OXIDATION STATE OF THE EARTH'S UPPER MANTLE DURING THE LAST 3800 MILLION YEARS: IMPLICATIONS FOR THE ORIGIN OF LIFE.

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"The gossamer web of life, spun on the loom of sunlight from the breath of an infant Earth, is Nature's crowning achievement on this planet." [1]

A popular, as well as scientifically rigorous, scenario for the origin of life on Earth involves the production of organic molecules by interaction of lightning (or other forms of energy) with a chemically reducing atmosphere in the early history of Earth [e.g., 2-7]. Experiments since the 1950's have convincingly demonstrated that the yield of organic molecules is high when the atmosphere contains molecular hydrogen, methane, ammonia, and water vapor. Additional work has also shown that such a highly reducing atmosphere might not, however, have been sufficiently long-lived in the presence of intense solar ultraviolet radiation [e.g., 8-13] for life to have formed from it. One way of maintaining such an atmosphere would be to have a continual replenishment of the reduced gases by prolonged volcanic outgassing from a reducing Earth's interior. The length of time that this replenishment might need to continue is in part constrained by the flux of asteroids onto the Earth's surface containing sufficient energy to destroy most, if not all, life that had developed up to that point in time. If a reducing atmosphere is a key ingredient for the origin of life on Earth, the time of the last environmental sterilization due to large impacts would be an important constraint. In a deep marine setting (e.g., hydrothermal vent), the last global sterilization might have occurred at 4200-4000 Ma [14]. On the Earth's surface, the last global sterilization event might have occurred at 4000-3700 Ma [14-16]. If these are meaningful constraints, how likely is it that a reducing atmosphere could have survived on the Earth until about 3800 Ma ago? Due to the importance of replenishing this atmosphere with reducing components by volcanic outgassing from the mantle, geochemical information on the history of the mantle's oxidation state would be useful for addressing this question. Geochemical and experimental data discussed in this abstract suggest that extrusive mafic volcanics derived from the upper mantle have had oxidation states near the fayalite-magnetite-quartz buffer throughout the last 3800 Ma. At magmatic temperatures, the gases released from volcanoes having this oxidation state would have been, as they are today, composed dominantly of carbon dioxide and water vapor [e.g., 17-20], and hence would not contain the ingredients for maintaining a reducing atmosphere. Consequently, geochemical data do not favor the survival of a reducing atmosphere until about 3800 Ma. Alternative venues and pathways for the origin of life need to be investigated (e.g., hydrothermal vents along oceanic ridges; 21-25).

To constrain the oxidation state of mafic volcanics throughout the last 3800 Ma of Earth history, a new method will be relied upon that still needs additional experimental calibration. The principal concept of this approach is the following: the abundance of chromium (Cr) in a spinel-saturated, mafic magma is a strong function of oxidation state and temperature [e.g., 26,27]. Experimental data conducted during the current investigation, as well as that from earlier workers [26,27], has been used to define the IW (iron-wustite) and FMQ (fayalite-magnetite-quartz) buffers in Figure 1. The parameter MgO in Figure 1 is a proxy for temperature. The two groups of whole-rock data plotted in Figure 1 show the compositions of mid-ocean ridge basaltic glasses [open circles near FMQ; data from 28-34] and lunar mare volcanics (half-filled circles near IW). These data indicate, in agreement with other independent methods [e.g., 35-37], that modern terrestrial volcanics are relatively oxidizing (i.e., FMQ), whereas lunar mare volcanics are reducing (i.e., IW).

This approach can also be applied to older mafic volcanics in order to infer their ***original*** oxidation state, if subsequent metamorphism has not caused the whole rock to be an open system with respect to either Mg or Cr. For example, Figure 2 shows the compositions of Early Archean lavas [3000-3500 Ma; data from 38-40]. Those data suggest that these lavas had oxidation states near the FMQ buffer at the time of their eruption. This characteristic is observed in mafic volcanics throughout geologic history, including those from Isua, Greenland having an age of 3800 Ma.

In conclusion, these results suggest that the oxidation state of mafic volcanics derived from the Earth's upper mantle during the last 3800 Ma has been consistently near FMQ. If this accurately reflects the oxidation state of those portions of the mantle that contributed gaseous components to the early atmosphere, then these data indicate that a reducing atmosphere could not have been sustained by volcanic outgassing at 3800 Ma, or later. This same conclusion has been reached using other independent evidence [e.g., 41]. Although more reduced regions of the mantle may have existed [42], their contribution to the atmosphere may not have been significant

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since no ancient volcanics from such regions have yet been identified. The impact constraints on the old side of 3800 Ma, as well as the geochemical constraints on the young side of 3800 Ma, seem to make a "traditional" view of life's origin unlikely. Alternative scenarios for the origin of life need to be investigated.

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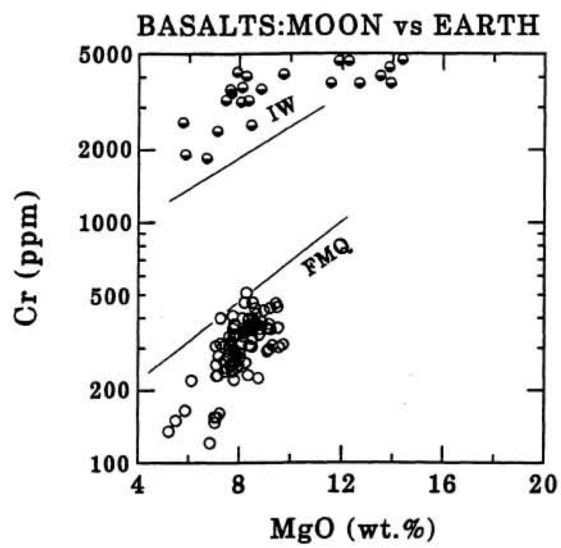

FIGURE 1
Compositions of terrestrial [26-34] and lunar basalts and glasses display evidence for different oxidation states.

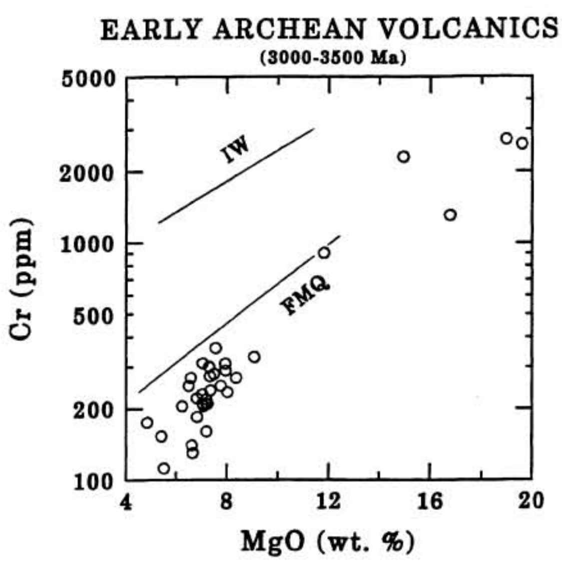

FIGURE 2
Mafic and ultramafic volcanics of Early Archean age [3000-3500 Ma; data from 38-40] were erupted having oxidation states near FMQ.