

**CHROMIUM PARTITIONING BETWEEN OLIVINE/MELT IN EXPERIMENTAL PARTIAL MELTS OF THE ALLENDE AND MURCHISON CHONDRITES.** James M. Karner. <sup>1</sup>Dept. of Earth, Environmental, and Planetary Sciences, Case Western Reserve University, Cleveland, OH 44106 (jmk207@case.edu).

**Introduction:** We are interested in the partitioning of multivalent elements in basaltic systems as a way of estimating the oxygen fugacity ( $fO_2$ ) conditions under which basalts formed on planetary bodies (Earth, Moon, Mars, asteroids). Cr is a minor element in basaltic melts, partitions into several minerals that crystallize from basaltic melts, exists in multiple valence states at differing  $fO_2$  conditions, and is therefore a powerful oxybarometer for basaltic melts. Chromium is mostly 3+ in terrestrial basaltic melts at relatively high  $fO_2$  values ( $\geq IW+3.5$ ), and mostly 2+ in melts at low  $fO_2$  values ( $\leq IW-1$ ), such as those on the Moon and some asteroids [1]. At intermediate  $fO_2$ s, (i.e.,  $IW-1$  to  $IW+3.5$ ), basaltic melts contain both  $Cr^{3+}$  and  $Cr^{2+}$ . Understanding the partitioning of  $Cr^{3+}$  and  $Cr^{2+}$  into silicate phases with changing  $fO_2$  is thus crucial to the employment of Cr oxybarometers.

We take the opportunity here to examine the equilibrium partitioning of Cr between olivine/melt in experimental partial melts of natural meteorites at differing  $fO_2$  conditions [2]. The study will help add to the experimental data on  $DCr$  olivine/melt with changing  $fO_2$ , and also help us better understand the equilibrium partitioning of both  $Cr^{2+}$  and  $Cr^{3+}$  in natural basaltic meteorite melts.

**Samples and analytical techniques:** The samples used in this study are experimental partial melts of the Allende (CV) and Murchison (CM) chondrites produced by [2]. The melts were produced at varying temperatures,  $fO_2$  values, and run times. One of the significant findings from these experiments was that partial melts at low  $fO_2$  strongly resemble the composition of eucrites, while at high  $fO_2$  ( $IW+2$ ) melts have compositions that resemble angrites [2]. The approach to equilibrium for these charges was well considered and documented (see details in [2]) and thus we are confident in using these samples to evaluate the equilibrium partitioning of Cr between olivine/melt. The specific samples studied here are 1) Murchison at an  $fO_2$  of  $IW-1$  and temperature of  $1325^\circ C$  (M\_IW-1\_1325) 2) Allende at  $IW-1$  and  $1180^\circ C$  (A\_IW-1\_1180) 3) Allende at  $IW+1$  and  $1200^\circ C$  (A\_IW+1\_1200) and 4) Allende at  $IW+2$  and  $1200^\circ C$  (A\_IW+2\_1200). Figure 1 shows back-scattered electron images of two of the samples- all four samples studied here contained olivine grains and adjacent melt appropriate for the evaluation of Cr partitioning between the two phases.

Major and minor element composition of olivine and melt were determined using a Cameca SX100 electron microprobe. WDS was performed using a voltage of 15 kV, beam current of 20 nA, and beam size of  $1 \mu m$  for olivine grains, while glass (melt) was analyzed at 15 kV, 10 nA and a  $10 \mu m$  beam size. Counting times were 30 s for major and minor elements and 45 s for Cr. Natural minerals including forsterite, chromite and volcanic glass were used as standards. Exceptional olivine analyses were those that approached 100 wt.% oxide totals ( $\pm 1.5$  wt.%), a sum close to 1 cation per the tetrahedral site ( $\pm 0.02$ ), and a total of 3 cations ( $\pm 0.1$ ) overall, based on 4 oxygens per the olivine formula. Glass (melt) analyses were acceptable if oxide totals  $\sim 100\%$  ( $\pm 1.5$  wt.%). Both olivine and glass analyses were compared with those of [2] and found to be analogous.  $DCr$  values were determined by measuring several pairs of olivine rims and adjacent glass and then taking the average.

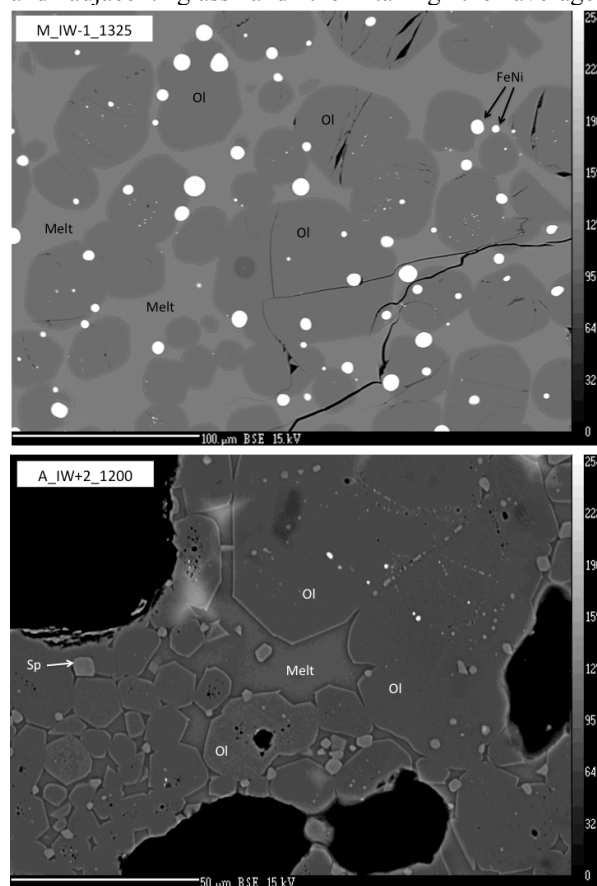


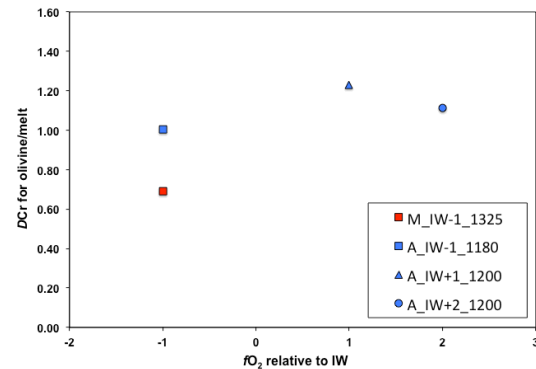
Figure 1. Back-scattered electron images of two of the four samples.

**Results:** Figure 2 charts the average  $DCr$  olivine/melt values against  $fO_2$ . The M\_IW-1\_1325 sample shows an average  $DCr = 0.69$  with a standard deviation of 0.02. The Allende samples range from  $DCr = 1.01$ , s.d. = 0.07 at IW-1, to  $DCr = 1.2$ , s.d. = 0.2 at IW+1, and  $DCr = 1.1$ , s.d. = 0.4 at IW+2.

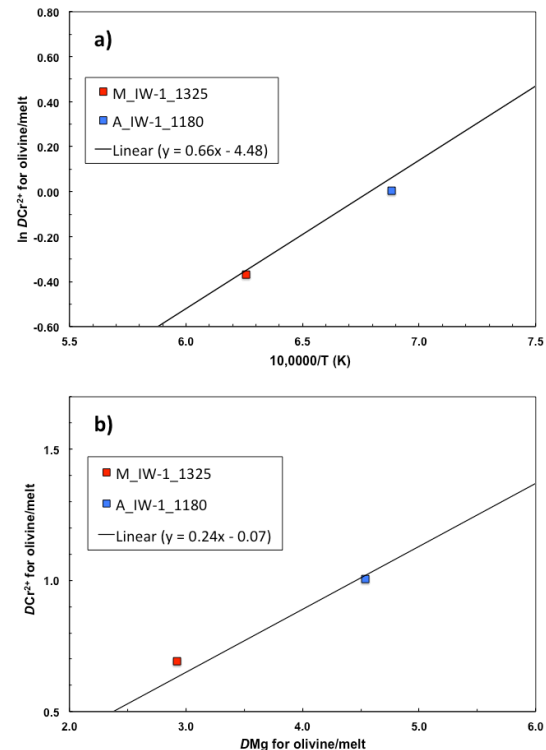
**Discussion:** In 1998, [1] performed a series of experiments in various Fe-free and Fe-bearing compositions over a wide range in  $fO_2$  in order to better understand  $Cr^{2+}$  and  $Cr^{3+}$  partitioning between olivine/melt. Their results show that at high  $fO_2$ , ( $\geq IW+3.5$ )  $Cr^{3+}$  dominates in basaltic melts, while at low  $fO_2$  ( $\leq IW-1$ ),  $Cr^{2+}$  dominates the melt. Hanson and Jones [2] then parameterized equations to model  $DCr^{3+}$  and  $DCr^{2+}$  between olivine/melt.  $DCr^{3+}$  covaries with the ratio of non-bridging oxygens to tetrahedrally coordinated cations (NBO/T), and  $DCr^{2+}$  is sensitive to liquid composition and temperature [1]. Figure 3a,b) show our measured values for M\_IW-1\_1325 and A\_IW-1\_1180 against the values predicted in [2], and show excellent agreement. Thus, we conclude that at IW-1,  $Cr^{2+}$  dominates in the system and  $DCr^{2+}$  olivine/melt is indeed sensitive to melt composition and temperature as predicted by [1].

Samples A\_IW+1\_1200, and A\_IW+2\_1200 were equilibrated at  $fO_2$  values where a mixture of  $Cr^{2+}$  and  $Cr^{3+}$  exist in the melt. Subsequently, our  $DCr$  values olivine/melt for these samples are equal to the sum of  $DCr^{2+}$  multiplied by the fraction of  $Cr^{2+}$  in the melt, and  $DCr^{3+}$  multiplied by the fraction of  $Cr^{3+}$  in the melt. The  $Cr^{2+}/Cr^{3+}$  ratio in the melt of our samples is unknown, and is very difficult to model in Fe-bearing systems [1]. As an approximation, [3] note at an  $fO_2$  of IW, the ratio of  $Cr^{2+}/Cr^{3+}$  in basaltic melts is approximately unity. Recently, [4] measured  $DCr$  olivine/melt at  $fO_2$ s from IW-1 to IW+3.4 and report  $Ds$  from 0.59 to 0.72 in a martian melt composition. Previous studies also show a lack of  $DCr$  variation with  $fO_2$  from IW to IW+4 with  $DCr$  olivine/melt  $\approx 0.6$  [5, 6]. The reason for this is that  $DCr^{2+}$  and  $DCr^{3+}$  olivine/melt are about equal [1]. This is because  $Cr^{2+}$  substitution into the olivine structure for  $Mg^{2+}$  or  $Fe^{2+}$  causes no charge balance problems but it is just a little big for the M1 site in olivine [3]. In contrast,  $Cr^{3+}$  fits nicely into the olivine M1 site but requires charge balance [3]. Our measured  $DCr$  values are greater than those of [4-6] but similarly lack change with  $fO_2$ . Our higher  $DCr$  values could be a consequence of measuring low Cr contents in olivine and melt in samples which contain relatively Cr-rich spinel; as such our measurements for these samples show significant standard deviations. We plan to remeasure these samples with longer counting times to alleviate this problem. We also note, however, that our samples were equilibrated at 1200°

C, 120° to 200° lower than those in [4-6], and this could have some effect. Lastly, we note that partial melts of eucrite meteorites (i.e., similar composition to our melts), yielded  $DCr$  olivine/melt of  $\sim 1.0$  at IW, IW-0.6 and IW-1.25 [7]. These results are very similar to our results for the Allende samples with varying  $fO_2$ .



**Figure 2.**  $DCr$  olivine/melt vs.  $fO_2$ .



**Figure 3a, b.** Our IW-1 samples against the linear regression predicted by [1].

**References:** [1] Hanson, B. and Jones, J.H. (1998) *Am. Min.*, 83, 1151–1154. [2] Jurewicz, A.J.G., et al. (1993) *GCA*, 57, 2123-2139. [3] Papike, J.J., et al. (2005) *Am. Min.*, 90, 277-290. [4] Bell, A.S., et al. (2014) *Am. Min.*, 99, 1404-1412. [5] Gaetani, G.A. and Grove, T.L. (1997) *GCA*, 61, 1829-1846. [6] Mikouchi, T., et al. (1994) *LPSC XXV*, 907-908. [7] Stolper, E. (1977) *GCA*, 41, 587-611.