## LETTER

## Valence state partitioning of V between pyroxene and melt for martian melt compositions Y 980459 and QUE 94201: The effect of pyroxene composition and crystal structure

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## ABSTRACT

A martian basalt (Yamato 980459) composition was used to synthesize olivine, spinel, and pyroxene at 1200 °C at five oxygen fugacities: IW-1, IW, IW+1, IW+2, and QFM. The goal of this study is to examine the significant variation in the value of  $D_{\rm pyroxene/melt}^{\rm pyroxene/melt}$  with changing Wo content in pyroxene. While most literature on this subject relies on electron microprobe data that assumes that if the Wo component (CaSiO<sub>3</sub>) is <4 mol%, the pyroxene is in fact orthopyroxene, we've made a more robust identification of orthopyroxene using appropriate Kikuchi diffraction lines collected during electron backscatter diffraction analysis. We compare augite (Wo  $\sim$  33), pigeonite (Wo  $\sim$  13), orthopyroxene (Wo <4), and olivine. In augite (Wo ~ 33), the M2 site is 8-coordinated, while in pigeonite (Wo ~ 13), the site is 6-coordinated. The larger (8-coordinated) M2 site in augite requires structural expansion along the chain direction. The longer chain is enabled by the substitution of the larger Al for Si. The  $Al^{3+}$  substitution for  $Si^{4+}$  causes a charge deficiency that is made up, in part, by the substitution of  $V^{4+}$  and  $V^{3+}$  in the pyroxene M1 site. This rationale does not fully explain the dramatic decrease in  $D_v^{\text{orthopyroxene/melt}}$ . In monoclinic pyroxenes, the TOT stacking is characterized by + + + + (indicating the direction), a stacking pattern that produces a monoclinic offset. In orthopyroxene, the stacking is ++--, which produces an orthorhombic structure. The M2 site is located between the reversed TOT units and is highly constrained to 6-coordination and thus cannot contain significant Ca that requires 8-coordination. Because the M2 site in orthopyroxene is small and constrained, it accommodates less Al in the tetrahedral chains and thus less V in the pyroxene M1 site.

Keywords: Vanadium, partitioning, pyroxene, orthopyroxene, augite, pigeonite, EBSD, valence