



# The solubility and oxidation state of tungsten in silicate melts: Implications for the comparative chemistry of W and Mo in planetary differentiation processes

Hugh St.C. O'Neill<sup>a,\*</sup>, Andrew J. Berry<sup>a,b</sup>, Stephen M. Eggins<sup>a</sup>

<sup>a</sup> Research School of Earth Sciences, Australian National University, Canberra 0200, ACT, Australia

<sup>b</sup> Department of Earth Science and Engineering, Imperial College London, South Kensington, London, SW7 2AZ, UK

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## ABSTRACT

The solubility of W in 18 melt compositions in the system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> in equilibrium with W metal was determined as a function of oxygen fugacity ( $f_{O_2}$ ) at 1400 °C and atmospheric pressure, using CO–CO<sub>2</sub> and H<sub>2</sub>–CO<sub>2</sub> gas mixtures to control  $f_{O_2}$ . Samples were analysed by both laser-ablation ICP-MS and electron microprobe. The variation of W solubility with  $f_{O_2}$  establishes that W dissolves predominantly as W<sup>6+</sup>, with a possible contribution from W<sup>4+</sup> only at the very lowest  $f_{O_2}$ s accessible to the experimental method, in which regime experimental difficulties make the reliability of the results uncertain. X-ray absorption near edge structure (XANES) spectroscopy at the L<sub>3</sub>-edge of representative samples confirms the oxidation state of W as 6+, and suggests that W<sup>6+</sup> occurs in tetrahedral coordination in silicate melts. Activity coefficients of WO<sub>3</sub> derived from the solubility measurements correlate exactly with those of MoO<sub>3</sub> obtained previously by similar experiments using the same melt compositions and temperature (O'Neill and Eggins, 2002). The effect of TiO<sub>2</sub> on W solubility is shown to be mainly one of dilution, from an investigation at one  $f_{O_2}$  in the pseudobinary between the anorthite–diopside eutectic composition (A<sub>Deu</sub>) and TiO<sub>2</sub>.

The solubilities of W and also Mo may be combined with thermodynamic data from the literature for Fe–W and Fe–Mo alloys to calculate partition coefficients for W and Mo between silicate melt and Fe-rich metal. The calculated partition coefficients for W and Mo differ by  $\sim 10^3$  over the range of  $f_{O_2}$  appropriate for equilibrium between liquid metal and silicate melt during planetary core formation at low pressures and moderate temperatures ( $\sim 1400$  °C). Because the ratio of  $D_W^{sil-melt/met}/D_{Mo}^{sil-melt/met}$  is predicted to decrease only moderately with temperature (e.g., to  $\sim 10^2$  at 2200 °C), and is independent of  $f_{O_2}$ , melt composition and degree of partial melting, the large fractionation of Mo/W expected for equilibrium conditions could provide a useful means of discriminating between models of heterogeneous and homogeneous accretion and core formation, once the effect of pressure is better understood. However, comparison of our calculated metal/silicate partition coefficients with direct experimental determinations reveals an apparent lack of internal consistency among the latter, which may partly reflect a strong influence of minor components in the metal phase (e.g., carbon) on partitioning, which will also need to be understood before Mo/W systematics can be applied with confidence.

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## 1. Introduction

Molybdenum and tungsten are positioned vertically adjacent to each other in group VIb of the periodic table, being the elements in this group from the 2nd and 3rd transition rows, respectively. Like other such “geochemical twins” (e.g., Y and Ho, Zr and Hf, or Nb and Ta), they consequently share very similar chemical properties. In the case of Mo and W, their chemical properties make them useful as monitors of core formation in planetary bodies, not least because they are the only two elements that are cosmochemically refractory while also being moderately siderophile. Their refractoriness means that Mo

and W may be assumed to have condensed into planetary bodies in the chondritic ratio, while their moderately siderophile nature means that a resolvable fraction of both elements should have remained behind in the silicate portion of planets after metal segregation and core formation. This latter behaviour is in contrast to the highly siderophile elements (i.e., the Platinum Group Elements plus Re and Au), which are partitioned so extremely into metal that their tiny residual concentrations in the silicate portion of a planet are likely to be obscured by later additions – the “Late Veneer” on Earth, for example, or meteoritic contamination in lunar soils. The Mo/W ratio in a planetary mantle therefore provides a critical clue as to how core formation occurred. For instance, the chondritic Mo/W ratio is  $10 \pm 1$ , whereas the Mo/W ratio in the Bulk Silicate Earth (BSE) is estimated as  $2.4 \pm 1.3$  (Palme and O'Neill, 2003), implying only a fairly modest fractionation of Mo from W during core formation (i.e., core formation

\* Corresponding author. Tel.: +61 2 6125 5159; fax: +61 2 6125 5989.  
E-mail address: [hugh.oneill@anu.edu.au](mailto:hugh.oneill@anu.edu.au) (H.S.C. O'Neill).

has depleted Mo only about four times more than W). The lunar Mo/W ratio is quite different, at about 0.1 to 0.2 (O'Neill, 1991a), recording a much stronger depletion of Mo over W. The Mo/W ratio of the eucrite parent body is similarly low (Newsom, 1985).

Less well appreciated is the fact that W and Mo appear to be considerably fractionated during continental crust formation in the Earth. The crust/mantle ratio for W is about 60 (it is one of the most incompatible of all elements), whereas that for Mo is  $\sim 30$ , implying a crust/mantle fractionation of the Mo/W ratio of a factor of two (see Palme and O'Neill, 2003, their Table 5). By contrast, other geochemical twins such as Zr/Hf, and Y/Ho are insignificantly, and Nb/Ta only slightly, fractionated by crust/mantle differentiation (Palme and O'Neill, 2003). One suggestion is that this may be due to the greater chalcophile tendencies of Mo relative to W, implying a role for residual sulfide during the processes leading to the extraction of the continental crust from the mantle (O'Neill, 1991b), which, if true, would have implications for the U–Th–Pb systematics of the Earth because of the chalcophile nature of Pb.

Unlike the other pairs of geochemical twins, Mo and W may occur in more than one oxidation state under redox conditions relevant to geochemical processes. The property that affects the geochemistry of heterovalent elements the most is the oxidation state in which they occur. For both Mo and W, the best known oxidation state under ambient laboratory conditions and also in most minerals is 6+, but both elements also adopt the 4+ oxidation state (e.g., Rollinson, 1973). If one of these twins were to occur in one oxidation state, say 6+, and the other in the other state, that is, 4+, then the large difference in chemical behaviour between the two states would be expected to produce large fractionations during any differentiation process. Previous experimental work in simple Fe-free systems has established that Mo dissolves in silicate melts in both its common oxidation states, Mo<sup>4+</sup> and Mo<sup>6+</sup>, under redox conditions relevant to planetary science, with Mo<sup>6+</sup> predominating under the redox conditions typical of the present-day terrestrial upper mantle (Holzheid et al., 1994; O'Neill and Eggins, 2002). This is consistent, at least approximately, with the oxidation states of Mo inferred from metal/silicate partitioning experiments (Schmitt et al., 1989; Walter and Thibault, 1995). The oxidation state of W in silicate melts is not so well constrained. From their study of the solubility of W in equilibrium with W metal in the anorthite–diopside eutectic melt composition, Ertel et al. (1996) concluded that W occurs exclusively as W<sup>4+</sup> in the oxygen fugacity range over which W metal is stable. In contrast to the results from the Mo solubility studies, no W<sup>6+</sup> could be detected. Yet W clearly occurs in most minerals as W<sup>6+</sup> (e.g., scheelite, CaWO<sub>4</sub>; hübnerite–ferberite, (Fe,Mn)WO<sub>4</sub>), and the 6+ state is the common one in molten salts, e.g., in the system Na<sub>2</sub>O–WO<sub>3</sub>. If W occurs as 4+ in equilibrium with metal but as 6+ at higher oxygen fugacities, then there should be an obvious transition between the two regimes, which has, however, never been reported. Moreover, most of the available direct studies of metal/silicate partitioning behaviour imply a distinctly higher average oxidation state for W in silicate melts (Schmitt et al., 1989; Hillgren, 1991; Walter and Thibault, 1995), although Ramensee and Wänke (1977) found W<sup>4+</sup> and Jaeger and Drake (2000) assumed W<sup>4+</sup> based on the results of Ertel et al. (1996).

In this study we measure the solubility of W in equilibrium with W metal at the same temperature (1400 °C) and in the same set of melt compositions as used previously for Mo (O'Neill and Eggins, 2002). This establishes the oxidation states of W at the low oxygen fugacities at which W metal is stable, as well as giving the activity coefficients of the W oxide components as a function of melt composition for comparison with the Mo data. We then use XANES spectroscopy to confirm the oxidation state of W in the solubility experiments, and determine it at higher  $fO_2$ s than those at which W metal is stable. We show, contrary to the findings of Ertel et al. (1996), that W occurs as W<sup>6+</sup> under nearly all conditions, except at the lowest  $fO_2$ s of our solubility experiments, under which conditions a

contribution to the solubility from a lower oxidation state, which we presume to be W<sup>4+</sup>, is arguably discernible. The dependence of the solubility of W as W<sup>6+</sup> on silicate-melt composition is identical within experimental uncertainty to that found by O'Neill and Eggins (2002) for Mo<sup>6+</sup>. An apparently similarly good correlation of the compositional dependence of the inferred W<sup>4+</sup> solubilities with those determined for Mo<sup>4+</sup> provides an argument that this oxidation state has been correctly identified. The solubility measurements are then used to calculate metal/silicate partition coefficients, which are about 10<sup>3</sup> less than those for Mo under equivalent conditions, i.e., W is very much less siderophile than Mo. The calculated partition coefficients provide a basis for testing direct measurements of W and Mo metal/silicate partitioning reported in the literature for internal consistency.

## 2. Experimental and analytical

### 2.1. Sample equilibration

The solubility of W as a function of oxygen fugacity ( $fO_2$ ) was determined in the same CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (CMAS) compositions previously used by O'Neill and Eggins (2002). These samples comprise three sets, called “AD6”, “CMAS7” and “CAS/MAS eutectics”. Samples were equilibrated in a conventional vertical tube furnace equipped for gas mixing, using the wire-loop method as described in O'Neill and Eggins (2002), with CO–CO<sub>2</sub> mixtures to control  $fO_2$ . Three additional experiments were done with H<sub>2</sub>–CO<sub>2</sub> mixtures in an attempt to access lower  $fO_2$ s. The loops were made from W wire of 0.4 mm diameter and 99.95% purity (Strem Chemicals). With the benefit of hindsight we report that the thinness of this wire was not optimal, with several samples dripping off. This difficulty was avoided in the analogous Mo experiments, which used metal strips cut from foil. For this reason, two particularly fluid compositions (AD+TiO<sub>2</sub> and CMAS7E) were run in only a few experiments. The effect of TiO<sub>2</sub> was studied by running four compositions in the binary ADeu–TiO<sub>2</sub> with 0, 5, 10 and 20 wt.% TiO<sub>2</sub> in one additional experiment.

All experiments reported in this paper were at 1400 °C. The time needed to reach steady-state solubilities was taken from the Mo investigation, and was confirmed by replicate experiments at  $fO_2 = 10^{-12}$  bars at 24 to 74 h for the AD6 compositions and 27 to 70 h for the CMAS7 compositions (see Table 2 below). The range in  $fO_2$  covered 10<sup>-13.21</sup> to 10<sup>-11.0</sup> bars using CO–CO<sub>2</sub> gas mixes, corresponding to 99.5% to 94% CO. This range of  $fO_2$  is on average lower than that used in the Mo experiments (10<sup>-11.6</sup> to 10<sup>-9.0</sup> bars), and is below the limit of Nernstian behaviour for zirconia oxygen sensors (Mendybaev et al., 1998). Imposed values of  $fO_2$  were therefore calculated from the input gas composition only. Due to the extreme ratios of the gas mixes, the non-systematic uncertainty in log  $fO_2$  is estimated to be about  $\pm 0.05$  log-bar units (cf.  $\pm 0.02$  log-bar units in the Mo study). At the extreme ratios used it is also possible, perhaps even likely, that there may exist a systematic error biasing the reported  $fO_2$ s towards being higher than the actual  $fO_2$ s, due to contamination of the input gases with small amounts of oxygen, e.g., from tiny quantities of air that may permeate over a long time through the tubing used to carry the input gases. The effect would be to increase erroneously the solubility of W compared to its true value at the nominal  $fO_2$ , thereby inflating the seeming importance of the 4+ oxidation state.

To try to check the inference of significant W<sup>4+</sup> at the lowest  $fO_2$  of the CO–CO<sub>2</sub> experiments, three additional experiments were made using H<sub>2</sub>–CO<sub>2</sub> gas mixtures. At 1400 °C, the value of  $fO_2$  at 0.5% CO<sub>2</sub> in H<sub>2</sub> is 10<sup>-14.24</sup> bars whereas that at 0.5% CO<sub>2</sub> in CO is 10<sup>-13.21</sup> bars, so a lower  $fO_2$  is accessed by H<sub>2</sub>–CO<sub>2</sub> mixtures for a given mixing ratio. The activity of carbon in H<sub>2</sub>–CO<sub>2</sub> mixtures is also much lower at a given  $fO_2$  than in CO–CO<sub>2</sub> mixtures, so an additional advantage of using the alternative gas mixture is to check that alloying of C into W metal or the formation of tungsten carbides do not affect the results.

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