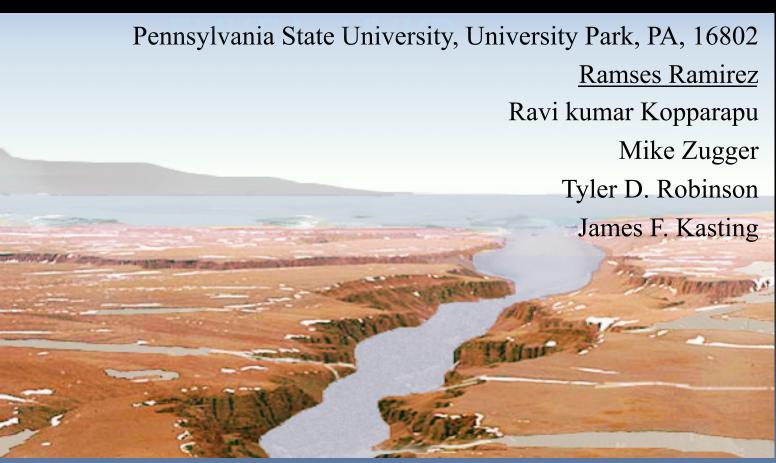
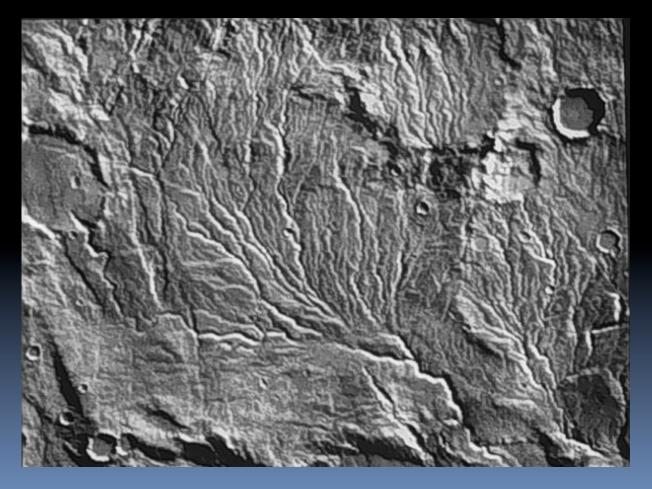


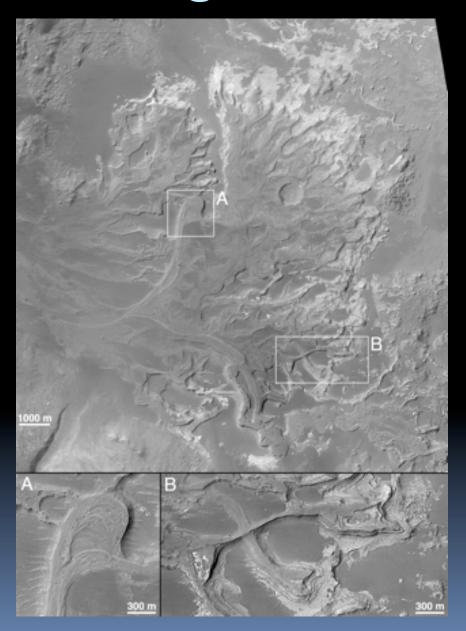
# A CO<sub>2</sub>-H<sub>2</sub> GREENHOUSE FOR EARLY MARS



 Presence of fluvial features on the martian surface suggest that early Mars was warm and wet



Warrego Vallis (Viking)



- A) Cutoff channel meander
- B) Cross-cutting channels

(inverted relief in both cases)

Malin and Edgett, *Science*, 2003

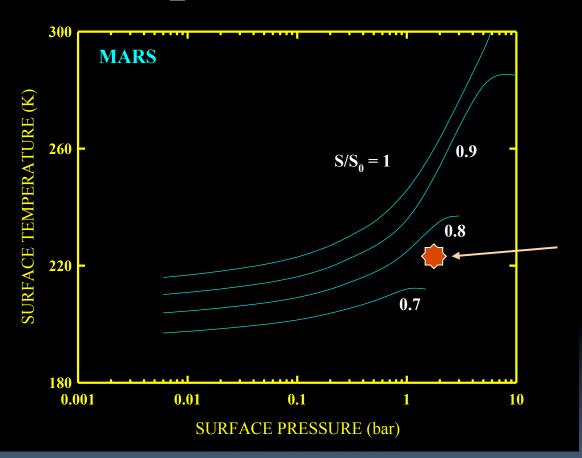


■According to Hoke et al., episodic intermittent runoff averaging ~10 cm/yr for (3-4)×10<sup>7</sup> yr, were needed to form the larger valleys (~> 3x10<sup>6</sup> m total runoff)

Grand Canyon

Nanedi Valles

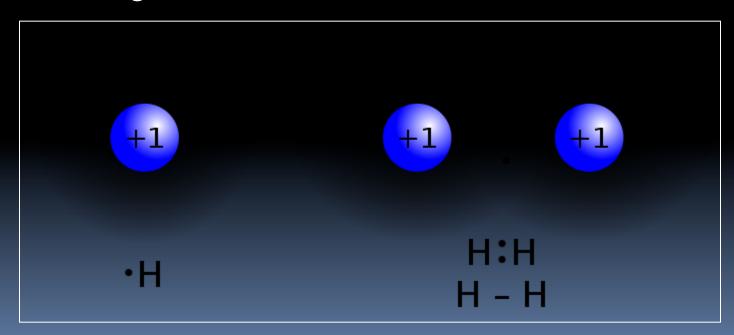
# Martian surface temperature vs. pCO<sub>2</sub> and solar luminosity



 $S/S_0 = 0.75$  at 3.8. b.y. ago, when most of the valleys formed

• Previous calculations showed that greenhouse warming by CO<sub>2</sub> (and H<sub>2</sub>O) could not have kept early Mars' mean surface above freezing J. F. Kasting, *Icarus* (1991)

- Unfortunately, a standard CO<sub>2</sub>-H<sub>2</sub>O greenhouse cannot warm early Mars
- However, H<sub>2</sub> has been a potent greenhouse in H<sub>2</sub>-dominated worlds (Pierrehumbert and Gaidos, 2011)
- We show that H<sub>2</sub> is also an effective secondary gas in warming the Martian surface



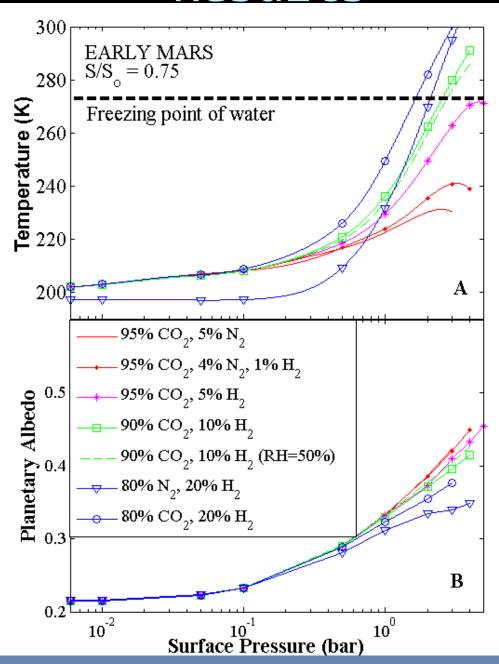
#### 1-D Climate model

- 1-D radiative-convective climate model
- Cloud-free
- Delta two-stream approximation parameterizes gaseous absorption in 38 solar intervals
- 55 IR intervals that use time-stepping routine that iterates until:
  - Absorbed and emitted fluxes in stratosphere are balanced
  - Surface temperature converges to steady state

#### Climate model updates

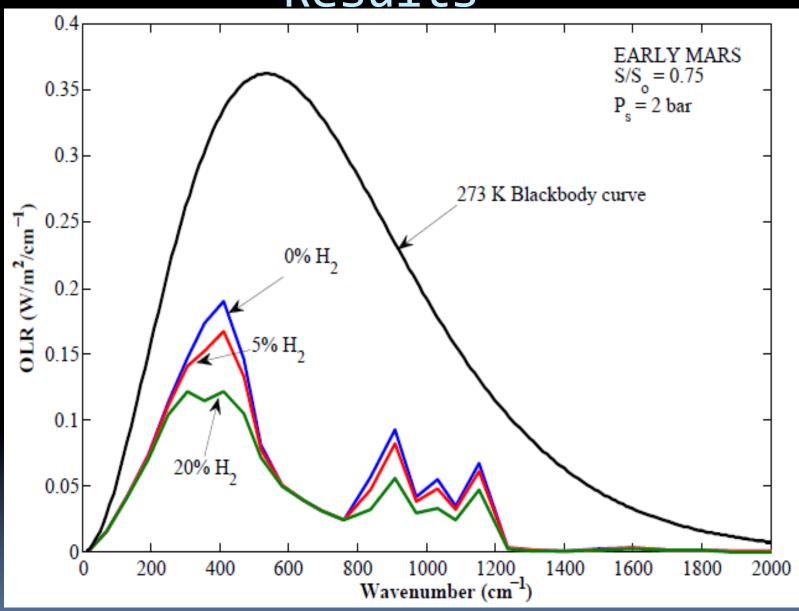
- We derived new HITRAN 2008 coefficients for CO<sub>2</sub>
  and HITEMP 2010 coefficients for H<sub>2</sub>O
- The H<sub>2</sub>-N<sub>2</sub> CIA data of Lothar and Frommhold (1986) are used as a proxy for H<sub>2</sub>-CO<sub>2</sub>
- Self-broadening by H<sub>2</sub>-H<sub>2</sub> pairs was also incorporated (Borysow, 2002)
- H<sub>2</sub> Rayleigh scattering was added (Dalgarno and Williams, 1962)
- The Shomate Equation was used to compute the heat capacity of H<sub>2</sub>

#### Results



Ramirez et al., (2013), in review





## Are high H<sub>2</sub> amounts possible?

$$2H_2O \Leftrightarrow^{K_{eq}} 2H_2 + O_2$$

$$K_{eq} = \frac{pH_2^2 f O_2}{pH_2 O^2}$$

$$K_{eq} = \frac{pH_2^2 fO_2}{pH_2 O^2}$$
 
$$\frac{pH_2}{pH_2 O} = \sqrt{\frac{K_{eq}}{fO_2}}$$

$$\left(\frac{pH_2}{pH_2O}\right)_{Earth} \approx 0.02$$
 At P = 5 atm and 1300C

At 
$$P = 5$$
 atm and 1300C

Grott et al. (2011) argue that early Mars's mantle fugacity state could gave been as low as IW-1 (or FMQ -5)

$$fO_2^{Earth} \cong 10^{-8} atm(FMQ)$$
$$fO_2 \cong 10^{-12} atm(IW)$$

Outgas more H<sub>2</sub> on Mars because of reduced mantle

# Are high H<sub>2</sub> amounts possible?

$$\Phi_l(H_2) = \frac{b_i}{H_a} \cdot \frac{f_T(H_2)}{1 + f_T(H_2)} \cong \frac{b_i f_T(H_2)}{H_a}$$

- For IW+1,  $H_2$  outgassing rates ~ 20x greater than that of Earth or  $4x10^{11}$  molec./cm<sup>-2</sup>s<sup>-1</sup>
- For a homopause temperature of 160K, bi/Ha~1.6x10<sup>13</sup> cm<sup>-2</sup>s<sup>-1</sup>
- So,  $f_t(H_2) \sim 2.5\%$ . Within a factor of 2 of 5%
- SNC meteorites (i.e. ALH84001) suggest IW-1 : f<sub>t</sub>(H2) >5% may be possible

-Works better for Mars than Earth because scale height (H<sub>a</sub>) for Mars is bigger

# Are high H<sub>2</sub> amounts possible?

In comparison with 1-D results (i.e. Tian et al., 2009), hydrodynamic escape would have been slowed down by two things:

- 1) Magnetic fields
- 2) Spherical geometry\*

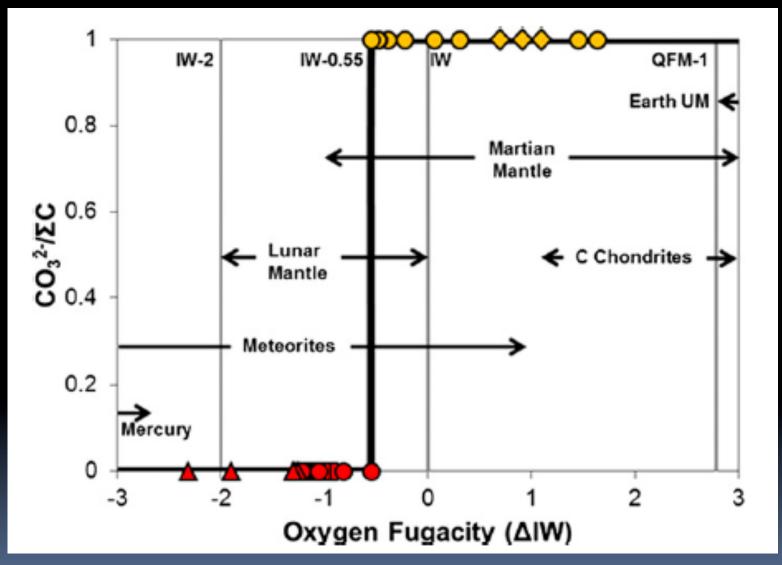
\* Stone and Praga (2009) show that spherical geometry would have reduced escape rates by a factor of 4, making  $20\% H_2$  achievable

### Degassing of C

- Grott et al. (2011) state that C would have remained in graphite form and not outgas as CO<sub>2</sub> in a very reduced early Mars atmosphere
- However, C could have outgassed as Fe-carbonyl  $(Fe(CO)_5)$  + minor  $CH_4$  and then get oxidized to  $CO_2$

#### Degassing of reduced carbon from planetary basalts

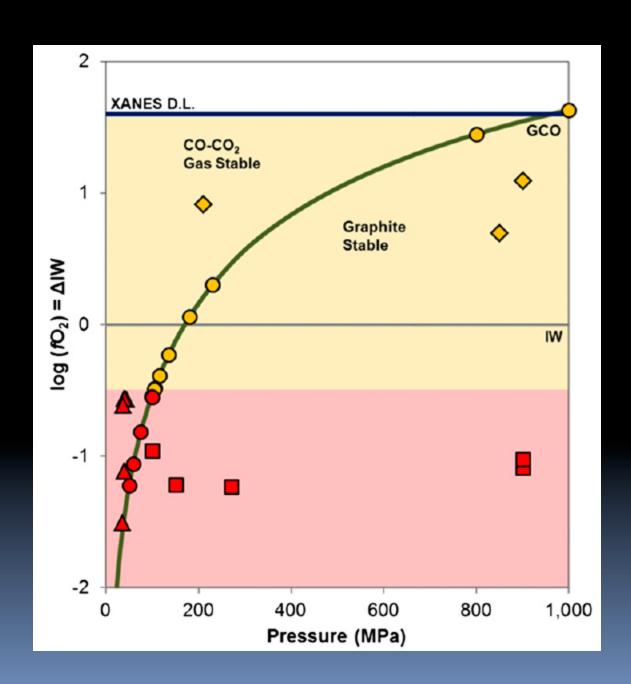
Diane T. Wetzel<sup>a,1</sup>, Malcolm J. Rutherford<sup>a</sup>, Steven D. Jacobsen<sup>b</sup>, Erik H. Hauri<sup>c</sup>, and Alberto E. Saal<sup>a</sup>



Wetzel et al., (2013), *PNAS* 

#### Conclusions

- The abundance of fluvial features suggests that early Mars (3.8 Ga) was once a warm, wet place
- In contrast to Segura et al. (2008), Hoke et al. (2011) show that voluminous amounts of water over long time scales are required to form the ancient valley networks
- Early Mars could have been warmed with a combination of CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>
- Future work requires a 2-D hydrodynamic model that includes spherical geometry
- Treatment of magnetic fields would require a 3-D model
- Come see me at my poster tomorrow to learn about this work's implications for the habitable zone



# Why is H<sub>2</sub> so effective?

- Consider the quantum mechanical linear rigid rotor:
- Rotational energy is represented by:

$$E_l = Bl(l+1)$$

The change in energy between levels is:

$$|\Delta E = 2B(l+1)|$$

$$B = \frac{\hbar^2}{2I}$$

$$I = \mu R^2$$

Where: 
$$B = \frac{\hbar^2}{2I}$$
  $I = \mu R^2$   $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m}{2}$ 

## Why is H<sub>2</sub> so effective?

- For  $N_2$ : B~ 2cm<sup>-1</sup> and both R and m are greater
- For  $H_2$ :  $B \sim 60 \text{cm}^{-1}$  and both R and m are smaller
- Thus,  $\Delta E$  is big for  $H_2$  and energy levels are widely-spaced
- For  $\Delta E$  is 1000cm<sup>-1</sup>, 1 = 6 for  $H_2$  and  $\sim 250$  for  $N_2$ !



