The Effects of Oxygen Fugacity on the Crystallization Sequence and Cr partitioning of an Analog Y-98 Liquid

A.S. Bell[1] (asbell@unm.edu), P.V. Burger[1], Loan Le[2], J.J. Papike[1], J. Jones[2], and C.K. Shearer[1]. [1]Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque New Mexico 87131, [2]ESCG, Houston, TX 77058, [3]KR, NASA/ JSC, Houston, TX 77058

Introduction: Interpreting the relationship between "enriched" olivine-phyric shergottites (e.g. NWA 1068/1110) and the "enriched" pyroxene-plagioclase shergottites (e.g. Shergotty, Los Angeles) is problematic. Symes et al. [1] and Shearer et al. [2]) proposed that the basaltic magma that crystallized to produce olivine-phyric shergottite NWA 1068/1110 could produce pyroxene-plagioclase shergottites with additional fractional crystallization. However, additional observations indicate that the relationship among the enriched shergottites may be more complex [1-3]. For example, Herd [3] concluded that some portion of the olivine megacrysts in this meteorite was xenocrystic in origin, seemingly derived from more reduced basaltic liquids. This conclusion may imply that a variety of complex processes such as magma mixing, entrainment, and assimilation may play important roles in the petrologic history of these meteorites. It is therefore possible that these processes have obscured the petrogenetic linkages between the enriched olivine-phyric shergottites and the pyroxene-plagioclase shergottites. As a first order step in attempting to unravel these petrologic complexities, this study focuses upon exploring the effect of fO_2 on the crystallization history for an analog primitive shergottite liquid composition (Y98). Results from this work will provide a basis for reconstructing the record of fO_2 in shergottites, its effect on both mineral chemistries and valence state partitioning, and a means for examining the role of crystallization on the petrologic linkages between olivine-phyric and pyroxene-plagioclase shergottites. A companion abstract [4] explores the behavior of V over this range of fO_2.

Experimental Details: Experiments were conducted in the 1 bar gas mixing laboratory at NASA JSC. The starting material was a synthetic mixture of oxides patterned after of martian meteorite Y98045 and doped with REE. The REEs were added as 0.6 % of their oxides. Scandium and vanadium were added as Sc_2O_3 and V_2O_3 and doped to 0.1 %. We recognize that the doping levels employed in this study do not realistically approximate the actual Y-98 bulk composition; however, such elevated concentrations of trace elements are required in order to make future XANES measurements of the valence states of various trace elements. Future efforts will concentrate on how the doping levels affect the behavior of the experimental system.

Experimental fO_2 was controlled CO-CO_2 mixtures that were calibrated with a Y-doped zirconia electrochemical oxygen sensor housed in a dedicated reference furnace. Experimental runs were conducted at the following relative fO_2 values: IW-1, IW, IW+1, and IW+3.4. Each experiment was initially run at super liquidus conditions for eight hours and subsequently dropped to target dwell temperature at a rate of $1000˚C sec^{-1}$. Experiments were held at target dwell temperature for a minimum of 48 hours and terminated by drop-quenching into distilled water. The experiments at IW+3 were performed on a Pt-Rh loop; all other experiments were done using Re loops to prevent Fe-loss.

Crystallization Sequence: All experimental run products consisted of some combination of quenched melt, olivine, low-Ca pyroxene, and Cr-enriched spinel. In order to assess whether or not the experiments had attained equilibrium, we have examined the olivine-liquid K_d values. The calculated K_d values for experimental olivine-liquid pairs range from 0.31-0.33, suggesting that the olivines have approached equilibrium with the liquid. The sequence in which the crystalline phases appear in the experimental system varies as function of fO_2 to a limited extent. For example, olivine appears as the liquidus phase between 1400˚C and 1300˚C in both the IW-1 and IW experiments and above 1400˚C in the IW+1 experiment. It is likely that the olivine appears as the liquidus phase at different temperatures for each investigated fO_2, but given the wide temperature range the experiments these differences have not yet been examined closely. However in the IW+3.4 experiment, a Cr-enriched spinel appears as the liquidus phase by 1400˚C. The change in the liquidus phase from olivine to spinel can be interpreted to reflect the fact that the liquid in the most oxidized set of experiments should contain the largest proportion of Cr^{3+} and Fe^{3+}. The elevated concentration of these trivalent cations in the liquids presumably causes spinel to precipitate from the liquid at higher temperature than in the more reduced experiments.

Mineral Compositions as a Function of Temperature: The major element compositions of the crystalline phases systematically change with decreasing temperature within a set of experiments conducted at the same relative fO_2 value. Expectedly, the MgO content of the olivine decreases continuously with decreasing temperature. In the IW+3 experiments the olivine compositions range from Fo_{81} at 1300˚C to Fo_{67} at 1100˚C; similarly the IW-1, IW, and IW +1 series experiments show a trend nearly identical to the to the IW+3.4 experiments in this respect. Spinel compositions show significant variability as a function

of decreasing temperature in the IW+3 series experiments. In this set of experiments the spinel composition becomes enriched in Al and Fe and simultaneously depleted in Cr and Mg with decreasing temperature.

Mineral Compositions as a Function of fO_2: In contrast to the significant variations of phase composition with temperature, the compositions of the silicate phases in a set of isothermal experiments at constant fO_2 show little significant systematic variability as a function of fO_2. We interpret this observation to reflect the fact that the range in $Fe^{3+}/\Sigma Fe$ ratios for the experimental melts is likely rather limited in a set isothermal experiments conducted across the fO_2 spectrum. We have verified this by calculating the $Fe^{3+}/\Sigma Fe$ of the experimental liquids with the Kress and Carmichael [5] model. The K and C model [5] predicts that the percentage of Fe^{3+} in the liquid (relative to total mole fraction Fe in the liquid) varies from less than 2% in the IW-1 and IW experiments to a maximum of 10% in the IW+3.4 experiments. Given the results of these calculations, it is of little surprise that the major element compositions for the olivine and pyroxene show such limited variability over the range of investigated fO_2 values. In contrast to the behavior of the crystalline silicate phases, the spinel compositions do display some compositional difference between the oxidizing and reducing runs. The spinel compositions from the 1200˚C experiments show a marked increase in the concentration of the Fe_3O_4 component as fO_2 is increased to IW+3. This result is consistent with the trend in spinel compositions reported in McKay et al [6]

Olivine-Liquid Partitioning of Cr: We have also calculated the olivine-liquid partition coefficient for Cr in all experiments containing olivine. The partitioning behavior of Cr has long been the subject of experimental investigation [i.e. 7-10] (add references here). The EPMA determined Cr content of the olivine ranges from a minimum of 700 ppm to a maximum of 4300 ppm; and similarly the Cr content of the quenched melts ranges from 600 ppm to 6300 ppm. The calculated partition coefficient values range from 0.58 to 1.29.

Interestingly, the calculated D values display strong systematic variation as function of temperature, whereas their (isothermal) variation as a function fO_2 is much less systematic and smaller in magnitude. The partition coefficients for all experiments (irrespective of fO_2) increase with decreasing temperature. Somewhat surprisingly, though, the trend observed for the decreasing bulk DCr is in excellent agreement with an empirical model for only DCr^{2+} [7]. The strong variation of bulk DCr with temperature is to be expected. DCr^{2+} increases with decreasing temperature and DCr^{3+} increases with decreasing NBO/T, which typically also decreases with

decreasing temperature. The small isothermal variation of DCr with fO_2 can also be rationalized because there is not a large systematic difference between DCr^{2+} and DCr^{3+} [7]

One particularly important aspect of the olivine-melt Cr partitioning behavior that has yet to be competed is a systematic and quantitative spectroscopic investigation of Cr valence in olivine. The coupling of quantitative measurements of Cr^{2+} and Cr^{3+} abundance in olivine with partitioning data will undoubtedly shed more light on this complex problem. Furthermore, relatively little is known about how the homogenous equilibrium between CrO and Cr_2O_3 is affected by temperature and fO_2 in the iron rich Y-98 liquids and how these effects might be manifested in the DCr values. Additional work to be carried out in the future will concentrate on disentangling the effects of each of these variables on the partitioning behavior of Cr with the intent of developing the Cr content of shergottitic olivines as useful petrologic indicators.
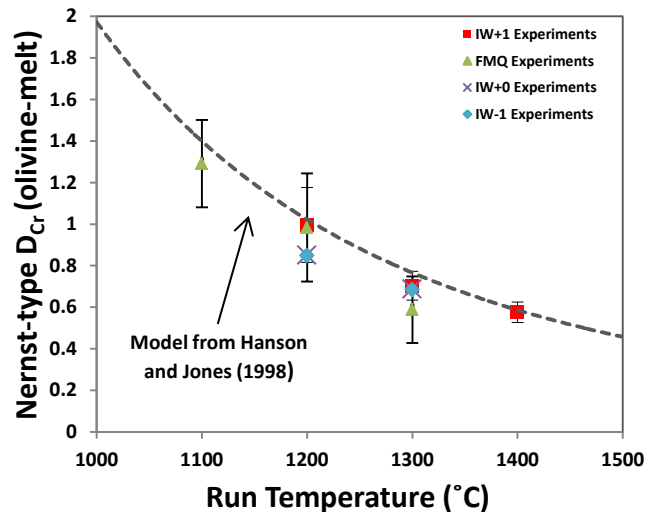
References: [1] Symes et al., (2008), *GCA* [2] Shearer et al., (2006), *Am. Min*. [3] Herd, (2006), *Am. Min.* [4] Papike et al., (2013), *LPSC 44* [5] Kress and Carmichael, (1991), *Contrib. Min. Pet.* [6] McKay et al., (2004), *LPSC 35* [7] Hanson and Jones, (1998), *Am. Min.* [8] Papike et al., (2005) *Am. Min.* [9] Gaetani et al., (1996), *GCA* [10] Schreiber and Haskin, (1976), *LPSC 11*