VENTILATION OF CO_2 FROM A REDUCED MANTLE AND CONSEQUENCES FOR THE EARLY MARTIAN GREENHOUSE. M.M. Hirschmann[1] and A.C. Withers[2], Dept. of Geology & Geophysics 108 Pillsbury Hall, University of Minnesota, Minneapolis, MN 55455 ([1]*Marc.M.Hirschmann-1@umn.edu*, [2]*withe012@umn.edu*)

Introduction: Because much or all of the Martian mantle is apparently quite reduced, with oxygen fugacities within 1 order of magnitude of the iron-wüstite (IW) buffer [1], the stable form of carbon in Martian basalt source regions is likely to be graphite. The presence of graphite limits the liberation of CO_2 from Martian mantle-derived magmas and thereby constrains volcanogenic fluxes of CO_2 to the Martian atmosphere.

Calculations: Thermodynamic calculations based on the models calibrated by Holloway et al. [2] for graphite-saturated basalt indicate that dissolved CO_2 concentrations near the Martian mantle solidus range from 5 ppm at IW-1 to 500 ppm at IW+1 and vary little with pressure along the solidus, but increase with increasing temperature (and melt fraction) above the solidus (**Fig. 1**).

For oxygen fugacities between IW-1 and IW+1, formation of the ancient (4.5 Ga) 50 km-thick Martian crust could therefore have produced a CO_2 atmosphere ranging from 70 millibars to 13 bars, depending chiefly on the mean oxygen fugacity during melting and, to a lesser extent, on temperatures and pressures of partial melting **(Fig. 2)**.

Subsequent volcanic outgassing associated with post-4.5 Ga magmatism could have contributed from 40 millibars up to 1.4 bars of CO_2 to the atmosphere, depending on oxygen fugacity and the details of melting conditions **(Fig. 3)**. Only at the higher end of oxygen fugacities and temperature are calculated cumulative CO_2 outgassing similar to previous models based on terrestrial volcanic CO_2 outputs [3,4] or treating CO_2 outgassing as a free parameter [5,6].

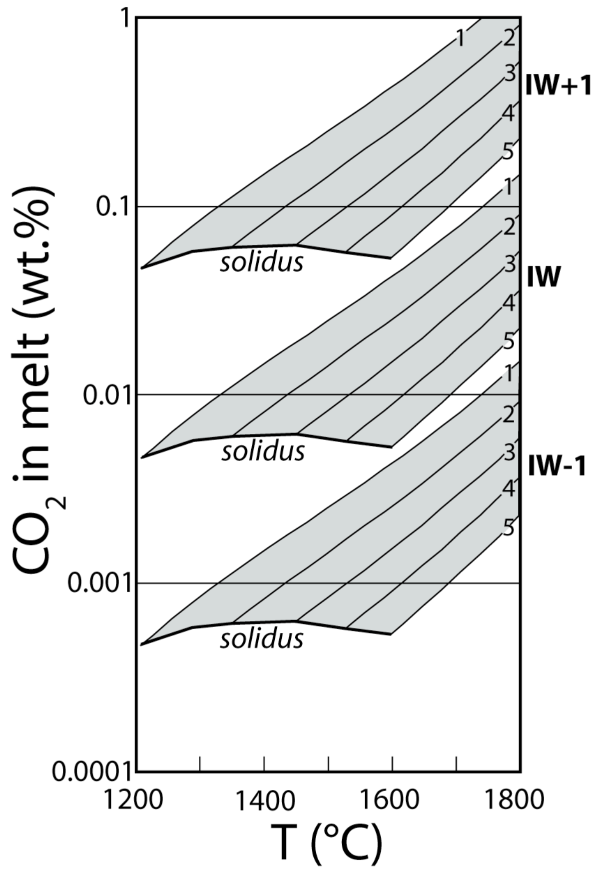

Fig. 1. Concentration of CO_2 in graphite-saturated basaltic melt as a function of temperature and pressure at conditions equal to the iron-wüstite buffer (IW) and both one log unit above and one log unit below IW (IW-1, IW+1) at 1, 2, 3, 4, and 5 GPa, calculated from the thermodynamic models of [2]. The Martian mantle solidus is indicated by the heavy curve at the low end of calculated values for each buffering condition.

Discussion: For both early (~4.5 Ga) and subsequent volcanic activity, large CO_2 fluxes outgassed to the mantle are probable only at the more oxidized and higher temperature extrema of plausible ranges. If the oxidation state of the Martian mantle is and has been more similar to more reduced estimates, ventilation of CO_2 to the Martian atmosphere has been quite limited and may not be sufficient to account for greenhouse conditions apparently required to support liquid surface waters. Other greenhouse gases, such as H_2S, SO_2 or CH_4 may have contributed significantly to equable climates in early Martian history [7,8]. Finally, low concentrations of CO_2 in graphite-saturated magmas under reducing conditions suggest that carbon in the Martian mantle may have originated by precipitation of graphite (or diamond) during solidification of a magma ocean.

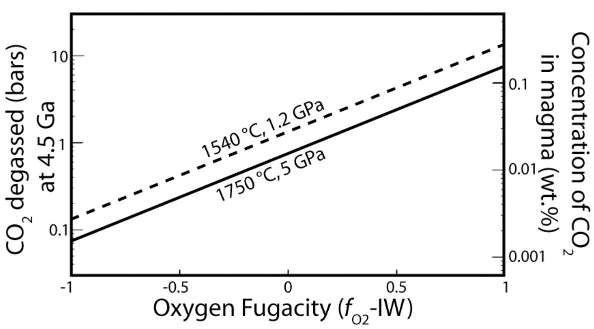

Fig. 2 Total CO_2 flux (left hand scale) and dissolved CO_2 concentration (right hand scale) associated with formation of the 50 km thick ancient (4.5 Ga) Martian crust, calculated as a function of oxygen fugacity relative to the IW buffer using mean conditions of 1750 °C and 5 GPa and 1540 °C and 1.2 GPa derived respectively, from the inverse experiments of Agee and Draper [9] and Musselwhite et al. [10].

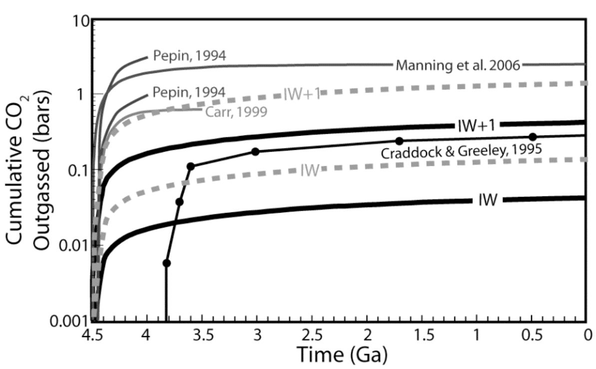

Fig. 3 Volcanic outgassing of CO_2 from 4.5 Ga to present on Mars estimated from this work compared to previous models. Our outgassing calculation uses a cumulative Martian magmatic production function linked to heat flow and to photogeologic estimates of Martian magmatism [11], with the mean concentration of CO_2 in partial melt of a graphite-bearing mantle at oxygen fugacities ranging of IW and IW+1 at 1320 °C, 1.2 GPa [12] (black solid curves)and 1540 °C and 1.2 GPa [10] (grey dashed curves). Also shown are models of Craddock and Greely [3], Pepin [5], Manning et al. [4], and Carr [6].

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