Probing the Earth’s Deep Oxygen Cycle with Vanadium: 
The Temperature Dependence of Partitioning

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Motivation

Oxygen cycles within the Earth influence rock chemistry, atmospheric evolution, and the structure of our planet. Nevertheless, this influence is more evident at subduction zones1,2,3. Figure 1, where the unique chemistry of arc lavas is attributed to their higher, more oxidized oxygen fugacity (fO2) relative to mid-ocean ridge basalt (MORB)1. However, the timing and mechanism by which arc lavas oxidize is unknown1,5.

We hypothesize that arc lavas are more oxidized than MORB because MORB sediments, and the oceanic lithosphere at all become oxidized as they transit the sea floor, and then contribute to arc melts. Heat and pressure during subduction metamorphose basalt to eclogite, which then contributes to arc lavas. We predict that natural eclogites will record this.

The fO2 of eclogites cannot be directly measured, so we must devise a proxy. The element vanadium (V) can take on multiple valence states (V (II), V (IV), V (V), V (VI)) and different fO2 (Figure 2). The concentration of V in the eclogitic mineral rutile (TiO2) relative to co-existing silicate melt (SiO2) depends on temperature and pressure. Using the Quantum-Rayleigh-Magnetic oxygen buffer (QFM-1) (Figure 2).

Here we present the results of laboratory experiments that quantify the dependence of vanadium valence on temperature; an important variable in subduction zone settings.

Methods

Starting Composition

CMAS, a synthetic composition, was made by mixing oxide reagents under ethanol in a mortar and pestle.

Table 1: Starting Composition by Weight Percentage

<table>
<thead>
<tr>
<th>Name</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>V2O5</th>
<th>TiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMAS</td>
<td>41.5</td>
<td>15.3</td>
<td>9.5</td>
<td>9.5</td>
<td>1.2</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Table 2: Experimental Run Conditions and Partition Coefficients

<table>
<thead>
<tr>
<th>Starting Comp.</th>
<th>∆QFM</th>
<th>Quench Temp (°C)</th>
<th>Time in Furnace (hr)</th>
<th>weight% V2O5</th>
<th>Dv(rutile/melt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMAS -1</td>
<td>1200</td>
<td>91.1</td>
<td>3.5</td>
<td>3.22</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>76.0</td>
<td>2.5</td>
<td>2.53</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>1375</td>
<td>65.3</td>
<td>3.5</td>
<td>2.32</td>
<td>0.78</td>
</tr>
</tbody>
</table>

We equilibrated rutile and silicate melt at 1200°C, 1300°C, and 1375°C. We observed no other phases.

The average weight percentages of V2O5 were used to calculate Dv(rutile/melt).

Dv(rutile/melt) = [V2O5 in rutile] / [V2O5 in melt]

As temperature increases, Dv(rutile/melt) decreases (Figure 6).

Figure 3: We suspended (3c) samples (3a, 3b) in a gas-mixing furnace (3d) at controlled T (1500°C) and fO2 (QFM-1). After glazing at 1500°C, we slowly ramped down the furnace at either 6 or 7°C/min to a final T and quenched the sample, producing a glass bearing the mineral rutile.

Sample Analysis

We set our samples in epoxy and analyzed with two methods:

- X-Ray Microprobe (Rigaku Tomo, JEOL JSM6490 SEM) at the Advanced Photon Source at Argonne National Laboratory, USA
- X-Ray Spectroscopy at the Advanced Photon Source at Argonne National Laboratory, USA

Figure 4: Sample set in epoxy

Figure 5: Reflective Light Images

Figure 6: Electron backscatter images of experiment at 1200°C (6a, 6b) and 1375°C (6c)

Figure 7: Vanadium-XANES spectra CMAS glass at QFM-1

This V XANES Spectra (Figure 7) is of a CMAS composition glass without any Ti. The pre-edge peak occurs at eV = 5467.9 and has intensity 287.0 (normalized to 1000).

Sutton et al. (2005) correlated V-XANES spectra with V (III), V (IV), and V (V) pre-edge peaks of rutile/melt experiments (Figure 7).

Figure 8: Vanadium valence vs. pre-edge peak intensity

We find that the vanadium partition coefficient between rutile and melt (Dv(rutile/melt)) decreases with increasing temperature. The effect is stronger than previously measured for other cations in rutile. We plan to conduct additional experiments at temperatures to more fully quantify the effect. We will also explore V partitioning at higher pressures, more closely mimicking rutile formation in natural systems. Ultimately, we will use these experiments to interpret V concentrations measured in natural eclogites from the National Rock Collection.

Discussion

Effect of Temperature on Partitioning

A series of rutile/melt partitioning experiments run at 1100°C and varying fO2 on a similar melt composition (Figure 9) show that Dv increases as fO2 increases.

Our new experiments indicate that temperature, as well as fO2, has a significant effect on the partitioning of V. At QFM-1, Dv increases by 88% as temperature drops 175°C.

This temperature dependence should be accounted for when applying the V-XANES oxybarometer presented by Holycross and Cottrell (2018).

Figure 9: Comparison of rutile/melt partitioning at 1100°C with previous data

Rutile Melt

Figure 10: Temperature effect on Dv(rutile/melt) for Hf, Zr, Nb, V

Our temperature-dependent vanadium partitioning data is plotted with the rutile/melt partitioning of 4+ (Hf, Zr) and 5+ (Nb) cations5,6. As temperature increases, Dv decreases, similar to the trend observed in V. The rutile/melt partitioning trend is not observed for Hf or Zr.

The literature data consists of experiments over a range of pressures, so it is unclear whether pressure may have played a role in partitioning.

Conclusions and Future Study

We find that the vanadium partition coefficient between rutile and melt (Dv(rutile/melt)) decreases with increasing temperature. The effect is stronger than previously measured for other cations in rutile. We plan to conduct additional experiments at temperatures to more fully quantify the effect. We will also explore V partitioning at higher pressures, more closely mimicking rutile formation in natural systems. Ultimately, we will use these experiments to interpret V concentrations measured in natural eclogites from the National Rock Collection.

Acknowledgements

I would like to thank Elizabeth Cottrell, Gene Hunt, and Virginia Power for their incredible dedication to the NHRE program. I would also like to thank the Department of Mineral Science at the Smithsonian National Museum of Natural History, and specifically Tim Gooding for the extensive help with sample preparation and troubleshooting. Susan Jackson for the assistance with the gas-mixing furnace, and Nicole Lunning for answering my many questions in the petrology lab. I would also like to thank everyone else involved in the NHRE program for your support and guidance. I am extremely grateful for the experience at the Advanced Photon Source at Argonne National Laboratory. I would also like to thank every other NHRE intern for all the adventures and the formation of some great friendships. I will miss you all so much. Also, Alan, thank you for the shrew commentary.

Funding for this research was provided by National Science Foundation OCE-1560088.

References