

## 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