

**PRESSURE DEPENDENCE OF GRAPHITE-C-O PHASE EQUILIBRIA AND ITS ROLE IN LUNAR MARE VOLCANISM.** M. G. Nicholis and M. J. Rutherford, Department of Geological Sciences, Brown University, 324 Brook St., Box 1846, Providence, RI 02912: [Mike\\_Nicholis@Brown.edu](mailto:Mike_Nicholis@Brown.edu) and [Malcolm\\_Rutherford@Brown.edu](mailto:Malcolm_Rutherford@Brown.edu).

**Introduction:** Many have argued that the Apollo 17 orange glass beads along with the other lunar glasses are products of gas-propelled mare fire-fountain eruptions [1,2,3]. Inferences made from the auto-reduction behavior of the orange glass endorse the oxidation of graphite as the principal gas generating mechanism [4,5]. Due to the low oxygen fugacity range of the lunar interior (IW +0.2 to -2.5), any carbon in the lunar interior would be stable in its reduced state, as graphite. Magma ascending through the lunar interior, due to buoyancy differences, may entrain graphite and carry it to shallower depths. Theoretical calculations on the Graphite-C-O (GCO) phase equilibria show strong pressure dependence. [6] deduced that at a critical pressure in the lunar interior the oxygen fugacity of ascending magma will eventually intersect an isothermal surface in  $f_{O_2}$ -P space where graphite will be in equilibrium with a CO-CO<sub>2</sub> gas mixture. When the orange glass magma ascends to this critical pressure, graphite suspended in the magma would oxidize, producing a gas-phase that would be in equilibrium with graphite, for given pressure. From the orange glass phase assemblage and chemistry, [7] inferred that the critical pressure at which entrained graphite would begin to oxidize was at a lunar pressure of 20 MPa (~ 4 km). Due to the high liquidus temperature (1320°C) of the orange glass the initial gas exsolved would be CO-rich [6]. Volatile partitioning into the gas would then evolve the gas-phase towards the complex composition of surface coatings found on the glass beads by [8], and propel the fire-fountain eruption that produced the orange glass.

The  $f_{O_2}$  of the graphite-CO gas equilibrium varies rapidly with decreasing pressure according to available data and calculations, particularly below 50 MPa (Figure 1). Very little experimental work has been done on GCO phase equilibria, and no experimental work to date has been done at P, T conditions corresponding to lunar fire-fountaining. Therefore, it is important to experimentally constrain the behavior of GCO phase equilibria for lunar fire-fountain conditions, and also determine whether or not graphite oxidation could be used as a process to generate a gas-phase in lunar magmas. In this experimental study we examine GCO phase equilibria for pre-eruption conditions applicable to the A17 orange glass magma and provide new constraints on the depth of gas production. This

same graphite oxidation process is also thought to be important in determining explosive eruptions on asteroidal bodies [9].

**Experimental and Analytical Methods:** Compressed sintered pellets of synthetic picritic orange glass composition were placed in Pt capsules lined with graphite powder. The C powder served multiple functions that included inhibiting melt contact with the Pt capsule walls, fixed the  $f_{O_2}$  to lunar conditions, and reacted with the melt to generate the CO-CO<sub>2</sub> gas phase. Isothermal (1350°C) decompression experiments were conducted in a Harwood internally heated pressure vessel. Experiments were equilibrated at an initial pressure of 80 MPa and then decompressed at a controlled rate to a final run pressure of 20-70 MPa for time duration of 3 hours. These experimental run conditions are designed to explore GCO phase equilibria at low pressures and locate the critical pressure of the graphite oxidation surface for the synthetic lunar orange glass composition.

In addition, similar decompression experiments are being run in TZM pressure vessels. The starting material in these experiments is either pure wüstite or magnetite. These experiments are designed to investigate the intersection of calculated isothermal GCO curves with Iron-Wüstite and Wüstite-Magnetite isothermal buffer curves, in the pressure range of 20-110 MPa.

Backscatter images and analysis of all experimental products were performed using the SX-100 electron microprobe.

**Results:** From our initial experiments at 70 and 41 MPa, we concluded that our experimental setup fixed the starting material  $f_{O_2}$  near lunar conditions. There were no changes in the melt composition, specifically in FeO content (~22 wt. %). Along with the absence of metal blebs in experimental products, this indicated that no graphite oxidation took place, and therefore the experiments did not intersect the GCO surface. All experiments decompressed to a final pressure of 39 MPa and below experienced a decrease in melt FeO content. Fe-loss increased significantly as experiments were decompressed to lower final pressures, Figure 2. Fe-loss in experiments was always associated with the formation of separate Fe-metal and gas phases. Both the production of a gas-phase and metal formation denoted that the GCO surface was intersected. In

these experiments, the metal/melt equilibrium  $f_{O_2}$  could be calculated from phase analyses using the method of [10], Figure 1. A correction in Fe activity was made for the presence of dissolved C in the metal blebs, which adjusted the  $f_{O_2}$  values.

In the second set of experiments, intersection of the GCO surface for isotherms ranging from 800-1100°C was indicated by the formation of a reduced reaction rim. In the wüstite experiments, a reaction rim of Fe-metal was generated. In the experiments with magnetite as the starting material, the reaction rim produced upon crossing the GCO surface was wüstite.

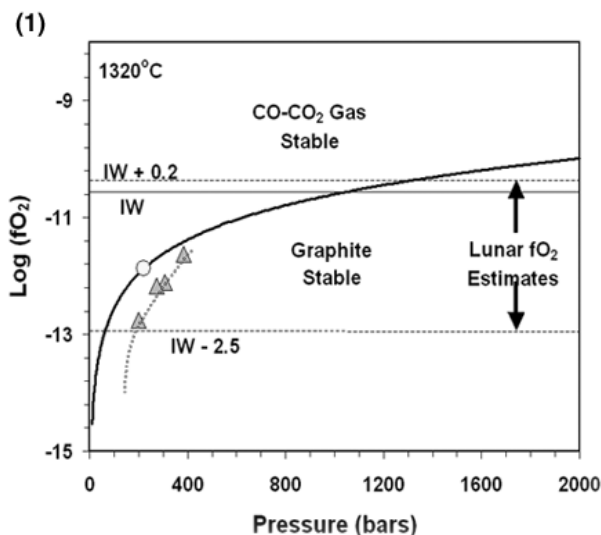
**Implications:** The results from this study illustrated that graphite oxidation could generate a gas-phase during magma ascent to the lunar surface. The intersection of the GCO surface at 40 MPa corresponds to a depth of 8 km on the moon. This is 4 km deeper than previously calculated by [4] (20 MPa).

The GCO surface represents the stability of both graphite and CO-CO<sub>2</sub> gas mixture. In the experimental setup used in this study, graphite was available in excess throughout the duration of the experiments. Therefore, when the GCO surface was intersected, a CO-rich gas-phase in equilibrium with graphite was produced for that given pressure. The amount of gas generated is represented by the increases in Fe-loss from melts held at lower pressures, Figure 2. As a result of graphite-gas equilibrium, each experiment, which generated a gas-

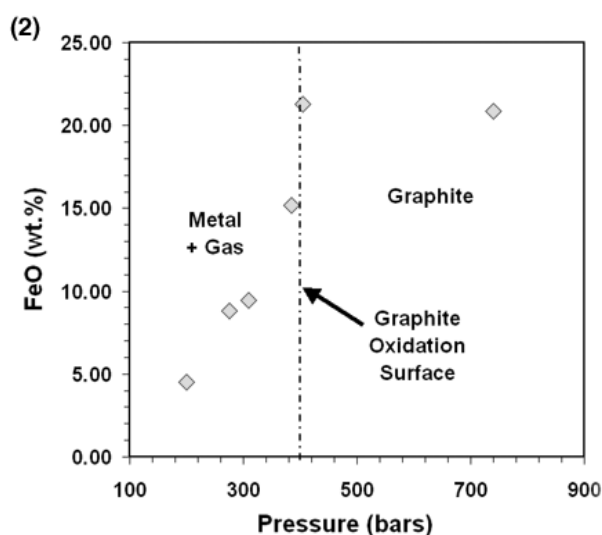
phase, represents a point on the GCO surface. These points are plotted against the calculated GCO surface in Figure 1. Our experiments indicate that the calculated GCO surface may be offset at low pressures by up to one order of magnitude in Log ( $f_{O_2}$ ) space. This offset contracts the stability field of graphite, and allows for oxidation to occur at higher pressures (deeper) in the lunar crust than previously thought. Contraction of the graphite stability field has also been verified in preliminary experiments on IW-GCO and WM-GCO intersection points. Offsets from calculated intersection points have been seen for pressures up to 110 MPa.

If GCO phase equilibria are shifted to greater depths/higher pressures, ascending magmas would be able to generate a gas-phase deeper in the crust of not only the moon but also asteroidal bodies, where C-bearing magmas may have been generated at depth.

**References:** [1] Ridley W. I. et al. (1973) *Phy. Earth Planet. Inter.*, 7, 133-136. [2] Heiken G. H. et al. (1974) *Geochim. Cosmochim. Acta.*, 38, 1703-1718. [3] Delano J. W. (1979) *LPSC X*, 275-300. [4] Sato M. (1976) *LPSC VII*, 1323-1344. [5] Sato M. (1979) *LPSC X*, 311-325. [6] Fogel R. A. and Rutherford M. J (1995) *Geochim. Cosmochim. Acta.*, 59, 201-215. [7] Weitz C. M. et al. (1997) *Geochim. Cosmochim. Acta.*, 61, 2765-2775. [8] Meyer C. (1975) *LPSC VI*, 1673-1699. [9] Warren P. H. and Kallemeyn G. W. (1992) *Icarus*, 100, 110-126 [10] Doyle C. D. (1989) *Geochim. Cosmochim. Acta.*, 53, 2631-2638.



**Figure 1.** P- $f_{O_2}$  plot of calculated GCO surface. Open circle -200 bar calculated intersection of GCO surface by [4]. Shaded triangles – experimentally determined GCO surface.



**Figure 2.** Plot of melt FeO content in experiments. Dashed line (400 bars) represents intersection of GCO surface.