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Chemical variability in vyacheslavite, $U(PO_4)(OH)$: Crystal-chemical implications for hydrous and hydroxylated U^{4+}, Ca, and REE phosphates

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Abstract

Particularly interesting chemical variability in the U^{4+} phosphate mineral vyacheslavite from Menzenschwand (Germany) has been discovered and investigated by means of electron-diffraction and micro-chemical methods. Suggested variability comprises the elevated contents of calcium and rare-earth elements (REEs or *Ln*). Based on the crystal structure refinement from 3D electron diffraction data, the structural formula of Ca-rich vyacheslavite studied is $U_{0.895}Ca_{0.105}PO_4(OH)_{0.790}(H_2O)_{0.210}$. In general, such compositional variability involving Ca^{2+} can be expressed as $U_{1-x}Ca_xPO_4(OH)_{1-2x}(H_2O)_{2x}$. Based on detailed electron-probe microanalysis, regions extremely enriched in Y and *Ln* have been discovered, characterized by the contents up to 11 wt% of Y_2O_3 and ~4.5 wt% of Ln_2O_3. In addition to the above-mentioned substitution mechanism, substitution involving Y and *Ln* can be expressed as $U^{4+} + OH^- \rightarrow REE^{3+} + H_2O$. Although the structure refinement has not provided direct evidence of H_2O in the studied nano-fragments of vyacheslavite, the presence of H_2O and its substitution at OH^- sites is a reasonable and necessary charge-balancing mechanism. One H atom site was located during structure refinements; however, an additional H-site is only partially occupied and thus was not revealed from the refinement despite the high-quality data. Substitutional trends observed here suggest possible miscibility or structural relationship between vyacheslavite, rhabdophane, and ningyoite that may depend strongly on OH/H_2O content, considering that all crystallize under similar paragenetic conditions.

Keywords: Vyacheslavite, crystal structure, chemical composition, electron-diffraction tomography, miscibility, rhabdophane, uranium deposits