations total = 12.621 ‰
K ⁺	0.380	
Sr ²⁺	0.013	
Overall salinity = 34.482 ‰		

take only 70 Ma for Na to reach its present concentration in the sea. This time is smaller still in the case of K, being 7 Ma (when corrected for cyclic salts the figures for Na and K are 210 and 10 Ma, respectively). These figures indicate that if the ocean had been there for hundreds of millions of years, it must be in some sort of chemical steady state since long. In other words, the present chemical composition of the sea dates back to the early period of its evolution and subsequent addition of salts has been in balance with their removal. Thus it is clear that the major constituents of the ocean are in chemical equilibrium since ~1.8-1.6 Ga (Grotzinger and Kasting, 1993). If so how did the ocean maintain the chemical steady state?

G Sillen in 1961 explained the steady state as due to thermodynamic equilibrium with sedimentary mineral phases in the seabed. That is to say, whenever there was any excess supply of a solute, an equal amount was transferred to the sedimentary minerals in the seabed to maintain equilibrium. He presumed for instance, that the Mg²⁺ concentration was regulated by the formation of Mg-clays on the sea floor. Sillen's model, however, did not stand detailed scrutiny by subsequent workers. We

know today that authigenic Mg-clays are not that abundant in marine sediments and that Mg^{2+} content of seawater is maintained primarily by removal of Mg^{2+} as seawater circulates through sea floor basalts. Further, river waters are HCO_3^- -rich and if they were the only source of salts, the sea would have become excessively alkaline. The fact that it is not indicates that there are HCO_3^- removal mechanisms. The predominant process of HCO_3^- removal today is by biogenic precipitation of $CaCO_3$ (inorganic precipitation of $CaCO_3$ is meager in today's marine environments except in the Bahama banks). But the riverine flux of Ca^{2+} is insufficient to meet this demand. Therefore, it requires the existence of some other process to supply the excess Ca^{2+} needed to maintain equilibrium. Similarly the abundance of Cl in continental rocks is insignificant and it cannot explain the high Cl^- concentration in seawater. Submarine volcanic activity and hydrothermal leaching of sea floor basalts supply bulk of the Cl^- . Thus it became clear that seawater is not merely a concentrated form of river water. There are additional supplies from elsewhere and important other sinks than seafloor sediments. It is now well understood that seawater circulating through seafloor hydrothermal systems (*Box 2*) is by far the most important source and sink for many constituents, second only to continental flux.

The degassed volatiles of the primitive Earth such as CO_2 , SO_2 , HCl, H_2S and HF are acid components and so would have rapidly reacted with primordial rocks. The pH of the early ocean was obviously more acidic due to these dissolved acid components. As anions like Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Fe^{2+} were soon leached from exposed continental rocks and transported to the sea, the pH increased rapidly. Condie 1984 considered that the Archaean continental crust was more basic. Therefore, more of Mg^{2+} , Ca^{2+} and Fe^{2+} would have been delivered to the early ocean than at the present time.

The oldest known marine sedimentary rocks are from the 3.86 Ga old Isua greenstone belt of Greenland. This suggests that the seawater had acquired a composition similar to modern seawater

Box 2. Hydrothermal Activity

Seawater seeps through cracks in ocean floor basalts and heats up at depths. The steam so generated escapes through other cracks as superheated jets. This is one of the chief mechanisms by which newly formed, hot oceanic crust is cooled. In the process some of its constituents are lost to the rocks while the rocks themselves are leached of their constituents, particularly the metals. The metal-laden hydrothermal solutions that escape into the sea floor shed their metals as sulphides on contacting the seawater. Some times settling sediment particles trap the metals and get deposited as metalliferous sediments.

There are minor variations in the abundance of individual sedimentary rocks and it is such variations that provide us clues to the compositional limits of the early ocean.

by Isua time. The absence of marine brucite ($\text{Mg}(\text{OH})_2$) in sedimentary records is considered to preclude a seawater pH of >10 . The continental crust had evolved to its present composition by about 2.7 Ga and therefore, the composition of continent-derived dissolved constituents to the sea remained by and large the same since then. The nature and relative abundance of sedimentary rocks remain largely the same in Precambrian and Phanerozoic successions: evaporites, bedded cherts, siderite rich sediments and carbonate rocks were deposited both in Precambrian and Phanerozoic times. This shows that the seawater composition has not greatly deviated since about 3.8 Ga. Nevertheless, there are minor variations in the abundance of individual sedimentary rocks and it is such variations that provide us clues to the compositional limits of the early ocean.

Carbonate Deposition

Archaean carbonates are rare in the rock record. We have seen earlier that the pCO_2 of Archaean atmosphere was high. This would have lowered the pH of the ocean prohibiting the deposition of carbonates; it would have also allowed more Ca^{2+} to go into solution at the same time. Since stable cratons were absent in the Archaean, carbonate sedimentation was probably confined to the deep sea. It is considered that these carbonates were biogenic, deposited by planktonic algae, which are believed to have played a role similar to foraminifera today. They were destroyed later by plate tectonic processes and so were not preserved.

It has been widely recognised that dolomite to calcite ratio in sedimentary carbonate decreases with time, reflected by the decreasing MgO/CaO ratio in carbonate rocks formed over the same time. A tendency for $\text{MgO}/\text{Al}_2\text{O}_3$ ratio in shales to increase during the same time has also been recognised (*Figure 2*). This suggests that Mg removal changed with time from carbonate reservoir to silicate reservoir. Further, silicate-carbonate equilibria are dependent on the availability of CO_2 in the ocean atmosphere system. When CO_2 availability was limited, Ca^{2+}



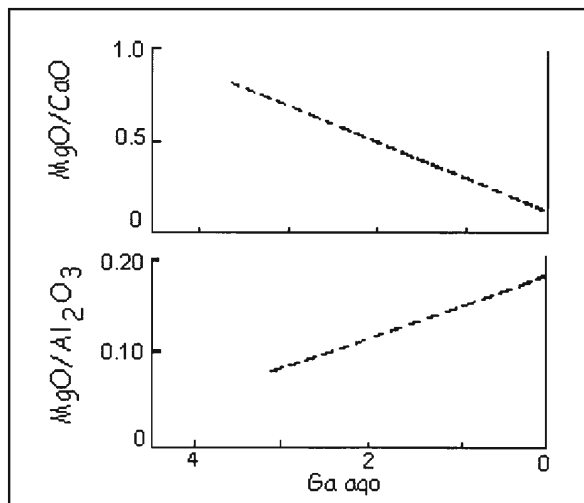


Figure 2. Variation of MgO/CaO in sedimentary carbonates and MgO/Al₂O₃ in shales with time.

was precipitated as calcite rather than as silicate; with the input of CO_3^{2-} to the ocean exceeding the rate of release of Ca^{2+} by weathering, both Mg^{2+} and Ca^{2+} were precipitated as dolomite. The dominance of dolomite in the Precambrian, therefore, reflects a CO_2 -rich atmosphere-ocean system in agreement with the Abelson model.

Marine Evaporites

The progressive evaporation of modern seawater leads to precipitation of minerals in a definite succession: crystallisation of calcite (CaCO_3) and/or limestone ($\text{CaMg}(\text{CO}_3)_2$) is followed by anhydrite (CaSO_4) and/or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Halite (NaCl) appears when over 90% of the initial water is evaporated. Sulphates and chlorides of Mg^{2+} and K^+ crystallise during the very end of evaporation.

The succession of minerals in marine evaporites in sedimentary sequences does not show any departure from the above since about 900 Ma, implying that seawater composition changed little during this period. Fluid inclusions in halite crystals from evaporite deposits reflect the composition of seawater when these deposits were formed and by careful extraction of these inclusions very valuable information can be derived on palaeosalinities.

The relative geochemical abundance of Fe is 12 times greater than S and therefore the flux of dissolved Fe to the early ocean exceeded that of sulphide.

Holland and coworkers in 1986 studied the crystallisation path followed by saline inclusions from the salt deposits of the Great Inagua Island, Bahamas and compared it with those in Miocene halite in DSDP cores from the Red Sea. Their data show that the evaporation path followed by Miocene seawater is remarkably similar to modern seawater. This observation is expected because the 5-6 Ma that have elapsed since the formation of Miocene halite is less than the oceanic residence time of Mg^{2+} (~10 Ma) and much less than that of Na^+ (~210 Ma) and Cl^- (~103 Ma; this residence time of Cl^- is uncorrected for cyclic Cl; when corrected it is nearly ∞). A similar relationship has been observed by Lazar and his group in 1985 for fluid inclusions in Permian (~290 Ma) halite. These observations confirm that the Permian seawater was chemically similar to modern seawater and that the similarity can be extended back to Silurian (~ 430 Ma) seawater.

Iron and Sulphur in the Precambrian Ocean

Walker and Brimblecombe in 1985 developed tentative geochemical budgets of Fe and S in the prebiologic ocean. Fe is a non conservative constituent in modern ocean while SO_4^{2-} is a conservative constituent. We have seen earlier that the prebiologic ocean was deficient in dissolved O_2 . Further, the volcanic sources of reduced gases and hydrothermal sources of reduced Fe were larger because of higher heatflow. The O_2 -poor early Archaean environments facilitated dissolution of Fe^{2+} during chemical weathering and its discharge into the sea. As continental landmasses were limited in extent in the prebiologic Earth, this source of Fe was probably less significant. Pyrite is the dominant sulphide mineral in sea floor basalt and seawater interactions with hot basalt dissolves pyrite, supplying both dissolved Fe and sulphide to the ocean. But basalt contains much more Fe-bearing minerals than pyrite, the dissolution of which provides Fe without sulphide to the sea. Besides, the relative geochemical abundance of Fe is 12 times greater than S and therefore the flux of dissolved Fe to the early ocean exceeded that of sulphide. Accordingly, the Fe concentration in

Archaean sea was high and sulphide concentration was low. The scarcity of BIF of early Archaean age suggests that the bulk of Fe^{2+} delivered to the ocean remained there in dissolved state. By early Proterozoic times, as O_2 level increased, the dissolved Fe^{2+} was oxidised and deposited as BIF. Ewer in 1980 estimated that the dissolved Fe^{2+} in seawater that deposited the BIF was in excess of 10^{-4} mole/ litre and the corresponding bisulphide concentration was below 10^{-8} mole/litre.

Geochemical evidence confirms that the early ocean had low SO_4^{2-} concentration. Walker and Brimblecombe in 1985 worked out the supply and removal fluxes of SO_4^{2-} in the Archaean ocean and compared them with the situation today. This is shown in Box 3. In the Archaean the chief source of SO_4^{2-} was photochemical oxidation of volcanogenic SO_2 and its transportation to the sea. This could have been higher in the early Earth when heat flow was higher. Contribution by rock weathering was negligible in the absence of large landmasses and when O_2 supply was limited. As against this, the SO_4^{2-} sink was dominant in hydrothermal systems, because of vigorous hydrothermal circulation in the Archaean. Limited biologic activity again would have made sedimentary sink (by bacterial oxidation of SO_4^{2-} to pyrite) negligible. Similarly evaporite deposition was also less significant because of limited landmass. Based on these fluxes, Walker and Brimblecombe arrived at a net SO_4^{2-} concentration of 10^{-3} mole/litre in the Archaean ocean.

Box 3. Sources and Sinks of Oceanic SO_4^{2-} (Figures in 10^{12} moles/year)

	Archaean	Present
Sources		
Volcanogenic	0.16	0.16
Weathering	Negligible	3.0
Sinks		
Sedimentary sulphide	Negligible	1.3
Hydrothermal system	0.16	0.16
Evaporite	Negligible	Negligible
Net SO_4^{2-} concentration	10^{-3} mole/litre	30×10^{-3} mole/litre

In comparison, present day sources of SO_4^{2-} to the ocean are dominated by weathering fluxes, obviously because of the O_2 rich atmosphere and availability of extensive continental areas. Volcanic contribution is of relatively lower importance. The principal removal flux today is bacterial reduction in anaerobic sediments to deposit pyrite. Hydrothermal circulation removes as much SO_4^{2-} today as is produced by volcanic activity. Evaporite deposition is not favourable in modern environments because of the absence of large isolated basins in arid regions. The net SO_4^{2-} concentration in modern oceans as arrived at by the above authors is 30×10^{-3} mole/litre. As is clear from *Box 3*, the budget is unbalanced and probably SO_4^{2-} is gradually accumulating in the ocean. Also apparent from *Box 3* is that the Archaean sea was deficient in SO_4^{2-} by a factor of 30 compared to the modern seawater.

Sulphur Isotopic Evidence

Stable sulphur isotopic ratios, $^{34}\text{S}/^{32}\text{S}$ (represented in terms of $\delta^{34}\text{S}$; *Box 4*) in evaporite sulphate, hydrothermal sulphides and sedimentary sulphides provide another clue to low SO_4^{2-} abundance in Archaean ocean. Inorganic reduction of SO_4^{2-} to sulphide fractionates sulphur in favour of the light isotope, ^{32}S ,

Box 4. Stable Isotope Ratios

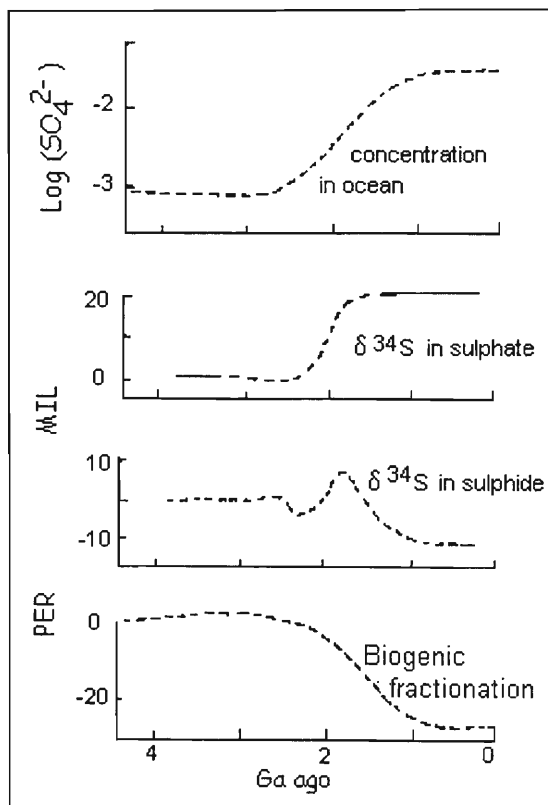
Stable isotope (non-radioactive) ratios most useful in geochemical studies are oxygen ($^{18}\text{O}/^{16}\text{O}$), carbon ($^{13}\text{C}/^{12}\text{C}$) and sulphur ($^{34}\text{S}/^{32}\text{S}$). Stable isotope ratios are expressed in terms of the δ notation as per mil ($‰$) difference relative to a standard. The commonly used standards are Peedee Belemnite (PDB) for C and O_2 , Standard Mean Ocean Water (SMOW) and Standard Light Antarctic Precipitation (SLAP) for O_2 and H_2 and Canyon Diablo Troilite (CDT) for S. Various natural processes fractionate these isotopes leading to variation in the ratios in a sample. For example, Calvin cycle photosynthesis fractionates C in favour of the light isotope so that organic C is depleted in ^{13}C . This is a powerful tool to look for the initiation of photosynthesis in the rock record.

The stable C isotopes are partitioned between reduced (organic) and oxidised (carbonate) C in sediments. Since production of organic matter fractionates C in favour of ^{12}C , the carbonate precipitated from the ambient water becomes enriched in ^{13}C . Periods of increased organic productivity and C burial are thus marked by deposition of isotopically heavy limestones in geological records.

leaving the residual sulphate enriched in the heavy isotope, ^{34}S . Incomplete reduction of SO_4^{2-} to sulphides as seawater circulates through mid-ocean ridge systems results in preferential removal of ^{32}S , enriching the seawater with ^{34}S . Evaporite sulphates formed from such residual seawater should be enriched in ^{34}S . Archaean evaporite sulphates, however, do not show any fractionation of the sulphur isotopes and their $\delta^{34}\text{S}$ values are close to the mantle values ($\delta^{34}\text{S}=0\text{‰}$). This implies that Archaean seawater-hydrothermal interactions resulted in incomplete and not partial reduction of SO_4^{2-} to sulphide leaving little SO_4^{2-} in the residual water.

The isotopic composition of hydrothermal sulphides from the Archaean to the present believed to have formed at the sea floor also confirms that the concentration of SO_4^{2-} in seawater has increased over time. Recent hydrothermal sulphides are isotopically heavier relative to the mantle values attributed to a mixture of mantle sulphide ($\delta^{34}\text{S} = 0\text{‰}$) and sulphide derived from partial reduction of seawater SO_4^{2-} in hydrothermal systems ($\delta^{34}\text{S} \approx -20\text{‰}$). On the contrary the Archaean and early Proterozoic hydrothermal sulphides show little isotopic fractionation, their $\delta^{34}\text{S}$ values being close to mantle source and to that of Archaean evaporite sulphate, implying complete reduction of sulphate and, therefore, little fractionation. Further, the Archaean hydrothermal fluids were deficient in sulphides and obviously contained excess Fe. This Fe would have precipitated any seawater SO_4^{2-} as sulphides, leaving the seawater with low dissolved SO_4^{2-} . The variation of SO_4^{2-} in the ocean and sulphur isotopic fractionation with time are given in Figure 3. Walker and Brimblecombe suggest that hydrothermal circulation of low-

Figure 3. Variation of SO_4^{2-} concentration in ocean, $\delta^{34}\text{S}$ in sulphate, sulphide and biogenic fraction, with time (adapted from Walker and Brimblecombe, 1985)



The transition from isotopically unfractionated sedimentary sulphides of the Archaean and early Proterozoic to ^{34}S -depleted Phanerozoic sulphides took place sometime between 2.32 and 2.2 Ga.

SO_4^{2-} seawater is likely to have removed the entire SO_4^{2-} without any isotopic fractionation.

Cameron in 1982 observed that isotopic fractionation in biologically mediated SO_4^{2-} reduction is small when the ambient SO_4^{2-} concentration is low and that isotopic fractionation is possible only when there is excess SO_4^{2-} . Laboratory culture experiments also confirm that sulphate reducers do not yield lighter sulphides when grown in media containing low SO_4^{2-} of $<10^{-3}$ mole/litre. The low fractionation of sulphur isotopes in Archaean and early Proterozoic sedimentary sulphides, therefore, suggests low SO_4^{2-} ion concentration in the seas of those times.

Cameron also presented data on the evolution of S isotopes in sedimentary sulphides of Archaean and early Proterozoic age from South Africa. He observed a distinct change in isotopic composition between 2.35 and 2.2Ga. It is at this time that sulphides strongly enriched in the light isotope first appear in the geological record. This reflects the initiation of biologically mediated SO_4^{2-} reduction during this interval. Isotopic fractionation became possible for the first time in this interval because of increased SO_4^{2-} concentration in the sea. This conclusion is corroborated by recent studies of Kristen S Habicht and Donald E Canfield in 1996, that sulphides precipitated from SO_4^{2-} -rich brines of Solar lake, Sinai ($\text{SO}_4^{2-} = 65$ milli mole) by cyanobacteria are depleted in $\delta^{34}\text{S}$ by more than 20 ‰. This depletion is distinctly higher than in sulphides precipitated bacterially from low- SO_4^{2-} media as observed in laboratory cultures. The transition from isotopically unfractionated sedimentary sulphides of the Archaean and early Proterozoic to ^{34}S depleted Phanerozoic sulphides took place sometime between 2.32 and 2.2 Ga. This period coincides with large-scale burial of organic C in sediments. The O_2 so released to the atmosphere forced accelerated SO_4^{2-} flux to the ocean consequent to oxidative weathering of sulphides exposed on land. The resulting enhanced SO_4^{2-} concentration in the ocean facilitated ^{34}S depletion in biochemically precipitated sulphides since then. The first indication of oxidative weathering in stratigraphic record

in the form of red beds also dates from about this period.

Unlike the unfractionated Archaean evaporite sulphates, early and mid-Proterozoic evaporite sulphates are enriched in ^{34}S by amounts comparable to recent sulphates ($\delta^{34}\text{S}$ of modern seawater SO_4^{2-} is $\sim 20\text{‰}$). This change is considered to be a consequence of either biological or inorganic SO_4^{2-} reduction to sulphide, as incomplete reduction by both processes leaves behind heavy sulphate. It is quite likely that with elevated SO_4^{2-} flux to the sea beginning with the early Proterozoic, biological and hydrothermal sulphate reduction occurred simultaneously, enriching the seawater with the heavy isotope.

In the next and final part of this series we will examine the concept of 'an early soda ocean' and new constraints on the evolution of the ocean based on reinterpretation of the evaporite-carbonate record.

Suggested Reading

- [1] H D Holland and others, Evolution of the atmosphere and oceans, *Nature*, 320, 27-33, 1986.
- [2] E Takahashi and others (Ed) Chemical Evolution of the Earth and Planets, American Geophysical Union, *Geophysical Monograph Series*, Vol. 74, 1993.
- [3] E M Cameron, Sulphate and sulphate reduction in early Precambrian oceans, *Nature*, 296, 145-148, 1982.
- [4] J C G Walker and P Brimblecombe, Iron and sulphur in the pre-biogenic ocean, *Precambrian Research*, 28, 205-222, 1985.
- [5] David Deming, On the possible influence of extraterrestrial volatiles on Earth's climate and the origin of the oceans, *Palaeogeography*, 146, 33-51.

Address for Correspondence

P V Sukumaran
Geologist (Sr)
Geodata Division
GSI, Seminary Hills
Nagpur 440 006, India.



"In the future, the revolutionary effect of Mendelism will be seen to flow from the particulate character of the hereditary elements. On this fact a rational theory of Natural Selection can be based, and it is, therefore, of enormous importance."

R A Fisher, 1930