THE CARBON CYCLE, CLIMATE VARIABILITY AND THE FATE OF AN EARLY MARTIAN OCEAN.
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Introduction: The surface of Mars preserves the record of a past climate in which liquid water was stable and apparently abundant [1]. We seek to understand the planetary-scale control of climate through the study of climatic perturbations and their relationship to the carbon cycle on Earth, making basic geological and geochemical observations and then comparing these data with simple models of biogeochemical cycles. We have previously applied this approach to a range of geological situations on Earth including the Neoproterozoic glaciations (i.e., Snowball Earth) [2,3] and a new theory for what causes oscillations in CO2 and climate on ~100 million year time scales [4].

Water and the Present Climate: Water is an essential ingredient for regulating climate. On Mars, as on Earth, there is substantial water on the surface at present, but it exists not as liquid water but as residual polar ice caps. Altimetric observations from the Mars Global Surveyor spacecraft showed that the Martian polar caps collectively contain the equivalent of approximately 85% the water in the Greenland ice sheet [5-7]. Mars has also long been thought to contain water ice in the subsurface [e.g., 8], and recent observations from the Mars Odyssey spacecraft have identified a substantial amount (in excess of 50 weight %) in the upper 2 meters of the Martian crust [9-11].

The CO2-rich atmosphere with 6 mb surface pressure is inadequate to keep Martian surface temperatures above freezing, (except, in the current epoch, for local equatorial areas for brief periods). What has limited the accumulation of atmospheric CO2 is not silicate weathering, but rather the lack of a modern volcanic source of CO2. If volcanism existed on Mars today as it likely does on Venus, CO2 would accumulate in the atmosphere until the ice caps melted. This in turn would limit the continued rise of atmospheric CO2 through the silicate weathering feedback.

Water and the Early Climate: Although liquid water is not stable at the surface today, there are a large number of observations that suggest that liquid water existed at least episodically at various times throughout Martian history [1]. Although most morphological evidence for liquid water on Mars is consistent either with episodic and rapid release of water at the surface, or else with liquid water in the subsurface that results in chemical weathering reactions, the presence of valley networks and the degradation of impact craters on ancient surfaces of late Noachian age imply weathering and erosion by liquid water at the surface, in some areas for substantial periods [e.g., 1, 12].

One particularly interesting aspect of Martian surface geology is the apparent discrepancy between the geological evidence for water on Mars during the Noachian and the lack of calcium carbonate on the surface [13]. If a large body of liquid water on Mars persisted for millions of years or longer, the high CO2 atmosphere would form carbonic acid, and react with the silicate crust, producing abundant calcium carbonate. However, carbonate minerals have not yet been detected on the surface in sufficient quantities to be consistent with this hypothesis [14].

The Carbon Cycle and the Early Ocean: A potential explanation for the observations is the possibility that climate episodes warm enough to maintain an active hydrologic cycle endured only long enough to produce the erosional features, but not long enough for calcium carbonate to reach saturation. Consider a scenario in which volcanic outgassing peaks during the Noachian, plausibly associated with the emplacement of a substantial fraction of the massive volcanotectonic Tharsis rise [15]. Such a volcanic event would have liberated significant water from the interior and raised atmospheric CO2. In this case, fresh water would flow to topographic lowlands, with crustal water and perhaps precipitation in highlands replenishing the fluvial systems [cf. 16]. Silicate weathering would commence, with streams and rivers bringing alkalinity from the sites of silicate weathering to the low-lying basins, exactly as they do on the Earth today. However, the delivery of alkalinity to the fresh water oceans would have a large effect on the atmospheric composition.

Fresh water with no alkalinity can hold very little dissolved inorganic carbon. As alkalinity increases, the pH rises, and more and more carbon enters the solution. On Mars, the result of the formation of large freshwater ocean would be the transfer of carbon from the atmosphere into the ocean as silicate weathering proceeded. The limit on alkalinity build-up in the Martian seawater would come when calcium carbonate became supersaturated and began to precipitate. However, if the ocean volume were of large enough mass relative to the atmosphere, the uptake of CO2 would have the potential to reduce atmospheric pCO2 sufficiently to lower the greenhouse forcing and plunge the planet back into a frost long before calcite saturation
was ever reached.

We are currently modeling this scenario for different ocean volumes \([e.e., 7, 17]\) and different atmospheric CO\(_2\) concentrations. The calculations assume simple calcium silicate chemistry for the crust and use equilibrium constants appropriate for the system CaO-CO\(_2\)-H\(_2\)O. The critical assumption made here is that volcanic outgassing at this time was not ongoing at a sufficient rate to replace whatever CO\(_2\) was lost from the atmosphere by ocean uptake.

In our model, the lack of observed abundant calcium carbonate on Mars today is due simply to the fact that oceans on Mars never lasted long enough for alkalinity to build up to saturation. The idea that carbon uptake by a Martian ocean would provide a sufficient negative feedback to destabilize an equable Martian climate is highly speculative. It represents one possible solution to the apparent contradiction between the clear evidence that liquid water existed on the Martian surface during the late Noachian and the low level of calcium carbonate so far detected on the Martian surface \([13, 14]\). Another class of hypotheses that we are exploring involves the possibility that calcium carbonate deposits were formed on the floor of a Martian ocean, but subsequent percolation of water into the subsurface dissolved the deposits, precipitating carbonate minerals in veins in the subsurface.

**References:**