

Implications of Oxidation on Martian Basalt Petrogenesis: Overprinting and Exsolution. N. Castle^{1,2} and C. D. K. Herd², ¹ Lunar and Planetary Institute, USRA, Houston, TX, USA ²Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, Canada (castle@lpi.usra.edu).

Introduction: A number of olivine-phyric shergottite basalts preserve evidence of an oxidation event having occurred between megacryst and groundmass formation [1-4]. Debate remains over the cause of the oxidation, but a leading hypothesis is that it is related to volatile loss [5], which ties oxidation to the presence of volatiles in shergottite magmas. Here we present the findings of an experimental study which have implications for the effects of oxidation on the petrogenesis of olivine-phyric shergottites.

Previous study examined the petrogenesis of the Tissint meteorite [1], a depleted olivine-phyric shergottite [6, 7]. A major conclusion of the earlier study was that Tissint had undergone an oxidation event, demonstrating that volatiles were present in both the depleted and enriched shergottite mantle reservoirs. Experimental charges that had undergone oxidation during crystallization (hybrid experiments) preserved a very different record of Cr in olivine than experiments that were performed under purely reducing conditions (**Fig. 1**). Notably, natural olivine in the Tissint meteorite has Cr profiles that strongly resemble the hybrid experimental result, suggesting that the overprinting is relevant to the natural system. Our aim here is to evaluate potential mechanisms for the overprinting of Cr in olivine via oxidation. The goal is both to help identify what elements are likely to be perturbed by oxidation, and to aid in identification of other shergottites that have been oxidized but where independent assessment of groundmass and phenocryst oxidation is not possible.

Methods: Experiments were conducted on the synthetic Tissint parental composition [1, 8] in GERO vertical tube furnaces using CO-CO₂ gas mixtures to control f_{O_2} , at conditions of QFM-1 and QFM-3.2, corresponding to estimated f_{O_2} values from the Tissint meteorite [1]. Mineral compositions were determined by standard electron microprobe analysis (EMPA), and further documented using backscatter electron (BSE) images and X-ray maps. Experiments were initiated at 1375°C, 12°C above the liquidus, at reducing conditions and cooled at 1°C/hr to a target temperature; a subset were oxidized during cooling (so-called “hybrid” experiments). Isothermal experimental results under oxidizing and reducing conditions, and natural observations were utilized for comparison with cooling rate results [1, 7]. A hybrid experiment was performed using a composition doped with V and Ni to examine the partitioning behaviors of these elements.

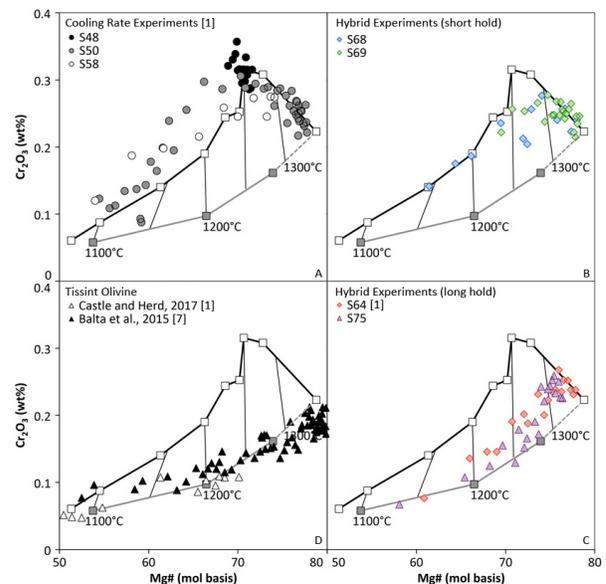
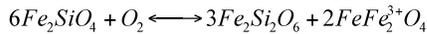


Figure 1: Compositions of experimental (A-C) and natural (D) olivines. A: Cooling rate experiments performed without an oxidation step. B: Two hybrid experiments quenched 24 and 50 hrs after oxidation. C: Two hybrid experiments quenched at ~100 hrs after oxidation; note that they have the same cooling profile as one of the experiments in (A). D: Compositions of Tissint olivine are most similar to hybrid experiments with the longest duration after oxidation (C).

Results: A number of systematic differences were observed between hybrid and reducing cooling rate experiments. Olivine is morphologically different if the system has been oxidized, changing from nearly euhedral without oxidation to completely anhedral in hybrid experiments. Accompanying the morphological change is a systematic difference in the olivine Cr profile (**Fig. 1**). A typical driver for a change in Cr content in olivine is the drawdown of Cr in the magma via formation of spinel; since much of the olivine had already formed before oxidation, this demonstrates that Cr in olivine is overprinted by oxidation [1, 9]. X-ray maps show a typical smooth variation in all elements, consistent with igneous zonation, except in Cr where fine-grained ‘hot spots’ are apparent (**Fig. 2**). Semi-quantitative chemical analysis indicates that these ‘hot spots’ are spinel grains.

Discussion: The change in olivine morphology is likely the result of a peritectic reaction, where olivine is resorbed into the liquid as additional pyroxene is stabilized. The olivine-pyroxene peritectic is a well-known phenomenon [10], and can be driven by oxida-

tion, for example as in the Fayalite-Ferrosilite-Magnetite buffer [11]:



The presence of a peritectic in shergottites is not surprising, but may explain why olivine is typically anhydrous in shergottites [12, 13].

The overprinting of Cr in olivine is a matter of concern for petrogenetic interpretation, as chemical profiles in olivine are typically used to trace magmatic histories [e.g. 2, 14, 15]. Diffusion operates too slowly to cause the overprinting, based on a calculated diffusion length scale of only 2-14 μm [16, 17] compared to the 500-800 μm measured olivine core-rim profiles in experiments. Peritectic resorption, discussed above, could potentially cause resorption of up to 84% of original olivine phenocrysts (based on differences in olivine abundances in isothermal experiments [1]), but our experimental olivines showed no evidence of having undergone substantial resorption.

The dusting of fine-grained Cr-spinel grains exclusively in hybrid (oxidized) experiments suggests another mechanism: oxidation-induced exsolution of spinel from olivine. X-ray maps (Fig. 2) show that the Cr-spinels are strongly concentrated in olivine rims in experiments with a shorter time between oxidation and quench, suggesting a rapid diffusion mechanism where the oxidation front penetrates the olivine at experimental timescales. A likely reaction causing the exsolution of spinel is the oxidation of Cr within the olivine, resulting in either structural breakdown into pyroxene and spinel, or formation of an oxidized-Cr olivine (similar to Laihunite) with spinel, for example:



Cr is not the only element likely to be overprinted: our doped hybrid experiment shows that V is also preferentially incorporated into the exsolved spinel, although a reduced cooling rate experiment was not performed to determine how strongly the V profile would be overprinted. Ni results were obscured due to experimental limitations where Ni was strongly partitioned into the Re-wire on which the sample was suspended, but a substantially higher partition coefficient in spinel over olivine [18-22] suggests that Ni would strongly partition into the spinel during exsolution. Co was not included in experiments, nor is there a clear partition driver for Co into spinel [23-25], but if it is partitioned strongly into spinel during exsolution then it would resolve a literature conflict between the observations of Herd [2] and Shearer et al. [15] where

opposite conclusions were reached on whether olivine megacrysts in Northwest Africa (NWA) 1068/1110 are phenocrystic or xenocrystic. Our results demonstrate that careful characterization of olivine grains to provide textural context is essential for accurate interpretations of melt evolution in planetary basalts.

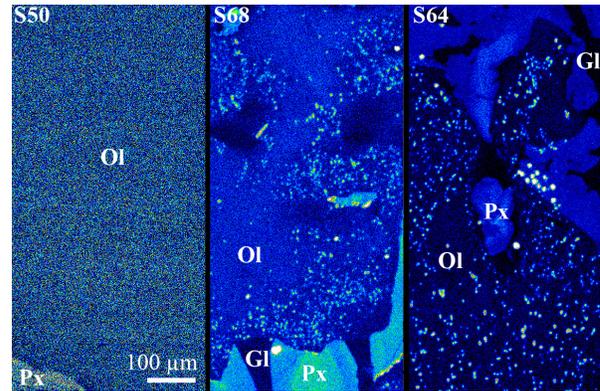


Figure 2: Stretched contrast X-ray Cr maps showing the presence of fine-grained spinel included in olivine in hybrid experiments. All three experiments were cooled from 1375°C to 1100°C. S50 was not oxidized; S68 was oxidized at 1150°C; S64 was oxidized at 1200°C. No fine-grained spinel is visible in S50, and the cores of S68 olivine are similarly spinel-free. All three images are at the same scale.

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