Solubility of C-O-H volatiles in graphite-saturated martian basalts and application to martian atmospheric evolution

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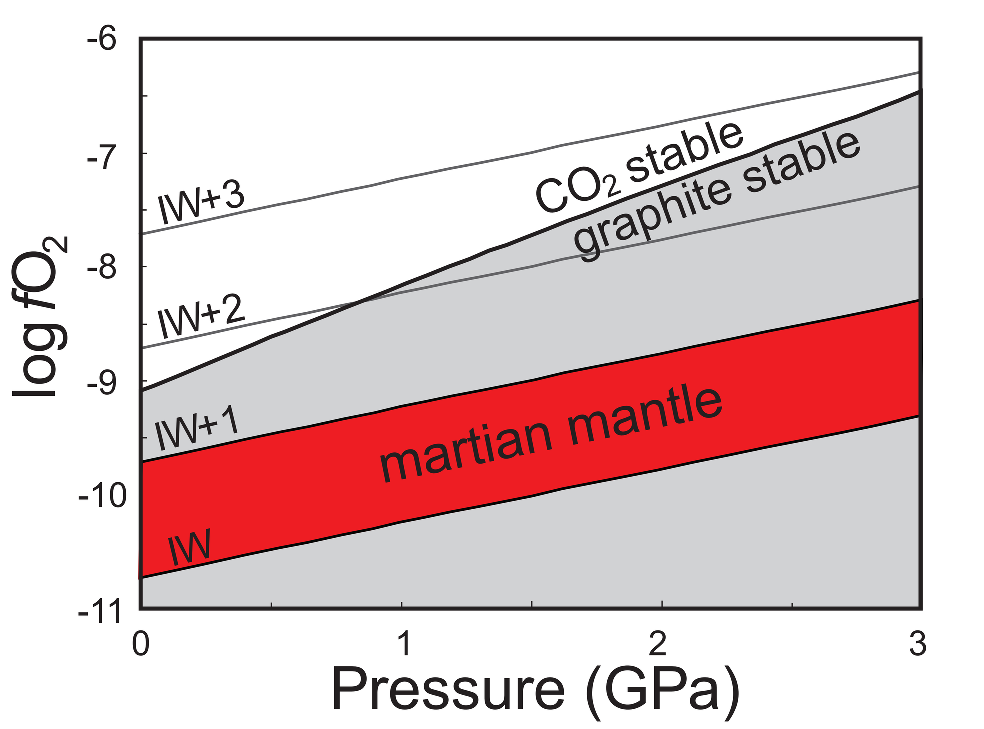
Introduction

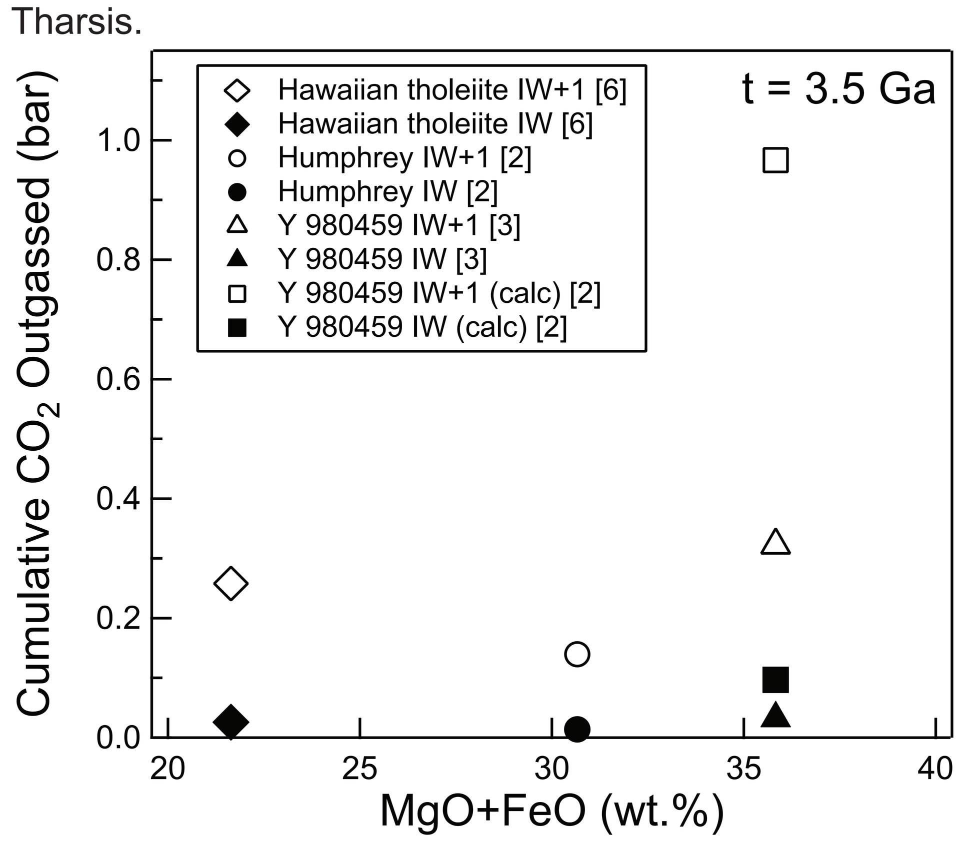
There is considerable evidence that liquid water was stable on the ancient martian surface during at least some parts of the late Noachian and early Hesperian epochs. Yet there remains uncertainty as to how this greenhouse was created and maintained and how it evolved to the current thin, modern atmosphere.



Oxybarometry of SNC meteorites suggests that the oxygen fugacity of much of the martian mantle is reducing (iron-wustite, IW, or IW+1) and so carbon is likely stored as graphite in a reduced martian mantle (After [1]).

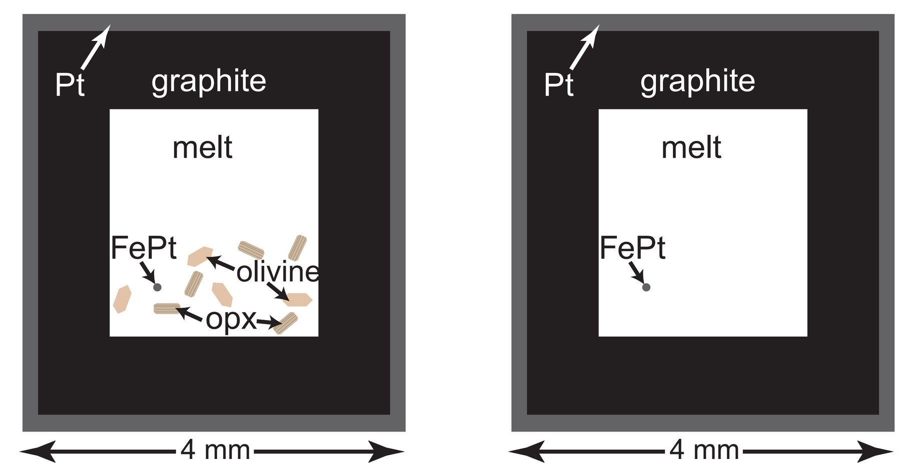
Previous Work

Our previous calculations [2-3] use the analysis developed by Holloway and co-workers [4-5], which predicts a linear relationship between CO_2 and oxygen fugacity (fO_2) in graphite-saturated silicate melts. At low oxygen fugacity, the solubility of CO_2 in silicate melts is therefore very low, which leads to small fluxes of CO_2 associated with martian magmatism. The figure below shows the critical importance of fO_2 on the solubility of CO_2 and the production of an early martian greenhouse by the creation of Tharsis.



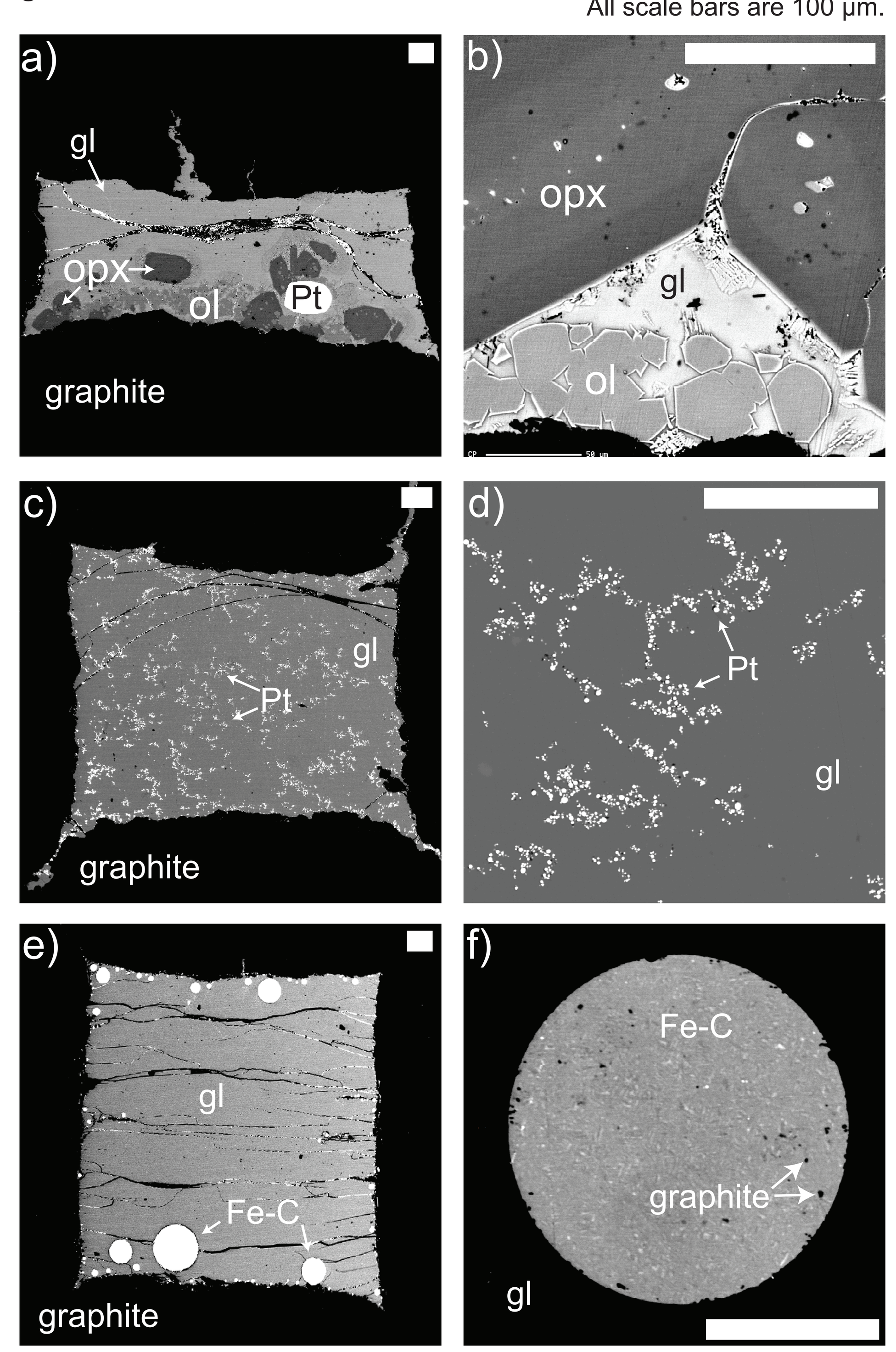
Experiments

Experiments were performed in 4 mm diameter Pt capsules with inner graphite containers at pressures of 1.0-3.0 GPa and temperatures of 1340-1600 ºC in a half-inch piston-cylinder apparatus. Run durations of 3-24 h were chosen to ensure equilibration of coexisting phases.

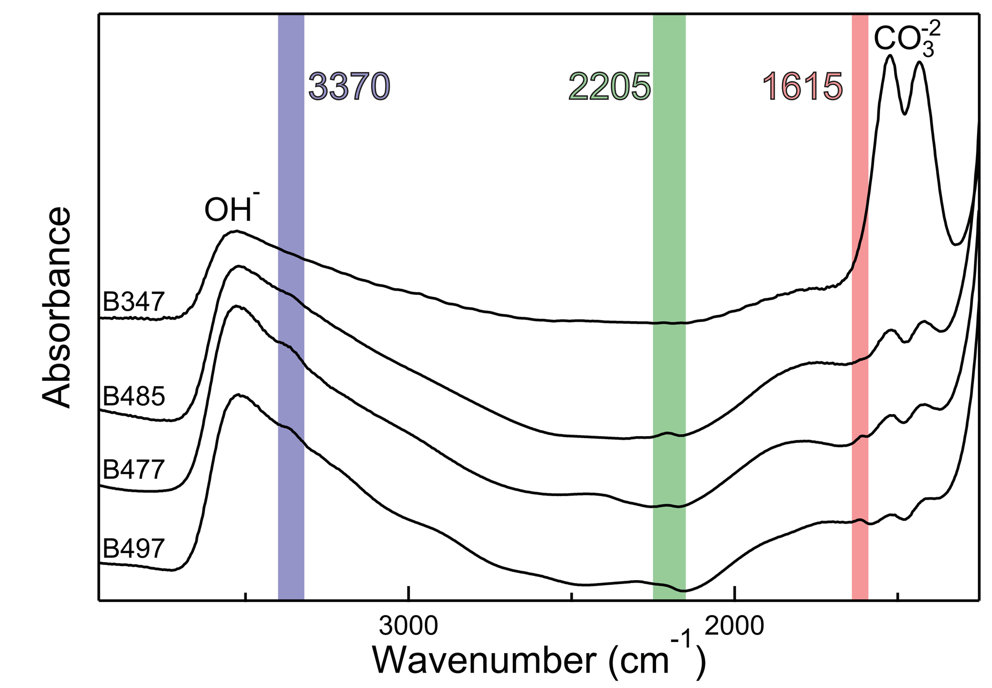


With graphite present, the prevailing oxygen fugacity must be at or below the carbon-CO-CO_2 (CCO) buffer [4]. To further constrain the redox conditions in our experiments, we relied on three different assemblages that define fO_2: olivine-pyroxene-FePt; glass-FePt; and glass-FeC.

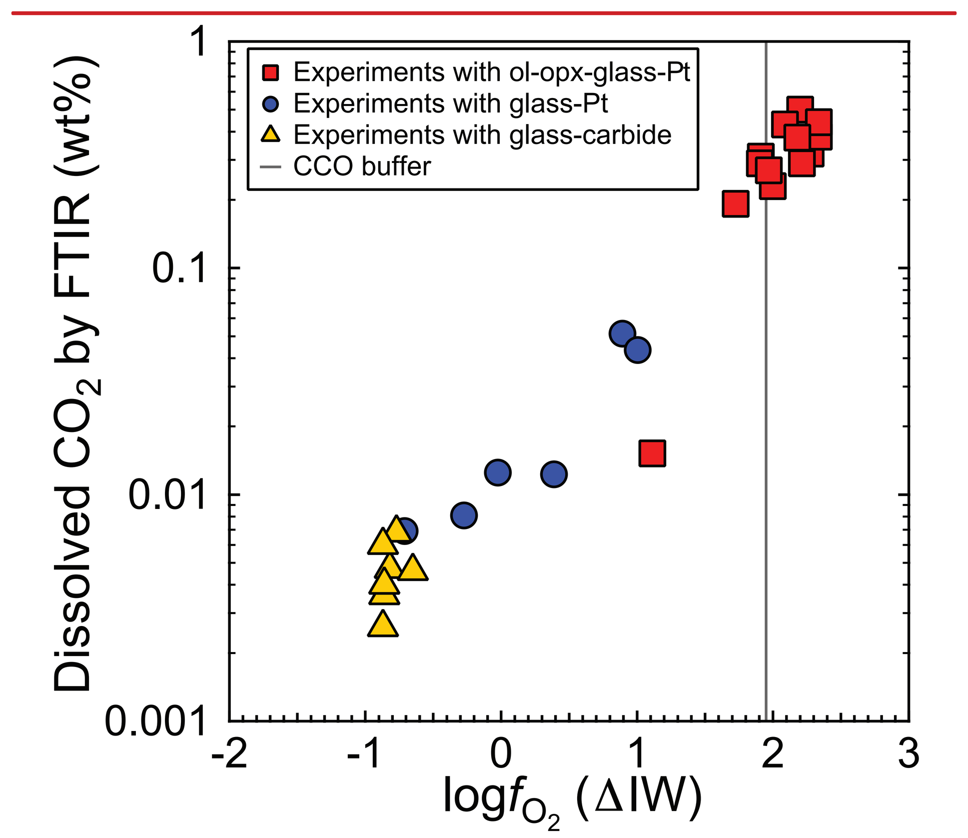
All scale bars are 100 μm.



FTIR Analysis



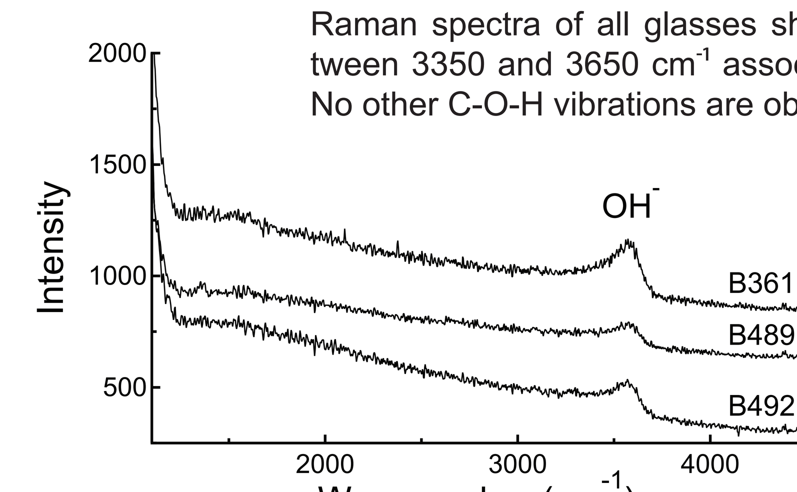
All samples show carbonate bands at 1430 and 1520 cm^{-1}, with CO_2 concentrations ranging from 0.0026-0.50 wt% and no evidence of molecular CO_2 at 2350 cm^{-1}. Spectra also have a wide peak at 3550 cm^{-1} indicating the presence of OH$^-$ with concentrations ranging from 0.26-0.85 wt%. Reduced experiments show additional peaks at 1615, 2205, and 3370 cm^{-1} not seen in oxidized samples.



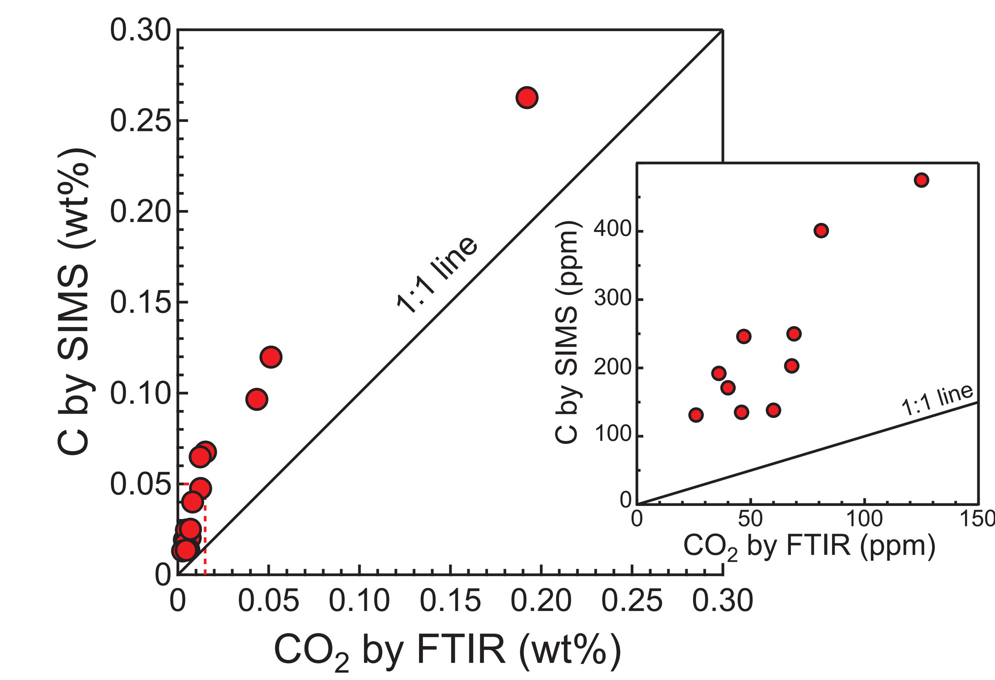
Experiments show a linear relationship between logfO_2 and CO_2 content in a graphite-saturated system, confirming the predictions of earlier models.

Raman Analysis

Raman spectra of all glasses show a band between 3350 and 3650 cm^{-1} associated with OH$^-$. No other C-O-H vibrations are observed.

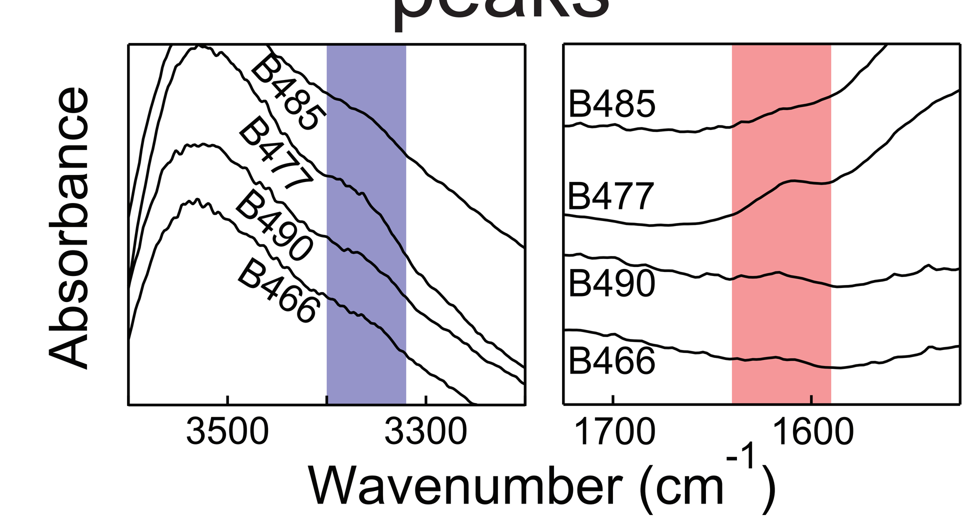


SIMS Analysis

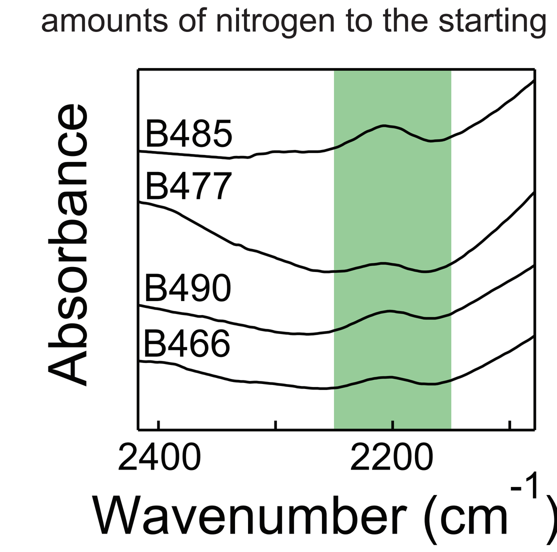


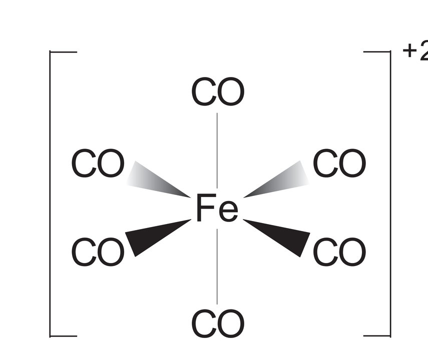
Secondary ion mass spectrometry (SIMS) determinations of C contents in glasses range from 0.0131-0.2626 wt%. C contents determined by SIMS are consistently higher than CO_2 contents determined by FTIR. This difference, termed excess C, is attributed to the presence of other reduced C-species.

Highlighted FTIR peaks



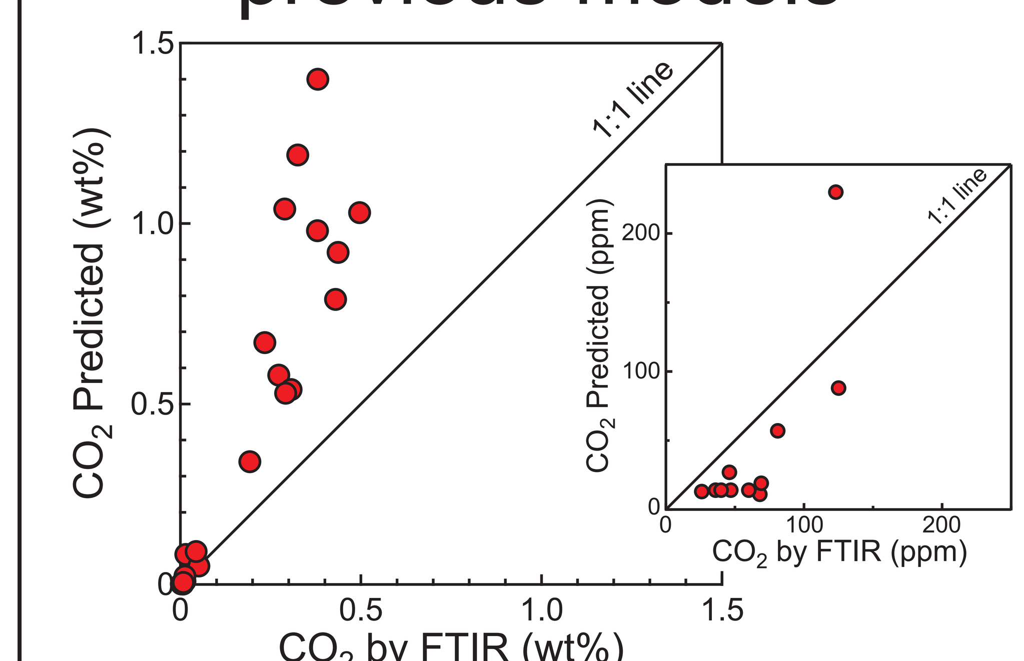
Two peaks at 1615 and 3370 cm^{-1} are difficult to attribute to a specific C-species. The 1615 peak is in a region dominated by many different molecules containing C=O bonds with none specific enough to single out [7]. The 3370 peak could be weakly associated with C-species or it could indicate the presence of N-H bonds, only seen in Raman in experiments that add large amounts of nitrogen to the starting material [8].





The peak at 2205 cm^{-1} is attributed to the Fe-carbonyl, $[Fe(CO)_6]^{+2}$ [9]. Though higher than the traditional range of metallic carbonyls, the large number of CO ligands and positive charge both increase the stretching frequency of the C=O bond [7].

Comparison to previous models



Applying our previous model [3] for CO_2 concentrations in graphite-saturated martian basalts to the experimental conditions of this study allows us to assess the viability of the model. At oxidized conditions experimental CO_2 contents are consistently lower than predicted, while more reduced conditions result in an underprediction of measured CO_2 concentrations.

Conclusions

- CO_2 solubilities change by one order of magnitude with an order of magnitude change in oxygen fugacity, as predicted by previous work. In a reduced martian mantle (between IW and IW+1), this leads to insufficient dissolved CO_2 to produce a thick martian greenhouse in the late Noachian.
- Other reduced species, such as carbonyls, are detected in reduced graphite-saturated martian basalts. An atmosphere produced by degassing of magmas similar to this study would be richer in C-O-H species than previously modeled using only CO_2 and could create a much warmer climate that could stabilize liquid water on the ancient martian surface.

References

[1] Hirschmann M.M. and Withers A.C. (2008) *Earth Planet. Sc. Lett.*, 270, 147-155. [2] Stanley B.D. et al. (2011) *Geochim. Cosmochim. Acta*, 75, 5987-6003. [3] Stanley B.D. et al. (2012) *Am. Mineral.*, 97, 1841-1848. [4] Holloway J.R. et al. (1992) *Eur. J. Mineral.*, 4, 105-114. [5] Holloway J.R. (1998) *Chem. Geol.*, 147, 89-97. [6] Pan V. et al. (1991) *Geochim. Cosmochim. Acta*, 55, 1587-1595. [7] Socrates G. (2001) *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*. [8] Kadik A.A. et al. (2011) *Geochem. Int+*, 49, 429-438. [9] Bley B. et al. (1997) *Inorganic Chemistry*, 36, 158-160.

Acknowledgements

This work is supported by NASA Mars Fundamental Research Program Grant 10-MFRP10-0069. Additional support for BDS came from the University of Minnesota's Doctoral Dissertation Fellowship. Electron microprobe analyses were carried out at the Electron Microprobe Laboratory, Department of Earth Sciences, UMN. Raman spectroscopy and glass thickness measurements were carried out in the Institute of Technology Characterization Facility, UMN, which receives partial support from NSF through the NNIN program. The SIMS analyses were obtained with the help of Richard Hervig and Lynda Williams at the Arizona State University National SIMS facility, supported by EAR0622775.