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New crystal-chemical data for marécottite

J. Plášil[1,*] and R. Škoda[2]

[1] Institute of Physics ASCR, v.v.i., Na Slovance 2, CZ-182 21 Prague 8, Czech Republic
[2] Department of Geological Sciences, Masaryk University, Kotlářská 2, Brno, 611 37, Czech Republic

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ABSTRACT

Marécottite, ideally $Mg_3[(UO_2)_4O_3(OH)(SO_4)_2]_2(H_2O)_{28}$, a triclinic, Mg-dominant member of the zippeite group, was described originally from a small uranium deposit at La Creusaz in Wallis (Switzerland). It has recently been found at Jáchymov (Czech Republic), where it forms exceptional crystals, up to 0.3 mm across. According to an electron microprobe study of these crystals, marécottite from Jáchymov is chemically similar to the material from the La Creusaz deposit. However, the Jáchymov crystals exhibit more cation substitution (Zn^{2+} and Mn^{2+} for Mg^{2+}). The chemical composition of marécottite from Jáchymov corresponds to the empirical formula $[(Na_{0.05}K_{0.07})_{\Sigma 0.12}(Mg_{1.83}Zn_{0.41}Mn_{0.41}Cu_{0.15}Ni_{0.08})_{\Sigma 2.88}Al_{0.07}]_{\Sigma 3.07}(UO_2)_8[(SO_4)_{3.77}(SiO_4)_{0.21}]_{\Sigma 3.98}O_6(OH)_{1.84}\cdot 28H_2O$ (the mean of four representative spots; calculated on the basis of eight U atoms and 28 H_2O per formula unit and 1.84 OH for charge balance). According to single-crystal X-ray diffraction, marécottite from Jáchymov is triclinic, $P\bar{1}$, a = 10.8084(2), b = 11.2519(3), c = 13.8465(3) Å, α = 66.222(2), β = 72.424(2), γ = 70.014(2)°, V = 1421.57(6) Å^3 and Z = 1. The crystal structure was refined from a highly redundant dataset (30,491 collected reflections) to R_1 = 0.0367 for all 7042 unique reflections. The refined structure confirms the previously determined structure for the crystal from the La Creusaz deposit. An extensive network of hydrogen bonds is an important feature that keeps the whole structure together, but the positions of H atoms had not been determined previously. The H-bond scheme proposed based on a detailed bond-valence analysis and the role of different types of molecular H_2O in the structure is discussed.

Keywords: Marécottite, uranyl sulfate, zippeite group, crystal structure, chemical composition, hydrogen bonds.

Introduction

Uranyl sulfates are common alteration products of uraninite and sulfides in oxide zones of most uranium deposits (Krivovichev and Plášil, 2013; Plášil, 2014). Minerals of the zippeite group are among the most common of the uranyl sulfates. Members of this group are paragenetically, chemically (Frondel *et al.*, 1976; Krivovichev and Plášil, 2013; Plášil, 2014) and structurally related (Burns *et al.*, 2003; Burns, 2005; Krivovichev and Plášil, 2013). Marécottite is the Mg-dominant triclinic member of the zippeite group and was originally described from the La Creusaz uranium deposit in Wallis (Switzerland) by Brugger *et al.* (2003). However, prior to that description, it had been known from Jáchymov, Czech Republic (Ondruš *et al.*, 1997), but the material available for study was not suitable for a full description for submission to the International Mineralogical Association Commission for New Minerals, Names and Classification. Recently, new specimens containing marécottite crystals of superb quality were found at Jáchymov. These crystals were used for the collection of new X-ray diffraction data along with a quantitative chemical analysis. A H-bonding scheme is proposed based on bond-valence considerations, as the positions of the hydrogen atoms could not be localized from the current X-ray data.

* E-mail: plasil@fzu.cz
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Occurrence

The specimens containing marécottite crystals originate from the Plavno mine, which is located in the southeastern part of the Jáchymov ore district (Ondruš *et al.*, 2003). The samples used in this study were collected from vein no. 13 on the 2nd level of the Vladimír shaft of the Plavno mine. Superior crystals were collected directly from the ore lens located on the hanging-wall of the adit. Samples consist of highly hematitized, clayey material (resembling mylonitic material) of dark reddish-brown colour. This material was situated directly below the ore lens, together with uraninite and pyrite. The uraninite was highly altered and fine-grained. Hundreds of isolated crystal aggregates, consisting of uranyl sulfates, were located in cracks within the clayey material and surrounding rocks. Magnesiozippeite, a phase similar to blatonite, based on powder XRD – and a new (K-Mn)-zippeite (still under investigation) were identified from this association. Marécottite forms crystalline aggregates consisting of perfect tabular crystals up to 0.3 mm across (Fig. 1*a*). Crystals are yellowish orange to orange in colour and usually form multiple intergrowths (Fig. 1*a*,*b*).

Chemical composition

Crystals of marécottite were analysed with a Cameca SX100 electron microprobe (Masaryk University, Brno), operating in wavelength dispersive spectroscopy mode using an accelerating voltage of 15 kV, beam current of 2 nA and a 15 μm beam diameter. The following X-ray lines and standards were used. *K*α lines: Na (albite), Mg (Mg_2SiO_4), S ($SrSO_4$), K, Al, Si (sanidine), Mn (spessartite), Zn (gahnite), Fe (almandine), Ni (Ni_2SiO_4); *L*α lines: Cu (lammerite); *M*α lines: U (uranophane). Other elements, such as Ca, Co, Pb, Ba, Y, As, P, V and F were sought, but were below detection limits (~0.05–0.2 wt.% with the analytical conditions used). Peak counting times were 10–20 s and the counting time for background was 50% of that of the peak. Matrix effects were accounted for using the *PAP* correction routine (Pouchou and Pichoir, 1985). The chemical composition of the marécottite crystals studied here (in wt.% of oxides) and the coefficients of the empirical formula calculated on the basis of eight U atoms per formula unit (a.p.f.u.) are given in Table 1. The empirical formula is $[(Na_{0.05}K_{0.07})_{\Sigma 0.12}(Mg_{1.83}Zn_{0.41}Mn_{0.41}Cu_{0.15}Ni_{0.08})_{\Sigma 2.88}Al_{0.07}]_{\Sigma 3.07}(UO_2)_8[(SO_4)_{3.77}(SiO_4)_{0.21}]_{\Sigma 3.98}O_6(OH)_{1.84}\cdot 28H_2O$ (mean of 4 analyses). The O^{2-} and molecular H_2O content were assumed from the ideal stoichiometry and the OH content was calculated to achieve charge balance. The calculated OH is close to the ideal content of 2 OH^- in the structural unit. According to the microprobe data, there is substantial substitution at the cationic site, the major substituting cations being Zn^{2+} and Mn^{2+}. Of significance for nomenclature issues, the divalent cations enter only a single site. The existence of Mn^{2+}- and Zn^{2+}-dominant (along with other divalent transition metal cations) triclinic members of the zippeite group seems very likely, and these will correspond to new minerals if discovered. Moreover, a Cu^{2+}-rich marécottite from Jáchymov has been described recently (Plášil *et al.*, 2014).

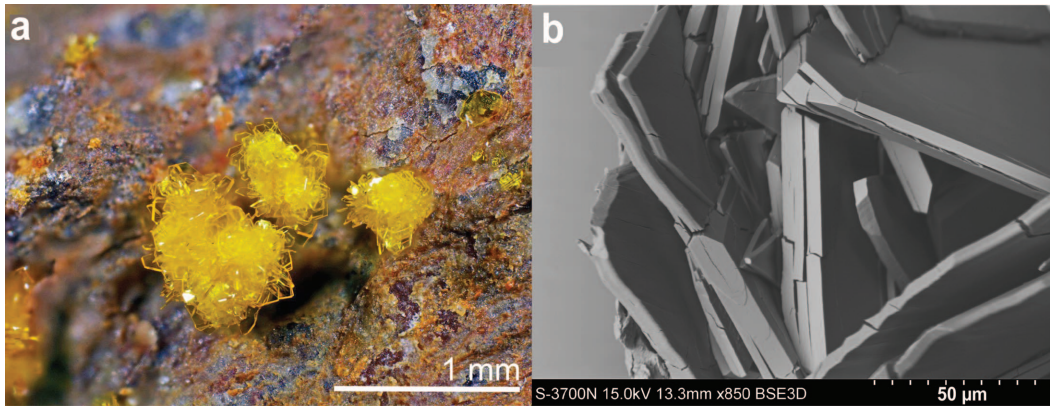


FIG. 1. Marécottite from Jáchymov. (*a*) Aggregate of perfectly developed marécottite crystals on hematitized gangue; (*b*) backscattered electron image showing detail of the tabular crystals.

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TABLE 1. Results of wavelength dispersive spectroscopy analyses of marécottite from Jáchymov.

Wt.% oxides	Mean	1	2	3	4
Na_2O	0.09	0.08	0.17	0.10	bdl.
K_2O	0.06	bdl.	bdl.	bdl.	0.16
MgO	2.30	2.66	2.28	2.17	2.06
MnO	0.83	0.97	0.70	0.82	0.82
FeO	0.07	0.18	bdl.	bdl.	0.10
NiO	0.14	0.13	bdl.	0.17	0.17
CuO	0.23	0.23	bdl.	0.12	0.56
ZnO	0.93	1.02	0.78	0.70	1.21
Al_2O_3	0.11	0.08	0.15	0.15	0.06
SiO_2	0.34	0.31	0.33	0.23	0.47
SO_3	9.04	10.43	8.48	8.78	8.47
UO_3	68.69	74.72	69.18	67.30	63.56
H_2O	15.64				
Total	98.48				
Composition calculated on the basis of eight U a.p.f.u.					
Na	0.054	0.083	0.181	0.109	
K	0.072				0.118
Sum M^+	0.126				
Fe	0.025	0.070			0.050
Mg	1.834	2.040	1.874	1.831	1.836
Cu	0.151	0.087		0.050	0.252
Ni	0.080	0.052	0.035	0.078	0.081
Mn	0.406	0.420	0.327	0.394	0.418
Zn	0.414	0.384	0.318	0.293	0.536
Sum M^{2+}	2.910				
Al	0.071	0.050	0.099	0.101	0.040
U	8	8	8	8	8
Si	0.206	0.160	0.182	0.130	0.282
S	3.768	3.988	3.502	3.727	3.808
Sum T site	3.974	4.148	3.684	3.857	4.090
H_2O+OH	29.837				

bdl. – below detection limit.

Single-crystal X-ray diffraction

A tabular, 0.15 mm × 0.08 mm × 0.04 mm, orange crystal of marécottite was selected for X-ray study on an Oxford diffraction Gemini diffractometer. Graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71073 Å) from a conventional sealed X-ray tube collimated with a fibre-optics Mo-Enhance collimator was detected by an Atlas CCD detector. The crystal studied is triclinic, with a = 10.8084(2), b = 11.2519(3), c = 13.8465(3) Å, α = 66.222(2), β = 72.424(2), γ = 70.014(2)°, V = 1421.57(6) Å^3 and Z = 1 (Table 2). The unit cell was refined from 17,785 reflections using a least-squares algorithm of the *CrysAlis* software (Agilent Technologies, 2012). The collected diffraction dataset contained a high redundancy of reflection measurements, with 30,491 reflections collected. Of these, 7042 were unique and 5847 were classified as observed. Integration of the data, including corrections for background, polarization and Lorentz effects, was carried out with the *CrysAlis RED* programs (Agilent Technologies, 2012). The absorption correction that combines the shape of the crystal and an empirical correction was performed using *Jana2006* (Petříček *et al.*, 2014), which led to a dataset with an R_{int} of 0.042. The structure of

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marécottite was solved independently from the previous structure determination (Brugger *et al.*, 2003) by the charge-flipping algorithm using the *Superflip* program (Palatinus and Chapuis, 2007). The structure was then refined using *Jana2006* (Petříček *et al.*, 2006, 2014) based on F^2. The structure solution provided a reasonable model involving a nearly complete uranyl sulfate structural unit and also several interstitial atom sites. Positions of the remaining atoms, namely oxygen, were located in difference Fourier maps. The refined low values of the isotropic displacement parameters for the Mg sites indicated substitution by heavier atoms. As the studied marécottite contains high concentrations of Mn (in addition to other divalent transition metals), according to the electron microprobe analysis (EMPA), the occupancy of the Mg sites was refined to allow the presence of Mn at the sites. Other divalent cation metals were omitted due to similar scattering curves. The sum of the Mn atoms at the mixed Mg/Mn sites obtained from the refined occupancies is 0.97 Mn a.p.f.u., which is similar to the sum of M^{2+} (excluding Mg^{2+}) obtained from the EMPA, 1.08 M^{2+} a.p.f.u. All atoms were refined with anisotropic displacement parameters during the last cycles of the refinement, which converged smoothly to $R_1 = 0.0284$ for 5847 observed unique reflections and $R_1 = 0.0367$ for all 7042 unique reflections (Table 2). Final atom coordinates and displacement parameters are listed in Table 3, selected interatomic distances in Table 4 and the bond-valence analysis (Brown, 1981, 2002) in Table 5. The original crystallographic information file (cif) has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

TABLE 2. Summary of data-collection conditions and refinement parameters for marécottite.

Structural formula	$(Mg_{2.03}Mn_{0.97})_{\Sigma 3.00}[(UO_2)_4O_3(OH)(SO_4)_2]_2(H_2O)_{28}$
Unit-cell parameters	
	a = 10.8084(2) Å
	b = 11.2519(3) Å
	c = 13.8465(3) Å
	α = 66.222(7)º
	β = 72.424(2)º
	γ = 70.014(2)º
V	1421.57(6) (Å^3)
Z	1
Space group	$P\bar{1}$
$D_{calc.}$ (g cm^{-3})	3.764 (applicable for the above given formula)
Temperature (K)	293(2)
Wavelength	Mo$K\alpha$, 0.71075 Å
Crystal dimensions (mm)	0.15 × 0.08 × 0.04
Limiting θ angles	2.85–29.27º
Limiting Miller indices	$-14 \leqslant h < 14$, $-14 \leqslant k \leqslant 15$, $-18 \leqslant l \leqslant 18$
No. of reflections	30,491
No. of unique reflections	7042
No. of observed reflections (criterion)	5847 [$I > 3\sigma(I)$]
Absorption coefficient (mm^{-1}), method	23.21, analytical+empirical
T_{min}/T_{max}	0.156/0.567
R_{int}	0.0422
F_{000}	1393
Refinement by *Jana2006* on F^2	
Parameter refined, constraints, restraints	382, 0, 18
R_1, wR_2 (obs)	0.0284, 0.0647
R_1, wR_2 (all)	0.0367, 0.0685
Goof (obs, all) 1.17, 1.12	
Weighting scheme	$1/(\sigma^2(I) + 0.0004I^2)$
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−1.51, 3.38

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General crystal-structure features

A general description of the marécottite structure is given by Brugger *et al.* (2003). The current X-ray study confirms the proposed structure model. Marécottite possesses a layered structure (Fig. 2), which consists of uranyl-oxo-hydroxy-sulfate sheets separated by an interlayer containing octahedrally coordinated Mg^{2+} cations and H_2O molecules. Adjacent sheets are linked by hydrogen bonds only. The structural unit (sheet) has the nominal composition $[(UO_2)_4O_3(OH)(SO_4)_2]^{3-}$ and hierarchically belongs to the zippeite topology (Burns, 2005). A structural unit of the same chemical composition was found in the structure of synthetic zippeite (Burns *et al.*, 2003); the chemical composition of the structural sheets of the zippeite-group minerals and compounds differs nominally, but they have very similar bond-valence requirements that are reflected in the same range of Lewis basicity, 0.14–0.25 valence units (vu) (Schindler and Hawthorne, 2008).

The interlayer of the marécottite structure is occupied by the Mg^{2+} cations and H_2O molecules. The crystal structure contains three symmetrically independent Mg sites (occupied by Mg^{2+} and Mn^{2+}), coordinated octahedrally by O atoms that belong to molecular H_2O (Table 6). $Mg(H_2O)_6$ polyhedra are non-polymerized, unlike the Cu^{2+} polyhedra in pseudojohannite (Plášil *et al.*, 2012, 2015), and they are linked into the structure by a network of H bonds only. There are also five additional O sites in the interlayer, which belong to molecular H_2O groups that are not bonded to any metal cation and are held in place by H bonds only. The high content of H_2O in marécottite is quite a unique feature among the zippeite-group minerals and is known only for sejkoraite-(Y) (Plášil *et al.*, 2011). The structural formula obtained from the structure refinement is $(Mg_{2.03}Mn_{0.97})_{\Sigma 3.00}[(UO_2)_4O_3(OH)(SO_4)_2]_2(H_2O)_{28}$, $Z = 1$, with $D_{calc} = 3.764$ g cm^{-3}.

Bond-valence analysis and proposed H-bond scheme

A complete bond-valence analysis of the marécottite structure is provided in Table 6. Calculated bond-valence sums for the cations in the structure show less scatter around ideal values, consistent with the formal cationic valences, than the sums provided by Brugger *et al.* (2003). However, this is quite reasonable, with regard to the refinement results, which are more accurate in the case of the current data.

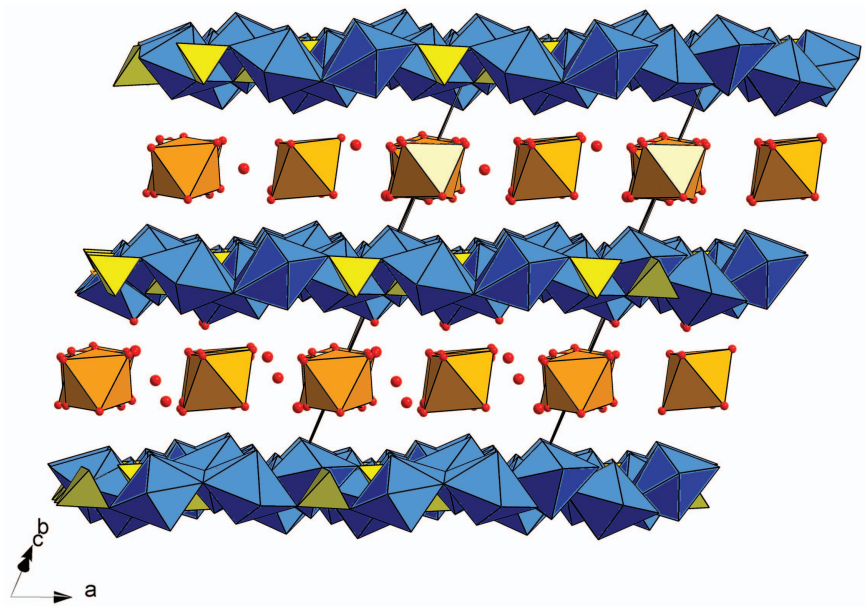


FIG. 2. The structure of marécottite. Uranyl sulfate sheets (UO_7 = blue, SO_4 = yellow) of the zippeite topology alternate with an interlayer occupied by the complex $[^{[6]}Mg_3(H_2^{[3]}O)_{18}(H_2^{[4]}O)_2(H_2^{[5]}O)_8]^{3+}$ ($Mg[H_2O]_6$ = orange, H_2O groups = red).

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TABLE 3. Atom positions and displacement parameters (U_{eq}, U_{iso}, in Å^2) for marécottite from Jáchymov.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.02895(2)	0.89959(3)	0.13719(2)	0.00962(11)	0.00791(13)	0.01126(14)	0.00812(13)	−0.00386(10)	−0.00316(10)	0.00066(11)
U2	−0.54463(2)	0.60681(3)	0.37149(2)	0.00995(11)	0.00852(13)	0.01133(14)	0.00805(13)	−0.00340(10)	−0.00363(10)	0.00090(11)
U3	−0.31085(2)	0.92124(3)	0.13502(2)	0.01001(11)	0.00805(13)	0.01168(14)	0.00861(13)	−0.00384(10)	−0.00335(10)	0.00064(11)
U4	−0.20569(2)	0.62775(3)	0.37745(2)	0.00997(11)	0.00867(13)	0.01177(14)	0.00797(13)	−0.00453(11)	−0.00347(10)	0.00112(11)
Mg1*	0	0	0.5	0.0226(12)	0.0277(16)	0.0169(15)	0.0224(16)	−0.0046(11)	−0.0003(11)	−0.0099(12)
Mg2*	0.5	0.5	0	0.0205(13)	0.0220(16)	0.0204(16)	0.0243(17)	−0.0052(12	−0.0055(12)	−0.0121(13)
Mg3*	0	0.5	0	0.0180(15)	0.0176(17)	0.0186(18)	0.0207(18)	−0.0064(13)	−0.0011(13)	−0.0096(14)
S1	0.37186(16)	0.88579(18)	0.13238(13)	0.0104(7)	0.0102(8)	0.0122(9)	0.0072(8)	−0.0052(7)	−0.0040(7)	0.0019(7)
S2	−0.87505(16)	0.62473(18)	0.37385(13)	0.0099(7)	0.0074(8)	0.0113(9)	0.0085(8)	−0.0040(7)	−0.0031(7)	0.0016(7)
O1	−0.3549(5)	1.0534(5)	0.1901(4)	0.017(2)	0.017(3)	0.019(3)	0.015(3)	−0.009(2)	0.002(2)	−0.007(2)
O2	−0.0516(5)	1.0434(5)	0.1804(4)	0.015(2)	0.012(2)	0.014(3)	0.018(3)	−0.004(2)	0.000(2)	−0.005(2)
O3	−0.4416(5)	0.4859(5)	0.3092(4)	0.017(2)	0.018(3)	0.015(3)	0.019(3)	0.001(2)	−0.005(2)	−0.008(2)
O4	−0.1220(5)	1.2474(5)	−0.1018(4)	0.020(2)	0.019(3)	0.024(3)	0.016(3)	−0.014(2)	0.000(2)	−0.002(2)
O5	−0.7345(4)	0.5742(5)	0.3269(4)	0.017(2)	0.009(2)	0.026(3)	0.016(3)	−0.006(2)	−0.001(2)	−0.007(2)
O6	−0.1814(5)	0.5376(5)	0.2911(4)	0.018(2)	0.013(3)	0.025(3)	0.016(3)	−0.013(2)	0.001(2)	−0.004(2)
O7	0.2273(5)	0.9321(5)	0.1709(4)	0.018(2)	0.010(2)	0.027(3)	0.016(3)	−0.011(2)	0.000(2)	−0.006(2)
O8	−0.1193(4)	0.9740(5)	0.0285(4)	0.014(2)	0.008(2)	0.020(3)	0.011(3)	−0.007(2)	−0.004(2)	0.003(2)
O9	−0.8861(5)	0.5923(5)	0.4899(4)	0.018(2)	0.020(3)	0.021(3)	0.007(2)	−0.006(2)	−0.004(2)	0.005(2)
O10	−0.3917(5)	0.5488(5)	0.4759(4)	0.014(2)	0.014(2)	0.013(3)	0.013(3)	−0.008(2)	−0.004(2)	0.004(2)
O11	−0.1460(4)	0.8030(5)	0.2307(4)	0.016(2)	0.011(2)	0.019(3)	0.013(3)	−0.007(2)	−0.003(2)	0.002(2)
O12	−0.9583(4)	0.5607(5)	0.3532(4)	0.016(2)	0.009(2)	0.020(3)	0.019(3)	−0.006(2)	−0.004(2)	−0.004(2)
O13	−0.4027(4)	0.7741(5)	0.3050(4)	0.016(2)	0.009(2)	0.021(3)	0.013(3)	−0.006(2)	−0.005(2)	0.002(2)
O14	−0.2251(5)	0.7136(5)	0.4668(4)	0.017(2)	0.015(3)	0.023(3)	0.015(3)	−0.006(2)	−0.001(2)	−0.008(2)
O15	−0.9206(5)	0.7712(5)	0.3254(4)	0.016(2)	0.018(3)	0.013(3)	0.012(3)	−0.006(2)	−0.007(2)	0.004(2)
O16	0.3974(5)	0.9030(5)	0.0180(4)	0.018(2)	0.015(3)	0.024(3)	0.005(2)	−0.004(2)	−0.003(2)	0.005(2)
O17	−0.1799(5)	0.4846(6)	0.1126(4)	0.026(3)	0.024(3)	0.036(4)	0.020(3)	−0.010(3)	−0.001(2)	−0.011(3)
O18	−0.0840(6)	0.4884(6)	−0.1107(5)	0.030(3)	0.037(3)	0.031(4)	0.029(3)	−0.014(3)	−0.009(3)	−0.011(3)
O19	−0.6588(5)	0.7345(5)	0.4230(4)	0.017(2)	0.018(3)	0.015(3)	0.020(3)	−0.007(2)	−0.001(2)	−0.007(2)
O20	−0.2861(5)	0.7977(5)	0.0779(4)	0.019(2)	0.014(3)	0.024(3)	0.017(3)	−0.009(2)	0.002(2)	−0.007(2)
O21	0.4241(5)	0.7413(5)	0.1874(4)	0.018(2)	0.021(3)	0.019(3)	0.011(3)	−0.010(2)	−0.008(2)	0.005(2)
O22	0.4407(5)	0.9638(5)	0.1528(4)	0.016(2)	0.012(2)	0.016(3)	0.021(3)	−0.005(2)	−0.006(2)	−0.004(2)
O23	−0.0620(6)	0.7095(6)	−0.0627(5)	0.034(3)	0.033(3)	0.021(3)	0.042(4)	−0.004(3)	−0.001(3)	−0.012(3)
O24	0.1532(6)	0.0072(6)	0.3610(5)	0.031(3)	0.039(4)	0.022(3)	0.027(3)	−0.002(3)	−0.003(3)	−0.008(3)
O25	0.3915(6)	0.4595(7)	0.1591(5)	0.039(3)	0.045(4)	0.046(4)	0.030(4)	−0.018(3)	0.003(3)	−0.020(3)
O26	−0.2452(7)	1.2275(7)	0.2769(6)	0.055(4)	0.065(5)	0.040(5)	0.059(5)	0.007(4)	−0.026(4)	−0.023(4)
O27	−0.1160(6)	0.6814(7)	−0.3110(5)	0.042(3)	0.057(4)	0.037(4)	0.035(4)	−0.010(3)	−0.010(3)	−0.016(3)
O28	0.6567(5)	0.3268(6)	0.0521(5)	0.031(3)	0.031(3)	0.028(4)	0.035(4)	−0.005(3)	−0.010(3)	−0.011(3)

O29	0.1037(6)	−0.1978(6)	0.5786(5)	0.035(3)	0.041(4)	0.029(4)	0.026(3)	−0.004(3)	−0.002(3)	−0.008(3)
O30	0.5914(5)	0.6208(6)	0.0261(5)	0.030(3)	0.024(3)	0.028(3)	0.048(4)	−0.005(3)	−0.011(3)	−0.020(3)
O31	0.1111(6)	0.0716(7)	0.5535(5)	0.041(3)	0.047(4)	0.048(4)	0.039(4)	−0.018(3)	−0.004(3)	−0.023(4)
O32	0.6674(8)	0.7806(7)	−0.1701(7)	0.074(4)	0.074(6)	0.029(4)	0.079(6)	−0.002(4)	0.019(5)	−0.013(4)
O33	−0.5925(9)	0.9782(9)	0.4108(7)	0.078(5)	0.105(7)	0.082(7)	0.073(6)	−0.069(6)	−0.029(5)	−0.004(5)
O34	−0.4993(9)	0.7999(10)	0.6043(9)	0.102(7)	0.096(7)	0.083(7)	0.133(9)	−0.047(6)	0.034(7)	−0.063(7)

* Refined occupancies: Mg1/Mn1 0.571(12)/0.429(12); Mg2/Mn2 0.640(12)/0.360(12); Mg3/Mn3 0.818(12)/0.182(12).

The structure of marécottite has a polar character and can be divided into two parts, held together by the weak H-bonding interactions. These are the structural unit, $[(UO_2)_4O_3(OH)(SO_4)_2]_2^{3-}$ and an interstitial complex, $[Mg_3(H_2O)_{28}]^{6+}$. In the following paragraphs the H-bond network is proposed and discussed using a bond valence approach (Schindler and Hawthorne, 2008).

We propose an H-bond scheme based on a reasonable bond geometry of the proposed bonds (D–H···A lengths and A–D–A angles) and thus an acceptable bond valence scheme (Table 6). We note that the contribution of the H bonds provide slightly higher bond-valence sums calculated for the anionic O sites. However, we point out that this is just an artefact of the chosen approach, assigning the same bond-valence distribution to each bond and thus the same bond-length distribution. In reality, the actual bonds will be more relaxed from the point of view of bond lengths and this results in much lower sums, closer to the ideal sums for the O anions. The proposed H-bond scheme involves an extensive network (Fig. 3*a*,*b*) that links the adjacent sheets together. This network consists of bonds between apical atoms of the $Mg(H_2O)_6$ octahedra and apical (uranyl) O atoms of the UO_7 bipyramids (Fig. 3*b*) and some of the H_2O groups coordinating Mg in the equatorial plane of the Mg octahedra. Some of the proposed bonds emanating from the $Mg(H_2O)_6$ octahedra are received by the O atoms shared between UO_7 bipyramids and sulfate tetrahedra (displayed in Fig. 3*b* as e.g. O22s = sheet), which are slightly undersaturated relative to their bond valence requirements, and thus they can accept at least one H bond (~0.2 vu). The oxygen atom in such an H_2O group has the coordination number [3] and belongs to the so-called 'transformer (H_2O) group' (Hawthorne and Schindler, 2008; Schindler and Hawthorne, 2008). Such a group acts as the bond valence transformer, transforming (splitting) the bond valence in the form of the single bond received from the cation into two separate bonds emanating towards the anionic parts of the polar structure. The O26 atom, which belongs to the H_2O molecule that is not bonded to any metal cation, is [4]-coordinate and thus belongs to the non-transformer (H_2O) group (Hawthorne and Schindler, 2008; Schindler and Hawthorne, 2008). Based on our model, the O atoms of the remaining H_2O groups are [5]-coordinate, receiving three bonds from metal cations or H bonds from other

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TABLE 4. Selected interatomic distances (Å) for the structure of marécottite*.

U1–O2	1.799(6)	U2–O3	1.779(6)	U3–O1	1.797(6)
U1–O4^{i}	1.790(6)	U2–O19	1.783(5)	U3–O20	1.770(7)
U1–O7	2.495(6)	U2–O5	2.488(6)	U3–O8	2.259(4)
U1–O8	2.249(5)	U2–O10	2.279(6)	U3–O11	2.254(5)
U1–O8^{i}	2.281(4)	U2–O10^{iii}	2.228(4)	U3–O13	2.416(4)
U1–O11	2.286(5)	U2–O13	2.543(6)	U3–O16^{i}	2.415(4)
U1–O15^{ii}	2.541(5)	U2–O21^{iv}	2.441(5)	U3–O22^{iv}	2.514(5)
<U1–O_{Ur}>	1.795	<U2–O_{Ur}>	1.781	<U3–O_{Ur}>	1.784
<U1–O_{eq}>	2.370	<U2–O_{eq}>	2.396	<U3–O_{eq}>	2.372
		U4–O6	1.770(7)		
		U4–O14	1.782(7)		
		U4–O9^{iii}	2.498(4)		
		U4–O10	2.298(5)		
		U4–O11	2.298(4)		
		U4–O12^{ii}	2.472(5)		
		U4–O13	2.411(4)		
		<U4–O_{Ur}>	1.776		
		<U4–O_{eq}>	2.395		
S1–O7	1.471(5)			S2–O5	1.472(4)
S1–O16	1.465(6)			S2–O9	1.473(6)
S1–O21	1.476(5)			S2–O12	1.475(7)
S1–O22	1.475(7)			S2–O15	1.470(5)
<S1–O>	1.472			<S2–O>	1.473
Mg1–O24	2.120(5)	Mg2–O25	2.105(6)	Mg3–O17	2.103(5)
Mg1–O24v	2.120(5)	Mg2–O25^{vi}	2.105(6)	Mg3–O17^{ix}	2.103(5)
Mg1–O29	2.114(5)	Mg2–O28	2.129(5)	Mg3–O18	2.068(8)
Mg1–O29v	2.114(5)	Mg2–O28^{vi}	2.129(5)	Mg3–O18^{ix}	2.068(8)
Mg1–O31	2.078(9)	Mg2–O30	2.117(8)	Mg3–O23	2.093(6)
Mg1–O31v	2.078(9)	Mg2–O30^{vi}	2.117(8)	Mg3–O23^{ix}	2.093(6)
<Mg1–O>	2.104	<Mg2–O>	2.117	<Mg3–O>	2.088
O1–O8	2.984(6)	O7–O16	2.402(7)	O17–O18^{ix}	2.961(10)
O1–O11	2.914(6)	O7–O21	2.443(6)	O17–O23^{ix}	2.881(7)
O1–O16^{i}	2.874(8)	O7–O22	2.377(8)	O17–O30^{iv}	2.759(8)
O1–O22^{iv}	2.965(9)	O7–O24^{viii}	2.889(9)	O18–O23	2.920(11)
O1–O28^{vii}	2.918(8)	O8–O8^{i}	2.655(7)	O18–O23^{ix}	2.964(8)
O2–O7	2.825(6)	O8–O11	2.678(6)	O18–O27	2.781(8)
O2–O8	2.866(10)	O8–O16^{i}	2.995(7)	O19–O24^{vii}	2.992(7)
O2–O8^{i}	2.966(7)	O8–O20	2.874(9)	O19–O29^{vii}	2.908(7)
O2–O11	2.964(9)	O9–O10^{iii}	2.958(7)	O19–O33	2.994(14)
O2–O26	2.835(9)	O9–O12	2.439(10)	O20–O23	2.776(7)
O3–O5	2.940(7)	O9–O12^{x}	2.696(7)	O21–O22	2.412(9)
O3–O6	2.982(8)	O9–O15	2.384(6)	O21–O30	2.902(9)
O3–O10	2.907(10)	O10–O10^{iii}	2.712(8)	O22–O32^{xiii}	2.790(10)
O3–O10^{iii}	2.926(7)	O10–O13	2.678(6)	O24–O29	2.991(7)
O3–O21^{iv}	2.815(6)	O10–O14	2.942(9)	O24–O29^{v}	2.996(8)
O4–O8	2.865(7)	O10–O19^{iii}	2.844(7)	O24–O31	2.904(11)
O4–O11^{i}	2.910(6)	O11–O12^{ii}	2.999(6)	O24–O33^{xiv}	2.914(13)
O4–O18^{viii}	2.828(10)	O11–O13	2.735(7)	O25–O28	2.989(8)
O4–O28^{vii}	2.839(7)	O11–O14	2.946(7)	O25–O28^{vi}	2.999(8)
O5–O9	2.394(7)	O11–O15^{ii}	2.956(8)	O25–O30	2.989(9)
O5–O12	2.384(7)	O11–O20	2.978(9)	O25–O30^{vi}	2.983(12)
O5–O15	2.430(6)	O12–O15	2.399(9)	O25–O32^{vi}	2.918(13)
O5–O21^{iv}	2.735(7)	O12–O27^{xi}	2.813(10)	O26–O29^{xii}	2.723(12)
O5–O25^{iv}	2.867(10)	O13–O19	2.839(7)	O26–O34^{xv}	2.803(11)

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Table 4 (*contd.*)

O6–O9^{iii}	2.982(7)	O13–O20	2.951(7)	O27–O29^{xvi}	2.857(10)
O6–O10	2.878(6)	O13–O22^{iv}	2.814(6)	O27–O32^{iv}	2.782(10)
O6–O11	2.887(9)	O14–O31^{xii}	2.953(11)	O28–O30^{vi}	2.978(10)
O6–O12^{ii}	2.911(9)	O15–O31^{iii}	2.828(9)	O29–O31	2.935(11)
O6–O13	2.937(7)	O16–O21	2.346(6)	O29–O31^{v}	2.994(10)
O6–O17	2.762(10)	O16–O22	2.438(10)	O30–O32	2.648(9)
O7–O8^{i}	2.975(8)	O16–O22^{xiii}	2.709(6)	O33–O34	2.852(13)
O7–O15^{ii}	2.683(7)	O17–O18	2.937(9)	O33–O34^{xv}	2.899(18)

* Symmetry codes: (i) $-x$, $-y+2$, $-z$; (ii) $x+1$, y, z; (iii) $-x-1$, $-y+1$, $-z+1$; (iv) $x-1$, y, z; (v) $-x$, $-y$, $-z+1$; (vi) $-x+1$, $-y+1$, $-z$; (vii) $x-1$, $y+1$, z; (viii) x, $y+1$, z; (ix) $-x$, $-y+1$, $-z$; (x) $-x-2$, $-y+1$, $-z+1$; (xi) $-x-1$, $-y+1$, $-z$; (xii) $-x$, $-y+1$, $-z+1$; (xiii) $-x+1$, $-y+2$, $-z$; (xiv) $x+1$, $y-1$, z; (xv) $-x-1$, $-y+2$, $-z+1$; (xvi) x, $y+1$, $z-1$.

TABLE 5. The bond-valence analysis for marécottite*.

	U1	U2	U3	U4	S1	S2	Mg1	Mg2	Mg3	ΣBV	Assignment
O1			1.63							1.63	O
O2	1.62									1.62	O
O3		1.68								1.68	O
O4	1.65									1.65	O
O5		0.42				1.51				1.93	O
O6				1.71						1.71	O
O7	0.41				1.51					1.92	O
O8	1.30		0.66							1.96	O
O9				0.41		1.50				1.91	O
O10		1.33		0.61						1.94	O
O11	0.62		0.66	0.61						1.89	O
O12				0.43		1.50				1.93	O
O13		0.38	0.48	0.49						1.35	OH^-
O14				1.67						1.67	O
O15	0.38					1.52				1.90	O
O16			0.48		1.54					2.02	O
O17									0.66	0.66	H_2O
O18									0.73	0.73	H_2O
O19		1.67								1.67	O
O20			1.71							1.71	O
O21		0.46			1.49					1.95	O
O22			0.40		1.50					1.90	O
O23									0.68	0.68	H_2O
O24							0.63			0.63	H_2O
O25								0.66		0.66	H_2O
O26										0.00	H_2O
O27										0.00	H_2O
O28								0.62		0.62	H_2O
O29							0.64			0.64	H_2O
O30								0.64		0.64	H_2O
O31							0.71			0.71	H_2O
O32										0.00	H_2O
O33										0.00	H_2O
O34										0.00	H_2O
ΣBV	5.98	5.94	6.03	5.94	6.04	6.02	1.98	1.91	2.06		

* Values are given in valence units (vu). ΣBV = sum of bond valences incident at the atomic site; U^{6+}–O bond-valence parameters (r_0 = 2.045, b = 0.51) are taken from Burns *et al*. (1997); Mg^{2+}–O, S^{6+}–O bond-valence parameters are from Brown and Altermatt (1985).

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TABLE 6. The bond-valence analysis of the model of the H-bonding network proposed for the structure of marécottite*.

	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	H12	H13	H14	H15	H16	H17	H18	H19	H20	H21	H22	H23	H24	H25	H26	H27	H28	ΣBV
O1									0.2																				1.83
O2														0.2															1.82
O3																				0.2									1.88
O4										0.2							0.2												1.85
O5											0.2																		2.13
O6															0.2														1.91
O7																													1.93
O8																													1.96
O9																													1.92
O10																													1.94
O11																													1.90
O12																					0.2								2.13
O13																													1.35
O14				0.2																									1.87
O15			0.2																										2.09
O16																													2.02
O17															0.8	0.8													2.26
O18																	0.8	0.8											2.33
O19	0.2																												1.87
O20													0.2																1.91
O21							0.2																						2.15
O22																							0.2						2.09
O23													0.8	0.8															2.28
O24	0.8	0.8																											2.23
O25											0.8	0.8																	2.26
O26					0.2											0.2			0.8	0.8									2.00
O27						0.2												0.2			0.8	0.8		0.2					2.20
O28									0.8	0.8																			2.22
O29					0.8	0.8																							2.24
O30							0.8	0.8																					2.24
O31			0.8	0.8																									2.31
O32								0.2				0.2										0.2	0.8	0.8					2.20
O33		0.2																							0.8	0.8	0.2	0.2	2.20
O34																			0.2						0.2	0.2	0.8	0.8	2.20

* Values are given in valence units (vu). ΣBV = sum of bond valences. The bond valence equivalent to the H-bond, ~0.2 vu, is taken into consideration after e.g. Hawthorne and Schindler (2008), consistent with bond-valence parameters provided for the H bond by Brown (2002): H^{+}–O (r_0 = 0.569, b = 0.94).

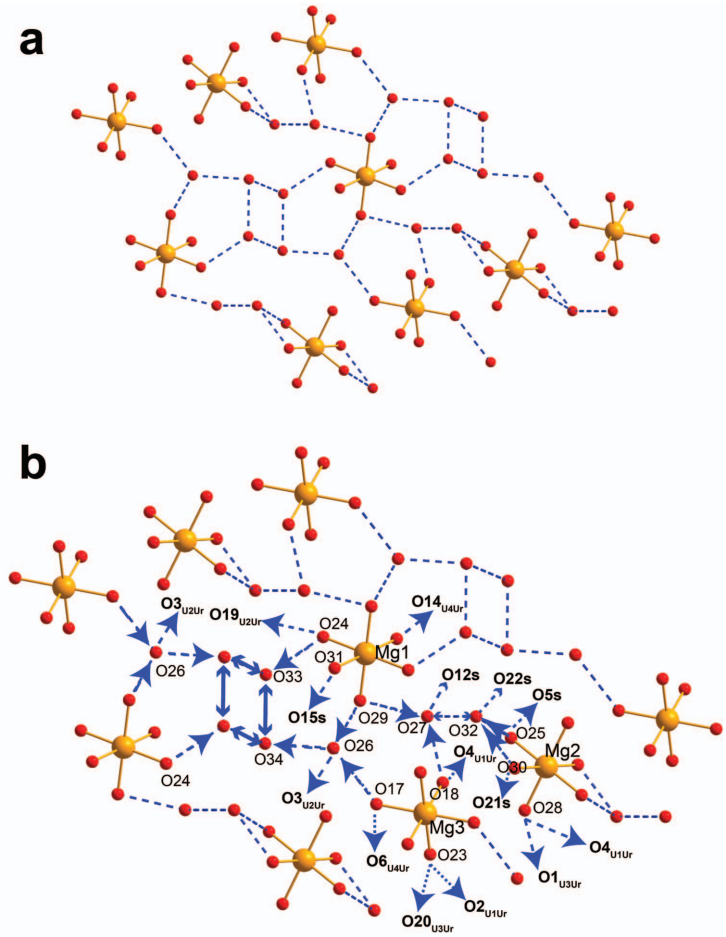


FIG. 3. An interstitial complex in marécottite. (*a*) Coordination of interstitial metal cation sites (orange = Mg^{2+}/Mn^{2+}), O atoms of the H_2O molecules (red) and linkage between them (dashed blue line); (*b*) proposed H-bond network. Blue arrows correspond to the particular H bond; acceptor atoms are displayed beside each arrow.

(H_2O) groups. Hence they are inverse transformer (H_2O) groups. Interestingly, the bond-valence calculations given by Schindler and Hawthorne (2008) do not suggest that there should be inverse transformer (H_2O) groups in the structure, but our model arising from the geometry of the possible H bonds support such a presence. Hence, based on the proposed model, the structure formula of the interstitial complex in marécottite can be written as $[^{[6]}Mg_3(H_2^{[3]}O)_{18}(H_2^{[4]}O)_2(H_2^{[5]}O)_8]^{3+}$.

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