

**Introduction.** While there is abundant evidence for flowing liquid water on the ancient Martian surface, a widely accepted greenhouse mechanism for explaining this in the presence of a faint young sun has yet to emerge. Gases such as NH<sub>3</sub>, CO<sub>2</sub> alone, SO<sub>2</sub>, clouds, and CH<sub>4</sub>, have sustainability issues or limited greenhouse power. Recently, Ramirez et al. [1] proposed that CO<sub>2</sub>-H<sub>2</sub> atmospheres, through collision induced absorptions (CIA), could solve the problem if large amounts are present (1.3-4 bars of CO<sub>2</sub>, 50-20% H<sub>2</sub>). However, they had to estimate the strength of the H<sub>2</sub>-CO<sub>2</sub> interaction from the measured strength of the H<sub>2</sub>-N<sub>2</sub> interaction. Recent ab initio calculations show that the strength of CO<sub>2</sub>-H<sub>2</sub> CIA is greater than Ramirez et al. assumed [2]. Wordsworth et al. [2] also calculated the absorption coefficients for CO<sub>2</sub>-CH<sub>4</sub> CIA and show that on early Mars a 0.5 bar CO<sub>2</sub> atmosphere with percent levels of H<sub>2</sub> or CH<sub>4</sub> can raise mean annual temperatures by tens of degrees Kelvin. Freezing temperatures can be reached in atmospheres containing 1-2 bars of CO<sub>2</sub> and 2-10% H<sub>2</sub> and CH<sub>4</sub>. The new work demonstrates that less CO<sub>2</sub> and reduced gases are needed than Ramirez et al. originally proposed, which improves prospects for their hypothesis.

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 required concentrations of H<sub>2</sub> and CH<sub>4</sub>. Possible sources of reducing gases include volcanic outgassing, serpentinization, and impact delivery; sinks include photolysis, oxidation, and hydrogen escape. 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 the Earth's [3,4]. Oxygen fugacities in Martian meteorites range from Iron-Wüstite (IW) all the way up to the Quartz-Fayalite-Magnetite (QFM) buffer [3]. If the early Martian mantle was at the low end of this range then a greater fraction of H<sub>2</sub>, CH<sub>4</sub>, and CO would have been included in the outgassed materials. However, the source of CO<sub>2</sub> would then rely more on the oxidation of CO from the photolysis products of water rather than direct outgassing.

Serpentinization is a mechanism in which ultramafic minerals (e.g., olivine) are hydrothermally altered to produce serpentine and magnetite, liberating H<sub>2</sub> in the process. If CO<sub>2</sub> is present in the water it can react with H<sub>2</sub> to produce CH<sub>4</sub>. Thus serpentinization

can produce both H<sub>2</sub> and CH<sub>4</sub>. Serpentine deposits have been identified on the surface [5] and extensive crustal serpentinization may have taken place early in the planets history [6].

Impacts might also be a source of reduced gases. The intense heat and rapid chemistry following an impact could produce H<sub>2</sub> and CH<sub>4</sub> depending on the composition, size, and entry velocity of the impactor, as well as the composition and strength of the target material [7,8,9].

**Sinks.** Sinks for reduced gases are more easily quantifiable. H<sub>2</sub> escapes while CH<sub>4</sub> is photolyzed and/or oxidized. If H<sub>2</sub> escapes at the diffusion limit, a simple analytical expression can be used to calculate escape rates as a function of mixing ratio and exobase temperature. Sinks for methane can be expressed in terms of lifetimes. Thus, models can be constructed with simple expressions for sources and sinks to estimate the potential for the development of reduced greenhouse gases on early Mars.

**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. A sample production plot for H<sub>2</sub> is shown in Figure 1.

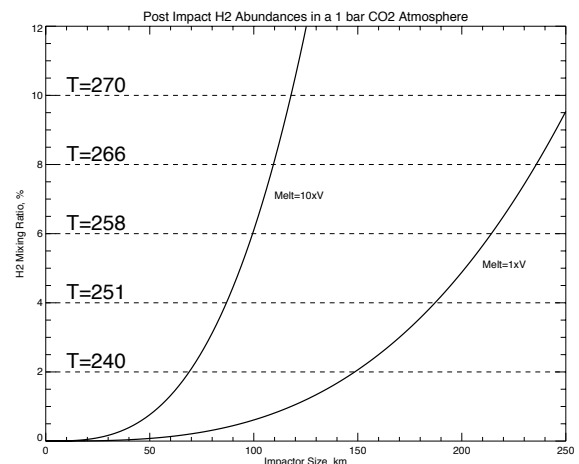


Figure 1. H<sub>2</sub> mixing ratios (%) vs impactor size (km). Dotted horizontal lines labeled T=270, 266, etc. correspond to the global mean temperatures from [2] for a 1 bar CO<sub>2</sub> atmosphere with the indicated hydrogen mixing ratio. Melt is the volume of melt material, and V is the volume of the impactor.

In this figure we have computed H<sub>2</sub> production by assuming a serpentinization-like process that uses the iron in an impactor to make H<sub>2</sub>. We assume a 10% mole fraction of iron, and that one H<sub>2</sub> molecule is produced for every three iron atoms that react with water. We show two curves: one for H<sub>2</sub> generated from the impactor alone (Melt=1xV, where V is the volume of the impactor), and one where the H<sub>2</sub> comes from a volume target material equal 10xV.

For small melt volumes, significant H<sub>2</sub> production occurs only for sizeable impactors, i.e., impactors greater than ~150 km. For larger melt volumes hydrogen production increases sharply for impactors greater than ~70 km. Larger impactors occur less frequently than the smaller impactors so the next step is to map our production curves to crater distribution curves and sum up over all impactors to get the total input. We also need to add the sinks discussed above and include a timing profile. We can use the same approach for CH<sub>4</sub>. Our goal is to determine if impacts can build up and sustain the required reduced gas concentrations for solving the faint young sun paradox. Results of this simple model will be presented at the meeting.

**References:**

[1] Ramirez et al. (2014) *Nature Geo.* 7, 59-63. [2] Wordsworth, et al., (2017), *Geophys. Res. Lett.*, In press. [3] Wadhwa, M. (2008) *Rev. Mineral. and Geochem.* 68,493-510. [4] Hirschmann et al. (2008), *Earth and Planet. Sci. Lett.* 270, 147–155. [5] Ehlmann et al. (2010), *Geophys. Res. Lett.* 37, 6. [6] Chassefière et al. (2013), *J. Geophys. Res.*, 118, 1123-1134. [7] Schaefer and Fegley (2007), *Icarus*, 186, 462–483. [8] Schaefer and Fegley (2010), *Icarus*, 208, 438–448. [9] Hashimoto et al. (2007), *J. Geophys. Res.*, 112, E05010.