

A new spinel-olivine oxybarometer: Near-liquidus partitioning of V between olivine-melt, spinel-melt, and spinel-olivine in martian basalt composition Y980459 as a function of oxygen fugacity. J.J. Papike¹ (jpapike@unm.edu), L. Le², P.V. Burger¹, C.K. Shearer¹, A.S. Bell¹, and J. Jones³. ¹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque New Mexico 87131, ²ESCG, Houston, TX 77058, ³NASA/Johnson Space Center, Houston, TX

Introduction: Our research on valence state partitioning began in 2005 with a review of Cr, Fe, Ti, and V partitioning among crystallographic sites in olivine, pyroxene, and spinel [1]. That paper was followed by several on QUE94201 melt composition and specifically on Cr, V, and Eu partitioning between pyroxene and melt [2-5]. This paper represents the continuation of our examination of the partitioning of multivalent V between olivine, spinel, and melt in martian olivine-phyric basalts of Y980459 composition [6, 7]. Here we introduce a new, potentially powerful oxybarometer, V partitioning between spinel and olivine, which can be used when no melt is preserved in the meteorite. The bulk composition of QUE94201 was ideal for our study of martian pyroxene-phyric basalts and specifically the partitioning between pyroxene-melt for Cr, V, and Eu. Likewise, bulk composition Y980459 is ideal for the study of martian olivine-phyric basalts and specifically for olivine-melt, spinel-melt, and spinel-olivine partitioning of V as a function of oxygen fugacity.

Experimental: Experiments were run in a 1-atm Deltech gas mixing furnace. These runs were made using a spiked composition of martian meteorite Y980459. The REEs were added as 0.6 wt.% of their oxides (Ce as CeO₂). Scandium and V were added as Sc₂O₃ and V₂O₃ and doped to 0.1 wt.%. Experimental charges of the Y98 composition were pasted onto Re-wire loops at imposed oxygen fugacities of IW-1, IW, IW+1 and QFM. All experiments were held for 8 hours at 1500°C to ensure homogeneity and fO_2 equilibration. Charges were then cooled at 1000°C/hr to 1400, 1300 and 1200 °C, and held at the final temperature for at least 48 hrs, then drop-quenched into water. For experiments conducted at QFM, pressed pellet charges of Y98 were placed onto Pt₉₀Rd₁₀ loops and then air-quenched at the end of same thermal history as the other fO_2 experiments. The Pt-wire loop does not oxidize at high fO_2 , whereas the Re-wire loop prevents Fe loss at low fO_2 .

Results: Charges were analyzed using a JEOL 8200 electron microprobe (EPMA). At QFM the liquidus is above 1400°C with chromite being the first phase to crystallize. Of the four fO_2 's studied, QFM is the only one where chromite is the first phase on the

liquidus. This is likely because at this high oxygen fugacity, the Cr³⁺/Cr²⁺ is high and stabilizes chromite relative to olivine. At IW+1, the liquidus is also above 1400° C, and the liquidus phase is now olivine. At IW the liquidus falls to below 1400°C and again, olivine is on the liquidus, as is the case in the IW-1 experiment. Pyroxene and olivine major element chemistry for the 4 oxygen fugacities at 1200°C (not shown) illustrate the effects of fO_2 at the most oxidized run conditions. At QFM, olivine and pyroxene are displaced toward more Mg-rich compositions. This is likely because of minor Fe-loss to the Pt-Rh loop.

Spinel-melt partitioning of V as a function of oxygen fugacity: Our first efforts using spinel as an indicator of relative oxygen fugacity [7] was only qualitative. That study showed that using only zoned spinel, relative oxygen fugacities can be estimated. Our first insights into this technique resulted from acquiring EPMA traverses across spinel grains from core to rim on grains that showed zoning from chromite to ulvospinel. The zoning profiles showed the normal trends of core to rim decreases of Cr, Al, and Mg and increases of Fe, Ti, and Mn. However, the behavior of V is very different for Earth and Moon, with Mars in between. In terrestrial basalts V⁴⁺ > V³⁺, in lunar basalts V³⁺ > V⁴⁺, and in martian basalts V³⁺ and V⁴⁺ are both significant. The trends (core to rim) for the Moon show a strong positive correlation of V and Cr and negative correlation of V and Ti. For the Earth, the trends are just the opposite, with a strong negative correlation of V and Cr and strong positive correlation of V and Ti. Chromite in martian basalts shows trends in between. The spinel oxybarometer (e.g. Canil [8]) is very useful but requires coexisting spinel and melt in equilibrium. Results from this study are shown in Figure 1a and are compared to the results of Canil [8]. Note that our results agree very well with Canil's [8] results for high Cr/Al spinel. The dramatically increasing D_V with decreasing oxygen fugacity is a result of the strong structural preference for V³⁺ vs. V⁴⁺. Canil [8] shows the strong dependence of V Ds on the Al content of the spinel. High Al/Cr spinels have a much lower site preference for V³⁺ than high Cr/Al spinels. This is because V³⁺ and Cr³⁺ are very similar geochemically and have high crystal field

stabilization energy in octahedral coordination. Note Papike et al. [1], where spinel crystal chemistry is discussed. Diagrams presented in that paper show additional reasons why Cr^{3+} and V^{3+} are so highly correlated (size and charge).

Olivine-melt partitioning of V as a function of oxygen fugacity: Our results using V in olivine as an oxybarometer [6] gave an estimated oxygen fugacity of crystallization for Y980459 of IW+0.9. That work used 3 oxygen fugacities IW-1, IW, and QFM. The application of this oxybarometer requires the presence of melt in the meteorite. Our current study, adds an additional oxygen fugacity (IW+1). Note that the results for both studies are almost identical and that the high spike levels of REE in the present study had no apparent effect on V partitioning between olivine and melt.

Spinel-olivine V partitioning as a function of oxygen fugacity: We have been searching for an oxybarometer with application to olivine-phyric martian basalts that does not require the presence of melt [1-7]. One possible solution to this quandary is the partitioning of V between spinel and olivine. Both are near liquidus phases and commonly share grain contacts. We examined the partitioning of V between spinel and olivine and the results are shown in Figure 1c. Note that the spinel/olivine partitioning of V provides a powerful oxybarometer at low oxygen fugacities, over two orders of magnitude, from IW-1 to IW+1. Many of the martian olivine-phyric basalts fall in this range.

Discussion: Our previous attempts to determine martian magmatic oxygen fugacity involved martian meteorite QUE94201 [2-5]. In these studies, the partitioning of V, Cr, and Eu between pyroxene and melt was examined. Here, we apply the same oxybarometers to Y980459 and the results will be reported later. As with the previous studies, pyroxene will be analyzed via XANES to obtain high-precision measurement of V, Cr, and Eu valence. Our first priority, however, will be the application of the new spinel-olivine oxybarometers to many of the olivine-phyric martian meteorites in the collection. This will give a good overview of the range of oxygen fugacities using a single oxybarometer.

References: [1] Papike et al. (2005) *Am. Min.* 90, 277-290. [2] Karner, J.M. et al. (2007a) *Am. Min.*, 92, 1238-1241. [3] Karner, J.M. et al. (2007b) *Am. Min.* 92, 2002-2005. [4] Karner, J.M. et al. (2008) *MAPS*, 43, 1275-1285. [5] Karner, J.M. et al. (2010) *Am. Min.*, 95, 410-413. [6] Shearer, C.K. et al. (2006), *Am. Min.* 91, 1657-1663. [7] Papike, J.J. et al. (2004), *Am. Min.* 89, 1557-1560. [8] Canil, D. (2002) *EPSL*, 195, 75-90.

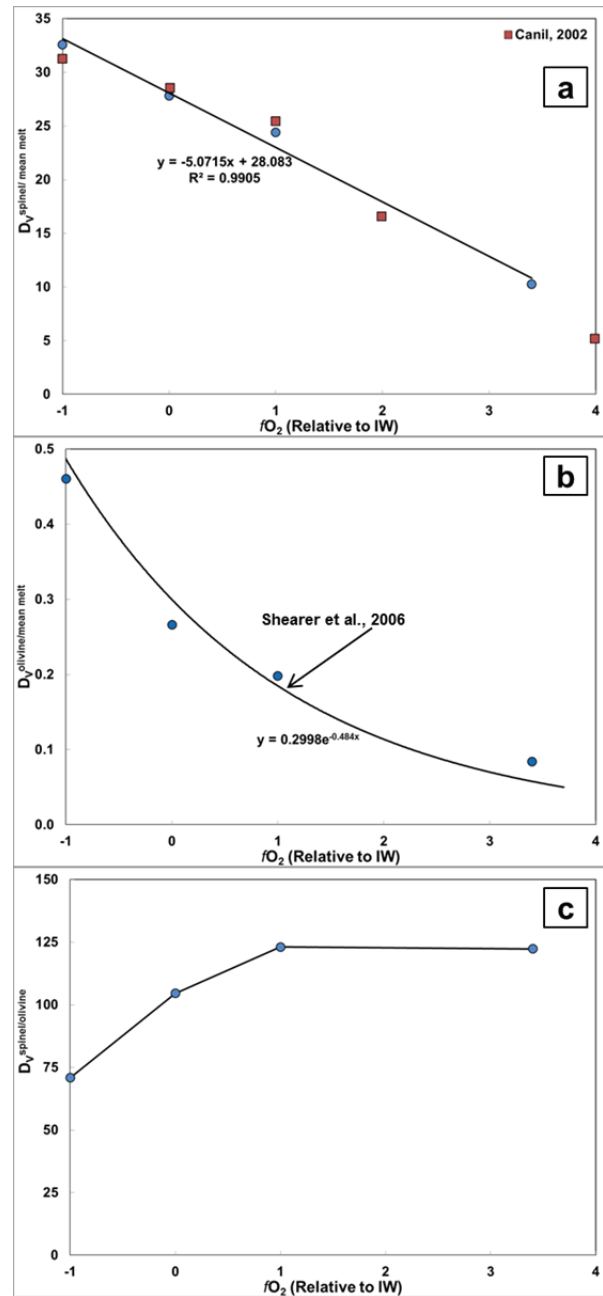


Figure 1. a. Mean V in spinels vs. glass; [8] data for comparison. b. Mean V in olivine vs. melt; [6] curve for comparison. c. Mean V in spinel vs. olivine.

Acknowledgements: This research was supported by NASA Cosmochemistry grants to CKS and J. Jones.