IMPACT DELIVERY OF REDUCED GREENHOUSE GASES ON EARLY MARS R.M. Haberle[1], K. Zahnle[1], and N. Barlow[2] , [1]Space Science and Astrobiology Division, NASA/Ames Research Center, Moffett Field, CA 94086, [2] Dept. Physics and Astonomy, Northern Arizona University, Flagstaff, AZ 86011.

Introduction. Reducing greenhouse gases are once again the latest trend in finding solutions to the early Mars climate dilemma. In its current form - as proposed by Ramirez et al. [1], later refined by Wordsworth et al. [2], and confirmed by Ramirez [3] - collision induced absorptions between CO_2-H_2 or CO_2-CH_4 provide enough extra greenhouse power to raise global mean surface temperatures to the melting point of water provided the atmosphere is thick enough and the reduced gases are abundant enough. To raise surface temperatures significantly by this mechanism, surface pressures must be at least 500 mb and H_2 and/or CH_4 concentrations must be at or above the several percent level. Both Wordsworth et al. [2] and Ramirez [3] show that the melting point can be reached in atmospheres with 1-2 bars of CO_2 and 2-10% H_2; smaller concentrations of H_2 will suffice if CH_4 is also present.

If thick weakly reducing atmospheres are the solution to the faint young Sun paradox, then plausible mechanisms must be found to generate and sustain the gases. Possible sources of reducing gases include volcanic outgassing, serpentinization, and impact delivery; sinks include photolyis, oxidation, and escape to space. The viability of the reduced greenhouse hypothesis depends, therefore, on the strength of these sources and sinks.

Sources. Volcanic outgassing of reduced gases is possible given that the Martian mantle appears to be more reducing than Earth's [4,5]. Oxygen fugacities in Martian meteorites range from Iron-Wüstite (IW) all the way up to the Quartz-Fayalite-Magnetite (QFM) buffer [4]. If the early Martian mantle was at the low end of this range then a greater fraction of H_2, CH_4, and CO would have been included in the outgassed materials. However, a reducing mantle will outgas less CO_2.

Serpentinization is a mechanism in which ultramafic minerals (e.g., olivine) are hydrothermally altered to produce serpentine and magnetite, liberating H_2 in the process. If CO_2 is present in the water it can react with H_2 to produce CH_4. Thus, serpentinization can produce both H_2 and CH_4. Serpentine deposits have been identified on the surface [6] and extensive crustal serpentinization may have taken place early in the planet's history [7] though evidence for this is not seen in the canyon walls of Vallis Marineris [8].

Impact degassing of asteroids and comets is a third source of reduced gases. The intense heat and rapid chemistry following an impact will produce H_2 and can produce CH_4 depending on the composition, size, and entry velocity of the impactor, as well as the composition and strength of the target material [9,10,11].

Sinks. Sinks for reduced gases are more easily quantifiable. H_2 escapes while CH_4 is photolyzed and/or oxidized. If H_2 escapes at the diffusion limit, a simple analytical expression can be used to calculate escape rates as a function of the volume mixing ratio (VMR) and exobase temperature. However if the H_2 VMR is high enough, escape becomes energy-limited; this too can be calculated from a simple expression [see, for example, ref 12]. The sink for methane can be expressed by its photochemical lifetime.

A Simple Model. In this work we focus on the production of reduced gases by impacts. Impact production is the least well understood source and the model we construct is meant to assess its potential. We employ a stochastic cratering model that reproduces the observed crater size frequency distribution of Noachian surfaces (Fig. 1).

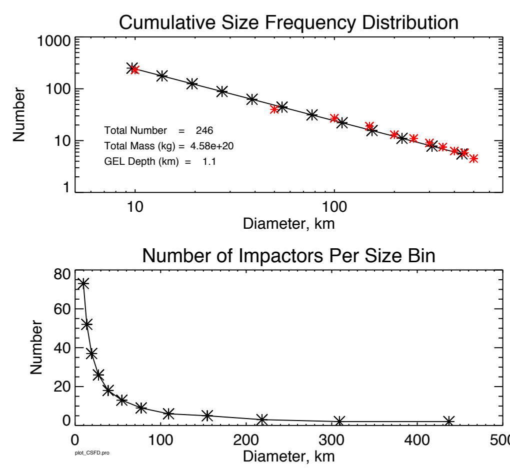

Fig. 1. Top: Cumulative size frequency distribution: modeled (black) observed (red, from Segura et al. [13]). Bottom: Number per size bin. There are 12 size bins.

For each simulation impactors are randomly assigned to the 100 model time bins which are chosen to emphasize early delivery. The model then marches through 400 My of time from 4.1-3.7 Ga keeping track of the reduced gases released into a 1 bar CO_2 atmosphere after each impact.

At present we focus on H_2 and simply specify that a fraction of the impactor mass, f_{H2}, is converted to H_2 with f_{H2} ranging from 0.04-0.4%.This is the range of values we estimate from the gas equilibrium calculations of [9] and [11] for several classes of asteroids, and from our own work for comets.

Escape of H_2 in the model, shown in Fig. 2, occurs at the rapid diffusion limit for low H_2 VMR's and at the slower energy limit for high H_2 VMR's. The transition between these two regimes, which depends on the Sun's XUV flux, occurs for a H_2 VMR ~1 at 4.1 Ga. VMR's this high can be achieved by volatile-rich cometary impactors, such as our f_{H2}=0.4% case, greater than 300 km in diameter. There are 4 such impacts in our model suggesting that H_2 escape may be throttled by energy limitations following such impacts.

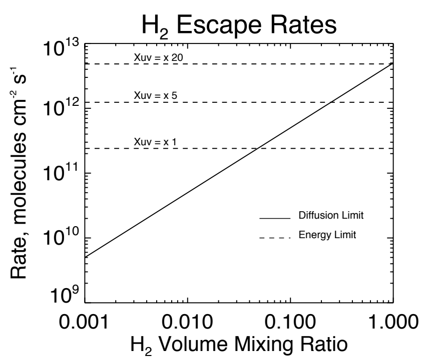

Fig 2. Hydrogen escape rates. Diffusion limit = (H_2 VMR) x b/H where b/H=10^{13} molecules cm^{-1} s^{-1}. Energy limited escape is shown for several values of the Xuv flux. For a given VMR, the model uses the minimum rate.

Results. Fig 3 shows a typical result for a single simulation with f_{H2}=0.04%, which is our estimate for the H-chondrites in ref [9] and is our least favorable case for H_2 production. H_2 VMR's are generally less than 10^{-3} throughout this simulation which is not high enough to significantly raise global mean surface temperatures. However, H_2 VMR's do spike following large impacts and in some cases exceed the 10% concentration level (horizontal dashed line in bottom panel of Fig. 3) required to raise global mean surface temperatures to the melting point – at least according to the models of [2] and [3]. For this particular simulation atmospheric VMR's > 0.1 (i.e., 10% concentration) are sustained for a total of 24 My. For cometary like impactors, where we estimate f_{H2}=0.4%, post-impact atmospheric VMR's > 0.1 are more frequent and the amount of time spent near the melting point can be doubled. Thus, the total time spent near the melting point from this simple model assuming a range of impactor types is in the 10s of millions of year range, which is an interesting result.

Discussion. There are, of course, many issues we have swept under the rug. The main ones are our assumed crater size distribution, the timing of delivery, the size of the early atmosphere, the mix of impactor types, and the details of H_2 escape.

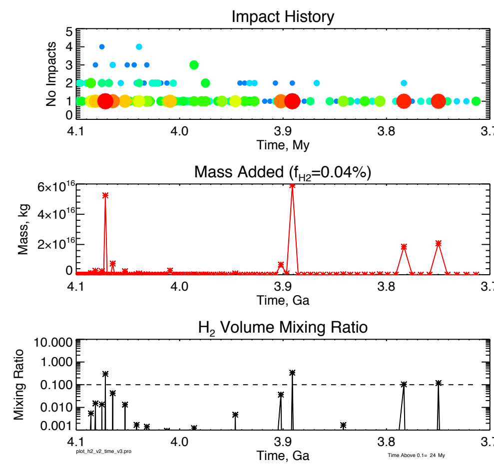

Fig 3. Top: Number of impacts vs time. Each filled circle is an impact event. Circle size and color are proportional to impactor diameter. Middle: Mass added after each event. Bottom: H_2 volume mixing ratio.

These are complicated, potentially show-stopping subjects, that need further study. Between now and the meeting, we plan to improve each of these aspects of the model. For example, to improve the impact size distribution information, we are utilizing Barlow's revised *Catalog of Large Martian Impact Craters* [14] to identify all impactors ≥10-km-diameter. For the moment, however, these simple calculations suggest that impact delivery of reduced greenhouse gases is a potentially important part of the early Mars story and may be part of the solution to the early Mars paradox.

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