# The Effect of Water on V and Sc Partitioning Between Mantle Minerals and Melt at Fixed Oxygen Fugacity

Christa Jackson[1,2], Elizabeth Cottrell[2], and Katie Kelley[3]

[1]Department of Geology, Humboldt State University, Arcata, CA; [2]Department of Mineral Sciences, Smithsonian Institution National Museum of Natural History, Washington DC; [3]Graduate School of Oceanography, University of Rhode Island, Kingston, RI

Motivation

The oxygen fugacity (fO_2) of the mantle beneath arc volcanoes, where tectonic plates converge, is poorly constrained. The fO_2 of the mantle beneath mid-ocean ridges, where tectonic plates diverge, can be determined using the $Fe^{3+}/\sum Fe$ ratio of volcanic glass as a proxy. This technique, however, may lead to a potentially false interpretation of fO_2 for the mantle at arcs due to interactions between mantle melt and the crust that can shift the $Fe^{3+}/\sum Fe$ ratio, potentially making arcs appear to be more oxidized than ridges. An alternate proxy for arc fO_2 is the V/Sc ratio of the melt. There is, however, some dispute among scientists over the validity of the V/Sc technique because it has shown (Lee *et al*, 2005) that the ridge and arc mantle have the same fO_2 which is in disagreement with the $Fe^{3+}/\sum Fe$ technique. There may be variables other than fO_2 that affect V and Sc partitioning. Here, we have used a new experimental technique to test the effect of water on the partitioning of V and Sc between mantle minerals and basaltic melts. Because arc volcanoes are much wetter than ridge volcanoes, we postulate that water could be the cause of the disagreement between the $Fe^{3+}/\sum Fe$ and V/Sc proxies for mantle fO_2.

Kelley and Cottrell, *Science*, 2009
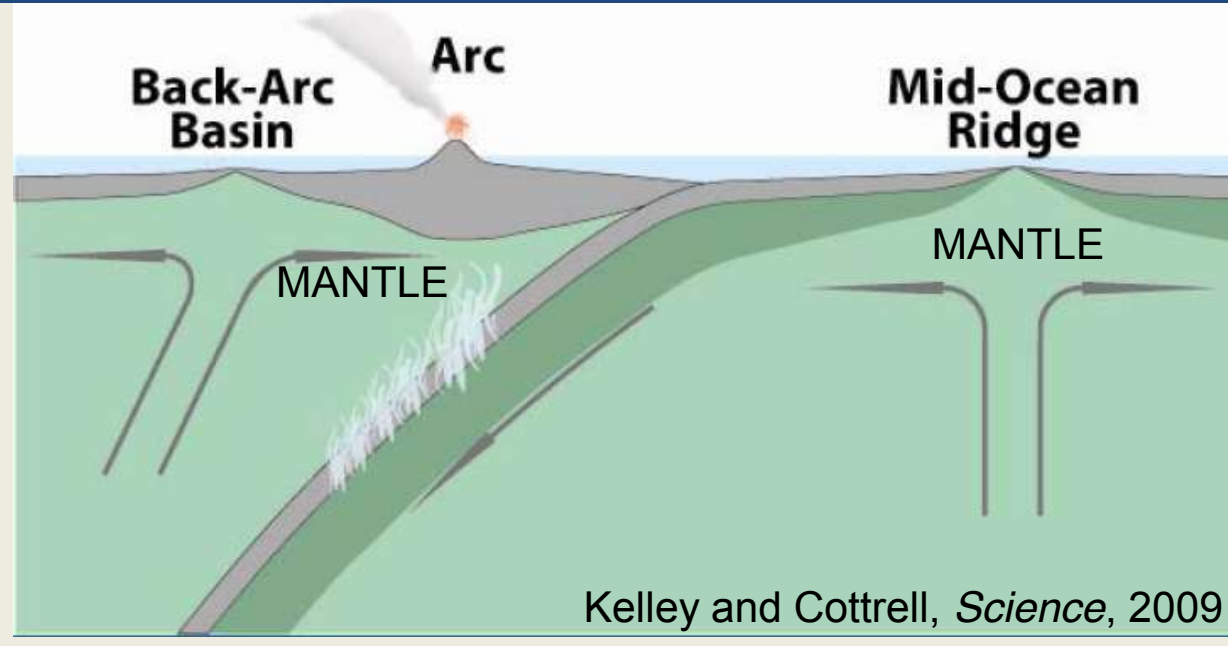
What is Oxygen Fugacity and Why is it Important?

Oxygen fugacity (fO_2) is an intensive variable, like pressure and temperature, that quantifies the redox potential of the mantle at equilibrium. Because fO_2 controls the speciation and mobility of redox-sensitive elements, it directly influences ore genesis and the composition of volcanic gases emitted into the atmosphere and ocean.
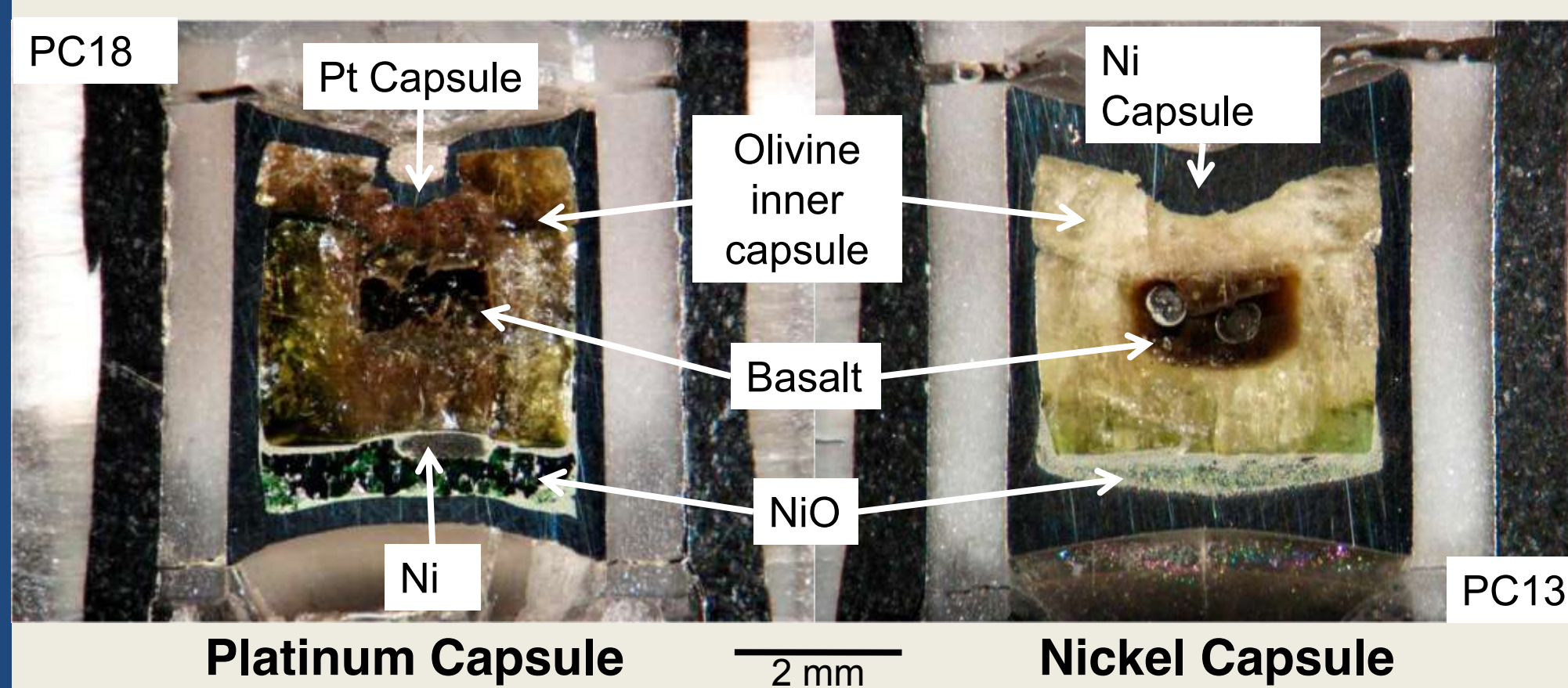Lee *et al*, *Journal of Petrology*, 2005

What are buffers?

When two compounds coexist in equilibrium through a redox exchange, it fixes the oxygen fugacity (fO_2) of the system. The coexistence of Ni metal and Ni oxide (the NNO buffer) is one example.

What is a Partition Coefficient?

A partition coefficient (D_x) is defined in a system as the ratio of the concentration of an element (x) in a mineral, to the concentration of an element (x) in the melt.

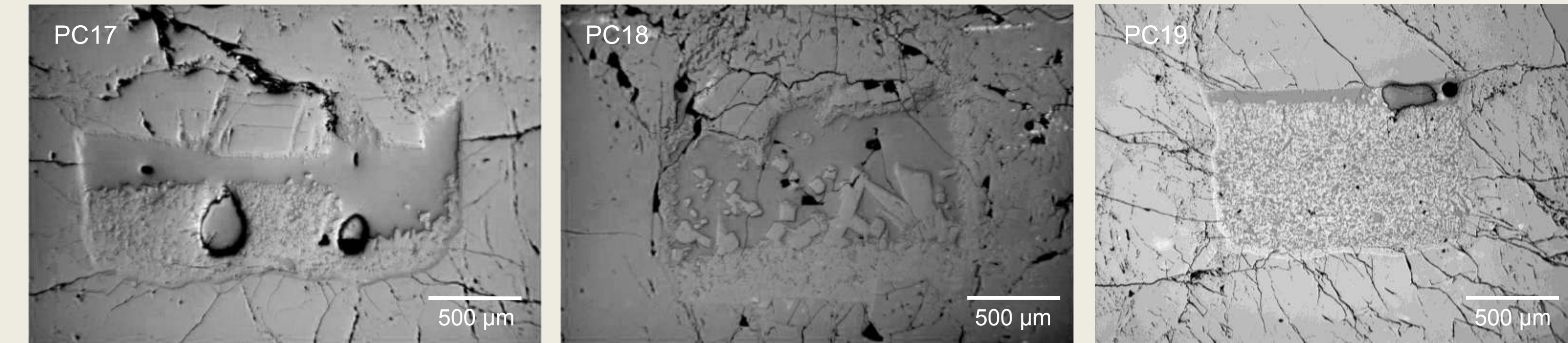$$D_x^{mineral/melt} = C_x^{mineral}/C_x^{melt}$$

fO_2 Buffers
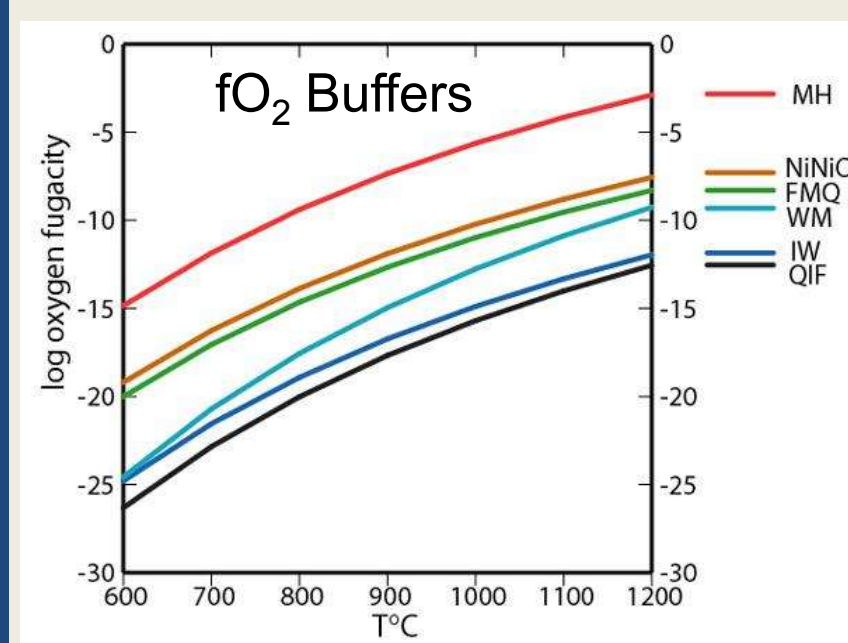
Experimental Products

- 6 experiments, lasting > 33 hrs each, were successful
- The phases present in the experimental products include olivine, orthopyroxene, clinopyroxene, CO_2 and H_2O vapor, plagioclase, and V-Fe phase, which are consistent with the expected phases
- NiO and Ni are still present at the end of each experiment
- Qualitatively, the melt fraction for each experiment correlates as expected with the added water volumes
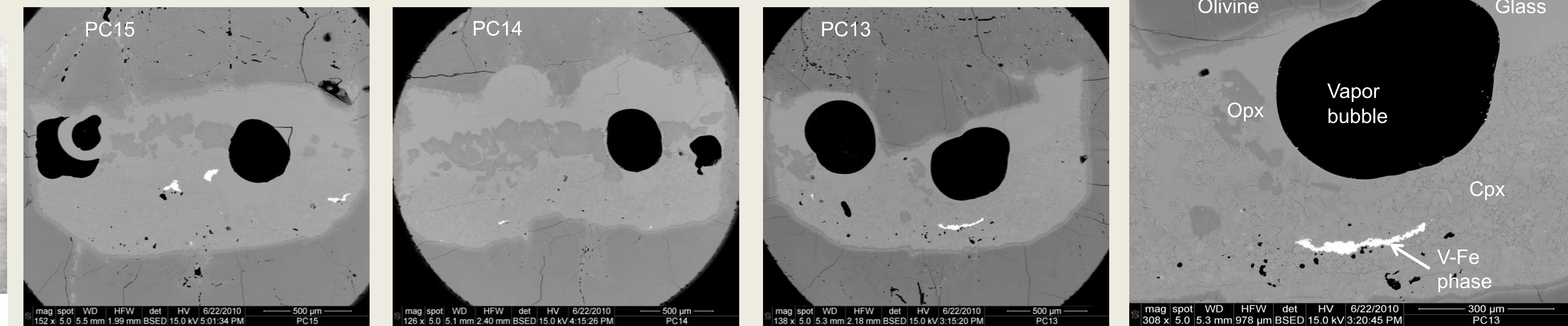
Reflected Light Images

PC17 — PC18 — PC19

Plane Light Images

PC18 — Pt Capsule, Olivine inner capsule, Basalt, Ni — Ni Capsule, NiO — PC13

Platinum Capsule — 2 mm — Nickel Capsule

SEM Backscattered Electron Images

PC15 — PC14 — PC13

PC13 Detail

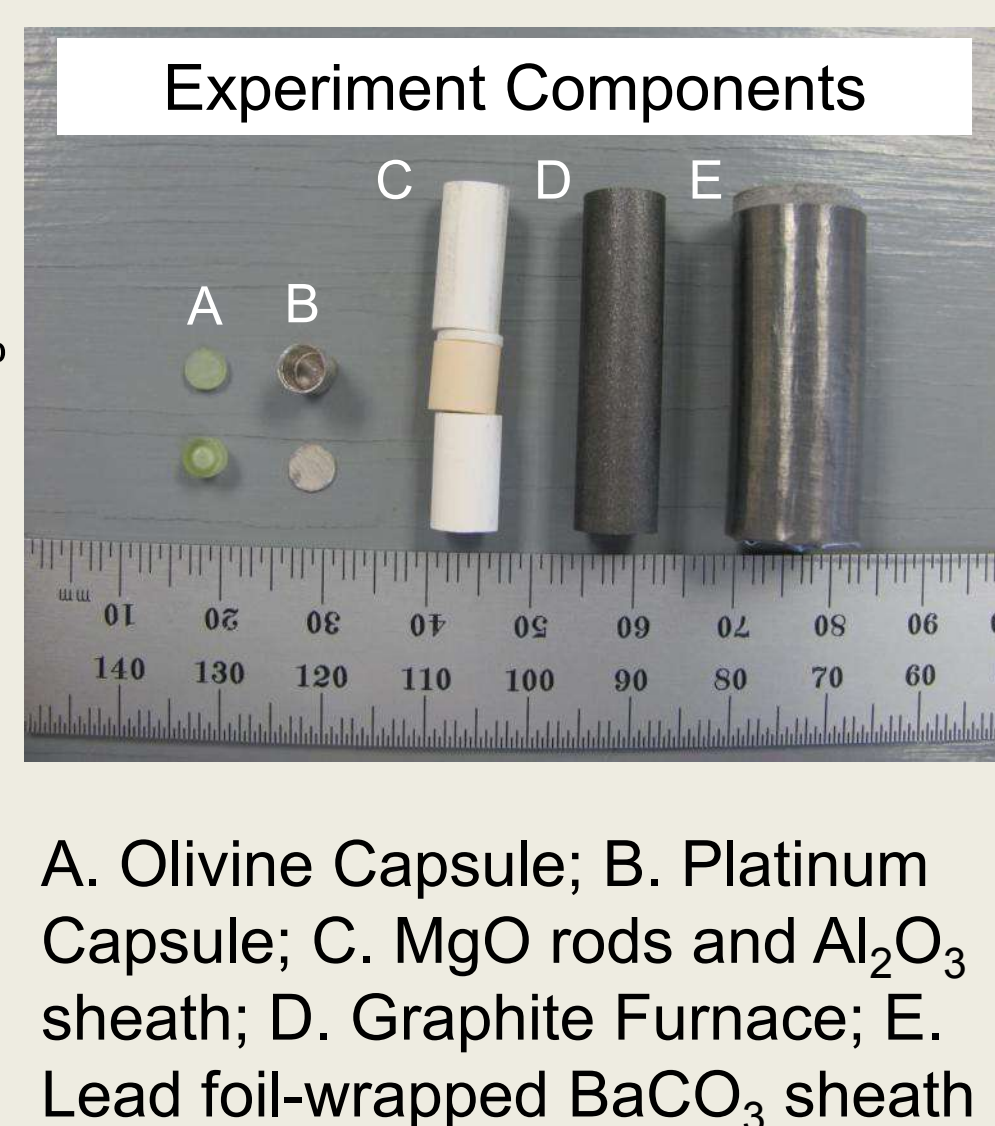Olivine — Glass — Opx — Vapor bubble — Cpx — V-Fe phase

Methods

Experimental

- Fix fO_2 at the NNO buffer through the reaction: $2Ni + O_2 \leftrightarrow 2NiO$
- Starting materials: Natural basalt (PC17-19) and basalt doped with 1 wt% of V and Sc (PC13-15)
- Hold temperature and pressure constant (1275°C, 1.5 Gpa), and vary H_2O through all experiments
- Ni outer capsule and Olivine inner capsule experiment design inspired by O'Leary *et al*, article in press, 2010

Experiment Components
A. Olivine Capsule; B. Platinum Capsule; C. MgO rods and Al_2O_3 sheath; D. Graphite Furnace; E. Lead foil-wrapped $BaCO_3$ sheath

A piston cylinder apparatus (pictures A and B) is used to simulate the high pressure and temperature conditions that exist in the Earth's mantle
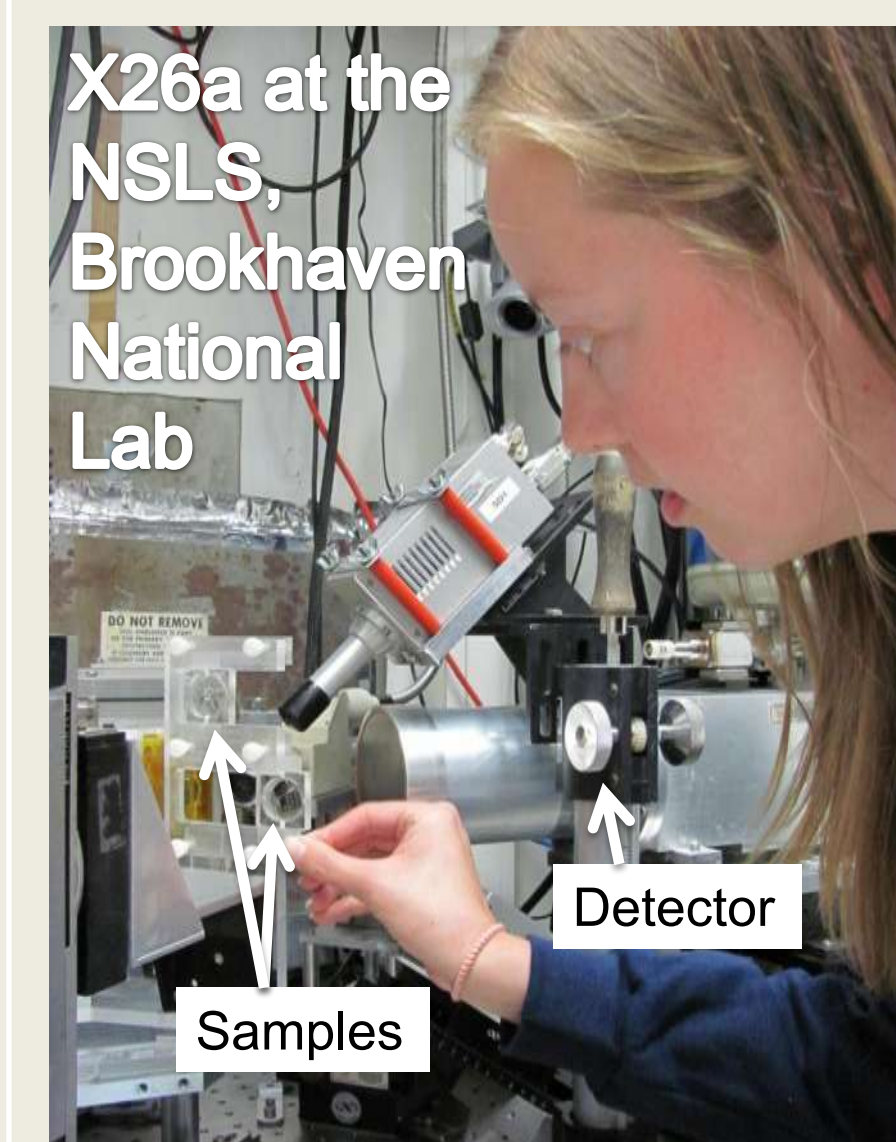
Microprobe

A high-precision technique used to quantify chemical composition. The detector is sensitive enough to measure trace elements like V and Sc

LA-ICPMS
(Laser Ablation Inductively Coupled Mass Spectrometry)

This technique, performed at the University of Rhode Island, Graduate School of Oceanography, is capable of detecting trace element concentrations in the experimental phases at the part per million level. LA-ICPMS serves as a check on the microprobe data collected here at the Smithsonian, and as the primary data source when concentrations are too low to detect with microprobe
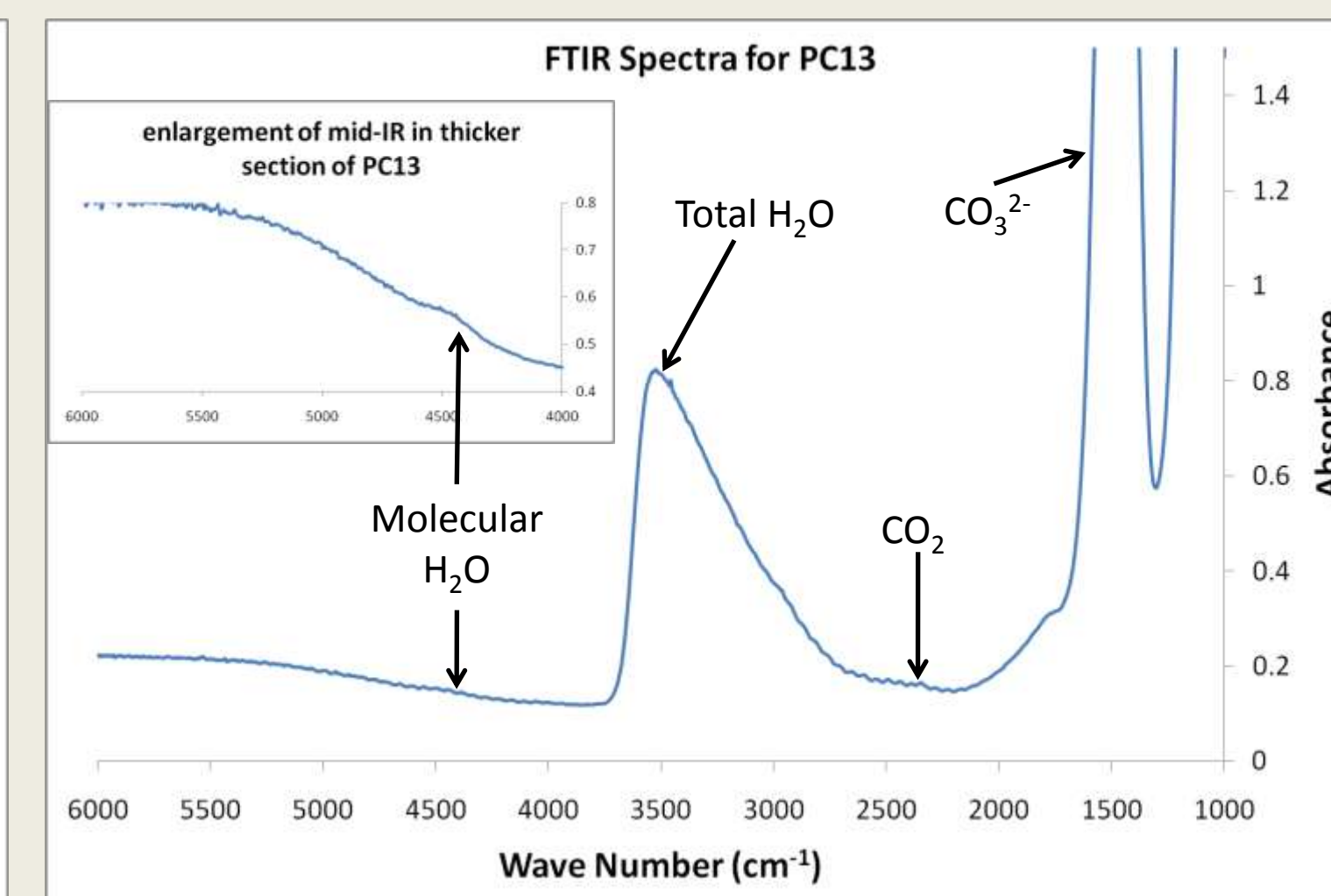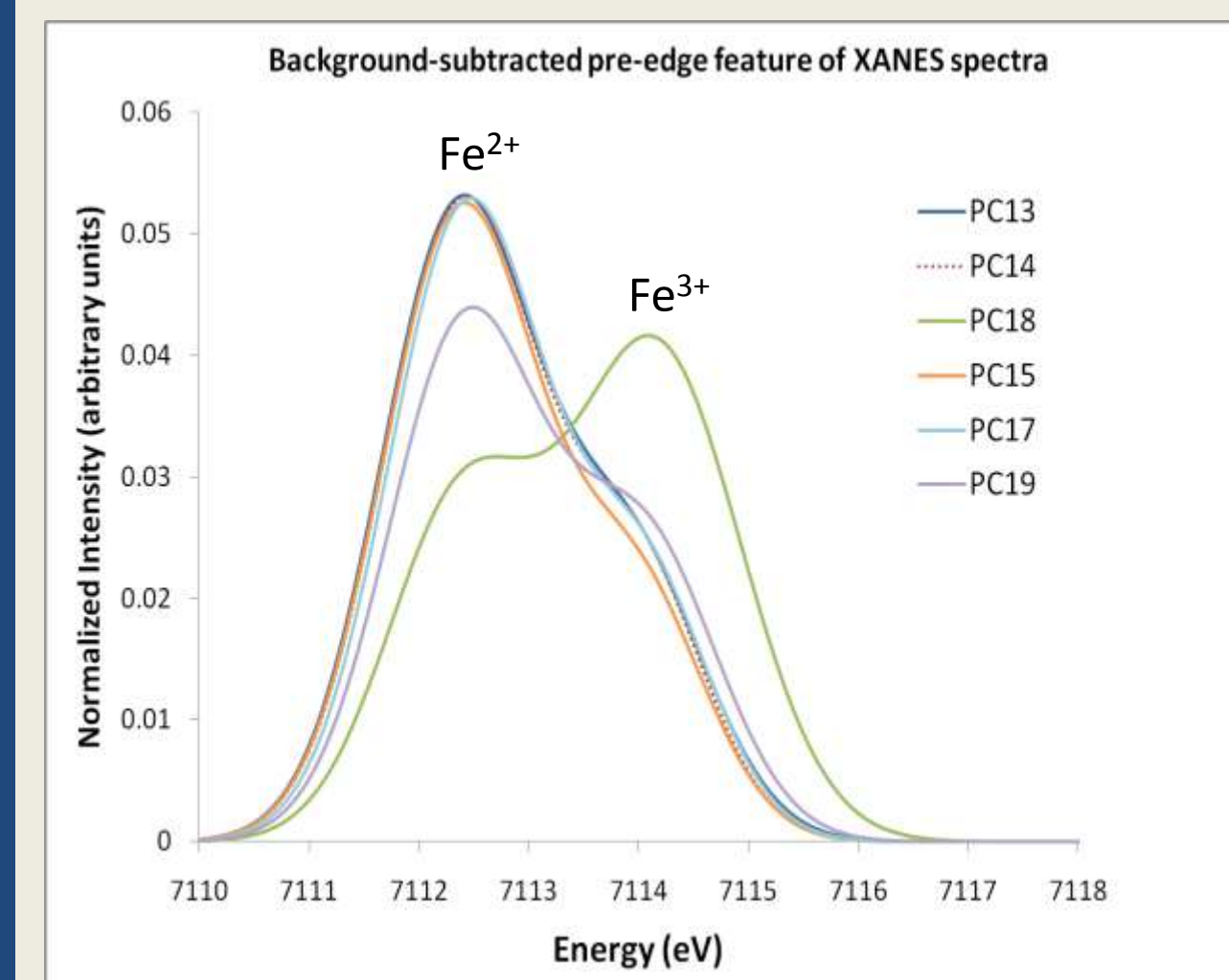
FTIR
(Fourier Transform Infrared Spectroscopy)

A spectroscopic technique used to quantify the concentration and speciation of molecules composed of the atoms O, C, and H, such as H_2O, CO_2, CO_3^{2-}, and OH^-

μ-XANES
(X-ray Absorption Near Edge Structure)

X26a at the NSLS, Brookhaven National Lab

XANES is an element-specific micro-beam absorption spectroscopy that is sensitive to the atomic environment of the absorbing atom. The spectra can be used to quantify the valence (oxidation state) of multi-valent elements. For our purposes, XANES was used to determine the oxidation state of iron ($Fe^{3+}/\sum Fe$) in order to calculate the fO_2 of the experimental products

Chemical and Spectral Results

- Preliminary FTIR results are not consistent with the quantities of added water or the textures observed in the experimental products. Nominally anhydrous experiments PC14 and PC19 show > 1 wt% dissolved H_2O
- FTIR results show large, unexpected, and unquantified amounts of dissolved CO_2 and CO_3^{2-}, which may account for the large vapor bubbles in the experimental products
- D_V and D_{Sc} are compatible in opx and cpx, and incompatible in olivine. D_V became incompatible in the oxidized experiment, PC18, while D_{Sc} remained constant, as expected
- Similar $Fe^{3+}/\sum Fe$ ratios (~ 0.11) are observed in all hydrous Ni capsule experiments, which are more reducing than the expected ratio of 0.13 for the NNO buffer
- It is unclear why the Pt capsule experiment is 3 orders of magnitude more oxidizing than NNO

Background-subtracted pre-edge feature of XANES spectra — Fe^{2+} — Fe^{3+} (PC13, PC14, PC18, PC15, PC17, PC19)

FTIR Spectra for PC13 — enlargement of mid-IR in thicker section of PC13 — Total H_2O — CO_3^{2-} — Molecular H_2O — CO_2

Sample Name	P (bars)	T (°C)	XANES $Fe^{3+}/\sum Fe$	XANES fO_2 ΔNNO	SiO_2	TiO_2	Al_2O_3	FeO^*	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total	FTIR H_2O	Dv-hyp	σ Dv	DSc-hyp	σ DSc	Dv-aug	σ Dv	DSc-aug	σ DSc	Dv-hyp	DSc-hyp	Dv-ol	DSc-ol	Dv-aug	DSc-aug
PC13	1.5	1275	0.112	-0.47	48.22	2.14	17.32	9.88	0.16	6.59	7.98	4.05	0.24	0.26	98.01	1.16	2.18	0.38	1.30	0.20	2.57	0.97	2.21	1.00	2.14	1.28	0.01	0.01	2.99	2.48
PC14	1.5	1275	0.108	-0.61	50.51	2.58	17.18	9.88	0.13	5.76	7.23	4.29	0.43	0.30	98.28		2.54	0.17	1.58	0.13	4.06	0.38	2.56	0.21	2.51	1.46	0.01	0.01	3.23	2.00
PC15	1.5	1275	0.107	-0.61	45.81	1.92	15.47	9.37	0.14	9.99	8.92	3.46	0.21	0.24	96.77	1.25	2.41	0.14	1.43	0.09	3.42	0.86	2.31	0.45					4.43	2.60
PC17	1.5	1275	0.114	-0.39	44.59	2.11	15.91	9.82	0.16	9.88	8.77	3.97	0.25	0.25	96.44	0.74	1.60	0.15	b.d	-	3.38	0.30	b.d	-					3.38	2.08
PC18	1.5	1275	0.392	3.12	45.97	2.24	17.01	9.95	0.14	7.92	8.08	4.36	0.26	0.30	96.22	>2	0.13	0.04	b.d	-	0.34	0.13	b.d	-	0.27	1.28	0.00	0.22	0.59	1.77
PC19	1.5	1275	0.160	0.49	46.80	2.17	16.78	9.75	0.16	7.58	8.08	4.19	0.26	0.28	97.19	1.15	0.44	0.34	b.d	-	0.56	0.38	b.d	-	1.03	1.30	0.02	0.26	1.31	2.39

Conclusions

- The new experimental designs did not fix fO_2 at the NNO buffer
- All experiments have dissolved H_2O and CO_2 in the melt, including those for which explicit attempts were made to exclude H_2O and CO_2. The source of the water is unknown.
- D_V and D_{Sc} between cpx and melt appear unaffected by water[1]
- D_V and D_{Sc} between opx and melt appear to increase in the presence of water[1]
- If water affects partitioning between the mantle mineral opx and melt, then the fact that arcs are wet and ridges are dry may explain the incongruence between the Fe and V/Sc proxies for fO_2

[1]Relative to anhydrous experiments from McDade *et al*, 2003, and Mallmann and O'Neill, 2009

Acknowledgements and References

Liz and Katie at BNL
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