

VALENCE STATE PARTITIONING OF CR AND V BETWEEN OLIVINE-MELT AND PYROXENE-MELT IN EXPERIMENTAL BASALTS OF A EUCRITIC COMPOSITION: PART II. J. M. Karner¹ (j.karner@utah.edu), and L. Le². ¹Dept. of Geology and Geophysics, University of Utah, Salt Lake City, UT. ²Jacobs Engineering, NASA Johnson Space Center, Houston, TX.

Introduction: The partitioning of multivalent elements helps clarify the oxygen fugacity (fO_2) conditions under which basalts formed on planetary bodies (Earth, Moon, Mars, asteroids). Chromium and V are two multi-valent elements that are useful in the above task as they; are minor and trace elements in basaltic melts, partition into several minerals that crystallize from basaltic melts, and exist in multiple valence states at differing fO_2 conditions. Chromium exists in the 3+ state in terrestrial basaltic melts at relatively high fO_2 conditions ($\geq IW+3.5$), and mostly 2+ in melts in low fO_2 settings ($\leq IW-1$), such as those on the Moon and some asteroids [1]. At intermediate fO_2 s, (IW-1 to IW+3.5), basaltic melts contain both Cr^{3+} and Cr^{2+} . Vanadium in basaltic melts is mostly 4+ at high fO_2 s, mostly 3+ at low fO_2 s, and a mix of V^{3+} and V^{4+} at intermediate fO_2 conditions [2].

In this abstract we continue to measure the equilibrium partitioning of Cr and V between olivine/melt and pyroxene/melt in new experimental charges of a Sioux County (i.e., eucrite) composition produced at differing fO_2 conditions. We also measure the partitioning of Sc, as Sc exists only in the 3+ state and therefore its partitioning should remain constant with changing fO_2 . Thus, DSc is used as a check on our charges and their approach to equilibrium. This abstract adds to the experimental data on DSc , DV , DCr (i.e., olivine/melt, pyroxene/melt) at differing fO_2 , and in turn these D -values can be used to assess the fO_2 of basalts from Vesta and other compositionally similar basalts.

Samples and analytical techniques: The new experimental crystallization products (SC-24 to SC-44) are of the Sioux County composition [3] doped with 1000 ppm V and Sc. These charges supplement those explored in [4]. The charges were produced at fO_2 values of IW-1, IW, IW+2 and include isothermal runs from 1190 °C down to 1120 °C at ten degree increments. The isothermal charges were produced by first homogenizing the mix at temperatures above the liquidus (~1195 °C) and then cooling to the desired temperature and holding for 24 to 48 hours.

Major and minor element compositions of minerals 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 μm for minerals and melt. Peak counting times were 20s for major and minor elements and 120s for V and Sc. Natural minerals were used as standards,

while V and Sc were calibrated on the respective metals of each. Olivine, pyroxene, and melt analyses were critically evaluated as to proper wt.% oxide totals, stoichiometry, and charge balance based on ideal mineral formulas. DCr , DV , and DSc values were determined by measuring elemental concentration in a crystal rim divided by elemental concentration in the adjacent melt. Several pairs of crystal/melt analyses were performed on each charge and the calculated D -values were averaged.

Results: In general, the charges shared a common silicate mineral occurrence of olivine crystallization at 1170-1160 °C, followed by olivine + pyroxene at 1160, 1150, and 1140 °C, and olivine + pyroxene + plagioclase in the 1130 and 1120 °C charges. Some specific differences were that the runs at IW-1 crystallized olivine at a higher temperature (1170 °C) than those at IW and IW+2 (1160 °C), and also the charge at IW-1 and 1130 °C contained no plagioclase while both charges at IW, IW+2 and 1130 °C did. Lastly, the runs at IW+2 crystallized pyroxene at 1160 °C, ten degrees higher than the runs at IW and IW-1.

Discussion: These new isothermal experiments (SC-24 to SC-44) supplement our previous experiments (both isothermal and cooling [4]) on the same composition (SC-7 to SC-20). The two sets of experiments share the same crystallization sequence of olivine, followed by pyroxene and then plagioclase, but differ slightly in the temperature of appearance of those minerals. Both sets of experiments show homogeneous olivine grains with olivine/melt $KD_{FeO/MgO} \approx 0.35$, which suggests the grains are approaching equilibrium with the melt for this iron-rich, (FeO = 17 wt.%) eucrite bulk composition [5].

Table 1 presents calculated DSc , DV and DCr olivine/melt vs. fO_2 , for both sets of experiments. DSc is pretty consistent at 0.4 for all three fO_2 conditions in the new experiments. This makes sense as DSc should not change with fO_2 as it only exists in the 3+ state. These values compare well to a linear equation by [6] relating DSc olivine/melt to $DMgO$ olivine/melt, which predicts $DSc = 0.32$ for eucrite compositions. Using the same equation and $DMgO$ olivine/melt from our samples, DSc computes to 0.32 to 0.37. We note that the Sc concentrations are about 0.02 oxide wt.% in olivine and about triple that in the glass, so we are measuring near probe detection limits and this almost certainly led to erroneous DSc olivine/melt values in

our first set of experiments (Table 1, SC-7 to SC-20). We increased peak counting times for these experiments and the results are obviously more consistent.

DV olivine/melt generally decreases with increasing fO_2 for both sets of experiments (Table 1). This is consistent with V^{3+} being more compatible in olivine than V^{4+} [7]. The reason for this may be due to the substitutional couple in which one vacancy can accommodate $2V^{3+}$ cations, while one vacancy can only accommodate one V^{4+} cation [1]. More specifically, our DV values are mostly consistent with those from [7,8], where calibration curves define DV olivine/melt of 0.5-0.6, 0.3-0.4, and 0.15, at IW-1, IW, and IW+2 respectively.

Table 1 finally shows DCr olivine/melt ≈ 1 at IW-1, IW, and IW+2 in nearly all the charges from both sets of experiments. DCr is steady even though the Cr^{2+}/Cr^{3+} ratio is decreasing with increasing fO_2 . The reason for this is that DCr^{2+} and DCr^{3+} olivine/melt are about equal; 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, while Cr^{3+} fits nicely into the olivine M1 site but requires charge balance [1]. These results are almost identical to those determined by [9,10] and are consistent with the predictions of [11].

Table 2 displays calculated DSc, DV and DCr pyroxene/melt vs. fO_2 for the experiments. All the pyroxenes measured here are low-Ca pigeonites, with Wollastonite (Wo) values increasing from 6 to 9 with decreasing temperatures from 1150 to 1120 °C. Our DSc values are pretty consistent at 2.3 to 3.0 for the new experiments. The regression of [6], using a eucritic DMgO for pyroxene and melt, predicts $DSc = 1.3$. The same equation using DMgO pyroxene/melt from our charges yields similar Ds of 1.2 to 1.5. So, our values are nearly double those of [6]; this could be related to the Wo content of the pyroxenes, or analytical error measuring low Sc contents in both mineral and melt. We are exploring both possibilities.

DV pyroxene/melt for the new charges (Table 2) generally decreases with increasing fO_2 . This is agreeable with the notion that DV^{3+} is more compatible in pyroxene than V^{4+} , which is probably because the charge balancing couple $M^{1+}V^{3+} - IVAl$ is more compatible than in the pyroxene structure than $M^{1+}V^{4+} - 2IVAl$ owing to the charge balance couples [1]. Our DV values at each fO_2 are broadly consistent with those of [12], but the leveling out of DV from IW to IW+2 warrants more detailed and careful analyses of the new charges.

Lastly, Table 2 shows DCr in the new experiments is consistent across all three fO_2 s at $DCr \approx 5.6$. This is not consistent with the idea that DCr should increase with increasing fO_2 , as Cr^{3+} is more compatible in py-

roxene than Cr^{2+} [1]. Widely varying Ds for the charges at each temperature contributes to our averages- a closer look at the mineral-melt pairs used to determine the DCr values is necessary. However, we note that DCr pyroxene/melt generally increases with increasing fO_2 in the first set of charges.

Conclusions: While the D-values for Sc, V, and Cr between olivine/melt and pyroxene/melt are reasonable, we may be able to understand the inconsistencies with further inspection of the temperature, analytical accuracy, and specific composition of the minerals in each of the charges that were measured.

Table 1. DSc, DV and DCr olivine/melt vs. fO_2 .

Temp	IW-1				IW				IW+2			
	DSc	DV	DCr	Exp.	DSc	DV	DCr	Exp.	DSc	DV	DCr	Exp.
1170	0.43	0.63	1.10	SC-26	0.36	0.21	0.94	SC-43	0.35	0.26	1.02	SC-31
1160	0.38	0.55	1.00	SC-27	0.42	0.29	1.09	SC-40	0.40	0.22	1.20	SC-33
1150				SC-30	0.46	0.16	1.05	SC-38	0.42	0.30	1.15	SC-34
1140				SC-32	0.46	0.16	0.88	SC-36	0.73	0.23	0.90	SC-39
1130				SC-35	0.68	0.18	1.18	SC-44	0.35	0.14	1.42	SC-41
1120												
	0.40	0.59	1.05	AVG	0.48	0.20	1.03	AVG	0.45	0.23	1.14	AVG
1190					0.45	0.38	1.06	SC-9				
1180	1.42	0.67	0.97	SC-15	0.18	0.38	1.01	SC-10				
1175					0.49	0.34	0.97	SC-13				
1170	0.45	0.62	1.03	SC-16	0.19	0.43	0.97	SC-11				
1163					0.19	0.45	1.01	SC-12				
1160	0.57	0.59	1.04	SC-17					0.42	0.29	1.24	SC-20
1150	1.22	0.56	1.04	SC-18								
1140												
1130	0.17	0.71	1.15	SC-7	0.21	0.42	1.08	SC-8				
	0.76	0.63	1.04	AVG	0.28	0.40	1.02	AVG	0.42	0.29	1.24	AVG

Table 2. DSc, DV and DCr pyroxene/melt vs. fO_2 .

Temp	IW-1				IW				IW+2			
	DSc	DV	DCr	Exp.	DSc	DV	DCr	Exp.	DSc	DV	DCr	Exp.
1170				SC-26				SC-43	2.28	2.11	4.64	SC-31
1160				SC-27				SC-42	2.24	2.03	6.13	SC-33
1150	2.22	2.21	4.82	SC-30	2.26	1.91	4.90	SC-40	2.24	2.03	6.13	SC-34
1140	2.45	2.16	4.04	SC-32	1.99	1.95	6.31	SC-38	1.35	2.00	7.07	SC-39
1130	4.41	3.24	8.04	SC-35	2.51	2.04	7.19	SC-36	3.10	2.13	5.00	SC-41
1120					2.87	2.26	4.42	SC-44	2.65	1.97	5.20	SC-37
	3.03	2.54	5.64	AVG	2.41	2.04	5.71	AVG	2.32	2.05	5.61	AVG
1190	2.40	2.12	2.31	SC-14					2.14	1.30	2.87	SC-21
1180	3.23	2.23	2.24	SC-15								
1170	1.92	2.15	3.34	SC-16								
1160	2.39	2.12	2.93	SC-17	0.77	1.87	2.79	SC-11				
1150	6.46	2.79	3.03	SC-18	1.32	3.17	4.26	SC-12	2.75	1.91	5.50	SC-20
1140												
1130	1.17	3.64	3.61	SC-7								
1100	1.28	3.32	3.52	SC-6	1.16	3.11	5.11	SC-8				
	2.69	2.63	3.00	AVG	1.09	2.72	4.05	AVG	2.44	1.61	4.18	AVG

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