CO_2-N_2-H_2 Atmosphere and Transient Habitability on Ancient Mars Indicated by C, N, Ar, and H isotopes

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Introduction:

Mars today is a frigid, arid planet with an atmosphere too thin to support liquid water on its surface. Yet abundant geologic evidence – valley networks, lakebed sediments, and hydrated minerals – shows that liquid water flowed on early Mars billions of years ago. This paradox implies that Mars's climate in the distant past was significantly warmer and wetter than today. A long-standing question is how Mars's atmosphere evolved from a potentially habitable state to the present thin, cold state. Recent advances have provided new clues: precise measurements of atmospheric isotopes (of carbon, nitrogen, argon, and hydrogen) by missions like Curiosity, mapping of carbonate and nitrate minerals that locked away atmospheric gases, and MAVEN's observations of ongoing atmospheric escape. These datasets, combined with modeling, allowed us to reconstruct the ancient atmosphere and climate state of Mars. Here we present a synthesis of this reconstruction, focusing on isotopic evidence and its implications for past climate and habitability.

Methods:

We employ an integrated modeling approach to trace Mars's atmospheric evolution from the late Noachian (~3.8 billion years ago) to present [1]. Our current models [2,3] track the inventories and isotopic ratios of major gases (CO_2, N_2, Ar, and H_2O) through key processes: volcanic outgassing, atmospheric escape to space, and sequestration of volatiles into rocks (e.g. carbonates, nitrates, hydrated minerals). Modern isotopic measurements serve as stringent benchmarks – for instance, Mars's atmosphere is enriched in heavy isotopes like ^{13}C, ^{15}N, ^{38}Ar, and D relative to the magmatic components of the Martian meteorites or initial solar system ratios, indicating preferential loss of lighter isotopes over time. We assimilate data on the current atmospheric composition, the size of present-day reservoirs (e.g., polar CO_2 ice, adsorbed gases in soil), and the estimated amounts of CO_2, H_2O, and N fixed in crustal minerals. We reevaluate the isotopic fractionation effects in the photochemical escape of C and N. A wide range of possible histories is explored via Monte Carlo simulations (on the order of one million runs) to identify scenarios that reproduce today's isotopic ratios and known volatile reservoirs. This multifaceted approach ensures consistency with both atmospheric chemistry and geological evidence.

Results and Discussion:

Emerging Paleo-Atmosphere Paradigm. Our results converge on a compelling picture of the Martian atmosphere through time. The late Noachian atmosphere (~3.8 Ga) was likely multi-component, composed of CO_2 on the order of ~1 bar or less, plus substantial N_2 (on the order of 0.1–0.5 bar) and occasional spikes of H_2 (up to ~10%). In fact, the modeling suggests an N_2-rich early atmosphere with N_2 partial pressure around ~0.3 bar [4]. This helps resolve the long-standing paradox of Mars's nitrogen: the moderate ^{15}N enrichment observed today can be explained without invoking an unrealistically thick (>3–4 bar) CO_2 atmosphere or extreme recent outgassing. The required CO_2 levels in the Noachian appear moderate, not tens of bars as once speculated. Scenarios with CO_2 much above 1–2 bars are only viable if nearly all that CO_2 was later removed into extensive carbonate deposits, which is inconsistent with the limited carbonates found on Mars. Thus, a moderately dense (~1 bar) atmosphere is favored.

Moreover, the isotopic and mineral evidence indicate that H_2 was likely present episodically in the ancient atmosphere [5,6,7]. Volcanic outgassing from a chemically reduced mantle and water-rock reactions (e.g., serpentinization, magnetite authigenesis) could have injected H_2 , perhaps accumulating to the few-percent level. A greenhouse atmosphere composed of ~1 bar CO_2 with ~0.3 bar N_2 and a few percent H_2 provides an elegant solution to Mars's climate puzzle: climate models show that CO_2–N_2 alone was insufficient to warm Mars, but adding several percent hydrogen greatly enhances the greenhouse effect [7]. Warming early Mars with CO_2 and H_2 alone requires hydrogen fluxes that stretch the limits set by geochemical constraints [8]. However, including 0.1–0.5 bar N_2 enhances the greenhouse effect through pressure broadening, thereby reducing the required H_2 abundance and making the climate scenario more consistent with volatile outgassing estimates.

Volatile Loss and Sequestration. Over time, Mars inexorably lost the bulk of its atmosphere. Isotopic fractionation records this loss: for example, high $\delta^{13}C$ and $\delta^{15}N$ values in the modern air imply that a large fraction of the original CO_2 and N_2 was removed via escape to space or trapped in rocks. Sputtering and photochemical escape driven by the solar wind stripped away lighter isotopes preferentially, enriching the remainder. Our model scenarios that match present-day $^{13}C/^{12}C$ ratios indicate Mars had already lost a substantial amount of CO_2 by the Hesperian period, with surface pressure likely dropping below a few hundred millibars by 3.5–3.0 Ga. Similarly, the enrichment of ^{38}Ar (which is inert) points to significant atmosphere escape over time.

In addition to escape, surface processes played a role: we find that carbonate formation in ancient lakes may have sequestered up to the equivalent of ~0.5–1 bar of CO_2 if an initial ~1–1.5 bar atmosphere is assumed. Much of Mars's water inventory may have also been lost to form hydrated minerals in the crust – D/H ratios ~6× higher than Earth's Ocean by a combination of loss to space and crustal sequestration. This reconciles the presence of widespread clay minerals with the idea of a gradually drying Mars. The end result of these processes is the thin CO_2 atmosphere we observe today, with only residual amounts of N_2 and Ar.

Climate and Habitability Implications. This CO_2–N_2–H_2 atmosphere in the late Noachian could raise mean surface temperatures toward the melting point of water and sustain intermittent (~10^5–10^6 year) warm periods consistent with the geologic record. During these windows, snow/ice deposits would melt and run off, carving the valley networks and feeding lakes, while global average conditions may have remained cooler overall – a scenario of transient habitability rather than a permanently tropical Mars.

Moreover, the inclusion of H_2 implies a more reducing atmospheric chemistry, which aligns with certain mineralogical observations (e.g., co-occurrence of oxidized and reduced iron minerals in the same strata) that suggest variable redox conditions in Martian history [7]. The presence of available nitrogen and sustained liquid water in these intervals also strengthens the case that early Mars was potentially habitable and perhaps briefly hospitable for life.

Implication for Future Exploration:

This synthesis of Mars's atmospheric evolution provides a framework for upcoming missions and studies. A priority will be to validate these atmospheric histories by searching for chemical and isotopic fingerprints in the Martian rock record. For example, carbonate minerals precipitated from ancient surface waters might trap a record of past atmospheric CO_2 isotope ratios, while nitrate deposits in sediments could reflect the abundance of N_2 and its isotopic composition in the Noachian atmosphere. NASA's Perseverance rover is currently collecting samples of ancient Jezero Crater rocks – including carbonates, nitrates, and clays – that, when returned to Earth, will allow laboratory measurements of these isotopic markers with high precision. Such samples could directly reveal the atmosphere's composition ~3.5–4 Ga and test the model of a CO_2–N_2–H_2 greenhouse. Additionally, continued orbital and in-situ measurements of atmospheric escape (e.g. MAVEN's ongoing observations of ion escape) will refine estimates of how fast Mars is losing gases today, improving our backward models of loss over time.

Understanding how Mars transformed from a wetter, thicker-atmosphere world to its present state also has broad implications. It informs how planetary atmospheres can be lost – a cautionary tale for Earth-like exoplanets in harsh environments – and it guides us in assessing the long-term habitability of terrestrial planets. In the coming decade, Mars sample return and advanced isotope analyses promise to fill remaining gaps in our timeline of Mars through time, bringing us closer to unraveling the mystery of how Mars went from blue to red. Each new piece of evidence will test and refine the emerging paradigm of a multi-component ancient atmosphere and its progressive depletion, sharpening our understanding of Mars's past climates and its capacity to support life.

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