Phase Relations and Experimental REE Partitioning using a Primitive Martian Basalt Composition at High Pressure. A. Blinova[1] and C. D. K. Herd[1], [1]Department of Earth and Atmospheric Sciences, 1-26 Earth Sciences Building, University of Alberta, Edmonton, AB, T6G 2E3, Canada (blinova@ualberta.ca)

Introduction: The bulk composition of the Yamato 980459 martian meteorite (Y98), has characteristics that make it a prime candidate for investigating phase relationships in the martian mantle using high pressure experimental petrology [1-3]. Phase relationships have been previously mapped up to 15 kbar [4,5]. We carried out experiments on Y98 in the 10-20 kbar range at 1350-1650ºC, thus extending the works of [4,5]. At the present there are several studies that use REE for Martian mantle modeling [e.g. 6]. However, no study has experimentally determined REE partitioning for Martian basalts at the estimated pressures and temperatures of basaltic melt generation in the Martian mantle (10-20 kbar and 1350-1650ºC). We present preliminary results from experimental determination of REE partitioning (D_{REE}) in olivine and orthopyroxene under these conditions. The results have implications for understanding melt generation in the martian mantle.

Experimental methods: The Y98 composition after [1] was chosen to approximate the bulk composition in terms of major and minor elements (Table 1). Reagent-grade oxide powders and carbonates were ground in appropriate proportions under acetone in an agate mortar and pestle, then melted in a platinum (Pt) crucible at 1500°C for several hours and reground to ensure homogeneity. Experiments were conducted using the end-loaded piston cylinder apparatus in the Chris M. Scarfe Experimental Petrology Lab at the University of Alberta with a half-inch diameter pressure assembly comprised of talc, Pyrex and graphite sleeves, and crushable ceramic internal parts. The sample was loaded into a graphite capsule which was placed in a triple-crimped Pt capsule. Temperature was monitored using a W5Re/W26Re (Type C) thermocouple. Pressure and temperature ramps were done "hot piston-in", i.e., the assembly was brought to half the run pressure and then ramped up to the target run temperature; once the temperature reached the required setting, the pressure was brought up to the final run pressure. The duration of each experiment was approximately 6 hours. Each run was quenched isobarically. Oxygen fugacity was controlled by initially presetting the starting material for Fe_2O_3 content in a CO/CO_2 gas-mixing furnace. This process lasted 220-264 hours at 900°C and log fO_2 = -14.53, and resulted in a calculated Fe_2O_3 concentration of 1.80±0.06 wt%. For partitioning experiments, reagent-grade, dry REE oxides were added to the unreduced Y98 composition. The target amount for REE doping was optimized for LA-ICPMS detection limits (1 µg/g for LREE; 3-4 µg/g fpr HREE) for the smallest achievable spot size (20 µm) and based on published D_{REE}. The doped Y98 composition was then reduced for 210 hours under similar conditions for the undoped composition, and reground in acetone every 24 hours to ensure a homogeneous distribution of REEs. Major and minor elements in all run products were obtained by electron probe microanalysis using a JEOL 8900 Superprobe at the University of Alberta. A Merchantek UP 213 UV laser ablation system connected to a Perkin Elmer Elan 6000 quadrupole inductively coupled plasma mass spectrometer (ICP-MS) was used for determination of REE concentrations in doped samples. NIST 610 and 612 were used as external standards. Both standards and samples were ablated using a 20 µm diameter spot size and 5 Hz repetitions with a dwell time of 50 milliseconds. A typical analysis consisted of a ~20 second background measurement followed by ablation for ~50 seconds.

Oxide (wt %)	This study	[1]	[5]
SiO_2	48.68	48.63	49.47
TiO_2	0.59	0.54	0.50
Al_2O_3	5.25	5.27	5.90
Cr_2O_3	0.55	0.71	0.68
FeO	17.67	17.32	16.00
MnO	0.51	0.52	0.55
MgO	19.98	19.64	18.91
NiO	0.00	na	0.01
CaO	6.57	6.37	6.85
Na_2O	0.56	0.48	0.75
K_2O	0.03	0.02	0.02
P_2O_5	0.28	0.29	0.34
FeS	na	0.26	na
S	na	na	0.01
TOTAL	100.67	99.86	100.00
Mg#	0.67	0.67	0.68

Table 1: Experimental starting composition.

Results: Run products and conditions are shown in Table 2 (SB01-017) and in Figure 1 (red symbols). We used the equilibrium correlation line from [7] and the average partition coefficient for Mg and Fe (D^{Fe} and D^{Mg}) to confirm equilibrium. In addition, we applied mass balance calculations to compositions of olivine, pyroxene and glass using a least-squares method [8] to confirm that our experimental olivine cores were in equilibrium with the melt. The liquidus from this study is 75-100ºC below that of [5] but consistent with results of [4], likely attributable to a small amount of H_2O (<0.5 wt%) dissolved in our experiments [4]. Run products and conditions for six experiments doped with rare earth elements (REE) are presented in Table 2 (REE01-06). LA-ICPMS analyses yield glass with

2,000-4,000 ppm REE. Olivine and pyroxene contain a large range of REE. For example, La in olivine and pyroxene ranges from 2.17(0.53) to 115.28(9.89) ppm and 176.77(9.57) to 1280(98) ppm, respectively (number in brackets is 1σ absolute error), likely due to rim effects [9] or incorporation of glass as melt inclusions. In some cases the laser spot size is comparable to the sizes of crystals. Non-Henrian behaviour of REE is a possibility that remains to be verified. Preferred D values, based on minimum concentrations, are given in Table 3.

Table 2: Summary of run conditions and run products for undoped and doped samples.

Run	P (kbar)	T (°C)	Results
SB01	13	1450	ol+px+gl
SB07	14	1450	ol+px+gl
SB08	16	1450	ol+px+gl
SB02	11	1450	ol+gl
SB06	14	1475	px+gl
SB016	17	1475	px+gl
SB017	19	1425	px+gl
SB03	13	1475	glass
SB014	14	1500	glass
SB09	18	1500	glass
REE01	18	1450	glass
REE02	19	1475	(ol)+px+gl
REE03	14	1425	ol+px+gl
REE04	12	1400	ol+px+gl
REE05	10	1447	glass
REE06	11	1450	ol+px+gl

Discussion: Our preliminary REE partition coefficients are the first D values determined on the composition of the most primitive Martian meteorite at high pressure conditions similar to that of the Martian basaltic sources, in contrast to previously published values, which are largely based on one atmosphere experiments or phenocryst/matrix studies [e.g., 9,10]. Known pressure effects on D_{REE} include increase of D-values with increase in pressure at constant SiO_2 levels [11]. Although such effects are not clearly seen in our preliminary data, overall D values are higher than reported previously. Models of Martian magma ocean (MMO) crystallization and basalt generation [e.g., 6,12,13] utilize D values from one atmosphere experiments [9], compilation of phen-matrix studies [10] and theoretical studies [14]. The higher D values and the lower D_{Sm}/D_{Nd} ratio for orthopyroxene reported here may have implications for MMO modeling as well as explaining discrepancies between time-integrated $^{147}Sm/^{144}Nd$ ratios of mantle sources and those measured in the Martian basalts [12,13].

References: [1] Misawa K. (2003) *NIPR Symp.,*84. [2] Mikouchi *et al.* (2004) *Ant.Met.Res.* 17, 13-34 . [3] McKay et al. (2004) LPS XXXV, #2154. [4] Norris J. and Herd C. (2006) LPS XXXVII, #1787. [5] Musselwhite D. et al. (2006) *MAPS*, 41, 1271-1290. [6] Borg L. and Draper D. (2003) *MAPS*, 38, 1713-1731. [7] Jones J. (1984) *Cont. Min. Pet.*, 88, 126-132. [8] Wright T. and Doherty P. (1970) *GSA Bul.*, 81, 1995-2008. [9] McKay G. (1986) *GCA*, 50, 69-79. [10] Fujimaki et al. (1984) *Cont. Min. Pet.*, 94, 42-45. [11] Green T. and Pearson N. (1983) *Nature*, 305, 414-416. [12] Borg L. et al. (2003) *GCA*, 67, 3519-3536. [13] Débaille et al. (2007) *Nature*, 450, 525-528. [14] McKenzie D. and O'Nions R. (1991) *JPet.*, 32, 1021-1091.

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Table 3: Preferred D values. 1σ % errors stated in brackets. D values for olivine and pyroxene used by [6] (original reference [14]) tabulated for comparison.

	P, T	D^{La}	D^{Nd}	D^{Sm}	D^{Eu}	D^{Gd}	D^{Yb}
Ol	11, 1450	0.0009 (27)	0.003(32)	0.008(38)	0.009(16)	0.014(18)	0.039(17)
	12, 1400	0.015 (9.4)	0.017(8.4)	0.019(16)	0.020(9.6)	0.025(11)	0.057(10)
	14, 1425	0.014 (6.9)	0.016(6.9)	0.019(11)	0.019(6.6)	0.016(9.1)	0.027(10)
	[6]	0.0004	0.001	0.0013	0.0016	0.0015	0.0015
Px	11, 1450	0.145 (15)	0.153(9.2)	0.148(18)	0.161(16)	0.135(16)	0.157(17)
	12, 1400	0.167 (12)	0.176(8.3)	0.165(14)	0.209(12)	0.151(13)	0.186(13)
	14, 1425	0.050 (7.1)	0.045(6.7)	0.046(9.2)	0.049(7.1)	0.057(8.7)	0.077(8.2)
	[6]	0.002	0.0068	0.01	0.013	0.016	0.049

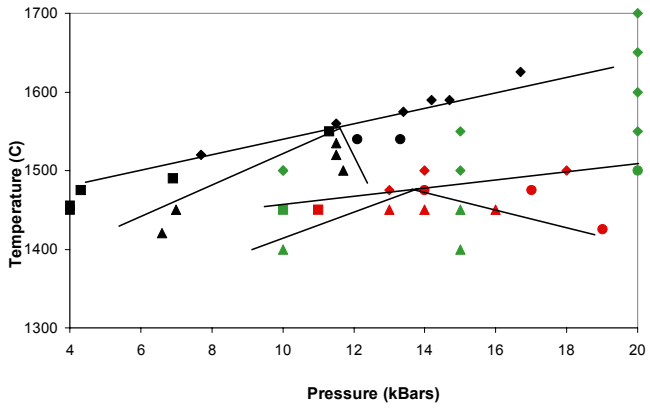

Figure 1: Experimentally determined phase relations for synthetic Y98 bulk composition. Green symbols are from [4], black are from [5], red are from this study. Diamonds = glass only, squares = olivine + glass, circles = pyroxene + glass, triangles = olivine + pyroxene + glass.