# DEPLETION OF VANADIUM IN PLANETARY MANTLES: CONTROLLED BY METAL, OXIDE, OR SILICATE?

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**Introduction:** Vanadium concentrations in planetary mantles can provide information about the conditions during early accretion and differentiation [1,2]. Because V is a slightly siderophile element, it is usually assumed that any depletion would be due to core formation and metal-silicate equilibrium (e.g., [3,4]). However, V is typically more compatible in phases such as spinel, magnesiowüstite and garnet. Fractionation of all of these phases would cause depletions more marked than those from metal. In this paper consideration of depletions due to metal, oxide and silicate are critically evaluated.

## Vanadium compatibility:

*Metal*: the partitioning of V between metal and silicate has been studied extensively at both low and high pressure and temperature conditions (e.g., [2, 3, 5-8], leading [3] to propose a predictive expression for D(V) met/sil, based on the S and C content of the metal, temperature and oxygen fugacity. This predictive expression does not include a pressure term because inspection of the data reveals no obvious pressure effect. This expression can be used to predict D(V) metal/silicate as a function of $fO_2$, at fixed T and metal composition (Fig. 1). The significant $fO_2$ effect shows that V switches from lithophile (D<1) to siderophile (D>1) at approximately 3 log $fO_2$ units below the IW buffer.

*Shallow mantle:* The partitioning of V during conditions of melting of the shallow terrestrial mantle has been studied extensively by [9], and is known to be controlled by spinel (see also [10]) and clinopyroxene. Similar to metal-bearing systems, V partitioning is strongly $fO_2$ dependent, and can switch from compatible to incompatible behavior within a range relevant to planetary mantles (Fig. 1).

*Intermediate mantle:* Both the martian and terrestrial mantles contain a large stability field for majoritic garnet and β $(Mg,Fe)_2SiO_4$ (e.g., [11]). There are very few data for these phases, and certainly not enough to assess whether there is also a dependence upon $fO_2$. However, given the available crystal chemical diversity in these phases, the interplay of 2+, 3+, and 4+ vanadium is likely to produce $fO_2$ dependent behavior.

*Deep mantle:* Several studies have measured the partitioning of V between deep mantle (terrestrial lower mantle) phases that may be relevant to early Mars as well. Magnesiowüstite is a significant host phase for V and can have D(V) as high as 4 to 6 [7]. Previous studies of both Mg- and Ca-silicate perovskite and melt have shown that D(V) may be as high as 2-3 [12-13]. The deep mantle may thus also be host to a significant amount of V, especially if there was early fractionation of these phases from a magma ocean.

*Summary of all phases:* To illustrate the potential for silicate and oxide phases to dominate the V budget, two different scenarios are illustrated in Figure 1: variation of D(metal/silicate) [3] and D(shallow mantle/silicate) [9], as a function of oxygen fugacity (the latter based on a mantle consisting of 49% olivine, 28% opx, 18% cpx and 5% spinel). Each of these scenarios shows that vanadium will be dominated by different phases depending on the environment of melting.

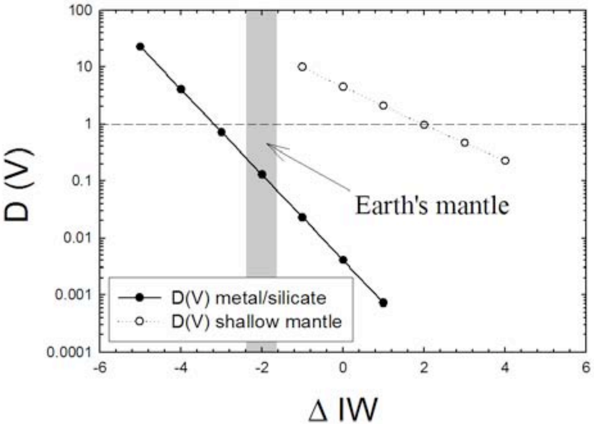

Figure 1: comparison of D(V) Metal/silicate liquid [3], and D(shallow mantle/silicate) [9], as a function of oxygen fugacity.

## Summary of depletions

Depletions of V in planetary mantles are best defined relative to an element of similar lithophile behavior – Al [14]. Correlations of V and Al are evident in terrestrial sample suites, but must be interpreted for other planetary bodies using data from basaltic rocks. As a result, there is some interpretation necessary. A summary of V depletions for Earth, Moon, Mars and Vesta is presented in Figure 2.

*Earth:* The V content of the primitive terrestrial mantle is defined by analyses of komatiites, peridotites and basaltic rocks. All of these samples define a small, but significant depletion of V relative to chondritic values.

*Moon:* The V content of the lunar mantle can be estimated from the many basalt samples we have from the Apollo, Luna and meteorite collections. Because many of these basalts have undergone fractionation, and some involving the V compatible phase chromite, only unevolved samples must be considered in these estimates. Consideration of available data by [10] shows that the Moon has only a small depletion of V relative to chondritic values.

*Mars:* The V content of the primitive martian mantle must also be estimated from a few basalt samples we have from meteorite collections. Because many of these basalts have also undergone fractionation involving chromite, only un-evolved samples must be considered in these estimates. One of the most primitive samples known is the shergottite Y980459 [15]. Consideration of available data by [10] shows that Mars has a higher V/Al ratio than chondritic values.

*Vesta:* The V content of the HED/Vesta mantle is lower than any other body known. However, our samples of the eucrites represent a suite of liquids of similar origin. These liquids may have been fractionated and thus seen the effects of chromite fractionation. On the other hand if they are primitive, unfractionated liquids, they may represent a severely depleted mantle compared to the Earth, Moon and Mars. The significant depletion of V in the HED mantle in Figure 2 is based on the assumption that no chromite has fractionated from the eucritic liquids and that they are primary derivatives from the HED mantle.

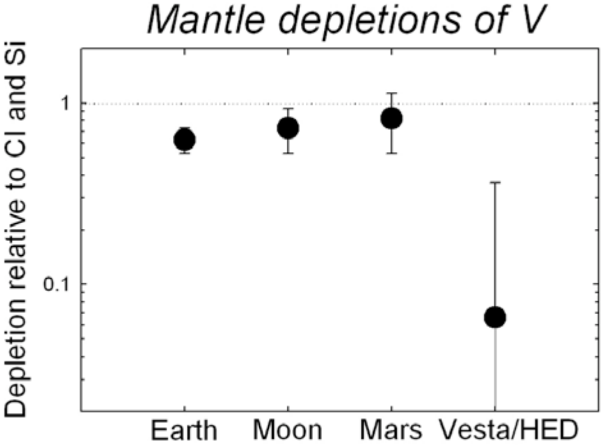

Figure 2: depletions of V for different planetary mantles. From Righter et al. (2006) [7].

**Models**

*Earth:* The ratios of lithophile elements such as Sm/Nd and Lu/Hf, as well and Hf and Nd isotopic compositions, in the primitive mantle can be satisfied by fractionation of 10-15% of an assemblage consisting of Mg-perovskite, Ca-perovskite and magnesiowustite [16]. Using published D(V) for these phases, and a CI chondrite as a starting material, it can be shown that the small depletions of V in the primitive terrestrial mantle could be caused by fractionation of these phases. This scenario is an alternative to the very high temperature and pressure models that have been proposed for V depletions [3,4].

*Moon*: Segregation of the small lunar core is unlikely to have caused a significant V depletion, as it did for other more siderophile elements such as Ni and Re [17]. Additionally, the D(V) met/sil for redox conditions relevant to the Moon (IW-2), is too small to have caused a depletion (Fig. 2). As a result, the lunar depletions must be attributed to a previous differentiation event, perhaps inherited from the mantle of the impactor that formed the Moon. Such an impactor could have been a large body, such as Mars or Earth, that underwent a V depletion due to silicate and oxide fractionation.

*Mars*: The depletion of V in the martian mantle, similar to the Earth and Moon, presents a problem for the high PT reduced core formation scenario proposed for the Earth [3,4]. A high PT scenario for Mars is inconsistent with most siderophile elements (Ni, Co, W, [18]). In addition, the 'reduced followed by oxidized' accretion scenario [4] won't work for Mars, since its mantle is not deep enough for a significant (or any at all) Mg-perovskite stability field [11]. Instead, V depletions produced by intermediate or deep mantle phases (oxides or silicates) can easily explain the martian V data.

**References:** [1] Ringwood, A.E. et al. (1990) Nature 347, 174-176 [2] Drake, M.J. et al. (1989) GCA 53, 2101. [3] Chabot, N.L. and Agee, C.B. (2003) GCA 67, 2077-2091 [4] Wade, J. and Wood, B.J. (2005) EPSL 236, 78-95 [5] Hillgren, V.J. et al. (1994) Science 264, 1442-1445 [6] Ohtani, E. et al. (1997) PEPI 100, 97-114 [7] Gessmann, C.K. and Rubie, D.C. (1998) GCA 62, 867-882; Ohtani, E. et al. (1992) High Pressure Research, eds. Y. Syono and M. Manghnani, AGU, Washington DC, 341-349 [8] Wade, J. and Wood, B.J. (2001) Nature 409, 75-78 [9] Canil, D. (2002) EPSL 195, 75-90 [10] Righter, K. et al. (2006) Amer. Mineral., in review [11] Bertka, C.M. and Fei, Y. (1997) JGR 102, 5251-5264 [12] Ohtani, E. and Yurimoto, H. (1996) GRL 23, 1993-1996 [13] McFarlane, E.A. et al. (1994) GCA 58, 5161-5172 [14] Newsom, H.E. (1995) Composition of the solar system, planets, meteorites, and major terrestrial reservoirs, in: T.J. Ahrens (ed.), *Global Earth Physics: A Handbook of physical constants: AGU Reference Shelf vol. 1*, AGU, Washington, p. 159-189 [15] Shirai, N. and Ebihara, M. (2004) AMR 17, 55-67 [16] Walter, M.J. et al. (2004) GCA 68, 4267-4284 [17] Righter, K. (2002) Icarus 158, 1-13 [18] Righter, K. et al. (1998) GCA62, 2167-2177.