American Mineralogist, Volume 96, pages 1278–1290, 2011

The effect of f_{O_2} on the partitioning and valence of V and Cr in garnet/melt pairs and the relation to terrestrial mantle V and Cr content

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Abstract

Chromium and vanadium are stable in multiple valence states in natural systems, and their distribution between garnet and silicate melt is not well understood. Here, the partitioning and valence state of V and Cr in experimental garnet/melt pairs have been studied at 1.8–3.0 GPa, with variable oxygen fugacity between IW-1.66 and the Ru-RuO_2 (IW+9.36) buffer. In addition, the valence state of V and Cr has been measured in several high-pressure (majoritic garnet up to 20 GPa) experimental garnets, some natural megacrystic garnets from the western United States, and a suite of mantle garnets from South Africa. The results show that Cr remains in trivalent in garnet across a wide range of oxygen fugacities. Vanadium, on the other hand, exhibits variable valence state from 2.5 to 3.7 in the garnets and from 3.0 to 4.0 in the glasses. The valence state of V is always greater in the glass than in the garnet. Moreover, the garnet/melt partition coefficient, D(V), is highest when V is trivalent, at the most reduced conditions investigated (IW-1.66 to FMQ). The $V^{2.5+}$ measured in high *P-T* experimental garnets is consistent with the reduced nature of those metal-bearing systems. The low V valence state measured in natural megacrystic garnets is consistent with f_{O_2} close to the IW buffer, overlapping the range of f_{O_2} measured independently by Fe^{2+}/Fe^{3+} techniques on similar samples. However, the valence state of V measured in a suite of mantle garnets from South Africa is constant across a 3 log f_{O_2} unit range (FMQ-1.8 to FMQ-4.5), suggesting that the valence state of V is controlled by the crystal chemistry of the garnets rather than f_{O_2} variations. The compatibility of V and Cr in garnets and other deep mantle silicates indicates that the depletion of these elements in the Earth's primitive upper mantle could be due to partitioning into lower mantle phases as well as into metal.

Keywords: Garnet, silicate melt, mantle, siderophile