

THE PARTITIONING OF CR AND V BETWEEN PYROXENE-MELT IN MARTIAN BASALT QUE 94201.

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Introduction: Studies on the partitioning of Cr and V between pyroxene-melt in both natural QUE 94201 and in synthetic charges of the QUE composition have provided clues to the 1) fO_2 of the natural sample, 2) behavior of V and Cr in both augite and pigeonite, and 3) valence state of these elements in pyroxene and melt under constrained fO_2 conditions.

Estimates of fO_2 for QUE 94201: Partitioning of Cr and V between pigeonite cores and bulk composition shows that QUE 94201 crystallized at an fO_2 between IW+0.2 and IW+0.9 [1]. These estimates are based on calibration curves for DCr , DV and DCr/DV (pyroxene/melt) derived from experimental charges that were synthesized at fO_2 conditions of IW-1, IW, and IW+1. Our fO_2 estimate is robust because 1) the fO_2 is measured in the earliest crystallizing pyroxenes 2) the calibration curves are based on the same bulk composition as the natural sample, and 3) that bulk composition represents a melt from the martian mantle, so an accurate DCr and DV are measured.

Valence state partitioning of Cr between pyroxene-melt: DCr augite/melt is approximately double that of DCr pigeonite/melt in synthetic martian basaltic samples equilibrated at the same fO_2 [2]. This increase is not related to changing fO_2 and the valence of Cr, but rather to the increased availability of elements for coupled substitution with the Cr^{3+} ion, namely Na and Al. The availability of Al and Na to partition into pyroxene is due to delayed nucleation of plagioclase for the QUE 94201 martian basalt composition. Direct valence determination by XANES shows that Cr^{3+} is dominant in pyroxene at IW-1, IW, and IW+1. Trivalent Cr is apparently much more compatible in the pyroxene structure than divalent Cr, and thus an increasing DCr for both augite/melt and pigeonite/melt with increasing fO_2 is a function of the increased activity of Cr^{3+} in the crystallizing melt.

Valence state partitioning of V between pyroxene-melt: D_V augite/melt is greater than D_V pigeonite/melt in samples equilibrated under the same fO_2 conditions [3]. This increase is due to the increased availability of elements for coupled substitution with the V^{3+} or V^{4+} ions, namely Al and Na. For this bulk composition, both Al and Na are higher in concentration in augite compared with pigeonite; therefore more V can enter augite than pigeonite. Valence state determination by XANES shows that the V^{3+} and V^{4+} are the main V species in the melt at fO_2 conditions of IW-1 to IW+3.5, whereas pyroxene grains at IW-1, IW, and IW+1 contain mostly V^{3+} . This confirms the idea that V^{3+} is more compatible in pyroxene than V^{4+} . The XANES data also indicates that a small percent of V^{2+} may exist in melt and pyroxene at IW-1. The similar valence of V in glass and pyroxene at IW-1 suggests that V^{2+} and V^{3+} have similar compatibilities in pyroxene.

References: [1] Karner et al. (2007) *Am. Min.* 92, 1238. [2] Karner et al. (2007) *Am. Min.* 92, 2002. [3] Karner et al. (2008) *MAPS*, in press.