

Evolution of the Atmosphere and Oceans: Evidence from Geological Records

4. The Early 'Soda Ocean' and New Constraints on Precambrian Ocean Evolution

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The Archaean ocean was probably a soda ocean rich in Na_2CO_3 and NaHCO_3 and continued to have high pH and Fe^{2+} , and low dissolved O_2 and SO_4^{2-} ; it was also probably highly oversaturated with CaCO_3 . SO_4^{2-} concentration reached modern levels by Palaeoproterozoic concomitant with the growth of atmospheric O_2 , which removed the Fe^{2+} . The ocean evolved to a chemical steady state with NaCl-dominated chemistry by about the late Palaeoproterozoic and remains so since then.

Compositional Limits of Archaean Ocean

The pCO_2 of Archaean atmosphere was suggested to be 100-1000 times those of the present to account for an equable climate in the wake of lower solar luminosity. From the persistence of gypsum and limestone in the rock record it is possible to examine whether this suggestion is compatible with the geologic record. Walker in 1983 made such an approach to set limits to the composition of the Archaean ocean. Carbonate rocks are present in sedimentary rocks of all ages, although rare in the Archaean. This means that the ocean has always been close to equilibrium with respect to CaCO_3 as it is today. Similarly sedimentary sulphate evaporites are known from rocks of all ages dating back to 3.5 Ga (the authenticity of early Archaean sulphate evaporites, however, has been questioned recently by Grotzinger, 1994). Evidences also show that the sequence of minerals precipitated in these evaporites remained unchanged with time. Estimates of the Archaean SO_4^{2-} concentration in the sea are $\sim 10^{-3}$ mole/litre. At a maximum evaporation rate of 10m/year in arid regions, this sulphate

Part 1. Evolution of the early atmosphere, *Resonance*, Vol. 4, No. 12, p.4-10, 1999.

Part 2. Enhancement of oxygen in the atmosphere, *Resonance*, Vol.5, No.5, p.6-14, 2000.

Part 3. Evolution of the early oceans, *Resonance*, Vol.5, No.9, p.8-21, 2000.



concentration is estimated to take 13500 years to precipitate a metre thick layer of gypsum. As the stability of evaporite environments longer than 100,000 years is unlikely, Walker concluded that SO_4^{2-} ion concentrations of $<10^{-3}$ mole/litre could not have given rise to massive evaporite gypsum.

In the normal sequence of evaporite mineral precipitation, gypsum follows calcite only if Ca^{2+} ion concentration is half the HCO_3^- ion concentration. Otherwise precipitation of carbonate will exhaust Ca^{2+} ions prohibiting gypsum formation. The presence of gypsum in evaporites of Archaean, therefore, sets an upper limit for the HCO_3^- concentration. From the above data pertaining to evaporites, Walker arrived at the composition of Archaean seawater. High pCO_2 on the early Earth would have yielded higher concentrations of Ca^{2+} , HCO_3^- and H^+ ions and lower concentrations of CO_3^{2-} and SO_4^{2-} ions. Evidently there is no inconsistency between the geologic record of evaporite sedimentation and the presumed high pCO_2 in the Archaean. However, in the absence of extensive continental masses, evaporite deposits could not have been widespread and presumably Cl^- and Na^+ concentrations were probably higher in Archaean ocean than the present. This argument supports the view that the ocean will be far from being saturated even if all known evaporite deposits are dissolved.

'An Early Soda Ocean'

On analogy with modern soda lakes (Box 1), Kempe and Degens 1985, postulated that the ancient sea was a soda ocean with high Na_2CO_3 and NaHCO_3 , high alkalinity, high pH and low Ca^{2+} and Mg^{2+} concentrations. The early soda ocean is believed to have evolved to a NaCl-dominated modern ocean.

It is well known that Na-, K-, Ca-, and Mg-silicates, on chemical weathering in the presence of CO_2 , produce alkaline solutions. The composition of the resulting solution depends on the composition of rocks undergoing chemical weathering. Even the basic Archaean crust is believed to have supplied the required Na

Box 1. Soda Lakes

Soda lakes are enriched in Na_2CO_3 and NaHCO_3 . High pH is a property of Na_2CO_3 and so the pH of soda lakes exceeds 9. They may also contain substantial concentrations of other salts, in particular NaCl. At such high pH Ca^{2+} and Mg^{2+} are effectively removed by calcite and dolomite precipitation. Several soda lakes are sited in volcanic and rift regions; Lake Van in eastern Anatolia, Turkey is the largest known soda lake on the Earth.

Subduction of pore waters and Na_2CO_3 -rich crust is believed to have caused soda depletion in the sea through generation of alkali-feldspars in accreting continents.

to form Na-carbonates for the soda ocean. However, the formation of soda ocean is controlled also by the relative abundance of CO_2 and Cl^- in the degassed volatile. Ca and Mg from such solutions can be removed easily by the formation of Ca-Mg bearing secondary silicates, and K will be incorporated in clay minerals; at high soda alkalinities Ca^{2+} and Mg^{2+} will also be removed by the precipitation of dolomite and calcite as in soda lakes. This will eventually lead to the enrichment of the solution in Na. Mass balance calculations by Kempe and Degens (1985) suggest that enough Na was available in Archaean crustal rocks to provide substantial Na_2CO_3 . The mantle degassing was also sufficient to supply the required CO_2 for the evolution of the soda ocean. As the high $p\text{CO}_2$ early atmosphere was not likely to have maintained for long, Kempe and Degens argue that oceanic pH would have increased significantly the moment $p\text{CO}_2$ decreased to levels of 0.1 to 0.01 atm, precipitating Ca and Mg carbonates and enriching the sea in Na.

Kempe and Degens believe that the early soda ocean evolved into modern ocean by shedding its Na_2CO_3 to the marine crust and accumulating NaCl by hydrothermal leaching. Some carbonates could have been extracted by organisms and buried in sediments. Subduction of pore waters and Na_2CO_3 -rich crust is believed to have caused soda depletion in the sea through generation of alkali-feldspars in accreting continents. Over several rock cycles, the degassed CO_2 extracted Ca and Mg formerly bound in secondary silicates and deposited them as Ca and Mg carbonates. As continents covered by sodium silicate sediments increased in size, rivers shifted more and more into Ca^{2+} - HCO_3^- dominated chemistry (Ca-silicates are leached faster than Na-silicates). This resulted in decreased Na flux to the sea and consequent waning of the soda ocean. The evolution of the soda ocean is given in *Figure 1*.

If the ancient sea was a veritable soda ocean one might expect Precambrian soda deposits. The complete absence of soda deposits according to Kempe and Degens is because Na_2CO_3 is thermally unstable and highly soluble and so was not preserved in the



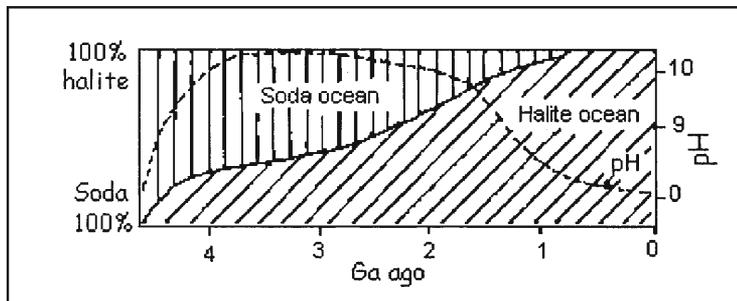


Figure 1. Evolution of the soda ocean (Adapted from Kempe and Degens, 1985).

rock record. In the Ca^{2+} -depleted soda lakes, no gypsum is precipitated; the occurrence of gypsum in Precambrian evaporites, therefore, argues against a highly alkaline ocean. The first occurrence of Precambrian marine gypsum should signal a transition from soda ocean to modern ocean. Gypsum and anhydrite pseudomorphs are known from the Proterozoics of Canada. Proterozoic evaporite gypsum is also reported from the Amadeus basin of Australia. But Kempe and Degens, based on geological evidences, consider these occurrences as diagenetic and not evaporitic. Massive true evaporite gypsum first appears almost at the beginning of Cambrian, as for instance the Hormuz series of Iran, the Valdai series of the Russian platform and the Vindhya of India, suggesting that the soda ocean persisted until about 800 Ma.

Kempe and Degens claim that the soda ocean model is capable of explaining several Precambrian geochemical problems: The dominance of dolomite in the Precambrian is due to high Mg/Ca ratio and high pH of alkaline solutions. Formation of widespread Precambrian cherts is attributed to transportation of dissolved SiO_2 in an alkaline medium followed by subsequent precipitation. It is suggested that above a $p\text{CO}_2$ of 0.3 atm a 'runaway greenhouse effect' would be triggered. Water would then exist only in gaseous state and would lose its H_2 through photolysis leading to its complete loss from the Earth. The calculated $p\text{CO}_2$ in the soda ocean is <0.03 atm, much lower than that required for a runaway greenhouse effect (Grotzinger and Kasting 1993, however, consider that such a low $p\text{CO}_2$ should freeze the ocean). In addition, the coexistence of chert, siderite

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and Fe-silicates in BIF is possible only under alkaline conditions. A soda ocean would be enriched in dissolved phosphate (the low Ca^{2+} would inhibit precipitation of phosphate as apatite) which would have fostered the evolution of life. Predominance of alkalophyllic cyanobacteria in Precambrian biota is taken as an indication of early soda ocean. Besides, the biogenic calcification, which began 600 Ma ago, is thought of as a natural response to build up of Ca^{2+} in the ocean as the soda ocean decayed; otherwise the Ca^{2+} in the ocean would poison vital cellular processes.

New Constraints

It was regarded for a long time that the composition of the ocean changed little since ~ 3.5 Ga. Kempe and Degens for the first time, based on theoretical considerations, challenged this myth in their soda ocean theory. Subsequently, Grotzinger in 1986 provided geological evidences against the concept of a constant ocean composition. Based on new interpretations of the evaporite-carbonate record Grotzinger and Kasting 1993 proposed new constraints on Precambrian ocean evolution as summed up below.

Carbonate and Sulphate

The Archaean carbonates are dominantly abiogenic, characterised by thick, massively precipitated dolomites and limestones. They are less spectacular in the Palaeoproterozoic and show progressive decline in Meso-through Neoproterozoic. Precipitation of massive abiogenic carbonate is unknown in modern marine environments, despite the seas being 3-7 fold over-saturated with respect to CaCO_3 . Modern carbonates are formed almost entirely by the process of bio-calcification, which began in the early Cambrian with the emergence of metazoans. The overwhelming abundance of massive carbonate in the Archaean suggests that the ocean was highly oversaturated with CaCO_3 and that saturation declined to modern levels at the end of the Proterozoic. In an oversaturated Archaean ocean slight perturba-



tion such as the uptake of CO_2 by microorganisms could trigger precipitation of CaCO_3 .

Precambrian evaporites on the other hand present evidences for curtailed sulphate precipitation. As mentioned earlier, Phanerozoic evaporites follow the crystallisation path of modern seawater. On the other hand, geological evidences confirm that early Precambrian evaporite precipitation proceeded straight from carbonate to halite bypassing the intermediate sulphate stage. Examples of this type of evaporite are reported from the late Archaean Grotescue basin of Australia and Palaeoproterozoic Rocknest Formation and Pethei group of Canada. Recent reviews of Precambrian evaporite by Grotzinger in 1989 show that sulphate minerals are absent in the Archaean and early Proterozoic and that gypsum-bearing evaporites first appear in the Mesoproterozoic (eg. McArthur basin evaporates of Australia). The first appearance of abundant gypsum also coincides with the disappearance of massive carbonates approximately at the Palaeoproterozoic-Mesoproterozoic boundary, 1.7 to 1.6 Ga. According to Grotzinger and Kasting, the absence of gypsum from evaporite sequence in Archaean and Palaeoproterozoic is either due to low SO_4^{2-} concentration or due to the removal of entire Ca^{2+} for the formation of carbonate which precedes gypsum formation. We have seen earlier that SO_4^{2-} in the Archaean sea was low. Walker 1983, and Walker and Brimblecombe 1985, argued that $\text{SO}_4^{2-} < \sim 10^{-3}$ mole/litre is unlikely because volcanic SO_2 and H_2S would have been oxidised even in the absence of free O_2 . Further, disproportionation of dissolved oceanic bisulphite and sulphite could also contribute to elevation of Archaean SO_4^{2-} to roughly 10^{-3} mole/litre. Holland and Buekes 1990, reported an abrupt rise in O_2 to 15% PAL between 2.2 and 1.9 Ga. This report is in agreement with the observed increase in $\delta^{34}\text{S}$ of oceanic SO_4^{2-} at about 2.2 Ga by Lambert and Donnelly in 1986. This implies rapid rise of SO_4^{2-} in the sea in response to rise in atmospheric O_2 . Quite possibly all sulphides were oxidised to SO_4^{2-} after about 2.2 Ga facilitating SO_4^{2-} concentration to reach modern levels. The rarity of Archaean and Palaeoproterozoic

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gypsum thus appears to be due to low SO_4^{2-} ion concentration in the sea.

In a normal evaporite situation gypsum precipitation can be bypassed if the HCO_3^- ion concentration exceeds twice the Ca^{2+} ion concentration. In such an eventuality precipitation of carbonate would leave no Ca^{2+} for sulphate formation. Kempe and Degens postulated such a scenario in their 'soda ocean' model. Grotzinger and Kasting 1993 argued that the soda ocean evolved to the modern NaCl-ocean by about 1.8-1.6 Ga rather than by 800 Ma as proposed by Kempe and Degens. Grotzinger and Kasting also estimated the composition of the Precambrian ocean based on the abundance/absence of carbonate/gypsum in evaporite deposits of Archaean and Palaeoproterozoic. Their estimates predict an atmospheric pCO_2 of 0.03 to ~ 5 atm and an oceanic pH of ~ 5.7 to 8.6, lower pH values being favoured by higher pCO_2 . The estimated bicarbonate concentration is ~ 70 milli moles /litre at a pCO_2 of 0.3 atm and a pH of 6.9. In comparison, the present day HCO_3^- ion concentration is 2.3 milli moles/litre. This means that HCO_3^- ion played a much more significant role in the Archaean and Palaeoproterozoic ocean than now.

Precipitation Inhibitors

Carbonate sediments exhibit secular variation in texture from bedded, herringbone texture in the Archaean to micrite in Neoproterozoic and later periods (*Box 2*). Earlier workers attributed these textural changes to a decline in carbonate satu-

Box 2.

Micrite: Micrite is a fine-grained crystalline limestone with crystal sizes of <4 microns. The crystals are believed to have precipitated, from an oversaturated solution, in the water column over numerous centres of nucleation. The crystals in turn settle on the sea floor to form an agglomerate of fine grained rock, or cemented by stromatolites to form micritic stromatolites.

Herringbone Texture: Limestone rocks sometimes display alternating layers of very coarsely crystalline calcite, each layer having a serrated surface over which the next layer rests. The serrated texture is something similar to herringbone textile fabric. The texture is considered to represent precipitation of calcite directly on the sea floor on preexisting surfaces unlike micrite.



ration state of the ocean from supersaturated in the Archaean to less supersaturated in Neoproterozoic. Sumner and Grotzinger 1996 ascribed these changes to secular variations in concentration of carbonate precipitation inhibitors in the sea.

Sumner and Bowring 1996, considered the sea floor encrusting fibrous calcite displaying bedded and herringbone texture from the ~2.5 Ga Gramohaan Formation of South Africa, to have been precipitated directly on the sea floor. Similar directly precipitated carbonates have been described from late Archaean sediments by several researchers, confirming that the late Archaean sea was supersaturated in CaCO_3 . Despite the supersaturation water column micrite formation was absent unlike the situation in carbonate-saturated modern basins. As a result micrite-textured Archaean carbonates are rare. Sumner and Grotzinger 1996, suggested that predominance of herringbone texture in Archaean carbonate at a time when the atmosphere and sea were O_2 deficient is indicative of the presence of calcite precipitation inhibitors in the sea of those times.

Many cations and anions act as calcite precipitation inhibitors, the most effective one being Fe^{2+} . The inhibitors maintain the supersaturated state of seawater by preventing the precipitation of calcite as micrite in the water column and promoting crystal growth on existing carbonate surfaces on the sea floor. The abundance of herringbone calcite in O_2 -depleted environments is indicative of Fe^{2+} as the principal inhibitor to calcite crystallisation in the Archaean ocean. The association of iron formations with Archaean carbonates and the enhanced concentration of Fe^{2+} in Archaean calcites but not in younger ones are cited as evidences supporting the presence of Fe^{2+} in carbonate depositing milieu. This argument is also consistent with the Archaean ocean being Fe^{2+} rich as a consequence of low atmospheric O_2 . With the growth of atmospheric O_2 , seawater Fe^{2+} decreased and calcite precipitation shifted from bedded sea floor carbonate to water column micrite.

To conclude, devolatilisation of accreting planetesimals and

The abundance of herringbone calcite in O_2 -depleted environments is indicative of Fe^{2+} as the principal inhibitor to calcite crystallisation in the Archaean ocean.



Suggested Reading

- [1] J P Grotzinger, Trends in Precambrian carbonate sediments and their implications for understanding evolution, S Bengston (Ed) *Early life on Earth*, Nobel Symposium, No.84, Columbia University Press, New York, p. 245-258, 1994.
- [2] S Kempe and E T Degens, An early soda ocean, *Chemical Geology*, Vol.53, p.95-108, 1985.
- [3] J P Grotzinger and J F Kasting, New constraints on Precambrian Ocean Composition, *Journal of Geology*, Vol.101, p. 235-243, 1993.

subsequent condensation of water vapour formed the proto-ocean. The Moon-forming impact event dissipated all of this proto-ocean while continued impact of comets from the Oort cloud/Kuiper belt delivered the water to the modern ocean, a process that is still continuing. With the atmosphere being dominated by CO_2 , deficient in O_2 , the Archaean ocean was probably a soda ocean, enriched in Na_2CO_3 , NaHCO_3 and Fe^{2+} and low in dissolved O_2 and SO_4^{2-} . The liberation of free O_2 and its invasion first of the hydrosphere in the Palaeoproterozoic heralded the transition of the soda ocean to NaCl-dominated modern ocean. Na^+ delivered from continental weathering and Cl^- supplied by submarine hydrothermal exhalations favoured the ocean to become NaCl-dominated. SO_4^{2-} concentration also reached modern levels by about the Palaeoproterozoic promoted by increased continental SO_4^{2-} fluxes in the wake of accelerated oxidative weathering. The invasion of the hydrosphere by molecular O_2 resulted in Fe^{2+} being totally removed from the ocean. The Archaean ocean was also supersaturated with CaCO_3 but dissolved Fe^{2+} inhibited water column carbonate precipitation suggested by extreme dearth of micritic limestone in Archaean geological records. The chemical steady state of the ocean dates back to the late Palaeoproterozoic period and is being maintained since then.

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