MOLYBDENUM VALENCE IN BASALTIC SILICATE MELTS. L. R. Danielson1, K. Righter2, M. Newville3, S. Sutton3, K. Pando1, Jacobs Sverdrup Co., Houston, TX 77058 United States (lisa.r.danielson@nasa.gov), 2NASA JSC, 2101 NASA Parkway, Houston, TX 77058 United States, 3Center for Advanced Radiation Sources and Dept. 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 FeO of interest for core formation (~IW-2) will be sensitive to changes in FeO 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 FeO 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.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>Pressure (kbar)</th>
<th>Δ IW</th>
<th>Mo, ppm</th>
<th>Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>hawaiite[3]</td>
<td>66</td>
<td>1300</td>
<td>-0.72</td>
<td>11.78</td>
<td>3.1</td>
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<tr>
<td></td>
<td>83</td>
<td>1300</td>
<td>-0.63</td>
<td>4.61</td>
<td>3.5</td>
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<tr>
<td>basalt[5,6]</td>
<td>cow1</td>
<td>1500</td>
<td>-1.44</td>
<td>2.9</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>cow3</td>
<td>1600</td>
<td>-1.48</td>
<td>4.2</td>
<td>3.9</td>
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<td>cow8</td>
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<td>-1.45</td>
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<td></td>
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<td>1800</td>
<td>-1.44</td>
<td>6.0</td>
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<tr>
<td>ankaramite</td>
<td>ankiW</td>
<td>1300</td>
<td>0</td>
<td>500</td>
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<tr>
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<td>1</td>
<td>500</td>
<td>5.4</td>
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<tr>
<td></td>
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<td>1300</td>
<td>2</td>
<td>500</td>
<td>6.0</td>
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<td>500</td>
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<td>-2</td>
<td>500</td>
<td>2.5</td>
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<tr>
<td>andesite[2]</td>
<td>KR-D</td>
<td>1190</td>
<td>11.5</td>
<td>0.13 wt%</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 1. XANES spectra for controlled FeO 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.

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

One andesite doped with 0.13 wt% MoO3 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 FeO, 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 FeO.

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.

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-
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$^{5+}$ 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 $f$O$_2$ 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].

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 (Figure 1) suggests more than 90% of the Mo$^{6+}$ is in tetrahedral coordination. This is the case for all $f$O$_2$ 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.

**Acknowledgements:** Portions of this work were performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation - Earth Sciences (EAR-0622171) and Department of Energy - Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.