

V oxidation state and coordination number in silicate glasses by XAS

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ABSTRACT

The local structure of vanadium (V) in synthetic glasses of basaltic composition has been studied by means of high-resolution V *K*-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy to obtain quantitative data on <V-O> distances, V coordination number (CN), and oxidation state. The compositions and experimental conditions were chosen so as to verify the effect of bulk-glass composition (using a diopside-anorthite composition, a sodium disilicate glass, and an iron-titanium-bearing basaltic glass) and V content (from 0.1 to 5 V₂O₅ wt%) on the structural role of V in these glasses.

The combined analysis of high-resolution XANES spectra and EXAFS data indicate that on average, the Fe-free glasses synthesized in air show vanadium in the V⁵⁺ state, mainly in tetrahedral coordination (less than 20% ⁵¹V⁵⁺) and with <V-O> distances of 1.697 (± 0.020) Å, in agreement with the values found for tetrahedral V in minerals. In contrast, the Fe-bearing basaltic glasses display a mixture of V⁵⁺ in fourfold and fivefold coordination, 40% ⁴¹V⁵⁺–60% ⁵¹V⁵⁺ in proportion, and the EXAFS-derived distances and coordination numbers are in agreement with this interpretation. No significant changes in the V local structure were found in the glasses analyzed as a function of V-contents in the 0.1 to 5 V₂O₅ wt% range. The data obtained suggest that the structural role of vanadium in these melts is rather insensitive to bulk composition, in terms of V and alkali content, but can be strongly affected by the presence of other transition elements, e.g., Fe³⁺ competing with V to enter the tetrahedral framework.