

Evolution of the Atmosphere and Oceans: Evidence from Geological Records

1. Evolution of the Early Atmosphere

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Molecular O_2 and H_2O are the vital requirements of contemporary life. The evolution of the atmosphere and oceans, therefore, necessarily predates metazoan evolution on the earth. The prebiotic primary atmosphere had CH_4 , NH_3 and H_2 as the chief components and was O_2 -deficient. Dissociation of CH_4 and NH_3 paved the way for the secondary atmosphere composed principally of CO_2 .

Introduction

The O_2 -rich atmosphere and H_2O -filled oceans are unique to the Earth in the Solar System. Oxygen and H_2O are basic requirements of multicellular life and so the metazoan evolution succeeded the evolution of the atmosphere and oceans. The oceans and atmosphere are in equilibrium with each other and regular transfer of gases and water takes place between them in order to maintain this equilibrium. Because of this intimate interrelationship, no discourse on the oceans and atmosphere can be exclusive of each other.

The atmosphere has an insignificant mass in comparison to the mass of the Earth, being 10^{-6} times the mass of the Earth. The composition of the present atmosphere is relatively simple. Three constituents, namely N_2 (75%), O_2 (23%) and Ar(1%) make up 99% by weight of the atmosphere. Among the minor constituents CO_2 forms roughly 0.04% but its role is very significant as it regulates the Earth's climate and provides the raw material for the sustenance of plant life on which is dependent the animal life.



The Primary Atmosphere

There is consensus of opinion that the Earth's atmosphere was formed from the volatiles supplied during early episodes of planetesimal impacts and gases released during subsequent mantle degassing. Current evidences point out that ~95% of rare gases were degassed by impact events during the Earth's accretion. The primordial atmosphere did not have its present composition. According to Oparin–Urey model, CH_4 and small amounts of NH_3 , H_2 , He and H_2O were the chief constituents of the atmosphere in the convulsive periods of the planet's evolution during the first 200 Ma (Mega annum = 10^6 years). In contrast to modern volcanic emanations, the early volcanoes must have belched out CH_4 , NH_3 and H_2 . This view is in agreement with H_2 and He being the most abundant elements in the universe and in the atmosphere of the giant planets. Further, CH_4 and N_2 have been detected in mantle-derived diamonds and kimberlites and are believed to represent trapped gases from the early period. This type of atmosphere is favoured for the Miller–Urey synthesis (Box 1) of prebiotic organic molecules. But this period, being very inhospitable, is too early to have fostered the origin of life.

It is regarded that the primordial magma ocean was deficient in O_2 and so would have contained Fe in a reduced form such as Fe metal. Metallic Fe reacts with H_2O releasing H_2 . The primeval atmosphere accordingly must have had more of H_2 than H_2O . Similarly CO would have dominated over CO_2 ; but in an H_2 -rich atmosphere CO would react with H_2 to form CH_4 . Thus the dominant C species in the primary atmosphere was CH_4 , while N_2 occurred as NH_3 and S as H_2S .

Hydrogen rapidly escaped from the atmosphere into space and unless enough H_2 was supplied through volcanoes and dissociation of water, the partial pressure of H_2 might not have been maintained for long. Besides, the diminishing volcanic activity and segregation of metallic iron in the core facilitated release of more oxidised species by volcanoes. As a result H_2 concentra-

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Box 1. Miller–Urey Experiment

The first laboratory experiment to synthesise organic molecules was performed by Stanley Miller and Harold Urey in 1953. They passed electric discharge through a gaseous mixture of CH_4 , NH_3 and H_2 . The electrical discharge represented lightning as the source of energy and the gaseous mixture the prebiotic atmosphere. The experiment yielded several amino acids confirming that these molecules were readily produced in the primitive atmosphere. Amino acids are the starting molecules for the origin of life.

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tion in the atmosphere decreased with time and inevitably that of CH_4 and NH_3 too. Further, both CH_4 and NH_3 can be easily dissociated by UV radiation releasing H_2 and N_2 and so the CH_4 - NH_3 -rich atmosphere was not stable for long. In a similar way H_2S was also destroyed by UV radiation or transferred by weathering reactions to the sedimentary reservoir.

With diminishing abundance of H_2 in the atmosphere in the wake of decreasing volcanic sources, CO_2 gained dominance by photodissociation of CH_4 in the presence of H_2O vapour. Similarly NH_3 dissociated into N_2 . In this way CH_4 and NH_3 enriched primordial atmosphere is believed to have given way to a volatile-enriched secondary atmosphere (the Abelson-type atmosphere). The water vapour condensed to form the early oceans while N_2 and noble gases, being chemically inert, went on accumulating to the present level. The Abelson model of the atmosphere had CO_2 , CO , N_2 , H_2 and HCl as the principal components. Neither Oparin nor Abelson model considers free O_2 as a constituent of the early atmosphere.

The Secondary Atmosphere

Geological evidence is consistent with the emergence of a volatile-rich atmosphere by the time stratigraphical record began ~ 3.8 Ga (Giga annum = 10^9 years) ago. These volatiles (H_2O , CO_2 and SO_2) are required for the chemical weathering of rocks to produce sedimentary rocks. These are also the chief gaseous components in modern volcanic eruptions, although these volatiles today are largely recycled through lithospheric subduction. The volatile-dominated Archaean atmosphere is considered to have evolved by the process of mantle degassing through volcanic and hydrothermal vents since the accretion of the Earth. However, the entire volatiles released through degassing are not in the atmosphere-ocean system today. A significant inventory of the volatiles, which were involved in weathering cycles, eventually got transferred to the sedimentary reservoirs as constituents of carbonates, clay minerals, organic matter and sulphides. Roughly a third of the outgassed H_2O and almost



all of C and S reside in the crust today while the remaining is in the ocean-atmosphere system. Nitrogen is chemically inert and was not considered to get transferred to the sedimentary reservoirs CO_2 or H_2O . However, Tolstikhin and Marty (1998), based on stable nitrogen isotope studies, concluded that the N_2 abundance of the early atmosphere was close to that presently observed, which means that N_2 level in the atmosphere did not increase over the years as has been thought till recently. Recent data show that the present N_2 outgassing flux is about five times lower than the subducted flux. This signals that atmospheric N_2 is slowly being swallowed by the mantle. The chief pathway of this trapping is through NH_4^+ ions in sediments undergoing subduction. Javoy (1998) considers the formation of very stable titanium nitride (osbornite, TiN) or substitution of nitrides for O_2 in mantle silicates as the principle storage form of N_2 in the mantle.

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Whether degassing and volatile accumulation in the atmosphere was a catastrophic early event or a continuous process is controversial. While there was certainly an early event of rapid degassing, there is overwhelming evidence to suggest that degassing has also occurred throughout geological time. Convincing evidence for gradual degassing comes from two sources, namely Ar accumulation and ^3He loss in the atmosphere. Atmospheric Ar is 99.6% ^{40}Ar formed by the decay of ^{40}K with a half life of 1.25 Ga. Such a long half life demands continuous production of ^{40}Ar throughout Earth's history. Besides, generation of the entire ^{40}Ar during an initial catastrophic degassing event would require a very high initial abundance of ^{40}K . This would have, in turn, led to high heat flow even today, much more than what is observed.

Helium has two isotopes: ^4He and ^3He . The ^4He isotope is produced by the radioactive decay of U and Th and accounts for 99.99% of that released from the Earth. The sources of ^3He are the decay of tritium (^3H) and interaction of cosmic rays with atmospheric gases. These sources account for only 10% of He lost annually from the atmosphere. Helium budget studies of



Suggested Reading

- [1] H D Holland and others, Evolution of the atmosphere and oceans, *Nature*, 320, 27–33, 1986.
- [2] E Donald Canfield and Andreas Teske, Late Proterozoic rise in atmospheric oxygen, Concentration inferred from phylogenetic and sulphur isotope studies, *Nature*, 382, 127–132, 1996.
- [3] Rob Rye and others, Atmospheric carbon dioxide concentrations before 2.2 b.y ago, *Nature*, 378, 603–605, 1995.
- [4] M Kenneth Towe, Aerobic respiration in the Archaean, *Nature*, 348, 54–56, 1990.
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Togersen in 1988 imply that the atmospheric ^3He content is dominantly due to mantle degassing of primordial ^3He by volcanic processes. ^3He is ubiquitous in submarine vent fluids, ridge basalts and deep waters while many deep sea hotspot volcanoes such as those in Hawaii, Iceland, Reunion, Galapagos and Kerguelen have high ^3He in the gaseous emanation. These data confirm that juvenile ^3He is being released from mantle sources even today and that the mantle is not yet completely degassed.

Both CO_2 and H_2O , the chief components of the secondary atmosphere, are green-house gases and their abundance in the atmosphere would have had much effect in regulating the surface temperature of the Archaean Earth. In 1986, Kasting calculated a $p\text{CO}_2$ of ~ 0.05 atmosphere (atm) in the Archaean or roughly 100 times the present atmospheric level of 360 ppm. His estimates also show that by the late Proterozoic times the CO_2 level had decreased 10 times.

Atmospheric CO_2

The atmospheric CO_2 concentration today is volumetrically insignificant. But the Archaean atmosphere was over 100 times more enriched in CO_2 than it is today. Thus the sources of CO_2 that existed then must have exceeded its sink in chemical weathering of crustal rocks. Higher CO_2 accelerates chemical weathering and so elevated CO_2 in the early atmosphere was a transient phenomenon; it would have adjusted itself over geologically short periods of time. Chemical analysis of sedimentary rocks formed at different periods of Earth's history indicates that nearly all CaO and half of all MgO of igneous rocks have always been converted to carbonates by weathering since about 3 Ga. Further, the organic C to carbonate C ratio in sediments has also remained constant over the same period. It is the CO_2 abundance in the atmosphere that regulates these transformations. The above data according to many researchers are, therefore, indicative of a relatively constant atmospheric CO_2 since about 3 Ga, barring a few abrupt excursions such as in the terminal Cretaceous period (65 Ma).



The intensity of chemical weathering today is due largely to higher soil-air CO₂ generated by the bacterial oxidation of organic matter. In the absence of land plants, the soil-air CO₂ was much lower in the Precambrian (Box 2). The relatively constant rate of CO₂ output, as indicated by the chemistry of sedimentary rocks, on the other hand, is in agreement with a higher atmospheric CO₂ in the Precambrian.

Standard solar models suggest a lower solar luminosity in the Archaean. Newman and Rood 1977, and Gough 1981, concluded that the luminosity increased from ~70% of its present value 4.6 Ga ago to 82% of its present value at the end of Archaean. The low luminosity would have lowered the surface temperature and triggered a runaway glaciation. However, there is no evidence of an Archaean glaciation in the geological record. One possibility is that a higher concentration of greenhouse gases could have mitigated the effect of reduced solar flux. Among the greenhouse gases, CO₂ is the most stable and likely candidate for the Archaean atmosphere. In 1987, Kasting showed that the pCO₂ during the Huronian glaciation (dated ~2.3 Ga) was between 0.03 to 0.3 atm, enough to produce a mean surface temperature of 5°C to 20°C. Somewhat higher pCO₂ is necessary to account for the warmer Archaean surface. The reasonable lower and upper limits estimated by Grotzinger and Kasting in 1993 are 0.03 atm and 5 atm, respectively. Lower than this would have frozen the Archaean oceans, whereas higher concentrations would have evaporated the entire ocean by greenhouse warming as is believed to have happened on Venus which possibly had a primordial ocean. By early Proterozoic times this had decreased to 0.02–0.25 atm and to 10⁻⁴–0.025 atm by late Proterozoic.

Another line of evidence for atmospheric CO₂ in the Precambrian comes from the examination of fossil weathering profiles called *palaeosols*. Occurrence of *palaeosols* has been reported from many Precambrian terranes. Using *Palaeosol* data, Rob Rye and coworkers (1995) constrained atmospheric pCO₂ between 2.75 Ga and 2.2 Ga. The Fe lost from the top of these profiles is

Box 2. The Precambrian

The Precambrian Era of geologic time encompasses a vast span of time from the origin of the Earth ~4.6 Ga ago to the explosion of life in geologic history at about 600 Ma. The era that followed is called Phanerozoic and includes the remaining time. The Precambrian is divided into an older Archaean and a younger Proterozoic period with the boundary taken at 2.5 Ga. The Proterozoic is sub-divided further into Palaeoproterozoic (2.5 – 1.7 Ga), Mesoproterozoic (1.7–0.9 Ga) and Neoproterozoic (900 – 600 Ma).

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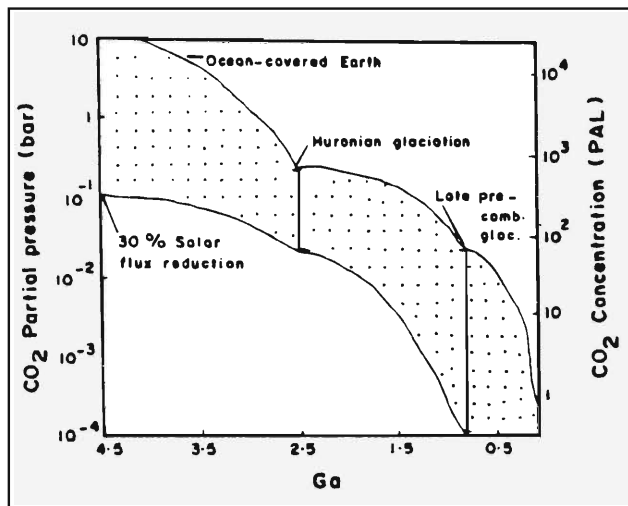


Figure 1. The variation of atmospheric CO₂ through time (J A Kasting, 1992).

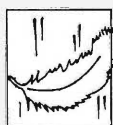
reprecipitated lower down in the profiles as Fe-silicate minerals rather than as Fe-carbonates. From this observation they calculated that atmospheric CO₂ during this interval was about 100 times today's level. This figure is still five times lower than that required to compensate for the lower solar flux at 2.7 Ga. Therefore, these authors postulate that greenhouse gases other than CO₂ must have contributed significantly to the atmospheric warming during the late-Archaeon-early-

Proterozoic. Ammonia, CH₄ and H₂O vapours, all greenhouse gases, are unlikely to have contributed to warming as all of them are unstable under UV irradiation, in the absence of an O₃ shield. A combination of CO₂ and CH₄ in the opinion of these authors, in an O₂-free late-Archaeon-early-Proterozoic atmosphere, would have maintained a high Earth-surface temperature required to offset the low temperature due to reduced solar radiation. Buick and colleagues reported in 1995 an important *palaeosol* older than 3.46 Ga from the Pilbara craton of Australia. Preliminary studies of this *palaeosol* predict a pCO₂ substantially higher at 3.46 Ga than at 2.75 Ga indicating that the CO₂ level decreased towards late Archean concomitant with increase in solar radiation. The variation of atmospheric CO₂ through Earth's history is shown in *Figure 1*. The dotted area in the *figure* represents the range of pCO₂ consistent with the predicted climatic model of Kasting, 1992.

In the next part, we take up processes leading to the enhancement of oxygen in the atmosphere leading to its present levels.

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"It is as fatal as it is cowardly to blink facts because they are not to our taste"
wrote Tyndall in "Science and Man".