Chemical variability in vyacheslavite, U(PO₄)(OH): crystal-chemical implications for hydrous and hydroxylated U⁴⁺, Ca and REE phosphates

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ABSTRACT

Particularly interesting chemical variability in the U⁴⁺ phosphate mineral vyacheslavite from Menzenschwand (Germany) has been discovered and investigated by means of electron-diffraction and micro-chemical methods. Suggested variability comprises namely the elevated contents of calcium and rare-earth elements (REEs). 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 Ca²⁺ can be expressed as $U_1$-$xCa_xPO_4(OH)_{1-2x}(H_2O)_{2x}$. 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 $U^{4+} + OH^- \rightarrow REE^{3+} + H_2O$. Though 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

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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 of 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$_2$O content; considering that all crystallize under similar paragenetic conditions.

Keywords: vyacheslavite; crystal structure; chemical composition; electron-diffraction tomography; miscibility, rhabdophane, uranium deposits.

INTRODUCTION

Only two U$^{4+}$ phosphates without additional metal cations are known from nature: lermontovite U$^{4+}$(PO$_4$)(OH)(H$_2$O) (Melkov et al. 1984), and vyacheslavite, U$^{4+}$(PO$_4$)(OH) (Belova et al. 1984). These minerals form as products of reduction of U$^{6+}$ to U$^{4+}$ in the supergene enrichment areas of the oxidation zones of U deposits. Together with the other U$^{4+}$-containing mineral, ningyoite, CaU$^{4+}$(PO$_4$)$_2$(H$_2$O)$_2$, they are substantial constituents of secondary U deposits and are of considerable economic importance (Doinikova 2007). Nevertheless, they have remained poorly defined, due to the fact that they are usually poorly crystalline or only form nanocrystals, preventing them from being characterized by conventional methods. Recently, Steciuk et al. (2019) reported the first structure determination of vyacheslavite from natural nanocrystals using 3D electron diffraction technique (Vincent and Midgley 1994; Gemmi and Lanza 2019; Gemmi and Mugniaoli 2019). Additionally, Density-Functional-Theory (DFT) calculations (Steciuk et al. 2019) showed that vyacheslavite contains no molecular H$_2$O, in contrast to previous findings.
(Belova et al. 1984). During crystal structure studies, we observed significant chemical variability in specimens of vyacheslavite originating from the Menzenschwand uranium deposit (Black Forest Mts., Germany). Here, we report on the results of this study, documenting that (Ca,REE)-rich vyacheslavite may represent an intermediate partially hydrated member related to U$^{4+}$, Ca$^{2+}$, Ln$^{3+}$-bearing hydroxyl phosphates, such as ningyoite and rhabdophane.

**MATERIAL DESCRIPTION**

Samples we investigated in this study originate from the Menzenschwand (Krunkelbach) uranium deposit, Black Forest Mountains, Germany, and were retrieved from the former Dietre Nicolai collection via Carsten Slotta (Mintreasure.com). The matrix of the specimen consists of quartz (partially smoky-quartz), which crystallized into cavities. The pyramidal terminations of quartz are covered by limonite overgrown by dark-green to the green crusts of vyacheslavite. Abundant hematite is also present. Crusts of vyacheslavite revealed upon trimming cover primary ore minerals, which have a metallic or semi-metallic luster. Uraninite and pyrite occur intimately associated.

**CHEMICAL ANALYSIS**

Vyacheslavite and related minerals were analyzed by electron microprobe using a Cameca SX100 electron microprobe (Masaryk University, Brno) operating in wavelength dispersive spectroscopy mode using an accelerating voltage of 15 kV, and a beam current of 20 nA for vyacheslavite and 40 nA for uranium. The beam diameter was set to 15 μm for vyacheslavite and 5 μm for (Ca, REE)-rich vyacheslavite and uranium. The beam diameter was set to 15 μm for vyacheslavite and 5 μm for (Ca, REE)-rich vyacheslavite and uranium. Concentrations of elements other than those reported in Table 1 were below detection limits (ca 0.05–0.10 wt. %). Standards used for
calibration are listed in Table 1. Raw X-ray intensities were corrected for matrix effects with a
\( \Phi(\rho z) \) algorithm of \textit{X-PHI} routine (Merlet 1994).

Uraninite was measured using prolonged counting times on Pb \( M\alpha \) (240s), and on U \( M\beta \), Th \( M\alpha \) and Y \( L\alpha \) (60s) in order to improve the statistics for chemical dating. Additionally, the
concentration of Pb and U were corrected for spectral interferences, see Škácha et al. (2009) for
details. Assuming that the total Pb in uraninite is radiogenic, the chemical age was calculated by
the equation published by Montel et al. (1996).

\textit{Laser ablation-ion-coupled-plasma mass spectroscopy (LA-ICP-MS)}

The trace-element content of vyacheslavite and uraninite was investigated by LA-ICP-MS
using an Agilent 7500ce quadrupole ICP-MS with an attached UP 213 laser ablation system. The
sample was ablated using a Q-switched Nd:YAG laser operating at a wavelength of 213 nm
(pulse duration of 4.2 ns). Ablated material was transported from the sample chamber using
helium carrier gas (1 L/min) and mixed with argon (0.6 L/min) prior to the torch. Potential
polyatomic interferences were minimized by a collision reaction cell in He mode (2 mL/min).
The contents of major to trace elements were determined after laser ablation of individual spots at
the following conditions: diameter 55 \( \mu \text{m} \), fluence of laser beam 7 J.cm \textsuperscript{-2}, frequency 10 Hz and
spot ablation time 60 s. The contents of elements of interest were determined using SRM NIST
610 as a standard, NIST 612 as an internal control and U and Ca as an internal reference element.
Calculations were performed after baseline correction and integration of peak areas.

\textit{Vyacheslavite}
Vyacheslavite is, along with uraninite, a dominant component of the studied section (Fig. 1). Locally grains of clausthalite, PbSe, are sparsely embedded. In general, vyacheslavite is chemically homogeneous in BSE images, except of very narrow rims at the border with uraninite grains which are darker, qualitatively, possibly due to less enrichment in REEs or higher Ca:U content. These rims adhere to a (Ca, REE)-rich vyacheslavite (see below). Typical vyacheslavite, nevertheless, also contains Ln and Y, up to ~1.5 wt. % Ln2O3 and ~ 3 wt. % Y2O3 and a slightly elevated content of Ca (~0.8 wt. % CaO). Elemental maps in Fig. 2 demonstrate the chemical variability and textural relations among these phases. The occupancy of the octahedral site of vyacheslavite is shown in Fig. 6. The sum of the analyzed oxides is ~96.5 wt. %. The corresponding empirical formula calculated from 9 individual analyses on the basis of 2 cations pfu is: U_{0.87}Ca_{0.05}Y_{0.08}Ln_{0.02}[(PO_4)_{0.80}(SiO_4)_{0.10}(AsO_4)_{0.05}(AlO_4)_{0.02}(SO_4)_{0.01}](OH)_{0.87} The sum of Ln, determined by LA-ICP-MS, is ~14000 ppm, where the dominant Ln^{3+} is Dy, at ~3500 ppm, see Table 2). The REE pattern normalized to post-Archean Australian Shale (PAAS, McLennan, 1989) shows a strong depletion in light REE and only a small Eu anomaly (Eu_N/Eu*_{N} = 1.57), see Fig. 4.

(Ca, REE)-rich vyacheslavite

In the polished-section studied, (Ca, REE)-rich vyacheslavite has been identified forming thin (~5 µm) rims and isolated aggregates at the border with uraninite. From observations in BSE images (Fig. 1, 2), it is also apparent that locally, this rim is surrounded by a thin “crust” of uraninite. In places, uraninite forms isolated globular aggregates in vyacheslavite. This type of vyacheslavite is characteristic by increased contents of Y (up to 11 wt. % of Y2O3), Ln (~4.5 wt. % of Ln2O3), and Ca (3.8 wt. % CaO). It also contains less As but more Si (Table 1) than...
vyacheslavite, which is more distant from uraninite. The empirical formula calculated from 3 individual analyses on the basis of 2 cations pfu is:

$$U_{0.64}Y_{0.29}Ca_{0.20}Ln_{0.07}[(PO_4)_{0.66}(SiO_4)_{0.11}(AsO_4)_{0.02}(AlO_4)_{0.01}](OH)_{1.47}$$ (where the dominant Ln$^{3+}$ is Dy). The small size of this phase did not allow trace-element measurements for the suite of Ln by LA-ICP-MS. The occupancy of the octahedral site based on these analyses is shown in Fig. 3.

**Uraninite**

Uraninite is a mixed-valence uranium oxide with a defective fluorite-type structure, which can accommodate a large amount of di- and trivalent elements (Ca$^{2+}$, REE$^{3+}$), and thus the structural formula can be expressed as $$(U^{4+}_{1-x-y-z}U^{6+}_{x}R^{3+}_{y}R^{2+}_{z})O_{2+z-x-y-z}$$ (Janeczek and Ewing 1992). The presence of Si in uraninite analyses is typically ascribed to coffinitization; however, a high content of V, As, P, and Zr has been occasionally reported (Škácha et al. 2009, Alexandre et al. 2015, René et al. 2019). Usually, high P, As or Zr content is concurrent with elevated Si content.

Uraninite aggregates associated with vyacheslavite are homogeneous in BSE images, lacking apparent features of alteration (besides replacement by vyacheslavite along the rim) and encloses pyrite fragments in the central parts. The chemical composition of uraninite is characterized by high As content (3.9 wt. % of As$_2$O$_5$) and P (2.3 wt. % of P$_2$O$_5$) and an elevated content of Ca (0.3 wt. % CaO), Al (0.5 wt. % of Al$_2$O$_3$) and Y (0.2 wt. % of Y$_2$O$_3$) and remarkably low Si (0.3 wt. % SiO$_2$), see Table 1. Considering U as tetravalent, the total is 97.4 wt. %; the presence of U$^{6+}$, which was not measured but is very likely present, would lead to slightly higher calculated totals. Low chemical variability and limited number of analyses do not allow for an elucidation of the substitution mechanisms involving As and P into the uraninite structure. The content of Ln's in uraninite obtained from LA-ICP-MS is ~2000 ppm again,
containing Dy as the most abundant element (Table 2). Distribution of REE normalized by Post Archean Australian Shale (PAAS; McLennan 1989) and its comparison with the REE pattern of uraninite I–III form Menzeschwand (Göb et al. 2013) is shown in Fig. 4. Concerning uraninite II and III (Göb et al. 2013), uraninite associated with vyacheslavite is lean in light REE and enriched in medium to heavy REE. The shape of the REE pattern of studied uraninite, vyacheslavite, and (Ca, REE)-rich vyacheslavite are similar, but the latter phase has several times higher REE content with respect to uraninite (c.f., Fig. 4).

**STRUCTURE OF CA-RICH VYACESLAVITE**

*Single-crystal 3D electron diffraction*

For transmission electron microscopy (TEM) investigations, the sample was crushed without solvent and deposited on a Cu-grid with a thin film of holey amorphous carbon. The grid was plunged into liquid nitrogen and then transferred to a FEI Tecnai 02 transmission electron microscope (TEM) (acceleration voltage of 200 kV, LaB₆) using a Gatan cryo-transfer holder. Precession-assisted 3D electron diffraction (3D ED) data sets of non-oriented patterns (see Vincent and Midgley 1994; Kolb et al. 2007, 2008; Gemmi et al. 2019) were recorded at 100K on several crystals with the precession device Nanomegas Digistar and a side-mounted CCD camera Olympus Veleta with 14bit dynamic range energy-dispersive analyzer Octane silicon drift detector (SDD) EDAX (Fig. 5). The precession angle was set to 1° with a tilt step of 1°. To preserve the crystal during the data acquisition, low illumination setting were used (condenser aperture of 10 μm with a spot size 7 or 8 μm). 3D ED data were analyzed using the computer programs PETS2.0 (Palatinus et al. 2019), Superflip (Palatinus and Chapuis 2007), and Jana2006 (Petříček et al. 2014). For each 3D ED data set, two hkl-type files are obtained with associated
intensities and estimated standard deviations based on counting statistics: one for structure
solution and the kinematical refinement, and another file dedicated to the dynamical refinement
where each ED frame is considered independent (Palatinus et al. 2015a, b). We focused our
attention on the Ca-rich areas of vyacheslavite that can be easily located via EDS coupled to our
TEM.

Data processing and refinement

All the data sets were processed using the new options available in PETS2.0: especially
the optimization of the frame orientation that improves data reduction and refinement. The
refinement of Ca-rich vyacheslavite was first performed without the hydrogen position to
determine the proportion of calcium (Fig. 6). All refinements have been done using Jana2006.
The refinement against the four 3D ED data sets independently gives a Ca proportion
ranging from 0.057(7) to 0.123(5) Ca, and the combination of all data leads to Ca = 0.104(3).
These refinements were carried out, assuming only Ca and U in the site. Refinements with and
without Ca substituting for U provided similar $R_{\text{obs}}$ values: $R_{\text{obs}}$ (without Ca) = 0.0919, $R_{\text{obs}}$ (with
Ca) = 0.0910 (Table 3). However, the values of atomic displacement parameters decreased
significantly to reach a more relevant value. The presence of a maximum corresponding to the
expected hydrogen position in the difference electrostatic potential map is an indication of the
high data quality (Fig. 6). As the next step, refinement, including hydrogen, was done by
combining all four data blocks in order to improve the statistics. Yttrium was not considered in
the refinement as it was not relevant to introduce a third atom (Y) having a scattering power
between Ca and U. It means that the refined amount of Ca is most likely overestimated in this
study. However, the evolution of the atomic displacement parameter for the U site after
introduction of Ca clearly indicates the presence of atom with a lower-scattering power than that of U (meaning those of Ca+Y).

Structure description

Generally, the structure of Ca-rich vyacheslavite is similar to that of vyacheslavite reported already (Steciuk et al. 2019). It contains a $U^{4+}$ cation coordinated in the form of a distorted square antiprism. The U polyhedra share edges with PO$_4$ tetrahedra to form chains extending parallel to [100]. The chains polymerize along the [010] by sharing edges between U polyhedra, and by U polyhedra sharing corners with the PO$_4$ tetrahedra of the adjacent chains. The structure thus contains complex uranium phosphate sheets running parallel to (001). These are interlinked by PO$_4$ tetrahedra that share corners with U polyhedra from the next layer. The result is a robust framework with cavities.

In the case of the Ca-rich vyacheslavite the strongest residual electrostatic potential maxima obtained after inclusion of the H atom into the refinement is most likely a Fourier-series artifact stemming from the symmetry. After several tests, we concluded that it cannot correspond to any additional oxygen position present instead of the O4 atom when the U is substituted by Ca. The first attempts showed that it is not compatible with reasonable bond valence values calculated then for Ca (>3.5 $v_u$). Moreover, it led to negative ADPs for this additional O site.

The final structural parameters for the Ca-rich vyacheslavite can be found in the CIF file given as supplementary. The refined structure model is displayed in Fig. 6; refinement parameters are listed in Table 3. With an average $x$ value of 0.105, the composition can be written as $U_{0.895}Ca_{0.105}PO_4(OH)_{0.790}(H_2O)_{0.210}$ (assuming no Y). The bond-valence analysis supports the
assumption that locally, H$_2$O substitutes for OH$^-$ in the structure to compensate for Ca$^{2+}$U$^{4+}$ substitution (Table 3).

**DISCUSSION**

$Ca^{2+}$ and REE$^{3+}$ for U$^{4+}$ substitution mechanism

When U$^{4+}$ is substituted by Ca$^{2+}$, two positive charges have to be compensated to keep the structure electroneutral. The first option would comprise a partially occupied O4 (and corresponding H1o4) as (OH)$_{1-2x}$ (where $x$ is the Ca-fraction). Nevertheless, it is not likely, namely, because the hydrogen position was evident from the difference Fourier map, it is likely then that it cannot correspond just to a partially occupied H site. The second option to be considered: an H$_2$O instead of the OH is present when the Ca substitution takes place, leading to an aqua-hydroxo calcium complex. Therefore, the vyacheslavite composition as studied by electron diffraction, may be expressed as $U_{1-x}Ca_xPO_4(OH)_{1-2x}(H_2O)_{2x}$. The conclusion is that the additional H-site is only partially occupied, possibly disordered and cannot be thus revealed from the refinement despite the high-quality data. The electron-probe microanalysis, nevertheless, documented high concentrations of REE$^{3+}$ along with Ca$^{2+}$, at least at some regions of the studied section. Similarly, to the substitution of Ca$^{2+}$ for U$^{4+}$ as $U^{4+} + 2OH^- \rightarrow Ca^{2+} + 2H_2O$, the substitution involving Y and Ln can be simply given as $U^{4+} + OH^- \rightarrow REE^{3+} + H_2O$.

Structure implications for ningyoite

Ningyoite has been described by Muto et al. (1959) as the main ore mineral in exogenic U deposits near Ningyo-Toge, Japan. They ascribed to it the formula $U_{1-x}Ca_{1-x}REE_{2x}(PO_4)_2(H_2O)_{1-2x}$, where $x$ ranges from ~0.1 to 0.2. Later on (see, e.g., Doinikova 2007), the formula was...
expressed in a simplified form, CaU(PO_4)_2·2H_2O. The official IMA formula kept today is (U,Ca,Ce)_2(PO_4)_2·1–2H_2O. The structure of this mineral has not been solved so far. Nevertheless, Muto et al. (1959) based on the similarity of the ningyoite powder XRD data and rhabdophane, concluded that ningyoite has a rhabdophane-type structure and possibly can form a solid solution. Based on current work it is impossible to decide if ningyoite adopts the rhabdophane- or vyacheslavite-type structure. The close chemical relationship of these minerals with churchite-(Y), and its potential connection with other Ca, U^{4+}, REE-phosphate mineral equilibria cannot be ignored, although it adopts an entirely distinctive crystal structure (Kohlman et al. 1994). Notwithstanding, both the structural and WDS investigations led us to the hypothesis that a solid-solution or at least a close topological similarity may exist between vyacheslavite and ningyoite (Fig. 4). Its extent is dependent on the capability of the vyacheslavite structure to accommodate H_2O. On close inspection of the structure of rhabdophane-(Ce) (Money 1948), we can distinguish certain significant differences, namely in the connectivity between Ce and PO_4 in rhabdophane and U/Ca and PO_4 in vyacheslavite (Fig. 6). In summary, the accommodation of REE and Ca, along with H_2O incorporation due to the charge-balance requirements into the vyacheslavite structure is possible, but the extent remains unknown as well as the answer to the question of whether ningyoite has a rhabdophane-type of structure or it is just somewhat similar. These questions remain open for future research.

Chemical analyses of natural ningyoite commonly show enrichment in REE, via the substitution Ca^{2+} + U^{4+} → 2REE^{3+} and a departure from the ideal stoichiometry in the octahedral site, as well as between octahedral and tetrahedral sites, and commonly contains elevated amounts of Fe, Pb (common), Zr, Si, and S (Scharmova and Scharm 1994; René et al. 2019). The tetrahedral-site deficiency also observed in the (Ca, REE)-rich vyacheslavite from
Menzenschwand and elevated Si, Fe and S supports that the observed compositional variation
trends towards a substantial chemical similarity with ningyoite.

Based on the high Ca and P content in coffinite, \( \text{U}^{4+}\text{SiO}_4(\text{H}_2\text{O})_n, 0<n<2 \) (Deditius et al. 2008), from Bangombé, Gabon, Janeczek and Ewing (1996) suggested a solid solution between coffinite and ningyoite. However, TEM observations of similar phases from the same locality instead revealed xenotime-type substitution and nanoscale intergrowths of amorphous coffinite and (U, Ca, \( \text{REE} \)) phosphate (Utsunomiya et al. 2008, Deditius et al. 2009). Considering these observations, we are unable to conclude whether elevated Si contents in vyacheslavite and (Ca, \( \text{REE} \)-rich vyacheslavite could represent participation of the coffinite-moiety \textit{via} a different substitution vector, or whether it represents a nanoscale intergrowths with the Si-rich phase.

Vyacheslavite occurrence at Menzenschwand: conditions of formation

The Menzenschwand U deposit in the Black Forest Mts. (Baden-Württemberg, Germany), is famous for various supergene uranium minerals; the zone of the supergene oxidation is extensively developed (Markl and Wolfsried 2011). Among the known supergene U minerals that occur there, two contain U in the reduced form: vyacheslavite and the uranyl-oxide mineral ianthinite, \( \left[\text{U}^{4+}_{12}\text{UO}_2\text{O}_6(\text{OH})_4(\text{H}_2\text{O})_4\right](\text{H}_2\text{O})_5 \) (Burns et al. 1997). Both minerals occur in a somewhat similar association, which is, however, relatively common at Menzenschwand. In the quartz gangue there is abundant fluorite, hematite, and sulfides, and among others, unusually large amounts of pyrite. The significant role of pyrite (and other sulfides) and its oxidation has been stressed by Göb et al. (2013). The presence of both vyacheslavite and ianthinite is tightly linked either to the relative abundance of pyrite (and uraninite) in the gangue or to the abundance of goethite and other Fe-supergene oxidemehanismplausible for the formation of vyacheslavite.
in the corresponding step no. 3: “If the reaction with sulfide proceeds, it can lead to a significant
decrease of $f_{O_2}$ and finally to the reduction of $U^{6+}$ to $U^{4+}$ and precipitation of uraninite. The
observed pseudomorphs of uraninite III after secondary uranyl minerals (especially ianthinite) or
pyrite are nicely explained by this scenario, which would occur if water percolating through the
rock gets trapped in a vug and reacts under the closed-system conditions and low-fluid/mineral
ratios with the sulfides in direct contact.” The vuggy (cavernous) quartz gangue seems to be an
ideal trap, where such micro-conditions can develop. For the formation of vyacheslavite, the
presence of PO$_4^{3-}$ is necessary to be within the system. As noted by Göb et al. (2013), phosphate
minerals are abundant in Menzenschwand in general. However, phosphate concentrations in the
(recent) mining waters are low (Göb et al. 2013), which can be explained by the effective
removal of phosphate from the Menzenschwand waters, most probably by precipitation of
phosphates. They further claimed that the hypothesis is further supported by the fact that, besides
uranyl phosphates, other phosphates are common at Menzenschwand, namely the REE-phosphate
churchite-(Y) and the Ba-Al phosphate gorceixite (Hofmann 1989; Göb et al. 2011, 2013; Markl
and Wolfsried 2011). Nevertheless, it is very likely that phosphate necessary for the formation of
vyacheslavite originates from the dissolution of torbernite as the pH of the solution decreases by
the continuing massive pyrite oxidation (c.f. step I in Göb et al. 2013). Phosphorus, can be,
however, also derived from the dissolution of apatite (e.g. in the host rock), which is unstable
under the low pH.

Based on SEM/BSE observations, it is likely that vyacheslavite replaces uraninite in-situ,
forming pseudomorphoses that adopt the colomorph texture of the original pitchblende (Fig. 1),
or that it assumed this shape by growing along the surfaces of uraninite grains. The REE patterns
of vyacheslavite and pitchblende are very similar (Fig. 4); the only difference is the magnitude of

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REE concentration, which is much higher in vyacheslavite, i.e., in the product of the reaction. It seems that little to no REE fractionation takes place during its formation, as there is no or only weak positive anomaly in Ce content. We think this supports the scenario mentioned above (step #3 in Göb et al. 2013), which comprises local and isolated systems. While the phosphate was obtained from locally dissolved torbernite, U could be derived both from torbernite and uraninite and REE is unambiguously sourced from altered uraninite. We note that normalized REE pattern of vyacheslavite from Menzenschwand is entirely distinct from those reported for uranyl silicates by Göb et al. (2013), but similar to uranyl phosphates and arsenates as well as the waters sampled in mine (Göb et al. 2013), that differ in the magnitude of concentration. This can, however, suggest that it formed from the same fluids percolating at Menzenschwand (and from uranyl phosphates and arsenates formed there, in general). This is in line with the conclusion of Göb et al. (2013): “Their REE patterns reflect those of the host-rock derived waters (Fig. 7), which suggests input from the host rock. However, since fluorite from the vein has an REE pattern similar to those observed in the uranyl phosphates and arsenates, an influence from the vein is also possible.” It is possible that both mechanisms contributed (depending on local conditions) to vyacheslavite formation.

Chemical dating of uraninite

The Menzenschwand deposit is located at the vicinity of the Krunkelbach fault in Bärhalde granite (14 ppm U; Hofmann and Eikenberg 1991), which hosts magmatic uraninite (uraninite I following the terminology by Göb et al. 2013) which is believed to be a source of hydrothermal uraninite (uraninite II) of Menzenschwand deposit. Its formation was dated to roughly 300 Ma by various isotopic techniques (Hofmann and Eikenberg 1991; Meshik et al. 2000) with a lower
limit U–Pb uraninite II discordia intersection at ca. 50 Ma, indicating the age of Pb-loss.

Hoffmann and Eikenberg (1991) also reported chemical ages of uraninite in the range 41–49 Ma, which agree reasonably well with the discordia intersection age, indicating it was likely formed during tertiary hydrothermal activity. Various secondary uranium minerals were dated between roughly 0.3–1.75 Ma (Hoffmann and Eikenberg 1991; Pfaff et al. 2009). Electron microprobe chemical dating of uraninite associated with vyacheslavite yields a consistent age of 18 ±4 Ma (n = 5). This is significantly lower than has been reported by Hoffmann and Eikenberg (1991). The uraninite studied here is typically enriched in As₂O₅ (3.9 wt. %), P₂O₅ (2.3 wt. %) with low SiO₂ and CaO content. Such composition differs from eight morphological and genetic types of uraninite analyzed by Hoffmann and Eikenberg (1991). The REE content and pattern of this uraninite differ from uraninite I–III published by Göb et al. (2013), both in the shape of the normalized pattern and in character of the Eu anomaly. Göb et al. (2013) used the plot of Gd₉/Lu₉ vs La₉/Gd₉ ratios to discriminate uraninite I–III generations, reproduced here in Fig. 7. Uraninite associated with vyacheslavite does not fall into the uraninite I and II fields, and is distinct from the two analyses of uraninite III. Thus, the uraninite associated with Ca-rich vyacheslavite may represent a separate generation formed by later hydrothermal Miocene event at 18 Ma. As there is no isotopic control in the chemical dating method, it might also represent an older uraninite reworked during a hydrothermal event which caused a Pb loss. If we follow this scenario, the consistent age of individual uraninite analyses (SD = 1.4) could indicate a complete age resetting during the hydrothermal event at 18 Ma.

There were no inclusions of Pb-rich phases within uraninite, which would provide evidence for the remobilization of radiogenic lead. On the other hand, the Pb-selenide mineral clausthalite occurs as small inclusions within vyacheslavite, spatially related to the contact with
uraninite. Their formation during uraninite replacement by vyacheslavite is likely because the
vyacheslavite structure obviously does not prefer the incorporation of Pb. Its content in
vyacheslavite is below the DL of electron microprobe (<0.10 wt. % Pb). Co-precipitation of
clausthalite and vyacheslavite is in accordance with reducing conditions necessary for the
formation of both phases.

**IMPLICATIONS**

Though vyacheslavite had been documented to be anhydrous, i.e. U(PO₄)(OH), our current study
has indicated this phase exhibits more significant chemical variability, manifested namely by the
incorporation of Ca²⁺ and REE³⁺. This variability is connected with the substitution of H₂O for
OH, necessary for charge balance. Such substitution plays an important role in the formation of
(and substitutions of) related uranyl oxysalts formed under low pT conditions.

Interestingly, vyacheslavite does not accumulate Pb, despite the fact that in the currently
investigated system lead is abundant – manifested by the presence of clausthalite, PbSe. In
general, both ningyoite and rhabdophane accommodate higher amounts of Pb, much higher than
the amount of radiogenic Pb formed from U-decay. The reason why is, unfortunately, beyond the
scope of this study. Nevertheless, we found it particularly interesting and useful for radiometric
dating.

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REFERENCES


FIGURE CAPTIONS

**Figure 1.** BSE image of the studied part of polished section containing vyacheslavite, Ca-REE-rich vyacheslavite and associated minerals.

**Figure 2.** X-ray (WDS) maps of the elemental distribution within the part of the analyzed section (see Fig. 1).

**Figure 3.** Ternary plot showing the occupancy of the octahedral site of vyacheslavite and (Ca, REE)-rich vyacheslavite form Menzenschwand.

**Figure 4.** REE patterns of vyacheslavite, (Ca, REE)-rich vyacheslavite, and associated uraninite normalized by PAAS (McLennan 1989). For comparison uraninite I-III (Göb et al. 2013) are shown: uraninite I represents magmatic uraninite from Bärhalde granite; uraninite II-hydrothermal uraninite, var. pitchblende; uraninite III, late uraninite replacing ianthinite.

**Figure 5.** Crystals used for the 3D ED experiments and the refinements.

**Figure 6. a)** Projection along the a-axis of vyacheslavite structure with a superimposed difference potential map showing maxima at the position of the hydrogen atom (H1o4). Isosurface levels are $3\sigma[\Delta V(r)]$ (orange) and $2\sigma[\Delta V(r)]$ (grey). The difference potential map is obtained after the dynamical refinement using the combination of four 3D ED data sets. The maxima surrounded in green at position (0, 0.5, 0.5) corresponds to a symmetry artifact. **b)** Crystal structure of rhabdophane (after Mooney 1950) viewed down a.
Figure 7. Discrimination plot for uraninite and secondary uranium minerals from Menzenschwand adopted from Göb et al. (2013) based on La, Gd and Lu values normalized to PAAS (McLennan1989).
Tables

Table 1. Electron-probe microanalyses (WDS) of vyacheslavite, (Ca,REE)-rich vyacheslavite, and uraninite from Menzenschwand.

<table>
<thead>
<tr>
<th>Element</th>
<th>Vyacheslavite</th>
<th>(Ca, REE)-rich Vyacheslavite</th>
<th>Uraninite</th>
<th>EPMA Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n = 9$</td>
<td>$1\sigma$</td>
<td>$n = 3$</td>
<td>$1\sigma$</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>17.00</td>
<td>0.83</td>
<td>15.59</td>
<td>0.13</td>
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<tr>
<td>As$_2$O$_3$</td>
<td>1.56</td>
<td>0.06</td>
<td>0.85</td>
<td>0.15</td>
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<td>SiO$_2$</td>
<td>1.72</td>
<td>0.20</td>
<td>2.28</td>
<td>0.12</td>
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<tr>
<td>UO$_2$</td>
<td>70.75</td>
<td>1.63</td>
<td>57.26</td>
<td>1.08</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>0.34</td>
<td>0.03</td>
<td>0.15</td>
<td>0.02</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>2.73</td>
<td>0.31</td>
<td>10.82</td>
<td>0.19</td>
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<tr>
<td>Sm$_2$O$_3$</td>
<td>0.12</td>
<td>0.06</td>
<td>0.23</td>
<td>0.07</td>
</tr>
<tr>
<td>Eu$_2$O$_3$</td>
<td>bdl</td>
<td>0.11</td>
<td>0.03</td>
<td>bdl</td>
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<tr>
<td>Gd$_2$O$_3$</td>
<td>0.30</td>
<td>0.06</td>
<td>0.64</td>
<td>0.11</td>
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<tr>
<td>Tb$_2$O$_3$</td>
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<td>0.18</td>
<td>0.02</td>
<td>bdl</td>
</tr>
<tr>
<td>Dy$_2$O$_3$</td>
<td>0.41</td>
<td>0.06</td>
<td>1.13</td>
<td>0.05</td>
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<tr>
<td>Ho$_2$O$_3$</td>
<td>0.09</td>
<td>0.07</td>
<td>0.36</td>
<td>0.14</td>
</tr>
<tr>
<td>Er$_2$O$_3$</td>
<td>0.22</td>
<td>0.07</td>
<td>0.76</td>
<td>0.07</td>
</tr>
<tr>
<td>Tm$_2$O$_3$</td>
<td>bdl</td>
<td>0.16</td>
<td>0.04</td>
<td>bdl</td>
</tr>
<tr>
<td>Yb$_2$O$_3$</td>
<td>0.22</td>
<td>0.07</td>
<td>0.69</td>
<td>0.07</td>
</tr>
<tr>
<td>CaO</td>
<td>0.82</td>
<td>0.14</td>
<td>3.72</td>
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</tr>
<tr>
<td>FeO</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>PbO</td>
<td>bdl</td>
<td>bdl</td>
<td>0.23</td>
<td>0.02</td>
</tr>
<tr>
<td>Total</td>
<td>96.47</td>
<td>95.04</td>
<td>97.23</td>
<td></td>
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bdl – below detection limits
Table 2. Average REE concentrations in uraninite and vyacheslavite from Menzenschwand obtained from the ICP-MS (in ppm).

<table>
<thead>
<tr>
<th></th>
<th>uraninite</th>
<th></th>
<th></th>
<th>vyacheslavite</th>
<th></th>
<th></th>
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<td></td>
<td>$n = 6$</td>
<td>$1\sigma$</td>
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<tr>
<td>Sc</td>
<td>82.4</td>
<td>3.22</td>
<td></td>
<td>161</td>
<td>54.5</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>2108</td>
<td>231</td>
<td></td>
<td>25100</td>
<td>6429</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>7.86</td>
<td>1.39</td>
<td></td>
<td>9.7</td>
<td>3.04</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
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<td>7.17</td>
<td></td>
<td>163</td>
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<tr>
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<td>1.65</td>
<td></td>
<td>89.7</td>
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<tr>
<td>Nd</td>
<td>235</td>
<td>5.89</td>
<td></td>
<td>897</td>
<td>258</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
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<td>3.4</td>
<td></td>
<td>1073</td>
<td>287</td>
<td></td>
</tr>
<tr>
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<td>2.08</td>
<td></td>
<td>433</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>232</td>
<td>10.4</td>
<td></td>
<td>1926</td>
<td>519</td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>64.2</td>
<td>1.86</td>
<td></td>
<td>486</td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>450</td>
<td>14.6</td>
<td></td>
<td>3483</td>
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</tr>
<tr>
<td>Ho</td>
<td>80.9</td>
<td>3.41</td>
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<td>161</td>
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</tr>
<tr>
<td>Er</td>
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<td>9.9</td>
<td></td>
<td>2026</td>
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<tr>
<td>Tm</td>
<td>36.8</td>
<td>1.6</td>
<td></td>
<td>301</td>
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<tr>
<td>Yb</td>
<td>269</td>
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<td></td>
<td>2199</td>
<td>567</td>
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<tr>
<td>Lu</td>
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<td>1.56</td>
<td></td>
<td>301</td>
<td>80.5</td>
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<td>$\Sigma Ln$</td>
<td>2022</td>
<td></td>
<td></td>
<td>14039</td>
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</table>
Table 3. Summary of the Ca occupancy in Ca-vyacheslavite $\text{U}_{1-x}\text{Ca}_x\text{PO}_4\text{OH}_{1-x}\text{OH}_2$ in the 4 crystals refined from 3D ED data independently and combined.

<table>
<thead>
<tr>
<th>data</th>
<th>Crystal 1</th>
<th>Crystal 2</th>
<th>Crystal 3</th>
<th>Crystal 4</th>
<th>combined</th>
<th>combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{obs}/N_{all}$</td>
<td>1478/2440</td>
<td>2066/4414</td>
<td>1870/4217</td>
<td>1395/3537</td>
<td>6809/14608</td>
<td>6809/14608</td>
</tr>
<tr>
<td>$R(\text{obs})/wR(\text{obs})$</td>
<td>9.31/8.96 %</td>
<td>8.52/7.98 %</td>
<td>9.51/9.13 %</td>
<td>8.59/8.15 %</td>
<td>9.10/8.72 %</td>
<td>9.19/8.81 %</td>
</tr>
<tr>
<td>$x$</td>
<td>0.057(7)</td>
<td>0.104(5)</td>
<td>0.105(5)</td>
<td>0.123(5)</td>
<td>0.104(3)</td>
<td>0</td>
</tr>
</tbody>
</table>
- vyacheslavite
- (Ca, REE)-rich vyacheslavite
- uraninite, this study
- uraninite I (Göb et al. 2012)
- uraninite II (Göb et al. 2012)
- uraninite III (Göb et al. 2012)