

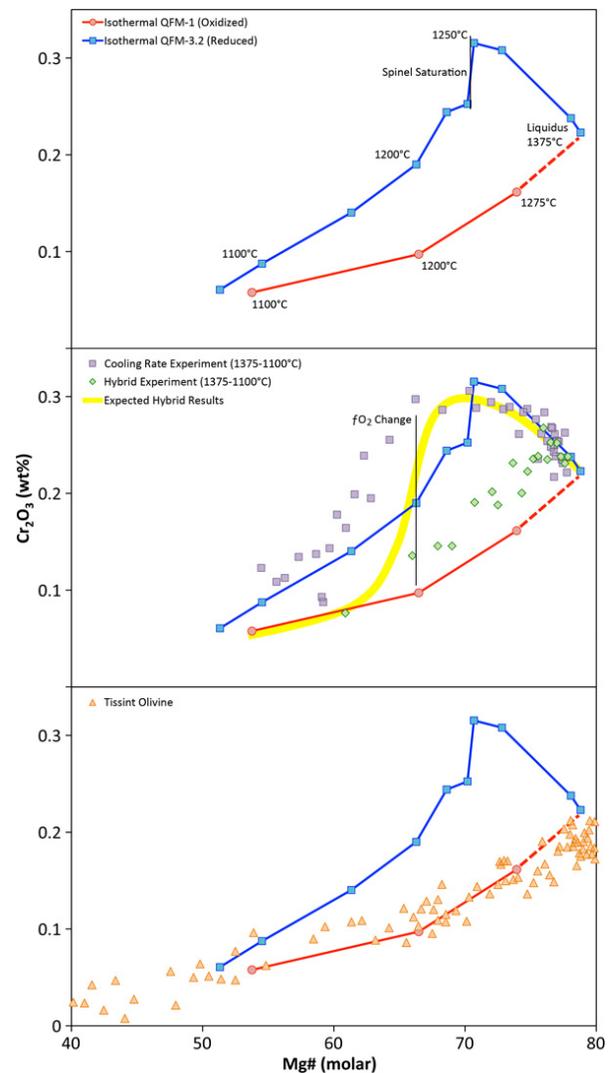
**Trace Elements in Martian Meteorites and the Olivine Peritectic Reaction: Insights from Tissint Experimental Petrology.** Nicholas Castle and Christopher D. K. Herd, Department of Earth and Atmospheric Sciences, 1-26 Earth Sciences Building, University of Alberta, Edmonton, Alberta, Canada ([castle@ualberta.ca](mailto:castle@ualberta.ca)).

**Introduction:** Trace element chemical zones in minerals have traditionally been used as tracers of magmatic history in all magmatic environments. Chemical zones have been used as tracers of the thermal and compositional history; they have been examined to determine the detailed history of oxygen fugacity ( $fO_2$ ) and mineral stability; they have even been used to argue for what part of the mineral assemblage is pheno- vs xenocrystic. In basaltic systems, like shergottites, olivine is especially important as the first silicate phase to form in many magmas.

In martian meteorites, near liquidus assemblages, where the parental composition can be readily determined, are rare [1]. The Tissint meteorite is a near liquidus assemblage, making it a good composition for experimentation. Previous estimates show that the Tissint magma started to crystallize at reducing conditions (QFM-3.5) but oxidized during cooling (QFM-1.4), likely due to open system behavior [2]. Tissint is thus a potentially useful natural sample in which to examine the effect of a redox change on trace element profiles during crystallization.

**Methods:** A series of isothermal (Iso) and cooling rate (CR) experiments were performed on a synthesized Tissint parental composition in CO-CO<sub>2</sub> gas mixing furnaces and analyzed by electron microprobe (EMP). Iso experiments were performed at QFM-1 (oxidizing) and QFM-3.2 (reducing); CR experiments were cooled at  $\sim 1^\circ\text{C/hr}$  with a set gas mixture averaging QFM-3.2 for each run, except one, referred to as the hybrid experiment, wherein the  $fO_2$  was abruptly increased to QFM-1 during cooling. This increase in  $fO_2$  is similar to what is hypothesized for the Tissint meteorite. See [3] for synthesis details; see [2, 4, 5] for experimental details and Tissint  $fO_2$  discussion.

**Results:** Iso experiments demonstrated different liquid lines of descent under reducing and oxidizing conditions, visible in olivine Cr-profiles (Fig. 1). CR experiments paralleled Iso experiments under reducing conditions, showing only minimal modification of the Cr-profile with experimental duration due to diffusion. It was expected that the hybrid experiment should evolve along the reducing curve until the  $fO_2$  change, after which it should follow the oxidizing curve (Fig. 1); however, this is not what was observed. Instead, the hybrid experiment follows the oxidizing curve, demonstrating that the original olivine profile was overprinted. Natural olivine profiles from Tissint [6] also parallel the oxidized Iso experiments, suggesting that the natural olivine zones were similarly overprinted.



**Figure 1:** Olivine Cr-content as a function of Mg#. Blue squares and red circles are the results of Iso experiments (top). Purple squares are olivine zones from a CR experiment; green diamonds are from the hybrid experiment (middle). Orange triangles are olivine compositions in Tissint, including literature data [6] (bottom). Each datapoint is the average of the three closest analyses, sorted by Mg#. Blue and red curves are the averages of all olivine analyses in each Iso experiment.

A peritectic relationship between olivine and pyroxene was elucidated by experiments, as evidenced by the modal mineralogies, where olivine abundance decreases as pyroxene stabilizes, and the petrologic textures where olivine converts from euhedral to embayed anhedral crystals. Oxidizing conditions greatly increase the extent of this reaction.

**Discussion:** Here we consider the possible mechanism for overprinting of trace elements, like Cr, in olivine. Diffusion is a potential mechanism to cause overprinting, but is not an adequate mechanism to cause all of the overprinting observed. Cr diffusion in olivine is apparent between the three CR experiments at constant  $fO_2$  where the peak Cr concentration decreases with increasing duration. Although this is a noticeable effect, all three experiments closely match the reducing curve from Iso experiments; substantially more Cr diffusion would be required to modify such curves until they match the oxidizing curve.

As diffusion alone is not adequate to overprint the olivine profile, olivine resorption may play a critical role. Although a relatively low fraction of olivine is resorbed at reducing conditions, a substantial fraction of olivine is resorbed under oxidizing conditions. For example, at 1200°C, the temperature the  $fO_2$  was changed in the hybrid experiment, there was 30% less olivine in the oxidized Iso experiment; by 1100°C the oxidized has 84% less olivine than the reduced Iso experiment, with a similar total crystallinity. A substantial resorption event should generate an abrupt compositional zone in the olivine, but diffusion has the potential to smooth the transition.

The resorption model requires an oxidation event during cooling to generate the olivine profile observed in the Tissint meteorite, and potentially other olivine-phyric shergottites [7]. Initial cooling generates large, relatively homogenous, olivine grains under reducing conditions. This is followed by an oxidation event, possibly gas escape during eruption [8]. The increase in  $fO_2$  causes a substantial fraction of the olivine to resorb, leaving behind anhedral cores out of equilibrium with the liquid, and stabilizes additional spinel, lowering Cr concentration in the magma. The olivine cores would be imparted with higher Fe rims, either as more olivine is stabilized during cooling or due to diffusion of Fe into the edges of the residual olivine cores. Faster diffusing elements, like Cr, would have a much deeper reequilibration before new olivine began to precipitate. With continued cooling, more olivine would precipitate either as rims on existing olivine grains or as discrete crystals in the groundmass. In the case of Tissint, the second stage of cooling was faster, yielding the finer-grained groundmass; however, cooling must have been sufficiently slow to cause modification of Cr in the olivine interiors.

Any elemental profile observed in olivine has the potential to be modified because the mechanism is driven by resorption rather than diffusion. The resorption itself may explain why olivine is commonly anhedral in shergottites [e.g., 9, 10]. Any slow diffusing element, like the Fe-Mg coexchange [11], may show

an abrupt change in the olivine profile, while a fast diffusing element, like Cr [12], may show a more gradual, but substantially modified, profile. Olivine in any shergottite that has undergone a substantial oxidation event is likely to have a modified profile. Whether a sample has undergone a substantial redox change may be demonstrated by mineral assemblages and oxybarometry (e.g., Tissint [2]); however, the presence of anhedral olivine may also be a strong indicator.

The mechanism described here may provide new insight into the petrogenesis of NWA 1068/1110, an enriched olivine-phyric shergottite. Previous work [13] concluded that olivine megacryst cores were xenocrystic because they formed under substantially more reducing conditions than the groundmass (QFM-2.5 and QFM+0.5, respectively). Supporting this was the anhedral nature of olivine cores, demonstrating that they were unstable in the magma. Contrasting with this, geochemical observations [7] concluded that olivine cores were in equilibrium with the melt on the basis of trace elements, and therefore likely phenocrysts. This work suggests that the olivine may have been phenocrystic, but substantially resorbed by the large oxidation event experienced by this basalt, before resuming crystallization at much lower Mg#. The similar redox histories of Tissint and NWA 1068/1110, belonging to the depleted and enriched chemistries respectively, implies that volatile content, and therefore the potential to oxidize during crystallization, is not tied to the enriched or depleted nature of the magmas, and may be a more common feature of olivine-phyric shergottites than previously known.

**Conclusions:** Overprinted olivine may lead to a number of erroneous petrogenetic interpretations if it is not accounted for. Olivine in any sample that has undergone substantial oxidation during crystallization is likely to be resorbed. Fast diffusing elements are likely to be overprinted, while slow diffusing elements are likely to preserve a reaction rim.

**References:** [1] McSween H.Y. and A.H. Treiman (1998) *Reviews in Min. and Geochem.*, 36, 6.1-6.53 [2] Castle N. and C.D.K. Herd, (2014) *LPSC*, #2334 [3] Herd C.D.K. et al. (2013) *LPSC*, #2683 [4] Castle N. and C.D.K. Herd (2013) *MaPS Supplement*, 76 [5] Castle N. and C.D.K. Herd (2015) *LPSC*, #1975 [6] Balta J.B. et al. (2015) *MaPS*, 50, 63-85 [7] Shearer C.K. et al. (2008) *MaPS*, 43, 1241-1258 [8] Shearer C.K. et al. (2013) *GCA*, 120, 17-38 [9] Barrat J.A. et al. (2002) *GCA*, 66, 3505-3518 [10] Basu Sarbadhikari A. et al. (2009) *GCA*, 73, 2190-2214 [11] Chakraborty S. (1997) *JGR: Solid Earth*, 102, 12317-12331 [12] Ito M. and J. Ganguly (2006) *GCA*, 70, 799-809 [13] Herd C.D.K. (2006) *American Mineralogist*, 1616.