Electronic supplement/Appendix A: Detailed description of experimental procedure

1. Starting materials and capsule preparation

Synthetic fluid inclusions were trapped in natural, inclusion-free quartz from Brazil. For each experiment, a quartz piece of ~7-9 mm^3 size was loaded into a $Pt_{95}Rh_{05}$ capsule together with powder of high purity WO_2 or MoO_3 and 19-26 µl fluid (Table 1). The length of the capsule was 8 mm, its inner diameter was 3.2 mm. The capsule design described by Audetat and Bali (2010) and Bali et al. (2011) was applied. As an approximately ~1 mm thick Pt plug is used to close the capsule during welding in this design the space for the sample load was approximately 4.4 mm in height. Note that the stoichiometry of the saturating Mo or W oxide was controlled by the equilibrium with the external buffer during the experiment. For the experiments at 600 and 700 °C fractured quartz was used to trap fluid inclusions. The aqueous fluid used for the MoO_3-bearing experiments had a salinity of 0.39 to 14.1 wt% $NaCl_{equiv}$. It was spiked with 860-998 ppm Cs, Rb and Ba, added as chlorides, to provide internal standards for LA-ICPMS analysis. Due to the addition of these minor components, the salinity is expressed as equivalent NaCl content ($NaCl_{equiv}$), in which the molar amount chlorine was recalculated as NaCl and added to the nominal NaCl-contents. One experiment was conducted with a solution containing 5 wt% HCl. The aqueous fluid used for the WO_2-bearing experiments contained variable amount of NaCl. The fluid salinity varied from 2.0 to 20.0 wt% $NaCl_{equiv}$. Oxygen fugacity was controlled by external Fe-FeO, Co-CoO, Ni-NiO and $Re-ReO_2$ buffers (Table 1).

Oxygen fugacity was buffered as described by Bali et al. (2011). The 8 mm long and 3.8 O.D. Pt-Rh capsule was placed into an outer metal capsule made of the metal buffer (Fe, Ni, Co). These outer capsules were 10 mm long and 5 mm in diameter. The remaining space in outer metal capsule (generally having a weight of ~ 1.4 g) was filled with the respective oxide powder (generally ~0.2-0.3 g) and water (generally ~0.04 g). For $Re-ReO_2$ buffer Re-foil and ReO_2 powder (both generally 0.3 g) was placed into an outer Pt-Rh capsule similar in size to the other buffering capsules. The presence of both buffering materials after the experiments was determined optically and by X-ray diffraction. Both buffers were present in all experiments.

We also determined the partitioning of W and Mo between aqueous fluid and major eclogite and peridotite minerals. For this, the solubility of W and Mo in diopside, garnet, and rutile was studied at variable fO_2 conditions. Approximately 40 mg of CMAS- or CMASTi-

oxide powder was encapsulated with 11-17 μl of fluid and the same WO_2 and MoO_3 powder was used in the synthetic fluid inclusion experiments. The CMAS-oxide powder had aluminous diopside bulk composition, the CMASTi-oxide powder was the same powder doped with 15 wt% TiO_2 (Table 2). The components of the powder were high purity oxides and Ca-carbonate. It was ground and mixed in an agate mortar under ethanol. The dry powder was slowly decarbonated in a high temperature oven and kept at 1000 °C overnight. We used the same capsule design as for synthetic fluid inclusion experiments. The experiments were buffered by Co-CoO, Ni-NiO and Re-ReO_2, and the fluid was pure water (Table 2). The addition of excess WO_2 or MoO_3 ensured W- or Mo-saturated fluid in equilibrium with the growing minerals, thus the composition of the fluid was constant during the experiments. This is especially important for Mo, as Mo alloys with the Pt-capsule relatively rapidly at T>800 °C (e.g.: Rooksby and Lewis, 1964; Walters and Covino, 1988). We confirmed this observation as we found ~1000 ppm Mo in the platinum capsule after one experiment. Similar alloying with W was not observed. Two experiments have been carried out in W-undersaturated conditions in order to check if the partitioning of W is constant even if the W-content of the fluid is an order of magnitude less than in saturated conditions. In these cases W was added to the experimental charge as $NaWO_4$ solution with 4940 ppm of W. This experiment was buffered by NiNiO.

2. High pressure experiments

The experiments were carried out in an end-loaded piston cylinder apparatus at the Bayerisches Geoinstitut, Bayreuth and at the Department of Experimental and Applied Mineralogy, University of Göttingen. In both cases we used ½ inch MgO-NaCl assemblies, with stepped graphite heaters. The capsule was placed in the assembly such that the top of the quartz crystal was in the hotspot, whereas its bottom was at a slightly cooler part of the assembly. The resulting slight temperature gradient (probably < 10 ˚C) enhanced crystal growth at the bottom part of the capsule. The temperature was measured by Pt/Pt-Rh ("S-type") thermocouple and monitored by a Eurotherm controller. A friction correction of 5% was applied. Pressure and temperature was raised simultaneously along a fluid isochoric path. This method and the use of MgO-NaCl pressure cells led to minimal deformation of the capsules. No water loss from inner capsules was detected.

Synthetic fluid inclusion experiments were carried out at temperatures of 600 to 800 °C at a constant pressure of 26.1 kbars (Table 1). Fluid pH is not explicitly buffered in these experiments. Experimental duration was 1 day. The runs were terminated by decreasing the

temperature from run temperature to room temperature within ~4 minutes, resulting in a pressure decrease by about 30%, and subsequently bleeding off the remaining pressure within 15 minutes. The Mo and W solubility experiments in mantle silicates and rutile were 48 to 72 hours long and quenched by shutting off the power and keeping the pressure constant during cooling. The pressure was lowered to room pressure within 20 minutes.

References:

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