

SOLUBILITY OF C-O-H VOLATILES IN WATER-POOR MARTIAN BASALT: THE EFFECT OF f_{CO} VARIATION. L. S. Armstrong and M. M. Hirschmann, Department of Earth Sciences, University of Minnesota, 310 Pillsbury Dr. SE, Minneapolis, MN, 55455 (larmstro@umn.edu).

Introduction: Magmatic C-O-H volatiles influence the evolution of planetary atmospheres and, when precipitated and stored in solidified mantles of terrestrial planets, the dynamical evolution of planetary interiors. The martian and lunar mantles are both reduced, with oxygen fugacities ranging from IW to IW+1 and IW-2 to IW, respectively [1-4]. During the Earth's accretion when the silicate portion of the planet was in contact with iron metal, the terrestrial mantle was also subjected to similar conditions. Consequently, volatile solubilities under reduced conditions are of importance to evolution of the terrestrial planets. At low oxygen fugacities the solubilities of reduced C-O-H species in silicate magmas increase, whereas the solubilities of CO_2 and H_2O [5-6], which dominate the volatile budget in magmas at more oxidizing conditions, decrease. As a result, oxygen fugacities of planetary interiors control the type of volatiles that are degassed during volcanic eruptions, and impact the composition and evolution of overlying planetary atmospheres.

Experimental studies have found that at f_{O_2} near and below the IW buffer, a variety of reduced volatile species are dissolved in magmas. Reduced magmatic species identified in recent studies include H_2 , CH_4 , CO , and $Fe(CO)_5$, but there remains significant disagreement regarding the identity and concentrations of these volatiles in natural magmas, as well as their dependencies on intensive variables (temperature, pressure, f_{O_2} , f_{CO} , and f_{H_2}) [5-9]. Previous experiments have documented the importance of CO-related species [5,9], but these studies been conducted over a limited range of f_{CO} and have had potentially interfering effects from poorly controlled variations in H_2O .

This study aims to experimentally constrain the solubility of C-O-H volatiles in basaltic magmas by reducing the water content of experiments as much as possible and controlling the hydrogen fugacity. Preliminary results constrain the relationship between volatile concentration f_{O_2} , and f_{CO} at a single pressure and temperature, laying the groundwork for a more extensive study at a range of conditions relevant to basalt generation in planetary interiors.

Experiments and analysis: A synthetic martian basalt based on the picritic Humphrey basalt from Gusev crater [10-11] was used as the starting material. All iron was added as FeO to reflect reducing conditions in the martian mantle. Iron metal (4 wt %) and platinum metal (5 wt %) were added to the basalt in

order to generate relatively reducing conditions and to monitor the f_{O_2} . The starting material was contained in a double capsule consisting of an inner graphite capsule surrounded by an outer platinum capsule, which ensured graphite saturation consistent with the conditions expected in the martian mantle [12]. While there were no volatiles added to the starting material, a nominal amount of H_2O is unavoidable in the experimental charge. The water content was minimized using drying techniques in which the Pt-C capsule was heated after loading but before being welded shut, at $400^\circ C$ for up to 48 hrs.

In preliminary experiments, samples were subjected to conditions of 1 GPa and $1400^\circ C$ for 6 hours in an end-loaded, half-inch piston cylinder apparatus at UMN. Upon quench, the experimental charge consisted of a basaltic glass coexisting with a metallic phase (Fig. 1). Recovered capsules were cut in half and singly- or double-polished for volatile and compositional analysis.

Phase compositions were determined using a JEOL JXA8900R electron microprobe, while volatile concentrations were measured using a Bruker H_2O and CO_2 concentrations were quantified using a Bruker Tensor 37 FTIR bench and Hyperion 2000 microscope. Confocal Raman spectroscopy provided a qualitative analysis of the volatiles present, using a Witec alpha300 R confocal Raman microscope with a UHTS300 spectrometer, DV401 CCD detector, and 514.5 nm Ar laser.

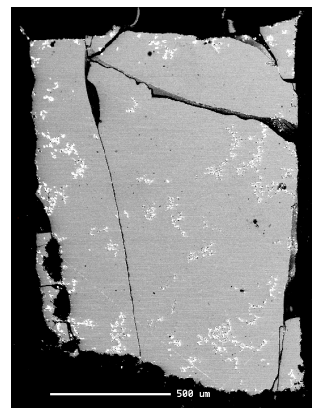


Figure 1. Backscattered electron image of experiment B527 (1 GPa, $1400^\circ C$, 6 hours). Scale bar is 500 μm .

Oxygen and CO fugacity: Oxygen fugacity was calculated from reaction (1) using the measured FeO concentration in the basaltic glass and the Fe concentration in the FePt alloy [13]:



Carbon monoxide fugacity was calculated from the model of Zhang & Duan [14], using the oxygen fugacity, pressure, temperature, and C activity.

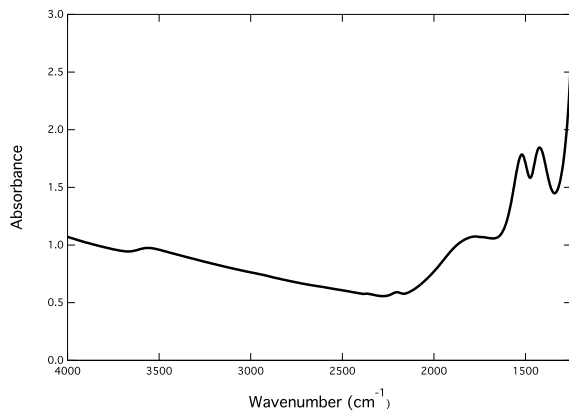


Figure 2. FTIR spectrum of experiment B530, containing 253 ppm H₂O (peak at 3550 cm⁻¹) and 653 ppm CO₂ (peaks at 1430 & 1520 cm⁻¹). There is an additional peak at 2205 cm⁻¹.

Results: A preliminary set of experiments was performed at 1 GPa and 1400 °C with H₂O concentrations ranging from 5581 ppm (nominally anhydrous starting material and no special drying) to 253 ppm (nominally anhydrous starting material with 48 hours drying at 400°C). FTIR spectra for all experiments showed a broad peak at 3550 cm⁻¹, a small peak at 2205 cm⁻¹, and a doublet at 1430 and 1530 cm⁻¹ (Fig. 2). H₂O concentrations were calculated from the broad peak at 3550 cm⁻¹, and CO₂ concentrations were determined from the carbonate doublet to be 50-627 ppm. The small peak at 2205 cm⁻¹ was also observed by Stanley et al. (in prep) in experiments on volatiles in martian basalt at similar conditions, and attributed to a C=O bond in the Fe-carbonyl Fe(CO)₆²⁺ [15].

The calculated oxygen fugacities of the experiments were between IW-0.67 and IW+1.12, which resulted in log *f*CO of 3-4 (Fig. 3). More hydrous experiments correspond to more reduced conditions. With increasing concentrations of H₂O and diminishing *f*O₂, CO₂ concentrations and the normalized intensity of the 2205 cm⁻¹ peak diminished. The latter observation is likely owing to diminished *f*CO (Fig. 3)

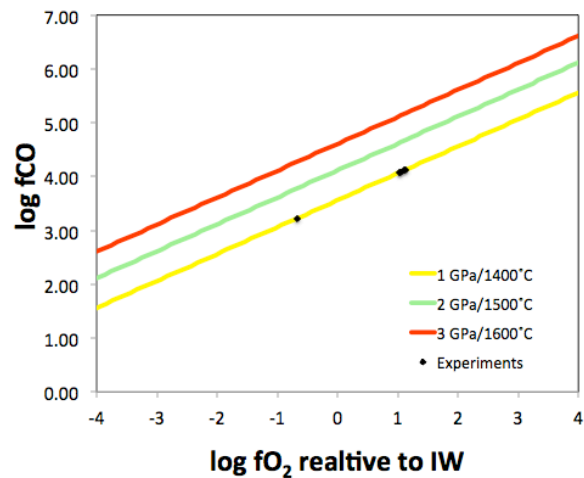


Figure 3. Relationship between CO and O₂ fugacities at 1-3 GPa and 1400-1600°C under graphite saturated conditions. Data points show the conditions of preliminary experiments.

Future work: Experiments in progress will document speciation and concentrations of dissolved C-O-H volatiles as a function of temperature and pressure over a wider range of *f*CO. Quantitative analyses of C concentrations in basaltic glass will be determined by SIMS.

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