Effect of silcate melt composition and fO_2 on metal-silicate partitioning of Si, Nb, Ta and V

N. RAI, M.J. WALTER, AND C.J. HAWKESWORTH

Dept. of Earth Sciences, University of Bristol, U.K. BS81RJ; glxnr@bris.ac.uk

High pressure experiments indicate that Nb and V have very similar metal-silicate partition coefficients and are slightly siderophile at reducing conditions [1]. It is postulated that the upper mantle depletion in V, and the depletion in Nb relative to Ta in mantle reservoirs, could be due to sequestering of V and Nb into the core [1]. Further, the mantle abundance of V together with high P-T partitioning data help to constrain the conditions of core segregation [2]. Nb, V and Ta can exist in variable and high oxidation states. As such, their partitioning behaviour is dependent on oxygen fugacity, and by way of analogy with other high-valence cations(Mo^{6+}, $W^{4+,6+}$), partitioning may also be sensitive to silicate melt composition [3]. Here we report new experimental results on the effects of silicate melt composition and oxygen fugacity on the partitioning behaviour of these elements along with Si. Experiments were made at 2 GPa and 2000 K and over a range of relative oxygen fugacities from ~IW-3 to IW-6. Silicate melts range from basaltic to peridotitic in composition. The melt compositional parameter, NBO/T, is used as a proxy for silicate melt composition, and has values from 0.7 to 4. Isobaric, isothermal data for each element were regressed using the equation: $\ln D^{met/sil} = a + bfO_2 + c(nbo/T)$. Regressions show that at the experimental conditions both Nb and V exist in 3+ valence states, Si exists in +4 state whereas Ta likely exists in a 5+ valence state. In contrast, higher pressure (25 GPa) partitioning data [1] show a 5+ valence state for Nb, which may imply a possible change in valence as the absolute fO_2 of the IW buffer becomes more oxidizing with pressure. Documenting such changes in valence is critical for parameterizations that rely on exchange partition coefficients [2]. Regressions indicate that melt composition has little effect on the partitioning behaviour of V, Nb and Ta although Si shows strong compositional dependency. For trivalent Nb and V this is generally consistent with findings that melt composition has a small effect on partitioning of lower valence elements such as Ni^{2+} and Co^{2+} [4]. A higher valence state of 5+ for Nb at higher pressures implies a greater effect of melt composition on partitioning. However, we find that Ta^{5+} shows virtually no compositional dependence, in marked contrast to Si^{4+}, and also that Ta^{5+} becomes siderophile at less reduced conditions than Si^{4+}.

References

[1] Wade et al. (2001), *Nature* **409**, 75-78. [2] Wade & Wood (2005), *EPSL* **236**, 78-95. [3] Walter et al. (1995), *Science* **270**,1186-1189. [4] Jaeger & Drake (2000) *GCA* **64**, 3887-3895.