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3	Characterisation of Vandenbrandeite: A Potential Alteration
4	Product of Spent Nuclear Fuel
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11	
12	Abstract
13	The use of copper canisters in the Swedish KBS-3 concept for spent nuclear fuel
14	disposal could result in the formation of copper-bearing uranyl phases should a canister suffer
15	from defects or if the containment were to fail before reducing conditions are established in
16	the repository. Most uranyl species would be expected to display higher solubility than the
17	original uranium(IV) dioxide fuel, leading to enhanced release, though this would depend on
18	the phase and prevailing groundwater conditions. Secondary alteration products may also be
19	poorly crystalline or even amorphous, making characterisation difficult during the pre-closure
20	period owing to the high radiation field close to the canister. Vandenbrandeite,
21	(CuUO ₂ (OH) ₄), is a rare mineral in nature but known to form by alteration of primary
22	uraninite through interaction with oxidising groundwater containing dissolved copper
23	Consequently, an attempt has been made to characterise two vandenbrandeite specimens of
24	varying crystallinity by luminescence and multiple-laser Raman spectroscopy; techniques
25	amenable to remote, robotic deployment and which have proved useful in discriminating

26 other uranyl oxy-hydroxides, silicates and phosphates. The first reported luminescence 27 emission and excitation spectra for vandenbrandeite revealed near-negligible luminescence, 28 with a slightly enhanced signal for the specimen displaying poorer crystallinity. This 29 observation agrees well with density functional theory calculations. The simulated projected 30 density of state and band structure show an unlikely transition from the U f-orbitals to Cu d-31 orbitals, or O states, would be required for luminescence to be detectable; this probably 32 improves for poorly crystalline specimens as the spatial overlap between the orbitals 33 increases. Further, negligible differences in the number of peaks and peak positions were 34 detected in the laser wavelength-dependent Raman spectra although again, variation in 35 background noise and peak shape was observed based on the degree of crystallinity. Good 36 agreement was obtained between experimental and simulated Raman spectra, particularly 37 with the environmentally sensitive axial uranyl stretching modes, validating the crystal 38 system derived in this study. The findings of this study suggest luminescence spectroscopy, 39 when combined with Raman spectroscopy, may be able to both identify vandenbrandeite and 40 distinguish between crystalline and amorphous forms based on their relative luminescence 41 intensity.

42 Keywords: Raman spectroscopy; time-resolved laser fluorescence spectroscopy;
43 density functional theory Raman simulation; projected density of states.

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Introduction

Understanding the processes governing uranium mobility is essential to minimise the environmental impact from nuclear decommissioning and waste management. The KBS-3 concept for disposal of spent nuclear fuel (SNF) proposed by Sweden (Rosborg and Werme 2008), adopted by Finland (King et al. 2010) and considered by Canada (Hall and Keech 2017; Hall et al. 2021) envisages a composite, copper-iron canister, surrounded by a

51 bentonite buffer, emplaced at depth in stable crystalline bedrock. Under anoxic conditions, 52 copper is thermodynamically stable, providing sulphide concentrations remain low (King 1995; Milodowski et al. 2000, 2002). Copper corrosion is enhanced under anoxic conditions 53 54 where sulphide concentrations are high (Marcos 1996; King et al. 2013: Hall and Keech 55 2017) or under oxic conditions (Rosborg et al. 2011) and in the presence of high radiation 56 fields (Björkbacka et al. 2013; Ibrahim et al. 2018). Even with the most stringent quality 57 control procedures in place, it is anticipated that a small proportion of the canister inventory 58 will be defective (Werme 1998) and that the copper barrier will be further compromised over the long disposal timescales (> 10^4 years) that have to be considered. Should the SNF to 59 come into contact with the exterior canister, water and products of water radiolysis, there is 60 61 potential for the uranium dioxide fuel to oxidise and form secondary uranyl phases, with the 62 composition of the alteration products being dependent on the pH and local water 63 composition (e.g., Moulin and Ouzounian 1992; Read and Hooker 1992; Read et al. 2008; 64 Plášil 2014; Wen et al. 2018). With abundant copper present (7.5 tonnes per canister), one 65 phase that might form is the naturally occurring mineral, vandenbrandeite ($CuUO_2(OH)_4$), 66 which is known to be stable in the presence of H₂O₂. Dehydroxylation and decomposition 67 products of vandenbrandeite may also need to be considered given the heat generating 68 potential of the SNF (Hall et al. 2021). Thermal analysis studies (Čejka 1994; Botto et al. 69 2002) indicate that vandenbrandeite dehydroxylates from around 250 °C, transforming into 70 crystalline CuU₃O₁₀ and CuUO₄ phases around 500 °C, before decomposing at 950 °C. Other 71 candidate copper uranyl phases that could form owing to incorporation of metal cations from groundwater, host rocks and the engineered system (e.g., Frondel 1958; Buck et al. 1996; 72 73 Roh et al. 2000; Plášil 2018; Qader and Kersten 2021), include silicates (e.g., 74 cuprosklodowskite) and phosphates (e.g., torbernite, metatorbernite).

Vandenbrandeite is defined by dimers of edge-sharing uranyl pentagonal bipyramids (**Figure 1**) joined by edge-sharing Cu atoms, which are conjugated to O in a square planar configuration. These layers are connected by the axially coordinated site of a Cu square planar in one sheet to a uranyl O atom in another. A clear feature distinguishing vandenbrandeite from other uranyl oxy-hydroxides is that the Cu cations are situated within the uranyl plane whereas metal cations in other uranyl oxy-hydroxides are typically positioned between the uranyl sheets.

A small number of laser-based characterisation studies have been undertaken on vandenbrandeite. Infrared (Čejka 1994; Botto et al. 2002) and Raman spectra (Botto et al. 2002; Colmenero et al. 2019) have been reported, but there are discrepancies between the number and position of the peaks as well as their modal assignment. No luminescence spectroscopy studies appear to have been published; indeed, an online database reports that vandenbrandeite does not fluoresce

88 (http://www.webmineral.com/data/Vandenbrandeite.shtml, accessed Sep. 1, 2021).

The work presented in this study, using traditional and laser-based techniques, aims to extend our knowledge of vandenbrandeite's structural and chemical characteristics using two specimens; one showing well-developed crystallinity and another where crystal order has been affected by metamictization, a process expected to occur in highly radioactive environments and through self-irradiation of the alteration products. Comparisons are made with published Raman data (Botto et al. 2002; Colmenero et al. 2019) and a simulated spectrum derived in this study in order to identify key distinguishing features. To the best of

223 tabular lozenge-shaped crystals were found lining small vuggy cavities in the dense matrix 224 (Figure 3b). The morphology of these crystals closely resembles that of a specimen of 225 vandenbrandeite (archived at the Royal Ontario Museum of Geology and Mineralogy, 226 Canada) from the type-locality at Kalongwe, in the Katanga-Copper Belt, that was described 227 by Milne and Nuffield (1951). The sample fragments are largely monomineralic, although 228 SEM-EDXA identified the presence of minor to trace amounts of fine-grained silica, 229 magnesium silicate and magnesium-aluminium silicate intergrown with the vandenbrandeite 230 (Figure 3a, b and Figure S.1 in the Supplementary Information). These may be clay mineral 231 impurities such as chlorite, talc, sepiolite and/or serpentine, although these were not detected 232 by XRD (Figure 5). No other uranium phases were identified in this specimen.

233 Under the SEM, the NMW specimen displays much poorer crystallinity than the BGS 234 specimen. It comprises a mixture of very fine-grained, porous, earthy-textured copper-235 uranium oxide or hydrated oxide (corresponding to the blue-green material seen optically), 236 which contains irregular patches of denser interlocking crystalline copper-uranium oxide or 237 hydrated oxide (corresponding to the greenish-black material seen optically; Figure 3c, d). 238 No well-formed crystals are present, although fracture surfaces within the denser material 239 display a single prominent cleavage, as also seen in the BGS specimen. No chemical 240 differences were identified by EDXA between the porous earthy and more crystalline 241 components, and the EDXA spectrum was very similar to that obtained from the BGS sample 242 (Figure 4). The NMW sample appears to be less pure than the BGS sample: SEM-EDXA and 243 EDXA elemental mapping show that the NMW sample commonly contains trace amounts of 244 finely-disseminated silica (probably quartz or chalcedony), magnesium-aluminium silicate 245 (possibly chlorite or other clay minerals), a magnesium-aluminium carbonate (possibly 246 hydrotalcite), and calcium sulphate (probably gypsum; cf. Figure 3c. d; Figure 6). Other 247 copper minerals are present as minor to trace impurities, including: black copper oxide

(probably tenorite, CuO), copper sulphide (possibly digenite, Cu₉S₅ or chalcocite, Cu₂S), copper selenide, and copper silicate (possibly chrysocolla, Cu_{2-x}Al_x(H_{2-x}Si₂O₅)(OH)₄·nH₂O). Although the presence of these phases has not been confirmed by XRD analysis (**Figure 5**), they are plausible contaminant phases, since they have all been recorded in association with vandenbrandeite from the supergene mineral assemblage in the Musonoï Mine (Dewaele et al. 2006; Barton et al. 2014). However, and crucially for this investigation, no other uranium phases were identified by SEM-EDXA in the NMW 83.41G.M3734 sample.

255 It should be noted that the SEM images obtained in this study found no evidence that 256 either of these two vandenbrandeite samples had suffered any crystal damage caused by 257 shrinkage due to dehydration either prior to or during SEM examination unlike some other 258 hydrated uranyl minerals (e.g., autunite and becquerelite; Frankland et al. 2020, 2021). 259 Published thermogravimetric (TG) and differential thermal analysis (DTA) data indicate that 260 vandenbrandeite does not readily undergo decomposition below 250 °C (Botto et al. 2002). 261 Further evidence for the lack of vandenbrandeite decomposition can be found in the d-262 spacing, corresponding to the distance between copper uranyl sheets; i.e., the perfect cleavage 263 plane. For the BGS and NMW specimens, this feature was detected at 4.499 and 4.450 Å 264 (Figure 5), respectively; similar to the distance obtained by Colmenero et al. (2019), in their 265 experimental and computational crystal structure analysis (4.44 and 4.43 Å, respectively), 266 and also by Rosenweig and Ryan (1977; at 4.45 Å). A shoulder at 4.460 Å was observed for 267 the BGS specimen but remains unassigned.

Comparison of the XRD patterns obtained in this study to those in the RRUFFTM database (Lafuente et al. 2015) suggests that neither sample contains any other uranium phase. However, differences in relative peak intensity were observed between these specimens and the reference XRD pattern (**Figure 5**). The reflection at 4.499 Å for BGS 756/1 is strongly enhanced and multiples of this plane were observed for both specimens at

273 2.234 and 2.187 (202) and 1.494 and 1.478 Å (303), respectively. The difference can be 274 explained by variations in sample orientation. In this study, the sample mounting method 275 resulted in a significant proportion of the crystal fragments being aligned along the perfect 276 cleavage plane; thus, the intensity of this lattice spacing (d) is enhanced. Discrepancies across 277 the literature result in various assignments of this perfect cleavage plane; some authors define 278 it as the (110(plane (Milne and Nuffield 1953; Rosenweig and Ryan 1977), others the (001) 279 face (Schoep 1932; Foshag 1933), whereas a third class this as the (101) plane (Colmenero et 280 al. 2019). The apparent confusion amongst published works possibly reflects vandenbrandeite 281 exhibiting multiple minor cleavage planes (Schoep 1932; Foshag 1933; Milne and Nuffield 282 1953).

283 A recent experimental and modelled XRD crystal structure study on vandenbrandeite 284 estimated the two uranyl U-O bond lengths as 1.786 and 1.801 Å in the axial direction and an 285 average of 2.38 Å in the equatorial plane (Colmenero et al. 2019). No peaks could be 286 attributed with any confidence to the uranyl axial bond length in this study; however, a few 287 peaks with very weak intensity were detected in the uranyl equatorial plane region for both 288 specimens. The peaks at 2.234 and 2.292 Å for the BGS and NMW specimens, respectively, 289 agree well with the Cu-O bond lengths derived experimentally (2.25 Å) and theoretically 290 (2.30 Å) by Colmenero et al. (2019), although shorter Cu-O bond lengths were obtained in 291 this study (see following sub-section). Another possible assignment for the peaks at 2.234 292 and 2.292 Å could be enhanced multiples of the perfect cleavage plane whereas the peaks located around 2.44 and 2.31 Å correspond to hydrogen bonding with the uranyl ion, based 293 294 on the XRD crystal structure analysis of Rosenweig and Ryan (1977).

The two broad peaks at 16 and 22° originate from the double-sided tape use to secure the fragments onto the silicon disc and partially obscure some of the X-ray reflections from vandenbrandeite, particularly for the NMW specimen. The resulting normalised patterns

clearly show a much weaker signal for the NMW specimen, even though the total exposure
time was eight times longer than that used for BGS 756/1 (12 hours compared to 1.5 hours).
The significant reduction in signal reflects the poor crystallinity of the NMW specimen as
shown by SEM observations, possibly due to metamictization.

302

303 Modelled Crystal Structure

Two different vandenbrandeite crystal structures were created initially based on previously reported X-ray structures (Colmenero et al. 2019). One was assigned to the paramagnetic state with no initial spin moments, and the other to an A-type antiferromagnetic state with opposing initial spins on the two Cu atoms in the unit cell. The forces on both systems were relaxed to 1 meV Å⁻¹ which revealed the antiferromagnetic state to be 0.3 eV more stable than the paramagnetic at 0 K, indicating the former as the ground state.

310 Few differences were observed between the vandenbrandeite antiferromagnetic 311 crystal system derived in this study (Figure 1) and the crystal structure published by 312 Colmenero et al. (2019). The most noticeable of these changes is that the equatorial O atoms form a more symmetrical pentagon around the U atom with a slightly longer U-O_{equatorial} 313 314 average bond-length of 2.46 Å, compared to 2.38 Å, with the longer bond length agreeing 315 better with the XRD findings obtained in this study (Figure 5). The uranyl U-O axial bond 316 lengths are estimated as 1.781 and 1.812 Å on the first U atom in the unit cell and 1.792 and 317 1.795 Å for the second giving an average U-O_{axial} bond length of 1.795 Å. Shorter Cu-O bond lengths are also predicted from the antiferromagnetic structure in this study at 1.88, 1.93, 2.01 318 319 and 2.02 Å compared to the values of 2.25 and 2.30 Å reported by Colmenero et al. (2019). A 320 value of 4.38 to 4.83 Å was obtained for the distance between the equatorially arranged O 321 atoms in neighbouring sheets, which corresponds to the perfect cleavage plane spacing in the 322 BGS and NMW XRD patterns (Figure 5). The corresponding U - U interplanar distance is 323 larger at 5.30 and 5.60 Å, as the uranyl copper sheets are not directly aligned with each other;
324 however, XRD peaks with corresponding d-spacing values, within experimental error, were
325 observed (Figure 5). Overall, the similarities between the experimental XRD patterns and the
326 simulated crystal structure suggest that the model system derived in this study correlates well
327 with the mineral phase. Further validation was obtained by comparing experimental and
328 simulated Raman spectra.

329

330 Luminescence Spectroscopy

331 While luminescence and Raman spectroscopy are classed as two different techniques, 332 the underlying processes resulting in their characteristic features are similar and can result in 333 the features of one appearing in the spectrum of the other. A relevant example is a Raman 334 spectrum obtained using a laser wavelength in the visible (especially the blue-green) region, 335 which tends to be masked by luminescence effects (Driscoll et al. 2014; Lin et al. 2014; Ho et al. 2015; Frankland et al.w 2019, 2020, 2021). Thus, exploration of the luminescence 336 337 emission and excitation spectra is essential when choosing laser wavelength settings designed 338 to minimise luminescence in Raman spectroscopy.

339

Emission and Excitation Spectra. Very weak luminescence emission spectra were obtained for the two vandenbrandeite specimens, whereas an excitation spectrum could be extracted only from the NMW specimen. The limited luminescence observed was not unexpected (http://www.webmineral.com/data/Vandenbrandeite.shtml, accessed Sep. 1, 2021) and probably accounts for the lack of previous studies on vandenbrandeite luminescence in the literature.

The emission spectra are displayed in **Figure 7**. For specimen BGS 765/1, the experimental data deviate slightly from the instrumental baseline between ~ 495 to 555 nm.

This deviation is more obvious for the NMW sample with a broad peak at ~500 to 605 nm. The more pronounced signal emitted by NMW 83.41G.M3734 could reflect metamictization and the presence of defect states or vacancies, and minor impurities within the microcrystal matrix, as revealed by the SEM-EDXA data described earlier in this paper.

352 Obtaining excitation spectra for vandenbrandeite was also difficult. Only the NMW 353 specimen exhibited any features above the instrument's detection limit (grey line in Figure 354 8), again possibly due to the poorer crystallinity and/or inclusion of minor species of this 355 sample. A broad excitation feature was observed around 500 nm, which roughly coincides 356 with the start of the emission feature in Figure 7b. Another broad, but less intense, excitation 357 feature was observed, centred around 440 nm. Only two peaks at 361.4 and 423.0 nm could 358 be resolved in the excitation spectrum with any degree of confidence. To the best of our 359 knowledge, no luminescence excitation spectra have been reported for vandenbrandeite; 360 however similarly positioned excitation features have been reported for other metal-bearing 361 uranyl oxy-hydroxides (Frankland et al. 2020, 2021) suggesting that the uranyl ion may 362 exhibit some common excitation energy levels that are independent of the incorporated metal 363 cation. If this is the case, vandenbrandeite should still absorb near-UV/blue photons. These 364 features are unlikely to be detectable with the TRLFS apparatus as the photon wavelength 365 would be close to the excitation wavelength. Overall, it is unclear from the emission and 366 excitation spectra alone if the vandenbrandeite crystal structure quenches luminescence or 367 whether the incorporated metal cations are shifting the emission features into another region 368 of the electromagnetic spectrum.

369

370 **Interpretation.** Simulating the projected density of states (PDOS) provides an insight 371 into the energies and character of the allowed states in a given system. Converting the 372 difference in energies of these allowed states into wavelengths indicates those regions of the

electromagnetic spectrum in which luminescence features could potentially occur. The PDOS results for vandenbrandeite are shown in **Figure 9a** and reveal significant deviation between the α - (spin up) and β - (spin down) channels, particularly the Cu d-orbitals near the Fermi level (0 eV) and at around 1.6 eV. This asymmetry is indicative of a magnetic ground system (e.g., Pakornchote et al. 2022), in this case an A-type antiferromagnetic ground state, which is 0.3 eV lower in energy than the paramagnetic state previously assumed to be the ground state by Colmenero et al. (2019).

380 The dominant features in the PDOS (Figure 9a) correspond to the U f-orbital, 381 positioned between 2.1 and 3.6 eV, which is situated across the expected luminescence 382 emission (650 to 450 nm) and excitation regions (500 to 350 nm) for uranyl-bearing species 383 (e.g., Amayri et al. 2004; Wang et al. 2008; Arnold et al. 2009; Frankland et al. 2020, 2021). The energy is highly sensitive to the value chosen for the Hubbard-U parameter, U_{eff} , and the 384 385 relatively conservative theoretical value used in this study could lead to an underestimate in 386 the position of these states. The paucity of states projected at energies of $\sim 2.7, 2.3, 2.0$ and 387 1.6 eV (i.e., 457, 532, 633 and 785 nm) suggests negligible fluorescence effects would be 388 observed in the multiple-laser Raman spectra employed later in this study (Figure 10). The 389 appearance of unoccupied states over these energy ranges in the simulated results indicate 390 that vandenbrandeite may also absorb photons in the near-UV region at similar energies as 391 other uranyl-bearing minerals (Frankland et al. 2020, 2021). However, despite the presence of 392 states within the 450 to 650 nm region, near-negligible luminescence was detected in the vandenbrandeite emission spectra (Figure 7). Possible explanations include, but are not 393 limited to, variations in crystallinity order, chemical quenching from the Cu²⁺ cation or 394 impurities. Evidence for Cu^{2+} chemical quenching has been found in other studies (Therien 395 396 2009; Warrier and Kharkar 2018) through the dramatic reduction in luminescence intensity as

397 the fluorescing molecule binds to the free Cu^{2+} ions; however, the lack of observable features

in the luminescence emission spectra (Figure 7) requires further investigation.

399 The simulated band structure indicates how the states vary in energy in reciprocal 400 space. Two wavelength axes are shown for vandenbrandeite (Figure 9b), one for excitations 401 from the highest occupied orbital of the α channel (red), and one for excitations from the β 402 channel (blue). In the α channel case, excitation at 357 nm raises the electron into the β state 403 situated between 2.8 and 4.4 eV above the Fermi level, from which decay can occur into one 404 of the α states situated between 2.2 and 2.4 eV (i.e., between 650 and 450 nm on the α 405 wavelength axis). Excitation from the α channel is less favourable as fewer states are 406 predicted at its highest occupied orbital compared to the β channel. Furthermore, the highest 407 occupied α orbitals have significant contributions from the Cu atoms (Figure 9a), which have 408 little spatial overlap with the U f-orbitals resulting in weak transitions, based on the Franck-409 Condon principle. Greater overlap of the U and Cu orbitals would be expected in poorly 410 crystalline vandenbrandeite, such as the NMW specimen, which might result in a very weak, 411 broad luminescence emission (Figure 7b).

Excitation from the α channel could also result in the electron decaying into the β states situated around 0.8 to 1.2 eV above the Fermi level (i.e., between 650 and 450 nm using the β wavelength axis; **Figure 9b**) if the electrons undergo inter-system crossing (ISC), which is possible due to the high strength of the spin-orbit interaction in a uranium-bearing mineral. However, this pathway decays into states dominated by either Cu or O orbitals (**Figure 9a**), both of which have little spatial overlap with the U f-orbitals, again, resulting in very weak transitions being observed.

In the case of the β channel, excitation is more probable as its highest occupied band lies entirely below the Fermi level and therefore, provides many more occupied states to act as the source for the excitation (β axis in **Figure 9b**). Following excitation, the electron may

422 drop into the highest occupied level of either spin channel located between 2.2 to 2.4 eV 423 above the Fermi level. However, contributions going to the α channel must first undergo ISC 424 and would lead to a peak in the 500 - 600 nm range, as observed in **Figure 7b**. Alternatively, 425 if no ISC occurs, the electrons may decay into the β states if a transition from the U f- to Cu 426 d-orbitals occurs. Both the U-f like states (2.2 to 2.4 eV range) and the Cu-d like states (0.8 to 427 1.2 eV) show a low degree of dispersion, which is indicative of a highly localised (almost 428 atomic-like) state, resulting in little overlap between these orbitals and decreasing the 429 probability of a transition occurring according to the Franck-Condon principle.

430

431 Summary of Luminescence Findings. Overall, the negligible luminescence features 432 observed for vandenbrandeite can be explained by its simulated PDOS and band structure. 433 The findings suggest that vandenbrandeite should absorb photons in the near UV region, 434 regardless of the spin channels used, but all the decay pathways require a transition from the 435 U f- to Cu d-orbitals or O states. Very little spatial overlap is predicted between the U f- to 436 Cu -d-orbitals or O states in a well crystalline system resulting in only very weak or 437 negligible emission features being detectable experimentally for the BGS specimen. 438 However, greater spatial overlap of orbitals is expected in poorly crystalline samples 439 increasing the probably of emission transitions being observed, which agrees well with the 440 NMW luminescence spectral data. Given that SNF alteration products are also expected to be 441 amorphous or poorly crystalline, the detection of vandenbrandeite (if present) may be 442 possible using luminescence spectroscopy when combined with other laser-based techniques 443 such as Raman and laser-induced breakdown (LIBS) spectroscopy to confirm chemical 444 structure and composition, respectively.

445

446 Raman Spectroscopy

447 The extraction of information on chemical structure from Raman spectra is wellestablished but can be prone to luminescence effects where regions of the spectrum are either 448 449 wholly, or partly, masked (Driscoll et al. 2014; Lin et al. 2014; Ho et al. 2015; Frankland et 450 al. 2019, 2020, 2021). The paucity of luminescence emission features for vandenbrandeite 451 implies that, in contrast to many other uranyl-bearing species, little if any luminescence 452 interference would be observed in the Raman spectral data, regardless of which laser 453 wavelength is used in the visible and near-IR region. Nevertheless, obtaining Raman spectra 454 using multiple lasers can be beneficial as the laser wavelength and energy will govern the 455 depth of penetration into the specimen enabling bulk and, if present, surface modes to be 456 assigned. Another aspect explored in this study is the effect of the degree of mineral 457 crystallinity on Raman spectra.

458

459 Experimentally-Obtained Multiple-Laser Raman Spectra. Raman spectra were 460 collected using lasers operating at 785, 633, 532 and 457 nm for the more crystalline BGS 461 756/1 specimen (Figure 10). All the spectra display a low, relatively flat background 462 indicating limited masking of Raman features by luminescence, as predicted from the 463 luminescence emission study above together with simulated PDOS and band structure. A raised background was observed in the 457 nm spectrum covering the 2000 - 4000 cm⁻¹ 464 465 region. Converting the wavenumbers, v, for this range into wavelength, λ_s , using the Raman 466 laser wavelength, λ_i , and **Equation 1** gives values of 503 - 560 nm, which coincide with the 467 similar feature observed in the luminescence emission spectrum (Figure 7a), suggesting 468 minor luminescence masking at 457 nm.

469
$$\lambda_s = 1/[(1/\lambda_i) - (\nu/1 \times 10^7)]$$
 (1)

470 Some variation was observed in the Raman spectra for the BGS specimen at different 471 laser wavelengths (**Figure 10**). Below 1500 cm⁻¹, the most well-defined features were

obtained using the 785 nm laser whereas the 457 nm laser gave better resolution for those
peaks positioned at wavenumbers above 1500 cm⁻¹, notwithstanding the minor luminescence
effects noted previously. This change in peak definition could be linked to laser penetration
depth. Typically, only water and hydrogen bonding modes are observed above 1500 cm⁻¹,
suggesting surface or near-surface modal activation, whereas those associated with the uranyl
moiety (i.e., the bulk crystal sheets) are known to be positioned below 1500 cm⁻¹ (e.g., Ho et
al. 2014; Lu et al. 2018).

479 Variation in the degree of crystallinity also needs to be considered as this may alter 480 the width and, through this, the degree of resolution of the Raman features. A Raman 481 spectrum for the weakly crystalline NMW specimen is shown alongside the BGS sample in 482 Figure 10; only the 785 nm laser was used to characterise the NMW specimen as it produced 483 the most well-defined uranyl features. The elevated background observed probably reflects a 484 combination of poor crystallinity, minor impurities, as identified by SEM-EDXA and XRD, 485 and geometric effects. It is unlikely to be due to luminescence since no corresponding 486 masking was observed for the BGS 756/1 spectrum at 785 nm (Figure 10).

487

488 Simulated Raman Spectrum and Modal Assignment. The peak positions and 489 assigned Raman modes for the simulated vandenbrandeite spectrum are compared to 490 available experimental data and another computational study (Colmenero et al. 2019) in 491 **Table 1**. Overall, there is good agreement between the simulated and experimental datasets. 492 No additional experimental features were observed when compared to the simulated 493 spectrum, implying an absence of surface modes, which were not included in the model. The 494 experimentally-obtained Raman modes are attributed using the empirical method, which is 495 based on molecular rather than crystal structure. Given that the PDOS for vandenbrandeite 496 reveals the U f-orbitals exhibit atomic-like states (Figure 9a), the perturbations with U

497 nearest neighbours will be restricted in the crystal matrix enabling the empirical method to be498 used as a first-order approximation.

More features were simulated than resolved experimentally, which can be explained by the following: First, there are several cases where close lying multiple simulated peak positions have been assigned to the same mode, though due to limited resolution, only one or two peaks were detected experimentally. Second, some modes are known to be Raman weak resulting in features close to the experimental background. Third, the artificial 'noise' generated in the simulated spectrum is lower than that obtained for real samples due to higher specimen purity.

506 The resolved Raman 785 nm spectra for the two vandenbrandeite specimens are507 displayed in Figure 11.

A sharp peak was observed at 805 ± 3 and 804 ± 3 cm⁻¹ for the BGS and NMW 508 509 specimens, respectively, with the error taken as the variation between repeats. Using the empirical method, this feature is attributed to the uranyl symmetric stretch, $v_1(UO_2)^{2^+}$, mode. 510 511 A similarly shaped feature positioned at coincident wavenumbers, within experimental error of those found in this study, have been reported in the literature (Table 1; Botto et al. 2002; 512 Colmenero et al. 2019). Empirically, this peak is attributed to the $v_1(UO_2)^{2+}$ mode (Botto et 513 514 al. 2002; Colmenero et al. 2019), although the simulated spectra (this study and Colmenero et 515 al. 2019) reveal an accompanying bending of the free-hanging H bond connected to an 516 equatorial uranyl O atom, δ (UOH), (Figure 1 and simulated Raman vector image in the supplementary information), probably due to the lightness of this element compared to its 517 nearest neighbours. The position of the empirical $v_1(UO_2)^{2+}$ feature (or the computationally 518 simulated $v_1(UO_2)^{2+}$ and $\delta(UOH)$ modes) is known to be highly sensitive to its local 519 520 environment (Bartlett and Cooney 1989). A relationship between the position of this feature

521 (in cm⁻¹) and the U-O bond length, d_{U-O} , in Å, was derived by Bartlett and Cooney (1989;

522 Equation 2) and appears to hold well for all minerals (Bartlett and Cooney 1989).

523
$$d_{U-0} = 106.5[\nu_1(UO_2)^{2+}]^{-2/3} + 0.575$$
 (2)

From the $v_1(UO_2)^{2+}$ mode peak position, d_{U-Q} was calculated as 1.81 ± 0.1 Å for both 524 specimens (with the error in d_{U-O} derived from the variation in the $v_1(UO_2)^{2+}$ mode peak 525 526 positions). Traditionally, d_{U-Q} values are extracted from XRD analysis; a technique restricted 527 to well-ordered crystalline materials but not those materials affected by, for example, 528 metamictization. Values of 1.786 and 1.801 Å (Colmenero et al. 2019) have been reported for 529 axial d_{U-Q} from XRD analysis (compared to 1.792, 1.795, 1.781 and 1.812 Å in this study) of which the largest value coincides with the single value extracted from the Raman spectra 530 531 here.

Another variable that can be estimated from the resolved $v_1(UO_2)^{2+}$ mode peak position is the U-O bond force constant, k_{U-O} , using Badger's law (**Equation 3**; Badger 1935; Jones 1959), which is expected to be useful to those modelling the alteration pathways of SNF. **Equation 3** calculates k_{U-O} in units of millidynes Å⁻¹ (1 millidyne Å⁻¹ equals 100 N m⁻¹) and gives values of 4.90 ± 0.07 and 4.88 ± 0.07 millidynes Å⁻¹ for the BGS and NMW specimens, respectively. These predicted values are lower than those calculated by Botto et al. (2002) from their Raman spectra due to differences in the formulae used.

539

$$k_{U-0} = [1.08/(d_{U-0} - 1.17)]^3$$
(3)

Bartlett and Cooney (1989) also derived another relationship linking the uranyl antisymmetric stretch, $v_3(UO_2)^{2+}$, mode to d_{U-O} (**Equation 4**). This equation is more commonly used with IR characterisation as the $v_3(UO_2)^{2+}$ mode is IR-strong and Ramanweak; however, both published Raman spectra display this mode (**Table 1**; Botto et al. 2002; Colmenero et al. 2019), suggesting that the uranyl bond deviates slightly from linearity. Further evidence for the non-linear nature of the axial uranyl bond is revealed by the

546 simulated crystal structure (Figure 1), displaying a bond angle of $\sim 176^{\circ}$. The predicted position of the $v_3(UO_2)^{2+}$ mode, based on our empirically assigned $v_1(UO_2)^{2+}$ peaks, are 872 ± 547 4 and 870 ± 4 cm⁻¹ for the BGS and NMW specimens, respectively. A weak intensity peak 548 was resolved nearby at 881 cm⁻¹ in the BGS specimen (Figure 11) and, based on this 549 evidence alone, is empirically attributed to the $v_3(UO_2)^{2+}$ mode. Other experimental Raman 550 studies have assigned this mode at 862 cm⁻¹ (Botto et al. 2002) and 844 cm⁻¹ (Colmenero et 551 al. 2019), again using the empirical method, whereas simulated spectra reveal that the 552 $v_3(UO_2)^{2+}$ mode is accompanied by $\delta(UOH)$ (**Table 1**). Given that the $v_3(UO_2)^{2+}$ feature is 553 554 known to be IR strong, the position of this peak can be estimated through comparison with IR spectra. The IR spectrum published by Botto et al. (2002) reported the $v_3(UO_2)^{2+}$ feature at 555 897 cm⁻¹, which is close to the experimentally observed peak position in this study. 556

557
$$d_{U-0} = 92.42 [\nu_3 (UO_2)^{2+}]^{-2/3} + 0.804$$
(4)

At higher wavenumbers, a broad but weak peak was resolved at 967 cm⁻¹ in the BGS 558 specimen and is empirically and computationally assigned to δ (UOH), which is an IR mode 559 560 and therefore, Raman-weak. It is plausible that this mode is present in the NMW specimen; 561 however, the overall Raman signal obtained was much lower preventing this very small peak from being observed. It should be noted that both IR (Botto et al. 2002) and simulated Raman 562 563 (this study and Colmenero et al. 2019) spectra report multiple peaks for this mode as does the 564 experimentally obtained Raman spectrum by Colmenero et al. (2019). However, the simulation of Colmenero et al. (2019) reports the environmentally sensitive $v_1(UO_2)^{2+}$ and 565 $v_3(\text{UO}_2)^{2+}$ modes, both with accompanying $\delta(\text{UOH})$, around 30 to 40 cm⁻¹ lower than 566 567 observed experimentally in this and other studies (Botto et al. 2002; Colmenero et al. 2019). 568 The discrepancy between Colmenero et al.'s (2019) simulated spectrum and that obtained 569 here could be due to differences in the magnetic configuration of the vandenbrandeite system 570 and the Hubbard-U corrections used.

Both resolved 785 nm Raman spectra in **Figure 11** reveal a single peak with weak intensity at 658 cm⁻¹ (**Table 1**) in good agreement with Colmenero et al.'s (2019) findings. No modal assignment is available using the empirical method; however, both simulated studies attributed this feature to the δ (UOH) mode.

Between 580 and 380 cm⁻¹, three and four peaks were resolved from the NMW and 575 576 BGS specimens respectively, and attributed to Cu-O vibrations, v(Cu-O) using the empirical 577 method. Other experimental studies have reported varying number of peaks for this feature 578 (Table 1; Botto et al. 2002; Colmenero et al. 2019), possibly due to differences in apparatus 579 detection limits given that all of these peaks exhibit weak Raman signals. Over the same 580 wavenumber region, ten peaks were simulated in this study, with all but one being attributed 581 to vibrations along the O-Cu-O or U-O-Cu part of the crystal structure (Table 1). It should be 582 noted that the computational modes in this region are accompanied by multi-directional 583 movements in the free-hanging H bond due to its small size (as shown in the Raman vector 584 images in the Supplementary Information), which would account for the general broadness of 585 these Raman features in the experimentally obtained spectra (Figure 11).

At lower wavenumbers, three peaks were resolved from both vandenbrandeite specimens (**Figure 11** and **Table 1**); all of which coincide, within experimental error, of those observed by Colmenero et al (2019) but could not be attributed to any Raman mode using the empirical method. Across this same region, ten simulated peaks were obtained (**Table 1**) with most of these peak positions attributed to either multi-directional bending of the δ (UOH) mode or asymmetric stretching of the uranyl bond in the equatorial plane, $v_3(UO_2)^{2+}_{equatorial}$.

⁵⁹³ Several peaks were resolved below 250 cm⁻¹ for both vandenbrandeite specimens 594 (**Figure 11** and **Table 1**). Two peaks were resolved at 248 and 219 cm⁻¹ for the BGS 595 specimen and at 248 and 216 cm⁻¹ for the NMW sample. These correspond to published

Raman spectra (Botto et al. 2002; Colmenero et al. 2019) where these peaks are attributed to the uranyl symmetric bending, $v_2(UO_2)^{2+}$, mode. Five peaks are reported for both simulated spectra, again corresponding well with those obtained experimentally (**Table 1**). These have also been assigned to the $v_2(UO_2)^{2+}$ mode in the axial plane. All features observed below 215 cm⁻¹ in this study, both experimentally and simulated, were assigned to lattice vibrations based on the Raman vector images (Supplementary Information).

602 The final Raman mode observed in this study corresponds to H-bonding vibrations, 603 $v(OH \cdots O)$, between the OH⁻ ions linking the copper-uranyl sheets (**Figure 1**). The definition 604 of the $v(OH \cdots O)$ mode was observed to increase with decreasing laser wavelength in the 605 visible region (Figure 12), probably due to the lower wavelength (457 nm) laser penetrating 606 into the bulk crystal (Lee et al. 2017). The $v(OH \cdots O)$ feature contains the broadest of all the 607 peaks resolved and can be explained as a combination of multi-directional vibrations (Raman vector images in the Supplementary Information). As with the $v_1(UO_2)^{2+}$ mode discussed 608 609 above, the position of the resolved $v(OH \cdots O)$ peaks is environmentally sensitive. A 610 relationship between the v(OH···O) peak positions and the H-bond length, $d_{(O-H \cdots H)}$, was 611 derived by Libowitzky (1999) and is shown in Equation 5. Using the most well-defined peaks (i.e., those at ~ 3505 and 3418 cm⁻¹), the H-bonding length in vandenbrandeite was 612 613 extracted as 2.90 and 2.81 Å for the BGS sample, respectively, in agreement with those 614 obtained in the simulated crystal structure (2.71 – 3.13 Å; Figure 1).

615
$$d_{(O-H\cdots O)} = -0.1321 \ln[(3592 - \nu(OH)_{water})/3.04 \times 10^{11}]$$
(5)

616

617 **Summary of Raman Findings.** Overall, the dominant Raman modes identifying 618 vandenbrandeite could be obtained with little, if any, luminescence effects present regardless 619 of which laser wavelength was used in the visible and near-IR region. The most well-defined 620 features were typically observed in the 785 nm spectrum and agree well with other

experimental and simulated vandenbrandeite Raman spectra (Botto et al. 2002; Colmenero et al. 2019). Significant differences were observed in the overall Raman signal intensity, possibly due to geometric effects and metamictization in the NMW specimen. It is likely that any SNF alteration products would be measured with variable sample geometry, and it is also possible that the specimen could be affected by metamictization where radiation levels are high. Nevertheless, provided the key Raman features are intense enough to be resolved, vandenbrandeite should be readily identifiable by this method.

628 Good agreement was found in the peak positions between the experimental and 629 simulated Raman spectra supporting the vandenbrandeite crystal structure derived in this 630 study. The smaller number of peaks observed experimentally may be explained by multi-631 directional vibrations from the same mode. Only minor variations were revealed in the 632 computational Raman modal assignment compared to the molecular based empirical method. 633 The lack of additional peaks observed in the experimental Raman spectrum suggests a near-634 IR laser penetrates far enough into the bulk crystal structure to prevent the detection of 635 surface modes.

636

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Implications

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Vandenbrandeite is known to form at uranium ore deposits through alteration of primary uraninite in oxidising groundwater containing dissolved copper. Thus, the proposed use of copper canisters in the KBS-3 concept for SNF disposal may result in the formation of similar secondary copper-bearing uranium phases if the containment fails and/or where an initial canister defect is present. These phases would be expected to display higher solubility than the ceramic UO_2 fuel, leading to enhanced uranium release. Secondary alteration products may also be poorly crystalline or even amorphous, making characterisation difficult

during the pre-closure period owing to the high radiation field close to the canister. An attempt has been made to characterise two vandenbrandeite specimens of varying crystallinity using laser-based techniques which are amenable to remote, robotic deployment and have proved useful in discriminating other uranyl oxy-hydroxides, silicates and phosphates. Raman and luminescence characterisation are useful techniques for identifying potential phases, both in pre-disposal canister evaluation and in confirmatory experimental studies provided reliable reference spectra for each potential phase are available.

653 Vandenbrandeite displays very limited luminescence, although the simulated PDOS and band 654 structure predict that this mineral should absorb photons in the near UV region, similar to 655 other uranyl-bearing species. The decay pathways which could result in luminescence 656 between 450 and 650 nm all require a transition from the U f- to Cu d-orbital or O states. As 657 there is little spatial overlap between U with Cu or O in vandenbrandeite, any emission 658 features observed would have very weak intensity. The relative absence of luminescence, 659 when compared to other uranyl-bearing species, is notable and simplifies interpretation of 660 Raman spectra. The resolved Raman features were similar for the two vandenbrandeite 661 samples and agree well with those published in the literature. Fewer peaks were resolvable in 662 the sample displaying poorer crystallinity, in part owing to elevated background. Good 663 agreement was found between experimental and simulated Raman spectra in terms of peak 664 position, particularly with the environmentally sensitive axial uranyl stretching modes. As 665 alteration products of SNF may also exhibit low or negligible crystal structure order, the 666 ability of Raman spectroscopy to extract useful structural information makes it a desirable 667 technique for incorporation into the nuclear waste management process. Furthermore, these 668 observations suggest luminescence spectroscopy, when combined with Raman spectroscopy (ideally obtained using a near IR laser wavelength), may be able to distinguish between 669

670 crystalline and amorphous forms of the same phase based on their relative luminescence671 intensity.

672

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List of Figure Captions

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Figure 1: Crystal structure image showing sheet plan (top) and side (bottom) view for
vandenbrandeite derived in this study: green represents uranium; blue the Cu²⁺ cation; red,
oxygen; white, hydrogen; and dashed lines, the hydrogen bonding interactions. The image
was created using VESTA 3 software (Momma and Izumi 2011).

Figure 2: Optical photomicrographs of selected vandenbrandeite fragments (a) Sample BGS 756/1 is relatively uniform, blue-green vandenbrandeite with a glassy or vitreous lustre; (b) Sample NMW 83.41G.M3734 is variably vitreous greenish-black, porous, earthy, dull blue-green vandenbrandeite. The yellow patches observed in both images are the effect of internal reflections from fracture planes positioned just beneath the surface of the sample.

Figure 3: BSE images of typical fragments of the vandenbrandeite samples BGS
756/1 (a and b) and NMW 83.41G.M3734 (c with highlighted area in the white box shown in
d). Both specimens show porous and etched crystal surfaces. Minor inclusions of dark Mg-Al
silicate (Mg) were observed in the BGS specimen whereas the NMW sample is intergrown
with patches Cu-oxide, Mg-Al silicate, hydrotalcite and silica.

Figure 4: Qualitative EDXA spectra for vandenbrandeite samples: (a) Sample BGS
756/1; (b) Sample NMW 83.41G.M3734. a.u. – arbitrary units.

Figure 5: XRD patterns for the two vandenbrandeite specimens. Peaks are labelled with the lattice spacings in Å. The two broad features centred around 16 and 22 20° are from the double-sided tape used to secure the fragments in place and were used to normalise intensities. A library XRD pattern for vandenbrandeite from the RRUFFTM database (Lafuente et al. 2015) is shown for comparison. a.u. – arbitrary units.

Figure 6: BSE image of a typical earthy vandenbrandeite fragment, with
corresponding EDXA element maps of the same area, from sample NMW 83.41G.M3734.
The elemental maps reveal the presence and distribution of inclusions of copper sulphide (S),
silica (Si), hydrotalcite (Mg-Al), and gypsum (Ca-S) as minor contaminant minerals within
the vandenbrandeite groundmass.

Figure 7: Emission spectra for vandenbrandeite (a) BGS Ref BGS 756/1 and (b) NMW Ref NMW 83.41G.M3734. λ_{ex} was held at 357.6 nm. The black line represents the experimental data with the red line providing an indication of baseline sensitivity in this λ_{em} region. a.u. – arbitrary units.

Figure 8: Excitation spectrum for vandenbrandeite specimen NMW 83.41G.M3734).
The thick black line represents the experimental data, the grey line an indication of
instrumental noise, the blue lines are the individual resolved peaks and the red line the overall
resolved fit. a.u. – arbitrary units.

Figure 9: a) PDOS of vandenbrandeite showing only those states with a non-zero contribution in the energy range plotted. Positive and negative density values indicate the α and β -spin channels, respectively. The black dotted line represents the Fermi energy. b) Band structure of vandenbrandeite with α - and β -spin states in red and blue, respectively. The two wavelength axes α) and β) are offset to the highest occupied orbital for their spin channel.

Figure 10: Raw vandenbrandeite Raman spectra for BGS 756/1, obtained at four laser
wavelengths (785, 633, 532 and 457 nm), and a single spectrum at 785 nm for NMW
83.41G.M3734. a.u. – arbitrary units.

Figure 11: Resolved Raman spectra for BGS 756/1 (top) and NMW 83.41G.M3734
(bottom). The thick black line represents the experimental data, the blue lines are the
individual peaks and the red line the overall resolved fit. a.u. – arbitrary units.

- 915 Figure 12: Comparison of resolved spectra for the BGS 756/1 specimen at high
- 916 wavenumbers. a.u. arbitrary units.

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920 Figure S.1 displays a backscatter electron (BSE) image of a typical well-crystallised 921 vandenbrandeite fragment, with corresponding EDXA elemental maps of the same area, from 922 sample BGS 756/1. The elemental maps reveal the presence and distribution of trace amounts 923 of fine intercrystalline particles of magnesium silicate (MgSiO₃) and quartz (SiO₂) as minor 924 contaminant minerals on the surfaces of the vandenbrandeite crystals. Al may be present in 925 some fine particles, indicating that some particles may be magnesium-aluminium silicate 926 ((Mg,Al)SiO₃). No other contaminant phases were detected by EDXA element mapping in 927 sample BGS 756/1.

928 Vector images for all the simulated Raman modes are displayed in Figures S.2 to 929 **S.11** revealing the dominant vibration occurring in the structure at each frequency. It should 930 be noted that very minor vibrations were observed occurring across the entire structure for 931 each mode; this is attributed to the presence of small residual forces following the geometry optimisation performed on the system (all forces less than 1×10^{-3} eV Å⁻¹). A summary table 932 933 listing all the simulated Raman peak positions and their modal assignment can be found in 934 **Table 1** in the main paper along with comparisons to experimental measurements obtained in 935 this study and those Raman spectra reported in the literature.

All eight images in **Figure S.2** reveal multi-directional H-bonding vibrations between the OH⁻ ions which link the Cu-uranyl sheets. The simulated $v(OH\cdots H)$ peak positions are at 3614, 3576, 3555, 3445, 3408, 3400, 3365 and 3229 cm⁻¹. **Figure S.3** shows eight multidirectional vibrations of the free-hanging H atom bonded to an equatorial uranyl O atom, $\delta(UOH)$, occurring at 1044, 1018, 1009, 974, 969, 947, 943 and 917 cm⁻¹.

941 The first three vector images displayed in **Figure S.4** (at 889, 878 and 850 cm⁻¹) are 942 the uranyl axial asymmetric stretch, $v_3(UO_2)^{2+}_{axial}$, whereas the latter three images (at 828,

800 and 791 cm⁻¹) are assigned to the uranyl axial symmetric stretch $v_1(UO_2)^{2+}$ axial. Both these 943 944 modes are known to be environmentally sensitive and are accompanied by $\delta(\text{UOH})$ 945 vibrations, probably due to the lightness of the H element compared to its nearest neighbours. 946 The first four vector images shown in **Figure S.5** are attributed to more δ (UOH) vibrations at 780, 760, 734 and 624 cm⁻¹. Figure S.5e and f are assigned to asymmetric and 947 symmetric stretches of the U-O-Cu bonds, v_3 (U-O-Cu) and v_1 (U-O-Cu), in the 948 vandenbrandeite sheets at 579 and 546 cm⁻¹, respectively. The final two vector images in 949 **Figure S.5** are asymmetric (at 496 cm⁻¹) and symmetric (493 cm⁻¹) O-Cu-O stretch, v_3 (O-Cu-950 951 O) and v_1 (O-Cu-O), modes, respectively. Some of the simulated Raman modes in Figure S.5 952 were also attributed to lower wavenumber positioned features shown in Figure S.6. The v_3 (O-Cu-O) is, again, simulated at 464, 446 and 430 cm⁻¹ (Figure S.6b-d), the v_1 (O-Cu-O) 953 mode at 403 and 382 cm⁻¹ (Figure S.6e-f) and another v_3 (U-O-Cu) peak at 372 cm⁻¹ (Figure 954 **S.6g**). The first vector image in **Figure S.6**, at 484 cm⁻¹, is attributed to asymmetric bending 955 of the uranyl ion in the equatorial plane, $v_4(\text{UO}_2)^{2^+}_{\text{equatorial}}$, whereas **Figure S.6h** is assigned to 956 another δ (UOH) vibration at 366 cm⁻¹. It should be noted that **Figures S.5e-h** and **S.6a-h** also 957 958 display multi-directional movements in the free-hanging H atom (i.e., the δ (UOH) mode) due 959 to the lightness of this element compared to its nearest neighbours.

Figure S.7a and **e** displays the simulated vector image for the asymmetric stretching of the uranyl ion in the equatorial plane, $v_3(UO_2)^{2+}_{equatorial}$, positioned at 350 and 293 cm⁻¹, respectively. Six further $\delta(UOH)$ vibrations are revealed at 345, 320 and 309 cm⁻¹ (**Figure S.7b-d**) and 290, 277 and 268 cm⁻¹ (**Figure S.7f-h**). All five Raman vector images shown in **Figure S.8** are assigned to the symmetric axial uranyl bending, $v_2(UO_2)^{2+}_{axial}$, mode with simulated peaks positioned of 246, 244, 239, 230 and 222 cm⁻¹. The remaining simulated vector images are assigned to general lattice vibrations in the vandenbrandeite crystal

- 967 structure at 215, 203, 196, 187, 175 and 162 cm⁻¹ (Figure S.9) 156, 147, 132, 121, 114 and
- 968 109 cm⁻¹ (**Figure S.10**) and 99, 97, 78, 72, 57 and 43 cm¹ (**Figure S.11**).

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972 Figure S.1: BSE image of a typical earthy vandenbrandeite fragment, with 973 corresponding EDXA element maps of the same area, from sample BGS 756/1. The 974 elemental maps reveal the presence and distribution of inclusions of copper sulphide (S), 975 silica (Si), hydrotalcite (Mg-Al), and gypsum (Ca-S) as minor contaminant minerals within 976 the vandenbrandeite groundmass.

977 **Figure S.2**: Raman vector H-bonding, $v(OH\cdots H)$, vibrations for vandenbrandeite at 978 a) 3614, b) 3576, c) 3555, d) 3445, e) 3408, f) 3400, g) 3365 and h) 3229 cm⁻¹. Blue 979 represents U, brown as Cu, red O and white H.

Figure S.3: Raman vector bending motions of the free-hanging H bond connected to an equatorial uranyl O atom, δ (UOH), for vandenbrandeite at a) 1044, b) 1018, c) 1009, d) 982 974, e) 969, f) 947, g) 943 and h) 917 cm⁻¹. Blue represents U, brown as Cu, red O and white H.

Figure S.4: Raman vector images of the axial asymmetric uranyl stretching vibrations, $v_3(UO_2)^{2+}_{axial}$, at a) 889, b) 878 and c) 850 cm⁻¹ and axial symmetric uranyl stretching vibrations, $v_1(UO_2)^{2+}_{axial}$, at d) 828, e) 800 and f) 791 cm⁻¹. All uranyl modes shown in this figure are accompanied by δ (UOH) vibrations. Blue represents U, brown as Cu, red O and white H.

Figure S.5: Simulated Raman vector vibration images for vandenbrandeite a) 780, b)
760, c) 734, d) 624, e) 579, f) 546, g) 496 and h) 493 cm⁻¹. Blue represents U, brown as Cu,
red O and white H.

Figure S.6: Simulated Raman vector vibration images for vandenbrandeite a) 484, b)
464, c) 446, d) 430, e) 403, f) 382, g) 372 and h) 366 cm⁻¹. Blue represents U, brown as Cu,
red O and white H.

995	Figure S.7: Simulated Raman vector vibration images for vandenbrandeite a) 350, b)
996	345, c) 320, d) 309, e) 293, f) 290, g) 277 and h) 268 cm ⁻¹ . Blue represents U, brown as Cu,
997	red O and white H.
998	Figure S.8 : Axial uranyl symmetric bending, $v_2(UO_2)^{2+}_{axial}$, simulated Raman vector
999	images for vandenbrandeite at a) 246, b) 244, c) 239, d) 230 and e) 222 cm ⁻¹ . Blue represents
1000	U, brown as Cu, red O and white H.
1001	Figure S.9: Simulated Raman lattice vibrations for vandenbrandeite at a) 215, b) 203,
1002	c) 196, d) 187, e) 175 and f) 162 cm ⁻¹ . Blue represents U, brown as Cu, red O and white H.
1003	Figure S.10: Simulated Raman lattice vibrations for vandenbrandeite at a) 156, b)
1004	147, c) 132, d) 121, e) 114 and f) 109 cm ⁻¹ . Blue represents U, brown as Cu, red O and white
1005	H.
1006	Figure S.11: Simulated Raman lattice vibrations for vandenbrandeite at a) 99, b) 97,
1007	c) 78, d) 72, e) 57 and f) 43 cm ⁻¹ . Blue represents U, brown as Cu, red O and white H.
1008	

Tables

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1010

*v*_{experimental} (cm⁻¹) **Empirical** <u>v_{model} (</u>cm⁻¹) Computational Assignment Published Assignment BGS **NMW** Colmenero This 756/1 83.41G. et al. (2019) Study (This Study) M3734 v(OH···O) 3614 **ν**(OH···O) -3576 _ 3510^b, 3505^b 3505 3555 3438 3445 3419^b 3418 3408 _ 3400 3300 3331 3365 3229 3311 3146 _ 2827^b 2775 δ(UOH) 1153^b 1224 δ(UOH) _ -_ 1044 _ _ 1014 1018 _ 1008^{b} 1009 967 ^b 991 967 974 969 -947 _ 941 ^b 936 943 917 _ _ $884\ ^{b}$ 894 $v_3(UO_2)^{2+1}$ 881 889 $v_3(UO_2)^{2+}_{axial} +$ _ - $862\ ^a$ δ(UOH) 878 _ -_ 844^{b} 834 850 _ $v_1(UO_2)^{2+}_{axial} +$ $v_1(UO_2)^{24}$ _ _ 828 _ 805 ^a, 803 ^b 805 δ(UOH) 804 _ 800 772 791 Unassigned 780 δ(UOH) --_ -_ 760 _ _ _ 734 _ 656 ^b 658 658 631 624 v(Cu-O) 579 v_3 (U-O-Cu) _ --554 ^b 556 546 v_1 (U-O-Cu) _ _ 496 $v_3(O-Cu-O)$ 516 492 ^b 492 $v_1(O-Cu-O)$ 496 493 $v_4(UO_2)^{2+}_{equatorial}$ 484 -_ _ 474 ^a, 463 ^b 466 467 474 464 $v_3(O-Cu-O)$ 440 446 433 429 430 _ 409 ^b 419 $v_1(O-Cu-O)$ 403 _ 394 382 Unassigned _ 372 v_3 (U-O-Cu) _ _ <u>36</u>2 ^b 367 _ _ 366 δ(UOH)

	DOI: 111	53.//doi.org/10	.2150/411-2022-0212. 1	mp.//www.mm30can	1.01g/	
	-	354	351 ^b	355	350	$v_3(UO_2)^{2+}_{equatorial}$
	-	-	331 ^b	348	345	δ(UOH)
	319	317	316 ^b	324	320	
	-	-	-	312	309	
	-	-	-	-	293	$v_3(UO_2)^{2+}_{equatorial}$
	-	-	-	-	290	δ(UOH)
	277	277	276 ^b	-	277	
	-	-	-	-	268	
$v_2(UO_2)^{2+}$	-	-	-	271	-	$v_2(UO_2)^{2+}_{axial}$
	248	248	252 ^a , 246 ^b	249	246	
	-	-	_	-	244	
	-	-	-	-	239	
	-	-	-	232,228	230	
	219	216	216 ^b	213	222	
	-	-	-	-	-	
Lattice	-	-	-	-	215	Lattice
vibrations	-	-	-	-	203	vibrations
	-	-	-	-	196	
	181	178	186 ^{°a} , 179 ^b	-	187	
	-	-	-	171	175	
	-	-	-	-	162	
	157	-	152 ^b	155	156	
	147	147	144 ^b	141	147	
	-	-	-	-	132	
	-	-	-	-	121	
	-	-	-	-	114	
	111	108	110 ^b	-	109	
	-	-	-	-	99	
	-	-	-	92	97	
	-	-	-	-	78	
	74	-	74 ^b	72	72	
	66	62	65 ^b	52	57	
	-	-	-	-	43	

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Table 1: Summary of experimental and simulated Raman data with literature comparisons for vandenbrandeite. The experimental error in the peak position for specimens BGS 756/1 and NMW 83.41G.M3734 is \pm 3 cm⁻¹ based on the variation between repeats. Superscript notation: ^a Botto et al. (2002), ^b Colmenero et al. (2019).

- 1016
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Figure 2 1028 a 1.0 mm 1029 1030 Figure 3 1031 З n Мa **BILLS** and etched crystal surfaces Mg Ma 100 µm 100 µm C porous and etched crystal surfaces 500 µm 150 µm 1032 Ŀ 1033

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