Introduction: Studies of the fractionation of non-condensable isotopes [1,2], fluvial and lacustrine systems on Hesperian-aged terrain [3,4] and climate studies with general climate models [5], suggest that 500 mbar or more of CO$_2$ prevailed during the Early Hesperian. How can we satisfactorily explain the transition from a thick early atmosphere to the thin atmosphere of today? The Mars Evolution Code (MEC) was written to address this question [6,7].

The goal of MEC is to incorporate an exhaustive set of sources, sinks, and reservoirs of CO$_2$, including an active regolith, whose evolution is constrained by the interconnecting fluxes, drawn from the literature, making a fully coupled system in energy-balance. Stepping forward in time in 500 year steps, MEC is driven by various synthetic obliquity sequences [6,7]. $^{14}$N and $^{15}$N have been incorporated in MEC as an additional constraint on CO$_2$ evolution since, given a fixed N$_2$ inventory, the rate of escape and fractionation of nitrogen is inversely proportional to P$_{CO_2}$.

Given an initial inventory and the uncertainties in the parameterizations of control variables for fluxes, and temperatures, program runs can generate a “solution space” at $t=0$ for comparison with actual data. Currently, the solution space does not circumscribe the data, as simulations were unable to reach the present with an exchangeable inventory of less than about 130 mbars [6].

While estimated photochemical plus sputtering escape is less than 80 mbars since 4 Ga [8], volcanic outgassing [9] is a source comparable to the escape rate to space during Hesperian Mars. Also, weathering loses its ability to draw down CO$_2$ below pressures of P$_{CO_2}$~150 mbar. Given this, and the 500 mbar inventory at 3.7 Ga, we suggest that an significant unanticipated sink of CO$_2$ will be needed to resolve the “missing CO$_2$” problem.

We suggest two previously neglected sinks of CO$_2$. First, the reflection-free zones (RFZ) detected within the South polar layered deposits (SPLD) using shallow radar [10] could represent many tens of millibars of buried CO$_2$, although only about 7 mbar under the residual cap have been verified [11]. Second, basal melting and possible sequestration of thick CO$_2$ caps on early Mars may occur [12,13]. While the former is relevant to the last ~100 Myr of SPLD growth [14,15], the latter is relevant to the Hesperian and Early Amazonian periods for which there is proxy climate data with which to judge atmospheric thickness. In this connection, there are indications that fluvial activity declined in discrete steps [3], as would be expected of intervening periods of basal melting and sequestration. However, between the Early Amazonian and the present, there is little to constrain collapses other than their effect on the isotope ratio of nitrogen or other non-condensable volatiles.

Stability of CO$_2$ deposits: Modern deposits need a thick (>20 m) water boundary layer to be stable against ablation from the maxima of obliquity fluctuations that occur between the minima [16,13]. For this to occur on today’s planet requires perihelion to be in the northern summer [17]. In this case, more water is sublimed from the cap, it migrates toward the equator and can rise to ~25 km, allowing it to become entrained in the rising Hadley circulation and transported into the southern hemisphere. Currently, with perihelion in the southern summer, saturation and freezing of water vapor and precipitation sets in at ~10 km – out of the reach of the Hadley cell. Hence, with perihelion in the northern summer, transport is enhanced 10-fold relative to current rates [17].

Following a prolonged period with high obliquity, water ice would be concentrated at mid-latitudes [18], and when the obliquity falls, as it did ~4.5 Ma [19], more water would likely be transported poleward since much water was already in the southern hemisphere. If the RFZs beyond the residual cap are CO$_2$, deposits formed early in the transition from a high to a low obliquity, the expected thicker boundary layers could have protected the deposits during the intervening high-obliquity periods. There appear to have been three such stages of SPLD construction [15].

Thermal structure of CO$_2$ deposits: Manning et al. [13] studied the thermal structure of CO$_2$ slabs buried under a surface boundary layer of about 20 m of water ice. In calculating CO$_2$ thermal structure, the thinner H$_2$O boundary layers can be neglected since, compressed under a massive CO$_2$ deposit, their thermal conductivity is high, and would negligibly affect CO$_2$ temperatures. We calculated the minimum thickness, $z^*$, of a single CO$_2$ slab that reaches the threshold for melting. We find that $z^*=(93.4/H) \ln(T_v/T_0)=25.1/H$ [13], where the base temperature, T$_v=216.6$ K, (the triple point), T$_0=163\pm3.4$ K (under 20 m of water ice),
is the top of the CO$_2$ slab, and the geothermal flux, $H=0.02$ W/m$^2$ [13]. Although the mean geothermal flux on Mars thought to be about 30 mW m$^{-2}$, it is closer to 20 mW m$^2$ [20] on the South pole. We conservatively estimate the geothermal flux in Hesperian Mars as 3 times the current value or $H=60$ mW m$^2$. If at this point, the atmosphere was 250 mbars, a thick deposit would be formed with a depth $z'\gg z^*$, implying robust basal melting.

**Melting rates of CO$_2$ deposits:** With slabs thicker than $z^*$, actual melting can occur. The melting flux, $d^2M/dAdt=(H-H_0)/\Delta H_0=\Delta T k_\text{eff}(z'-z^*)/z^*$, where $M$ is the mass of frozen CO$_2$, $\Delta H_0=1.897\times10^8$ J kg$^{-1}$, is the heat of fusion, $H_0=\Delta T k_\text{eff} z'$, with $\Delta T=216.6-165.5=52.1$ K, and $k_\text{eff}=0.5$ is the average thermal conductivity [13]. Consider a 250 mbar atmosphere (about $M=10^{18}$ kg of CO$_2$), collapsing onto the South pole. The current residual cap has an area of approximately $A_{\text{cap}}=4\times10^{11}$ m$^2$. The cap’s thickness would be, $z^*\approx M/(\rho A_{\text{cap}})$, where $\rho=1600$ kg m$^{-3}$ for CO$_2$; $z^*=1.56$ km. In this case, we find $z^*=25.1/0.06=420$ m. The vertical melting rate is $d^2M/dAt=2.38\times10^8$ kg m$^{-2}$ s$^{-1}$, or 7.53 kg m$^{-2}$ yr$^{-1}$. Over the whole cap the melting rate is $3\times10^{12}$ kg yr$^{-1}$, giving a time-scale for melting of $\tau_\text{melt}=3.3\times10^5$ yr. This suggests that a significant fraction of the entire cap could be melted over a 125 kyr obliquity cycle. However, melting is not sequestration.

**Sequestration Rates:** While we are able to calculate the melting rate, the fraction of melt that is sequestered is totally unknown. Although H$_2$O ice can be an effective barrier to sequestration, there are conditions under which the melted CO$_2$ could gravitationally penetrate to the regolith. For instance, after a long period of high obliquity ($\delta\geq40^\circ$), the polar areas would be effectively dessicated, allowing relatively direct access to the regolith after a downward obliquity swing ($\delta\leq20^\circ$). Also, if the base is unconsolidated, a previously emplaced water-ice cap could suffer differential settling from the CO$_2$ load, producing cracks through which the CO$_2$ could flow.

We define a parameter, $R_{\text{seq}}$, which describes the ratio of sequestered to melted CO$_2$, either as a function of geothermal flux, the exchangeable inventory, or both. The mass sequestered is $M_{\text{seq}}=M_{\text{melt}} R_{\text{seq}} \delta t$, where $M_{\text{melt}}$ is the melted CO$_2$ and $\delta t$ is the duration of the cap, while the fractionation and escape of nitrogen is determined only by $\delta t$. Thus, by varying, $R_{\text{seq}}$, the relative strengths of sequestration and nitrogen fractionation would be differentially affected, allowing one to guide $P_{\text{CO}_2}$ and $^{15}N/^{14}N$ toward current values.

Since it is the obliquity that controls atmospheric collapses, we must create a synthetic obliquity that distributes atmospheric collapses, perhaps 5 to 10 of them, by specifying a time and duration of each collapse throughout Mars history. We can define the obliquity, $\delta(t)$, as the sum of a mean obliquity, $\delta_\text{av}(t)$, with the quasi-periodic signal, QP, adjusted so that it has a net zero average value. Then, $\delta(t)=\delta_\text{av}(t)+\delta \text{QP}$. Our quasi-periodic signal comes from the last 2.28 Myr of the Laskar et al. [19] obliquity calculations. We can define $\delta_\text{av}(t)$ in a way that can explain the downward shifts in fluvial activity and crater rim weathering patterns in the Hesperian [3,4] that would come from CO$_2$ sequestration. For the last 100 Myr or so, we would place atmospheric collapses during the stages of SPLD building when low obliquity is required [15].

We expect that it would be difficult to rationalize basal melting and sequestration with an atmosphere smaller than about 50-75 mbar (i.e., $z'<z^*$ is likely). This problem may be alleviated if the more distal RFZs in the SPLD are in fact composed of CO$_2$.

If this study works as foreseen, then we will have found a way to explain the transition from a thick early atmosphere to the current thin one.

**Conclusion:** With the modernized MEC we will be able to test whether basal melting and sequestration, and the mysterious RFZ 1, 2, and 4 [10] deposits, are modes of sequestration that may answer the missing CO$_2$ problem.

The general utility of MEC is to provide a viable platform for testing this and other hypotheses of the evolution of the atmosphere of Mars.

**References:**