MOLYBDENUM VALENCE IN BASALTIC SILICATE MELTS. L. R. Danielson[1], K. Righter[2], M. Newville[3], S. Sutton[3,4], K. Pando[1], [1]Jacobs Sverdrup Co., Houston, TX 77058 United States (lisa.r.danielson@nasa.gov), [2]NASA JSC, 2101 NASA Parkway, Houston, TX 77058 United States, [3]Center for Advanced Radiation Sources and 4Dept. of Geophys. Sci., University of Chicago, Chicago, IL 60637 United States.

Introduction: The moderately siderophile element molybdenum has been used as an indicator in planetary differentiation processes, and is particularly relevant to core formation [for example, 1-6]. However, models that apply experimental data to an equilibrium differentiation scenario infer the oxidation state of molybdenum from solubility data or from multivariable coefficients from metal-silicate partitioning data [1,3,7].

Partitioning behavior of molybdenum, a multivalent element with a transition near the fO_2 of interest for core formation (~IW-2) will be sensitive to changes in fO_2 of the system and silicate melt structure. In a silicate melt, Mo can occur in either 4+ or 6+ valence state, and Mo^{6+} can be either octahedrally or tetrahedrally coordinated. Here we present first XANES measurements of Mo valence in basaltic run products at a range of P, T, and fO_2 and further quantify the valence transition of Mo.

Table 1. Experiments analyzed from this and previous studies. Silicate composition is indicated above experiment labels. Piston cylinder experiments [3,5,6] were metal-silicate partitioning studies, while controlled atmosphere experiments had no metal added to the starting composition.

	T deg C	Pressure	Δ IW	Mo, ppm	valence
hawaiite[3]					
66	1300	10 kbar	-0.72	11.78	3.1
83	1300	10 kbar	-0.63	4.61	3.5
basalt[5,6]					
cow1	1500	10 kbar	-1.44	2.9	3.9
cow3	1600	10 kbar	-1.48	4.2	3.9
cow8	1700	10 kbar	-1.45	4.9	4.2
cow20	1800	10 kbar	-1.44	6	3.8
ankaramite					
ankIW	1300	1 bar	0	500	5.3
ankIW1	1300	1 bar	1	500	5.4
ankIW2	1300	1 bar	2	500	6.0
ankIW-1	1300	1 bar	-1	500	3.7
ankIW-2	1300	1 bar	-2	500	2.5
andesite[2]					
KR-D	1190	1 bar	11.5	0.13 wt%	6

Experiments: Basaltic run products from 3 previous studies were selected for analyses, with attention to variation in temperature, pressure, fO_2, and amount of Mo dissolved in the silicate phase (Table 1). A new series of experiments were also conducted at controlled fO_2 in order to more fully explore fO_2 space.

One andesite doped with 0.13 wt% MoO_3 was analyzed from Righter et al. [2], a product that was melted in air. Another set of hawaiites from piston cylinder experiments by Righter and Drake [3] were run at near constant pressure, temperature, and fO_2, but contain low amounts of Mo from 0.11 ppm to 11.78 ppm by weight. Piston cylinder experiments using a basaltic silicate composition performed by Acuff et al. [5,6] were run at higher temperature and lower fO_2.

New experiments for this study were performed using ankaramite basalt at conditions similar to the previous study by Danielson et al. [8]. A small amount of Mo dopant (500 ppm) was added to natural ankaramite to ensure detection.

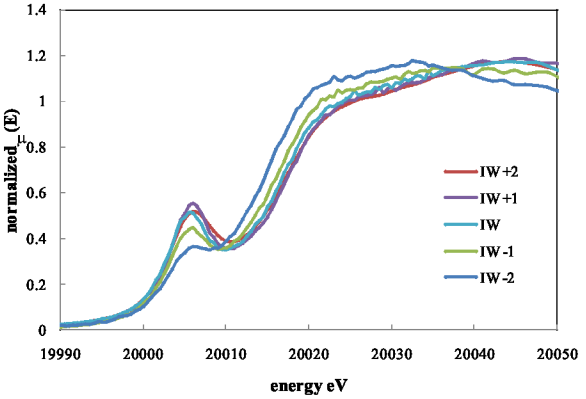

Figure 1. XANES spectra for controlled fO_2 experiments performed for this study, showing K-edge energy shift to lower energy with more reducing conditions. Pre-edge peak (at around 20007 eV) also decreases in intensity. An energy shift of the pre-edge peak to higher eV does not occur, indicating no change in Mo^{6+} coordination from tetrahedral to octahedral.

Analyses: A monochromatic X-ray beam from a Si(111) double crystal monochromator was focused onto the sample and the fluorescent X-ray yield was plotted as a function of incident X-ray energy (more detail can be found in [9]). Mo K XANES spectra were normalized to strontium as an internal reference ele-

ment, then normalized so that the below edge intensity was zero and the above edge intensity was unity. The oxidation state of molybdenum was then inferred from the energy of the K-edge position defined as the lowest energy where μ=1 in the normalized XANES spectrum (Figure 1) [after 10]. Energy shift and intensity of the pre-edge peak was used to determine coordination of Mo^{6+} [10]. Mo foil and experiment KR-D, the extreme oxidized end member Mo doped andesite were used as standards to form a linear trend for valence determination.

Results and Discussion: Ankaramite 1 bar experiments show a trend in average valence from Mo^{6+} at the most oxidizing condition (IW+2) to nearly Mo^{2+} at IW-2 (Figure 2). The transition from Mo^{6+} to Mo^{4+} occurs largely between IW and IW-1, in good agreement with [7], who concluded Mo changed dominant valence at around IW-1, from Mo^{6+} to Mo^{4+}. [7] also suggested that below IW, down to IW-3, Mo^{4+} and Mo^{6+} coexist in equal amounts. Our results narrow the field of Mo^{4+-6+} coexistence to IW+1 to just below IW. At the conditions of core formation, near IW-2, Mo^{6+} is no longer present. Farges et al. [10] suggested Mo^{5+} may be stable around IW. However, Farges et al. [10] evidence for stable Mo^{5+} (determined from additional electron paramagnetic resonance spectroscopy data) appears only in FeO-free systems, and thus Mo5+ is not likely to be present in experiments examined in this study.

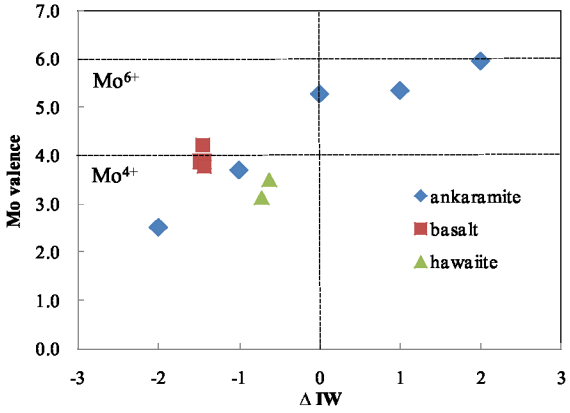

Figure 2. Molybdenum average valence as a function of oxygen fugacity relative to the iron-wüstite buffer for experiments in table 1.

The lack of energy shift of the pre-edge peak (Fig. 1) suggests more than 90% of the Mo^{6+} is in tetrahedral coordination. This is the case for all fO_2 where Mo^{6+} is present. Farges et al. [10] supported this system dominated by tetrahedral Mo^{6+} - octahedral Mo^{6+} only forms where network modifiers become scarce.

As oxygen fugacity decreases below IW-1, contributions from Mo metal increase although Farges et al. [10] maintained that some contributions from Mo^{2+} cannot be ruled out. Farges et al. [10] suggested the transition to Mo^0 dominance happens at around IW-3, with Mo metal becoming visible at IW-4. However, assuming a linear trend in the ankaramite data, Mo^0 may not be reached until near IW-5. More data will be collected at lower fO_2 to determine the amount of Mo^0 contribution.

The moderate increased pressure of the basalt and hawaiite experiments seems to have no effect on Mo valence, also observed in previous experiments [10]. ,W¶V□ XQNQRZQ□ ZKDW□ HIIHFWV□ SUHVVXUHV□ UHOHY (DUWK¶V□PDQWOH□PD\□KDYH□RQ□0R□YDOHQFH□DQG□ tion in silicate melts, but that will be studied in future experiments. Although hawaiites contain up to 1.36% water, this is unlikely to explain any valence differences in experiments around IW-1 [11].

Conclusions: Our data support the interpretation of previous authors [1,3,5,6] that Mo^{4+} is the dominant species at or below IW-1, with no Mo^{6+}, in contrast to the multi-YDOHQW□ PRGHO□ RI□ 2¶1HLOO□ DQG□ (JLQV□ Conditions below IW-1 may have a significant component of Mo^0. Even though the nugget effect has not been reported for Mo at IW-1 or below, a contribution from Mo metal (or even Mo^{2+}) may require modification of metal-silicate partitioning models.

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