



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

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REU Site, OCE-1560088

Motivation

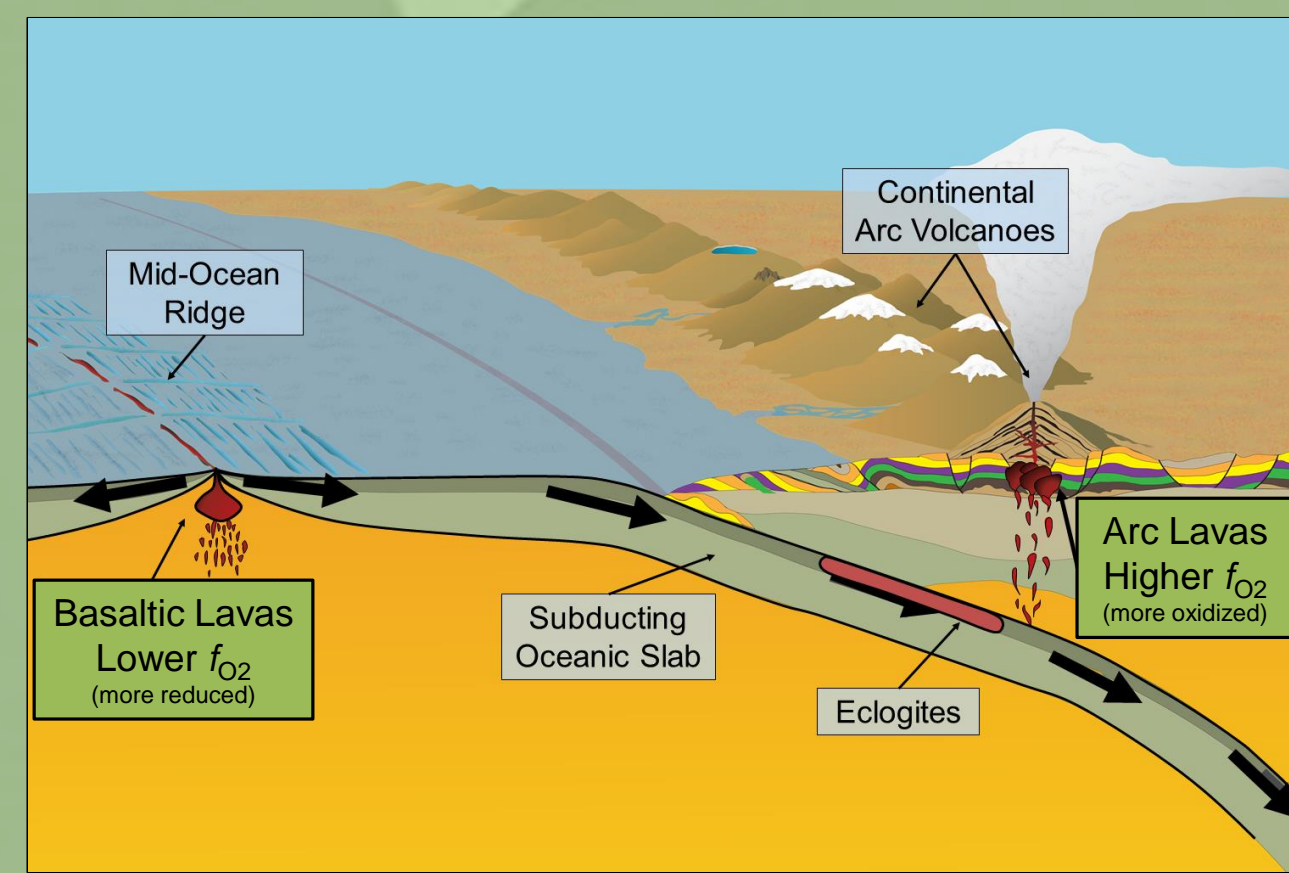


Figure 1: Diagram of subduction zone, modified after Ben Andrews, Smithsonian Institution

Oxygen cycles within the Earth influence rock chemistry, atmospheric evolution, and the structure of our planet. Nowhere is this influence more evident than at subduction zones (Figure 1), where the unique chemistry of arc lavas is attributed to their higher, more oxidized oxygen fugacity (f_{O_2} , analogous to p_{O_2}) relative to mid-ocean ridge basalts (MORB)¹. However, the timing and mechanism by which arc lavas oxidize is unknown^{2,3}.

We hypothesize that arc lavas are more oxidized than MORB because MORB, sediments, and the oceanic lithosphere 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 higher f_{O_2} .

The f_{O_2} of eclogites cannot be directly measured, so we must devise a proxy. The element Vanadium (V) can take on multiple valence states (V^{2+} , V^{3+} , V^{4+} , V^{5+}) at different f_{O_2} s (Figure 2). The concentration of V in the eclogitic mineral rutile (TiO_2) relative to co-existing silicate melt ($D_{V}^{rutile/melt}$) should change as a function of f_{O_2} , making V-in-rutile an excellent f_{O_2} proxy for eclogitic rocks.⁴

We predict that V^{4+} replaces Ti^{4+} . Sutton et al. (2005) show that this valence state occurs near one log unit below the Quartz-Fayalite-Magnetite oxygen buffer⁵ (i.e. $\Delta QFM-1$) (Figure 2).

Here we present the results of laboratory experiments that quantify the dependence of $D_{V}^{rutile/melt}$ on temperature: an important variable in subduction zone settings.

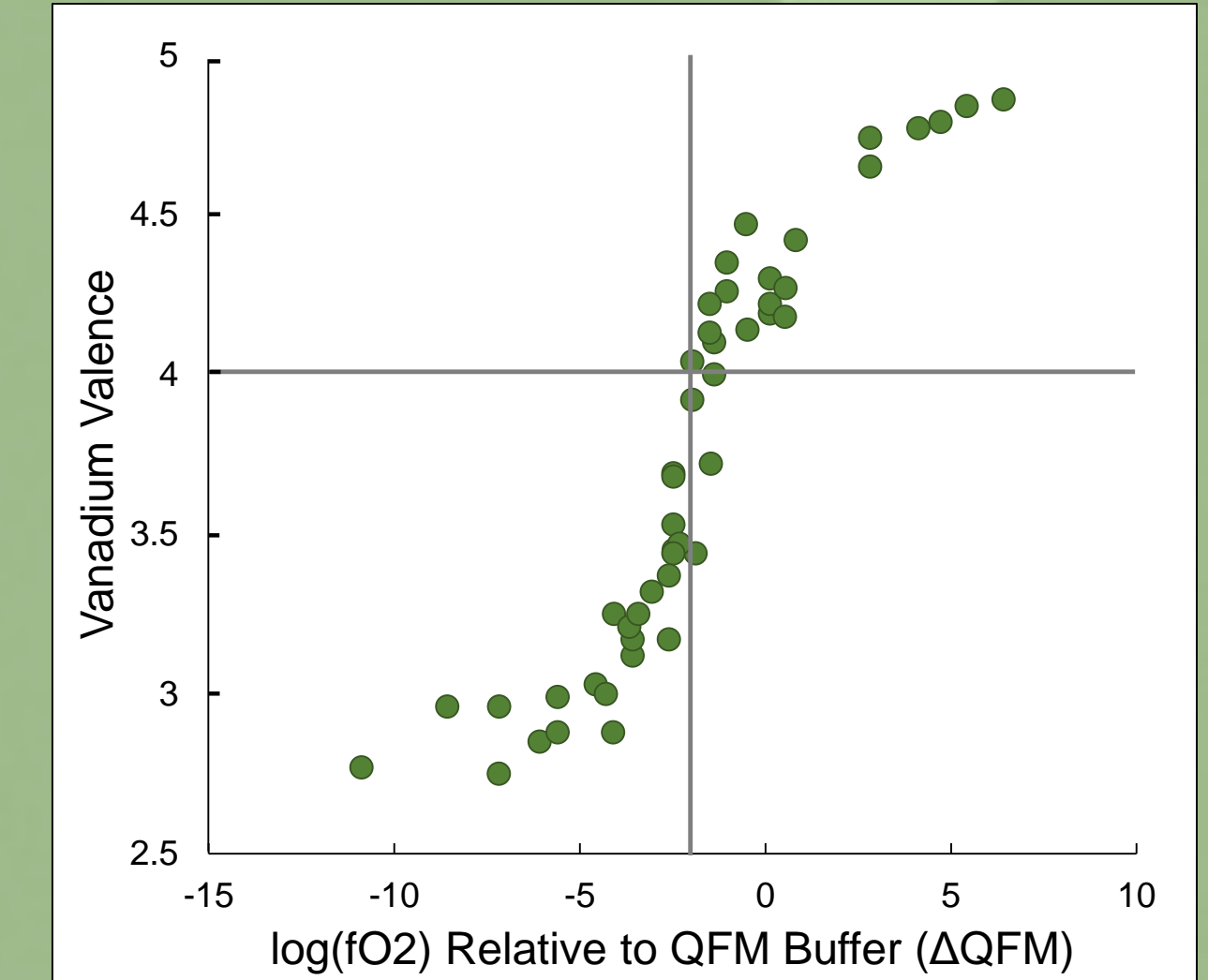


Figure 2: Vanadium valence vs ΔQFM (Sutton et al, 2005)

Methods

Starting Composition

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

Table 1: Starting Composition by Weight Percentage

Name	SiO ₂	Al ₂ O ₃	CaO	MgO	V ₂ O ₃	TiO ₂
CMAS	41.5	15.3	9.5	9.5	1.2	23.0

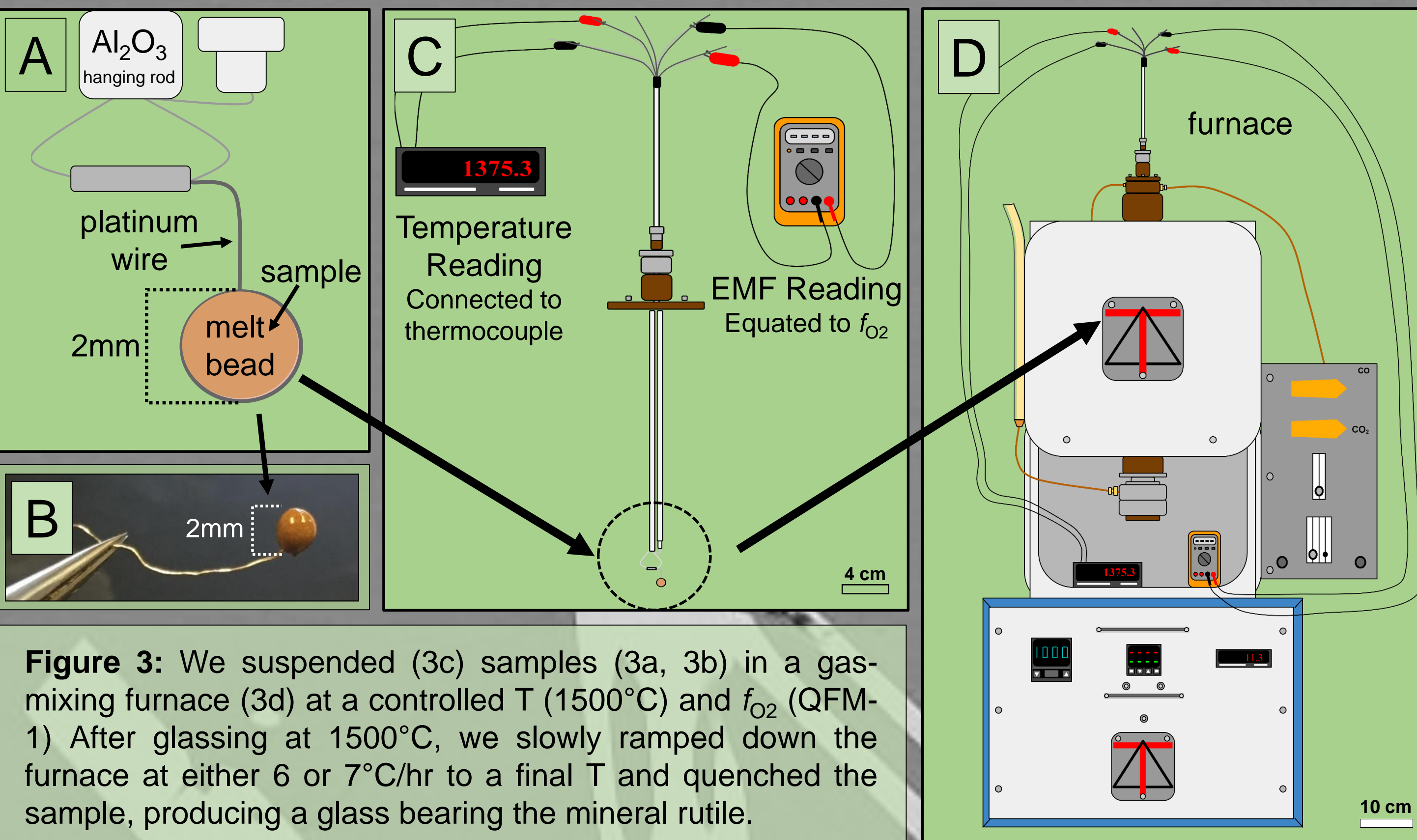


Figure 3: We suspended (3c) samples (3a, 3b) in a gas-mixing furnace (3d) at a controlled T (1500°C) and f_{O_2} (QFM-1) After glassing at 1500°C, we slowly ramped down the furnace at either 6 or 7°C/hr to a final T and quenched the sample, producing a glass bearing the mineral rutile.

Sample Analysis

We set our samples in epoxy and analyzed with two methods:
□ Electron Microprobe
□ X-Ray Analysis Near Edge Structure (XANES) Spectroscopy at the Advanced Photon Source at Argonne National Laboratory, USA

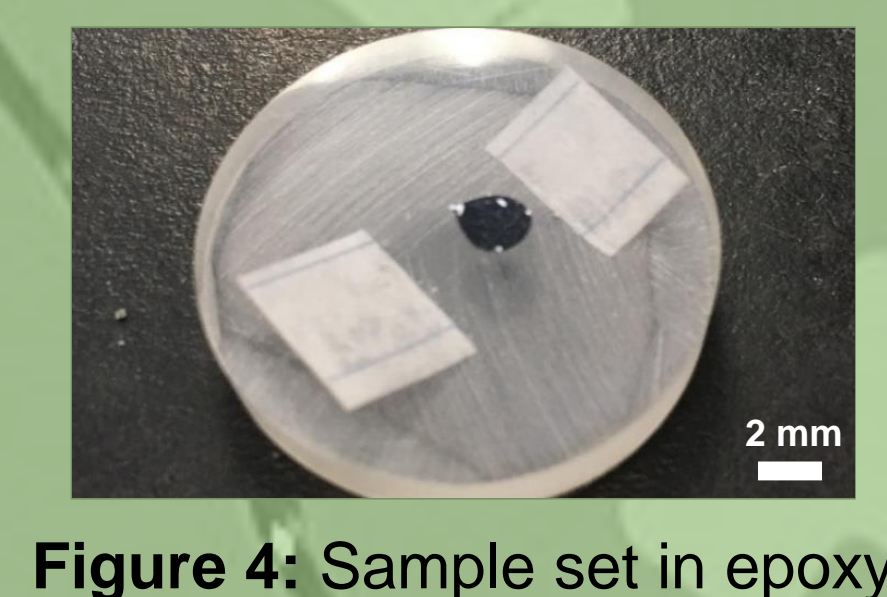


Figure 4: Sample set in epoxy

Results

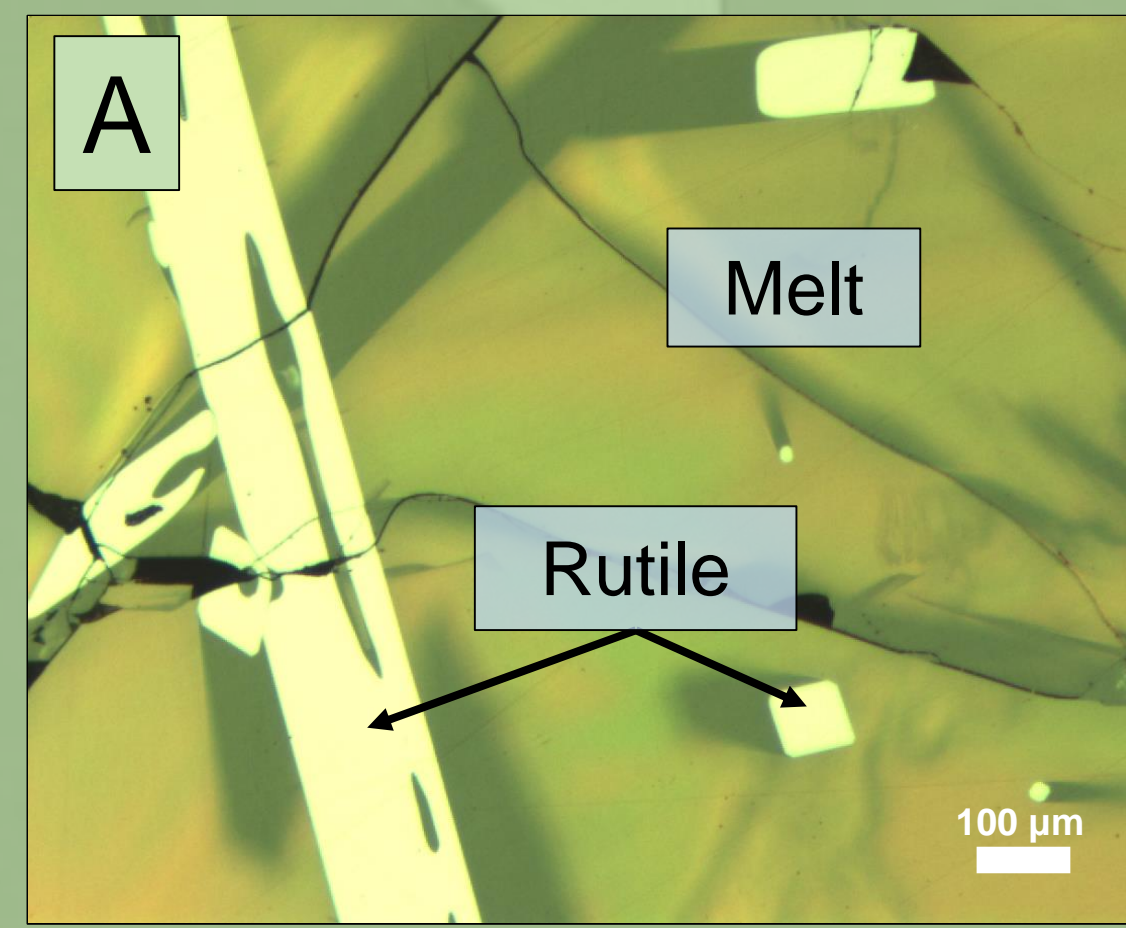


Figure 5: Reflected Light Images

5a: Sample created at f_{O_2} =QFM-1, T=1200°C

5b: Sample created at f_{O_2} =QFM-1, T=1300°C

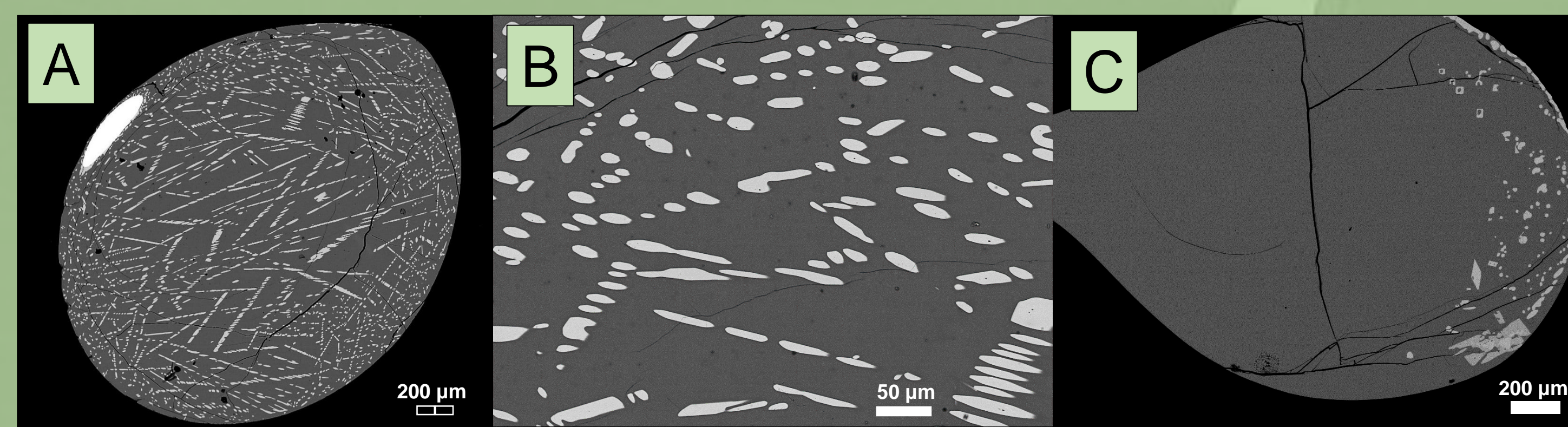
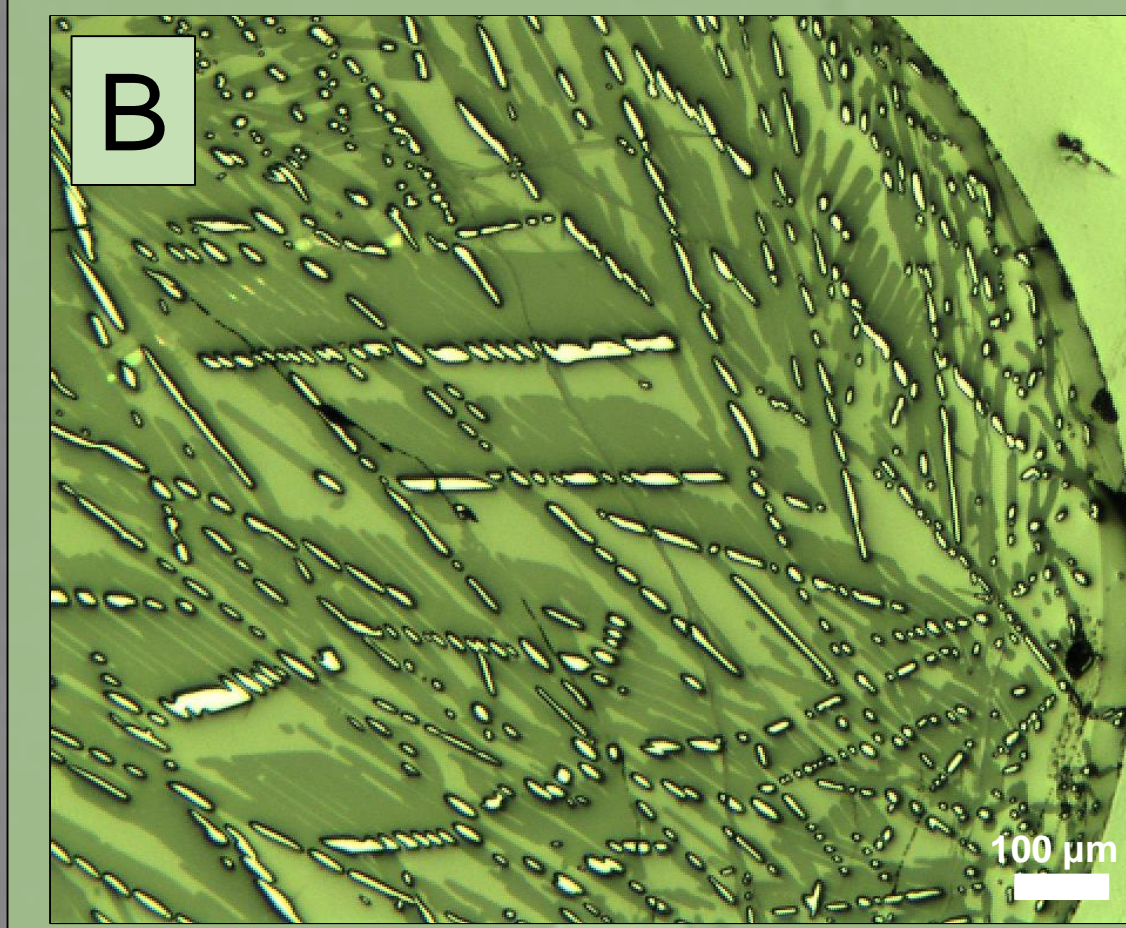


Figure 6: Electron backscatter images of experiment at 1200°C (6a, 6b) and 1375°C (6c)

Table 2: Experimental Run Conditions and Partition Coefficients

Starting Comp.	ΔQFM	Quench Temp (°C)	Time in Furnace (hr)	weight% V ₂ O ₃		$D_{V}^{rutile/melt}$
				Rutile	Melt	
CMAS	-1	1200	91.1	3.22	0.57	5.62
		1300	76.0	2.53	0.63	3.99
		1375	65.3	2.32	0.78	2.99

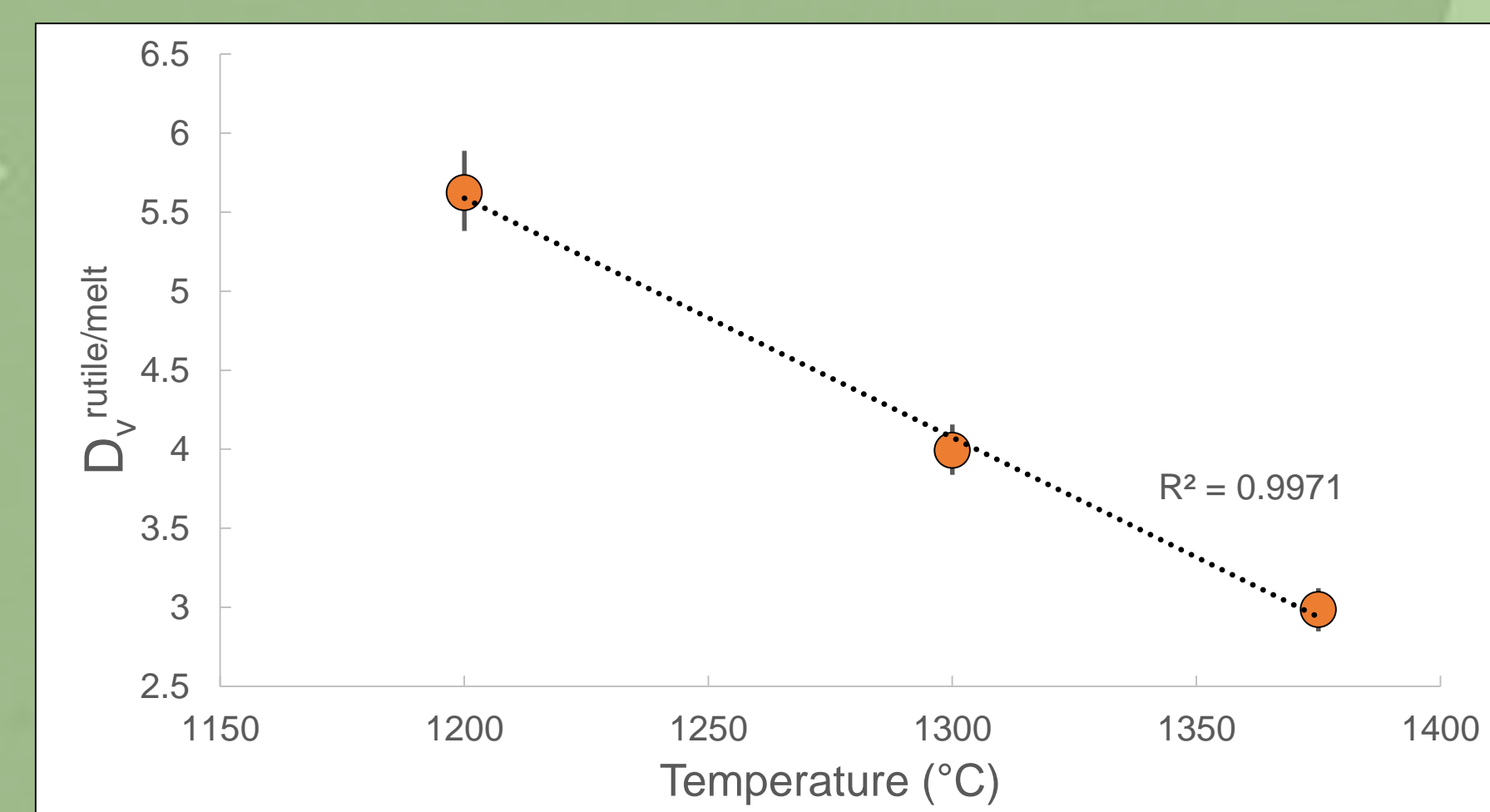


Figure 6: Temperature vs $D_{V}^{rutile/melt}$ in CMAS experiments

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

The average weight percentages of V₂O₃ were used to calculate $D_{V}^{rutile/melt}$.

$$D_{V}^{rutile/melt} = \frac{\text{wt\% V}_2\text{O}_3 \text{ in rutile}}{\text{wt\% V}_2\text{O}_3 \text{ in melt}}$$

As temperature increases, $D_{V}^{rutile/melt}$ decreases (Figure 6).

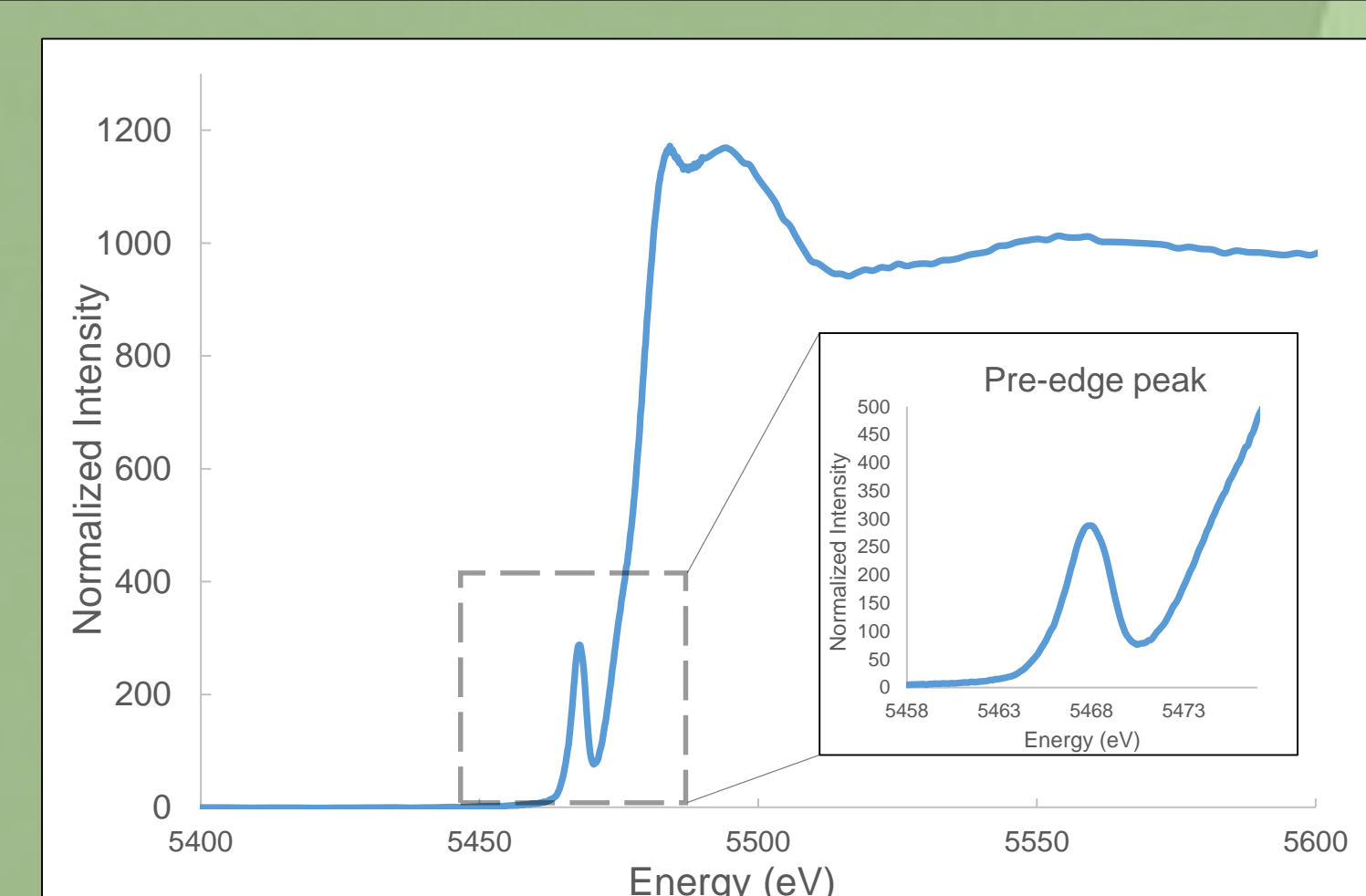


Figure 7: Vanadium-XANES spectra CMAS glass at $\Delta QFM-1$

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).

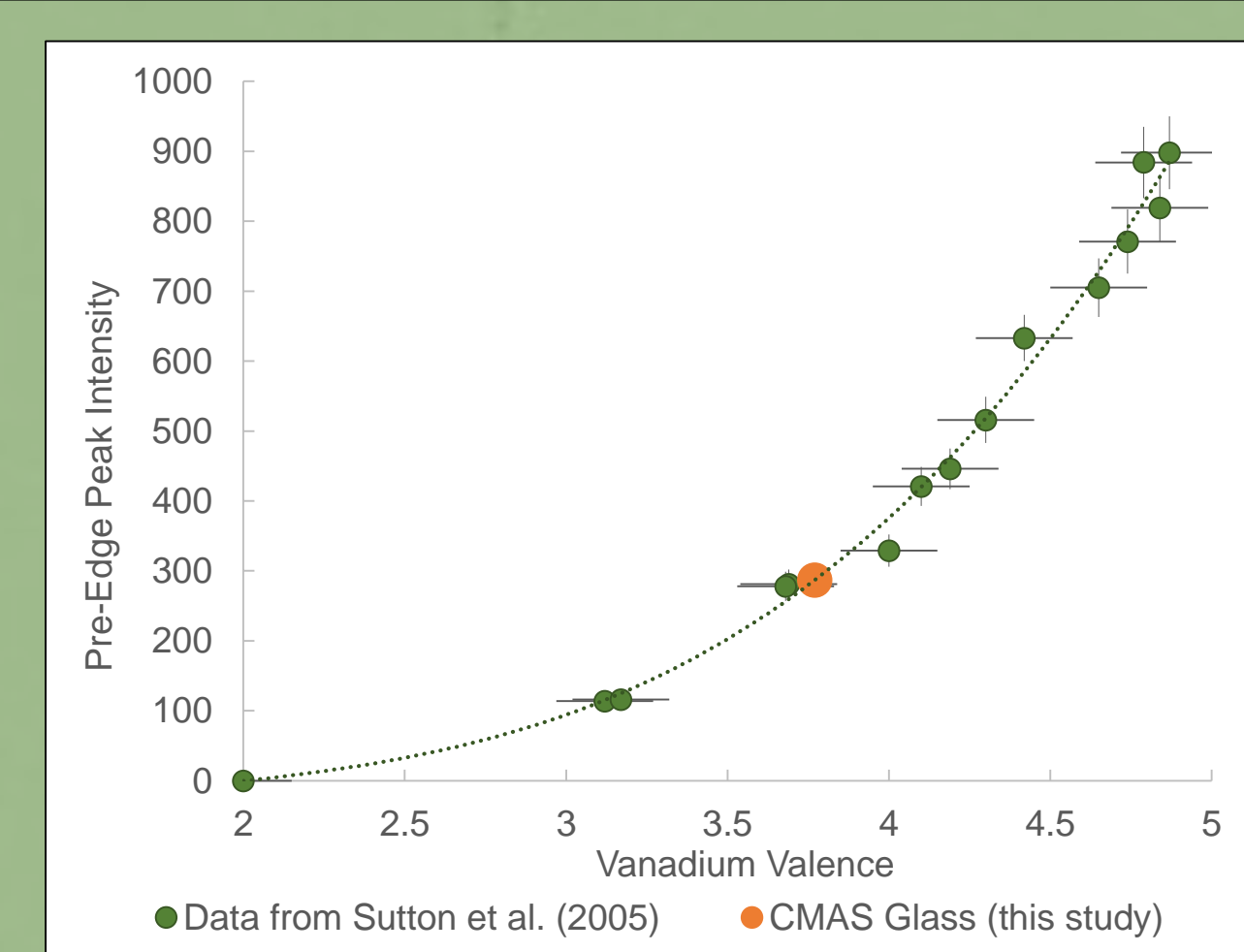


Figure 8: Vanadium valence vs pre-edge peak intensity

Sutton et al. (2005) correlated V-XANES pre-edge peak intensities directly to V valence. Using their calibration, the pre-edge peak intensity of our CMAS glass (Figure 7) indicates a valence of 3.77 (Figure 8)

Discussion

Effect of Temperature on Partitioning

A series of rutile/melt partitioning experiments run at 1300°C and varying f_{O_2} on a similar melt composition (Figure 9) show that $D_{V}^{rutile/melt}$ decreases as f_{O_2} increases.

Our new experiments indicate that temperature, as well as f_{O_2} , has a significant effect on the partitioning of V. At QFM-1, $D_{V}^{rutile/melt}$ increases by 88% as temperature drops 175°C.

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

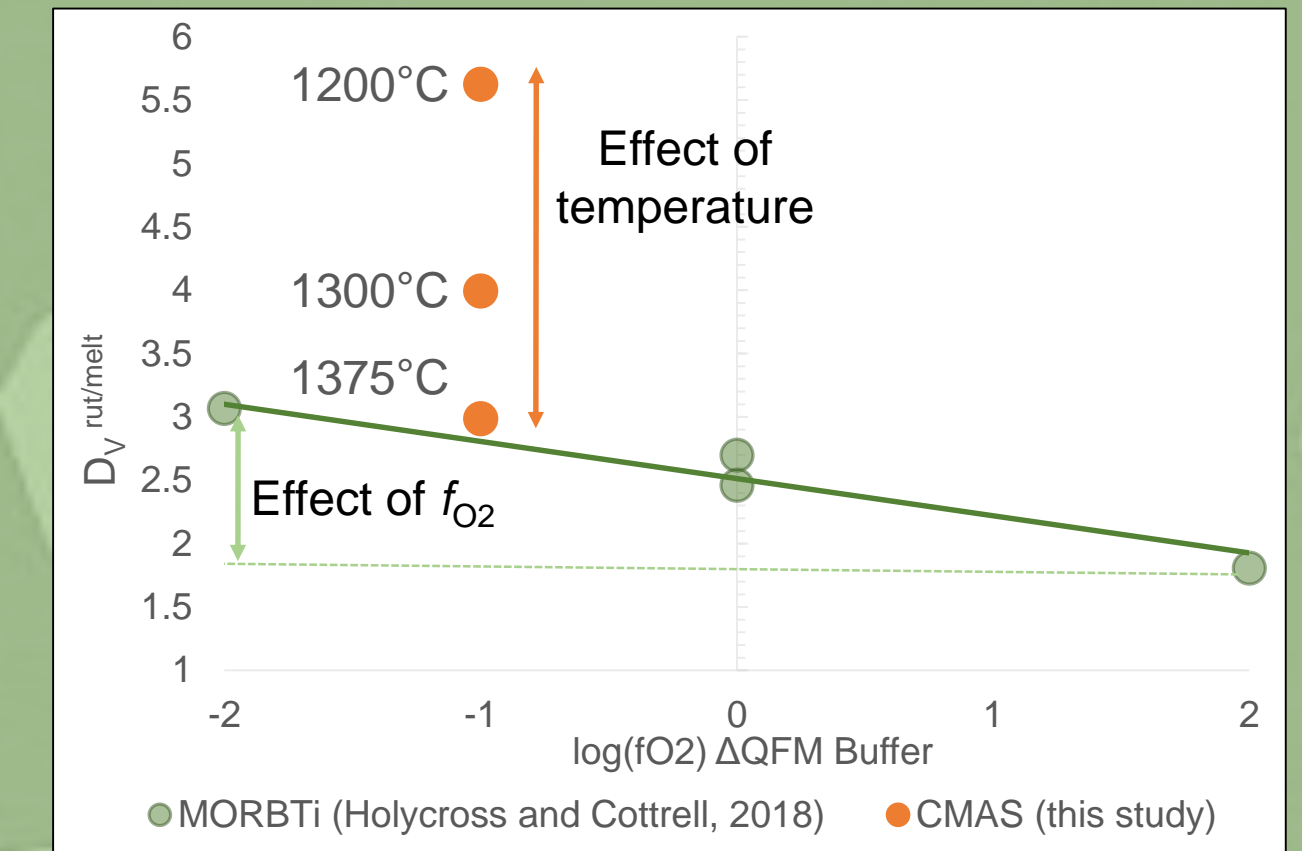


Figure 9: f_{O_2} vs D_V measured in this study compared with prior work performed on a similar composition at 1300°C.

Comparison to Temperature-Dependent Partitioning of other Cations

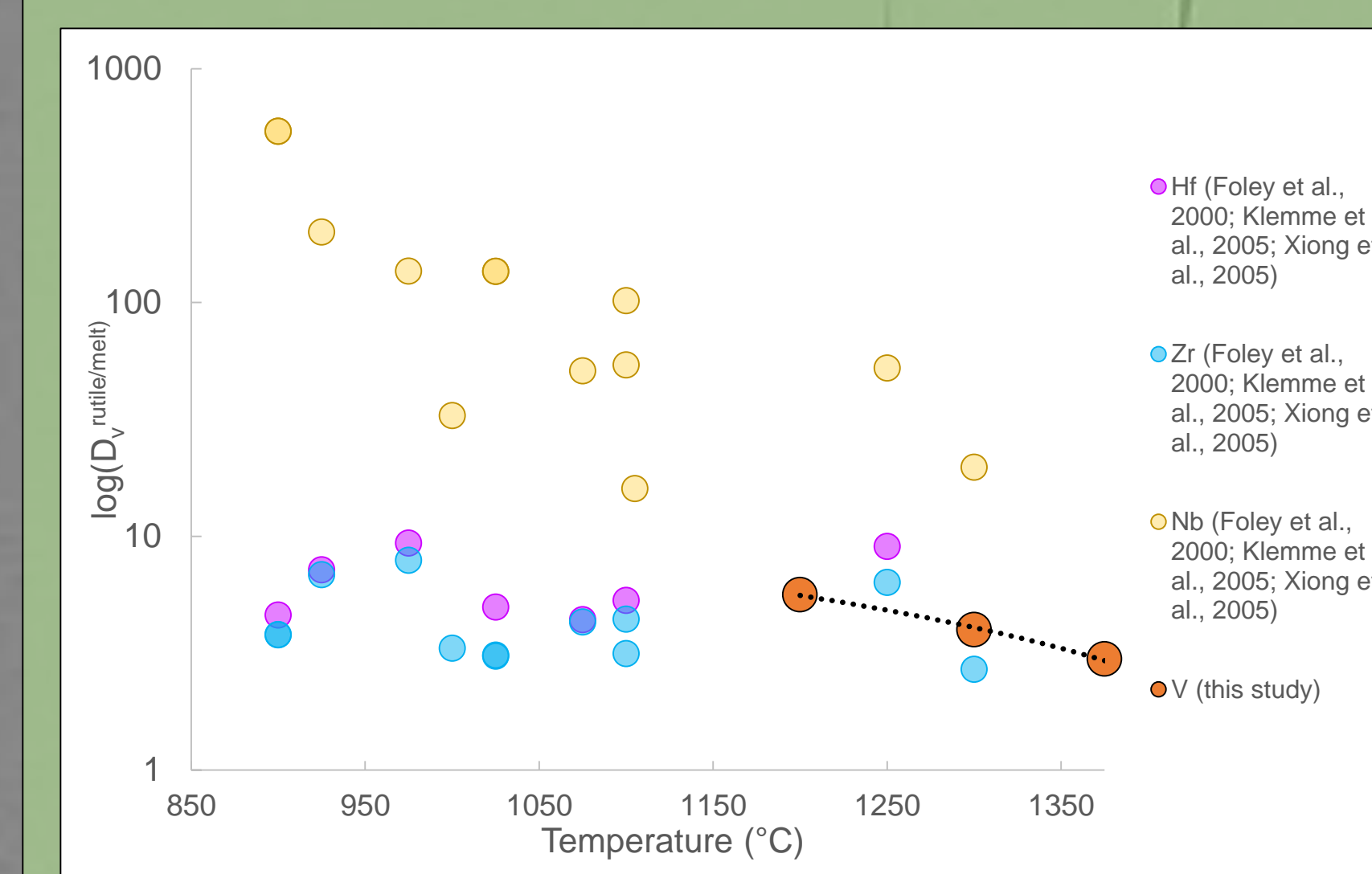


Figure 10: Temperature effect on $D_{V}^{rutile/melt}$ for Hf, Zr, Nb, V

Our temperature-dependent vanadium partitioning data is plotted with the rutile/melt partitioning of 4+ (Hf, Zr) and 5+ (Nb) cations^{6,7,8} (Figure 10).

As temperature increases, D_{Nb} decreases, similar to the trend observed in V. Such a 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 ($D_{V}^{rutile/melt}$) decreases with increasing temperature. The effect is stronger than previously measured for other 4+ cations in rutile. We plan to conduct additional experiments at lower 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.

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