



The oxidation state of tungsten in silicate melt at high pressures and temperatures

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ABSTRACT

Although at 1 atm pressure the oxidation state of W in silicate melts is 6+ at oxygen fugacities from air down to several $\log f_{\text{O}_2}$ units below Fe-FeO (IW) equilibrium, Cottrell et al. (2009) suggested that, at pressures above 6 GPa, W becomes predominantly 4+ in this oxygen fugacity range. Wade and Wood (2005), using a similar, but expanded metal-silicate partitioning dataset found, however, no evidence for an oxidation state change. In order to resolve the issue we collected tungsten L_3 edge XANES spectra of a series of synthetic tungsten-bearing glass standards and of silicates from a range of high-pressure (1.5 to 25 GPa) metal/silicate partitioning experiments. Glass standards were made at 1 atm pressure and equilibrated at oxygen fugacities spanning a range from approximately 5.5 log units below the Fe-FeO buffer (IW-5.5) to Air. Metal-silicate partitioning experiments were performed at oxygen fugacities between IW-6.2 and IW-1 and at pressures between 1.5 and 25 GPa. At low pressures and oxygen fugacities above IW-3.5, W exists in the silicate melt almost exclusively as W^{6+} (identical L_3 -edge energy to WO_3) with the progressive reduction to W^{4+} completed by about IW-6. The XANES spectra of W from experiments at 6, 7 and 25 GPa are completely consistent with those from 1 atm and 1.5 GPa experiments and with that of WO_3 . We conclude that there is no change of oxidation state with increasing pressure to 25 GPa and that modelling of the oxygen-fugacity dependence of core formation requires use of a +6 oxidation state of W.

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1. Introduction

The major phase of Earth accretion and core formation took place, according to ^{182}Hf - ^{182}W chronology, within approximately 30 My of Solar system formation (Kleine et al., 2002). During core segregation siderophile elements such as W were extracted into the liquid metal and transported to the growing core leaving lower concentrations in the silicate mantle. Based on what was known about metal/silicate partitioning behaviour at the time, Ringwood observed that the mantle is richer in siderophile elements, notably Ni, Co and Cu than expected (Ringwood, 1966) and argued that this indicates core-mantle disequilibrium during core segregation. More recently, however, experiments at higher pressures have shown that increasing pressure reduces the siderophile character of Ni and Co such that the mantle concentrations of these elements can be explained by equilibrium between core and mantle, but only at very high pressures (25–40 GPa) (Li and Agee, 1996; Kessler et al., 2008; Wood et al., 2008). These observations led to the “deep magma ocean” hypothesis whereby the core is presumed to have segregated from the mantle either continuously or discontinuously at intermediate depths in the growing planet.

Recent experimental data on a number of additional elements (V, Cr, Nb, W, Mo for example) have lent support to the deep magma ocean hypothesis (Wade and Wood, 2005; Wood et al., 2008; Corgne et al., 2009). The interpretation of metal/silicate partitioning requires consideration of the oxidation states of the elements of interest, however, because partitioning between the reduced form in the metal and oxidised form in the silicate depends on oxygen fugacity and hence on oxidation state. After Ni and Co, the element with the largest experimental database is W (Cottrell et al., 2009). Because of its highly refractory nature W is presumed to be present in the Earth in chondritic ratio to the other refractory elements (McDonough, 2003). Its moderately siderophile behaviour makes it relatively straightforward to study experimentally and its current mantle abundance should only have been marginally affected by any late “veener” of accreted material. However, at the oxygen fugacities that iron rich planetary cores formed under (below the iron-wüstite [IW] buffer), the free energies of oxide formation suggest that tungsten should exist in the silicate in both 4+ and 6+ valence states (Chase et al., 1985). This potential for mixed oxidation state greatly complicates the application of metal-silicate partitioning data to understanding core formation. The oxidation state of W in silicate melts must be known in order to apply such data realistically to understanding the process of accretion and metal segregation.

In a study using XANES spectroscopy of W-bearing glasses prepared at known f_{O_2} at 1 atm pressure O'Neill et al. (2008) found that W exists exclusively in the +6 oxidation state at oxygen fugacities down to 2.3

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$\log f_{O_2}$ units below IW. The metal-silicate partitioning data of Cottrell et al. (2009) at low pressure (0.5 GPa) are consistent with O'Neill et al.'s results but these authors found an apparent decrease in oxidation state with increasing pressure such that it approached +4 at 11–18 GPa. In contrast, Wade and Wood (2005) combined the Cottrell et al. high pressure data with their 15 new partitioning data from pressures of 6–24 GPa and concluded that W remains in the +6 oxidation state at all pressures to 24 GPa.

Because of the uncertainty discussed above, the large number of experimental data on metal-silicate partitioning of W and their potential application to core segregation models we have attempted to determine the oxidation state of W in the silicates from high pressure metal-silicate partitioning experiments. Experimentally, we employed micro-XANES spectroscopy to measure accurately the energy of the W L₃-edge in the high pressure silicates and compared the results with values for silicate standards synthesized at known oxygen fugacity and with the edge energies in WO₃ and WO₂.

2. Experimental

Silicate standards for XANES analysis were prepared by adding approximately 1 weight % WO₃ to a composition (An₅₀Di₂₈FeO₂₂) close to the 1.5 GPa eutectic in the anorthite-diopside-forsterite system (Presnall et al., 1978). This composition had previously been the basis of the silicates in most of our high pressure experiments (Wade and Wood, 2005), although the latter contain a much larger

range of W contents than our new standards (Wade and Wood, 2005). All compositions were prepared from reagent grade oxides, suitably fired and thoroughly homogenised under acetone. Samples were equilibrated with a gas atmosphere (either air or a more reducing CO-CO₂ mixture) using the wire loop method (O'Neill and Eggins, 2002) whereby a thick slurry of mixture was fixed to wire loops using a weak PVA solution diluted in ethanol and water. Loops were allowed to dry overnight before introduction into the furnace. Under relatively oxidising conditions Pt loops were used while at conditions at and below the Fe-FeO (IW) buffer loops of 95%W-5%Re wire were employed. Oxygen fugacities of the CO-CO₂ atmospheres were measured at the beginning of each experiment using an yttria-stabilised zirconia oxygen sensor, with continuously flowing air used at the reference junction. Gas mixtures were accurately controlled by mass flow controllers, calibrated for CO and CO₂, with mixtures cross-checked against published CO-CO₂ tables. The lowest f_{O_2} measured (pure CO) is an upper limit due to electronic conduction of the oxygen sensor at extremely low oxygen fugacities. For this reason we have assumed that experiments in pure CO actually reflect oxygen fugacities between the measured value and that of carbon saturation (about 1.6 log units lower). All experiments were run in excess of 16 hours at 1400 °C, except for one of the two most reducing (pure CO) which was run for 5 hours. Temperatures were measured using a type B thermocouple external to the furnace and checked against the temperature in the furnace hot-zone using a second internal type B thermocouple. Temperature control was better

Table 1
Experimental Results.

Sample	Pressure (GPa)	Temp (K)	$\log f_{O_2}$ (rel. IW)	Max in 1 st deriv. Positon (σ)	Composition									Total
					Na ₂ O (σ)	MgO (σ)	Al ₂ O ₃ (σ)	Si ₂ O ₃ (σ)	SO ₂ (σ)	CaO (σ)	FeO (σ)	Wppm (σ) (laser)		
0754	24	2433	-1.91	10205.76 (0.17)	0.07 (0.02)	35.58 (1.255)	3.43 (0.28)	47.83 (2.45)	-	2.69 (0.234)	11.63 (1.39)	1200 (600)	101.1	
1206	1.5	1923	-6.2	10203.18 (0.15)	0.03 (0.03)	31.42 (6.8)	15.03 (2.97)	37.1 (0.89)	-	17.1 (4.61)	0.07 (0.02)	31 (28)	100.8	
2665 ⁺	25	3000	-2.45	10205.70 (0.28)	-	38.54 (2.42)	-	46.93 (2.08)	-	-	7.42 (0.57)	144 (80)	98.8	
C29 [§]	6	2123	-2.45	10206.03 (0.05)	-	41.55 (9.0)	2.32 (1.23)	38.27 (2.12)	-	6.51 (5.67)	12.14 (5.05)	976 (113)	100.8	
0734	7	2073	-1.85	10205.87 (0.06)	0.53 (0.38)	32.63 (12.3)	0.62 (1.2)	42.68 (5.5)	-	7.1 (8.32)	16.06 (4.36)	958 (99)	99.7	
0736	7	2073	-3.09	10205.73 (0.05)	0.16 (0.12)	28.68 (14.59)	5.85 (6.46)	35.84 (5.3)	-	13.51 (11.7)	13.88 (6.13)	5070 (600)	97.9	
0738 ^a	1.5	1803	-2.21	10205.90 (0.00)	-	7.84 (0.73)	3.54 (0.25)	46.91 (1.45)	1.93 (1.67)	11.16 (0.43)	26.26 (1.57)	3540 (140)	97.8	
0745 [§]	1.5	1983	-1.77	10205.97 (0.06)	0.08 (0.01)	37.11 (10.3)	0.11 (0.11)	35.72 (3.4)	-	9.43 (6.20)	17.92 (1.48)	2686 (658)	100.4	
0748	1.5	1623	-3.49	10206.03 (0.06)	0.02 (0.01)	15.28 (2.16)	3.25 (1.63)	51.88 (1.41)	-	15.57 (1.09)	12.25 (1.63)	3520 (660)	98.3	
0942 [§]	1.5	2273	-1.1	10206.03 (0.06)	0.04 (0.01)	30.21 (3.9)	11.41 (1.2)	25.71 (0.83)	-	11.14 (3.05)	14.74 (1.74)	3995 (535)	99.2	
1116	1.5	1923	-2.1	10205.90 (0.00)	-	25.34 (8.70)	12.47 (3.12)	35.41 (1.55)	-	16.15 (5.05)	11.31 (1.31)	23701 (1997)	100.7	
1117	1.5	1923	-2.2	10205.80 (0.00)	-	33.14 (9.27)	11.70 (3.76)	33.98 (2.44)	-	11.02 (5.79)	10.34 (2.67)	44949 (9225)	100.2	
1205	1.5	1923	-3.6	10205.75 (0.07)	-	27.48 (4.67)	14.27 (1.88)	38.28 (0.41)	-	19.04 (3.06)	1.91 (0.09)	232 (119)	101.0	
W-5.5 (16 h)			-5.5 (0.8)	10203.35 (0.07)	-	15.96 (0.07)	20.84 (0.07)	44.70 (0.14)	-	18.68 (0.08)	-	26 (7)	100.2	
W+0.5			0.5	10205.87 (0.06)	-	17.06 (0.04)	20.73 (0.03)	45.82 (0.04)	-	17.73 (0.06)	-	508 (2)	101.4	
W+2			2	10206.03 (0.06)	-	16.86 (0.07)	20.52 (0.04)	45.37 (0.07)	-	17.53 (0.06)	-	7431 (70)	101.1	
W+4	0.1 MPa	1673	4	10206.00 (0.00)	-	16.42 (0.06)	20.5 (0.05)	44.96 (0.06)	-	17.45 (0.06)	-	12790 (250)	100.7	
Air			9	10205.90 (0.08)	-	16.37 (0.08)	20.03 (0.11)	44.20 (0.08)	-	17.1 (0.12)	-	12845 (160)	99.5	
W-1			-1	10205.88 (0.10)	-	16.36 (0.07)	20.36 (0.06)	44.54 (0.07)	-	17.35 (0.07)	-	17636 (123)	100.3	
W-5.5			-5.5 (0.8)	10203.58 (0.10)	-	16.93 (0.08)	20.85 (0.04)	45.35 (0.08)	-	17.94 (0.06)	-	121 (11)	101.1	
WO ₂			-	10204.00 (0.14)	-	-	-	-	-	-	-	-	-	
WO ₃			-	10205.80 (0.00)	-	-	-	-	-	-	-	-	-	

For full analyses see § – Wade et al. 2012 & + – Wade and Wood, 2005.

n.b. Maximum in first derivative position for WO₃ 3.9 eV below mean peak position.

^a - Denotes graphite capsule.

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