On a new occurrence of rapidcreekite from NW Romania

Tudor TĂMAŞ[1,2]

(1) Babeş-Bolyai University Cluj-Napoca, Dept. of Geology, M. Kogălniceanu 1, 400084 Cluj Napoca, Romania, tudor.tamas@ubbcluj.ro
(2) Montana Caving Club, Oituz 8A/15, 430202 Baia Mare, Romania, montanabm@yahoo.com

Abstract
Rapidcreekite, $Ca_2(CO_3)(SO_4)\bullet 4H_2O$ has only been reported from a handful of locations around the world. The mineral was discovered in 1983 on an affluent of Rapid Creek (Yukon, NW Canada) and since then in a few locations with different lithological settings, but usually associated with gypsum and another carbonate. Its first cave occurrence was reported in 2009 from Diana Cave, SW Romania. Here we present data on a new occurrence of rapidcreekite in a cave in NW Romania, where the mineral is associated with gypsum and calcite, as well as detrital quartz and muscovite. The cave filling consists of forest soil accumulated from the surface. Rapidcreekite occurs as tiny white crusts and nodules in cracks in the soil fill, or covering seeds, insects or older crusts consisting of calcite and gypsum, down to depths of 15-20 cm in the sediment (but never on the surface), more frequently in areas corresponding to drips from the ceiling. The rapidcreekite crystals form groups of 1-2 µm rhombic bipyramids and may also replace gypsum. The source of sulfur necessary for the formation of gypsum and rapidcreekite is most likely pyrite disseminated in the limestone.

Résumé
Sur une nouvelle occurrence de rapidcreekite du nord-ouest de la Roumanie. Rapidcreekite, $Ca_2(CO_3)(SO_4)\bullet 4H_2O$, n'a été signalée que dans une peu d'endroits dans le monde. Le minéral a été découvert en 1983 sur un affluent de Rapid Creek (Yukon, NW Canada) et depuis lors dans quelques endroits avec des paramètres lithologiques différents, mais généralement associé au gypse et à un autre carbonate. Sa première occurrence dans une grotte a été signalée en 2009 dans la grotte de Diana, dans le sud-ouest de la Roumanie. Nous présentons ici des données sur une nouvelle occurrence de rapidcreekite dans une grotte du nord-ouest de la Roumanie, où le minéral est associé au gypse et à la calcite, ainsi qu'au quartz et muscovite détritiques. Le remplissage de la grotte est constitué de sol forestier accumulé de la surface. Rapidcreekite se présente sous forme de minuscules croûtes blanches et de nodules dans les fissures du sol, ou recouvrant des graines, des insectes ou des croûtes plus anciennes constituées de calcite et de gypse, jusqu'à des profondeurs de 15 à 20 cm dans les sédiments (mais jamais en surface), plus fréquemment dans les zones correspondant aux gouttes du plafond. Les cristaux de rapidcreekite forment des groupes de bipyramides rhombiques de 1 à 2 µm et peuvent également remplacer le gypse. La source de soufre nécessaire à la formation de gypse et de rapidcreekite est très probablement la pyrite disséminée dans le calcaire.

1. Introduction

Rapidcreekite, $Ca_2(CO_3)(SO_4)\bullet 4H_2O$ was first described by ROBERTS et al. (1986), in the Rapid Creek area (Dawson mining district, Yukon, NW Canada), otherwise known for its diversity of phosphate occurrences (ROBERTSON 1982; ROBINSON et al. 1992; GUNTER 2020). In its type locality, rapidcreekite is a secondary mineral, associated with gypsum, aragonite and kulanite, another uncommon phosphate. Since its discovery, a few other natural occurrences of rapidcreekite have been reported from Czechia (cave occurrence - ŽAK et al 2010), Germany, Greece, Norway (in mines), Poland (mine and slag dump), and Romania (cave occurrence - ONAC et al. 2009, 2013). Its structure was refined in 1996 by COOPER & HAWTHORNE and in 2013 by ONAC et al. A new occurrence of rapidcreekite was discovered in the Plopiş Mountains on the Ponor karst plateau, situated at the limit of three counties from the NW part of Romania: Sălaj, Cluj and Bihor (Fig. 1). The karst plateau is formed on Triassic (Anisian) limestones and dolomites (GABRIAN et. al 2010). In May 2018, during a student field trip, a 1.3 m long “den” was discovered at 699 m a.s.l. on the southern side of the plateau and a short exploratory dig opened a relict phreatic passage, 0.8 m high and 0.6 m large, which is blocked by sediments after 10 m. The thickness of the sediments in the passage cannot be determined yet, however two short cores, covering the first 50 cm, were sampled. The cave filling consists of forest soil accumulated from the surface, with variable amounts of organic material (leaf fragments, seeds, charcoal, insect elitrae), bones, lithoclasts (limestone, dolomite, quartzites), and broken speleothems.

2. Materials and methods
The cores sampled from the sediment at the bottom of the passage were described in the laboratory and sub-sampled for charcoal, pollen, and clay mineral analysis. Several coatings and powdery deposits (tiny white crusts and

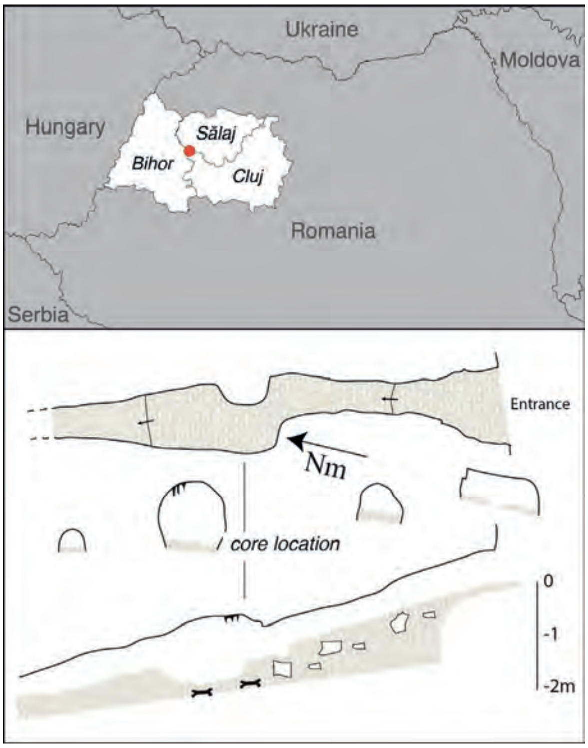

Figure 1: top: Location of the Ponor plateau in NW Romania; bottom: Passage map with the location of the core and samples described in the text.

nodules), as well as fragments of host rock, speleothems (stalactites and centimetric crusts), and bones were found when dividing the subsamples. They were selected primarily for X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses. XRPD analyses were done with a Bruker D8 Advance diffractometer, using Cu and Co tubes and a linear LynxEye detector. Selected powders from the samples were analyzed generally between 3.8 - 64˚ 2Θ. Pattern calculations were performed with the Mercury software using the *.cif* files available online. For clay minerals, XRPD analyses on the oriented mounts were achieved after air-drying, ethylene-glycol solvation for 24 h and thermal treatment at 400°C and 550°C for 1 h. The Bruker DiffracEVA 2.1 software with the PDF2 database from ICDD were used to identify the mineral composition. The clay minerals were identified in accordance with MOORE & REYNOLDS (1997). For SEM observations the samples were mounted on double-sided adhesive carbon tabs on aluminum holders and covered with a 10 nm gold layer, then observed with a Hitachi SU8230 electron microscope equipped with an Oxford Instruments elemental analysis system. Additional EDS analyses were done on uncovered samples using a specially designed sample holder with lateral clamps, to avoid bias from the adhesive carbon tabs.

3. Results and discussion

1. ***Rocks and clay minerals***. XRPD analyses of the rock fragments recovered from the sediment revealed the presence of both limestone and dolomite in the lithoclasts. The clay mineral analysis has shown a fairly uniform composition of the sediment samples taken from 5 different levels, with vermiculite, muscovite and kaolinite the minerals identified, similar to the soil samples collected from the plateau surface.
2. ***Speleothems.*** Considering the limited extent of the cavity and the type of samples retrieved from the sediments, the mineralogical composition of the samples was surprisingly diverse: aside from the clay minerals, *carbonates* (calcite, Mg-calcite), *phosphates* and *sulfates* were identified in various samples. As expected, centimetric stratified crusts and short stalactites buried in the sediment consisted primarily of calcite. Little calcite crusts were also found at or near the sediment surface. At several levels in the sediment we found phosphate crusts (separately hydroxylapatite and brushite) on bones and on broken calcite speleothems, indicating that a small source exists for phosphoric acid in the sediments. As brushite and gypsum are isostructural, the occurrence of one or the other was determined through SEM - EDS, the presence of P or S indicating the mineral present.
3. ***Sulfates***. The two sulfates identified were gypsum and rapidcreekite, in two different types of samples: a. *Gypsum and calcite centimetric crusts* (Fig. 2), containing white calcite on the outside part and translucent gypsum in a central millimetric band, separated by a thin layer of manganese oxides of bacterial origin (probably ranciéite). Rapidcreekite was first identified on the edges of this particular gypsum layer.
b. While separating subsamples for clay mineral analysis, we noticed *millimetric nodules and powdery deposits* on desiccation cracks, insect elitrae and small limestone fragments occurring at various depths in the sediment cores (more frequently between 10 cm and 20 cm, less frequent below 30 cm and never near the surface). 25 X-ray powder diffraction on 13 such deposits have shown they consist invariably of gypsum and rapidcreekite, with detrital quartz and muscovite. Rapidcreekite, identified from the reflections in the diffraction pattern at d-spacings 7.78 (100), 4.31, 3.88, 3.24, 3.10, 2.92 and 2,79, very close to

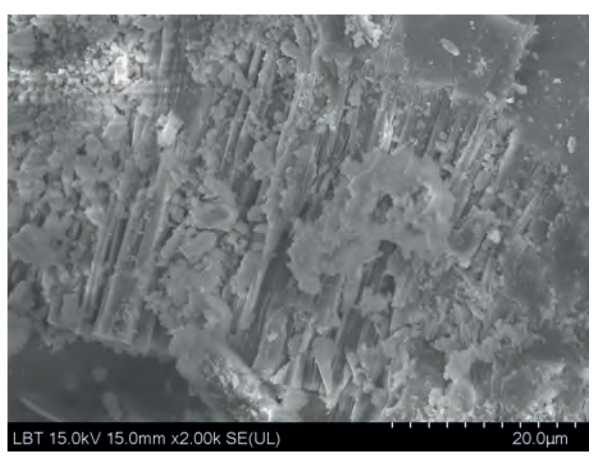

Figure 2: Fibrous gypsum in a calcite and gypsum crust

the pattern determined by ROBERTS et al. (1986), is however never occurring as the main mineral, some of the lines being partially masked by gypsum and quartz which have higher crystallinity (Fig. 3). As only 7 reflections in the diffraction patterns could be correlated to rapidcreekite with certainty, and due to its occurrence only in mixtures, calculating the crystal structure was not possible. Nevertheless, comparing the XRPD pattern with the structures available, we imply that the new phase is consistent with rapidcreekite. At SEM, rapidcreekite crystals form groups of 1-2 µm elongated rhombic bipyramids with perfect cleavage (Fig. 4). EDS analyses invariably show Ca, S, C and O as main constituents, with various elements also occurring in minor amounts, most likely from detrital contribution (Si, Fe, K and Al) and with variable amounts of P. In most instances gypsum may be identified by its larger (5 – 30 µm), typically monoclinic-prismatic crystals and by the lack of carbon in its composition.

An EDS spectrum similar to the rapidcreekite crystals is shown by slightly larger (up to 5 µm), monoclinic crystals, which may represent pseudomorphs after gypsum (Fig. 4). As we found both brushite and gypsum in different samples, we also verified if ardealite, with the chemical formula $Ca_2(SO_4)(HPO_4)\bullet 4(H_2O)$ and a somewhat similar diffraction pattern (first reflection at d=7.74 Å (100)), was not present. In 6 measurements done on the subsample taken from 9 cm in the core, the P content determined through EDS was 6.7 – 8% with C <2%, pointing to a likely presence of ardealite (which has ~9% P). However, all the other subsamples (i.e. from cm 10, 12, 14 etc) had a phosphorus content between 0.1 and 1.6% (with a mean of 0.5% for the crystals in Fig. 3), indicating the absence of ardealite.

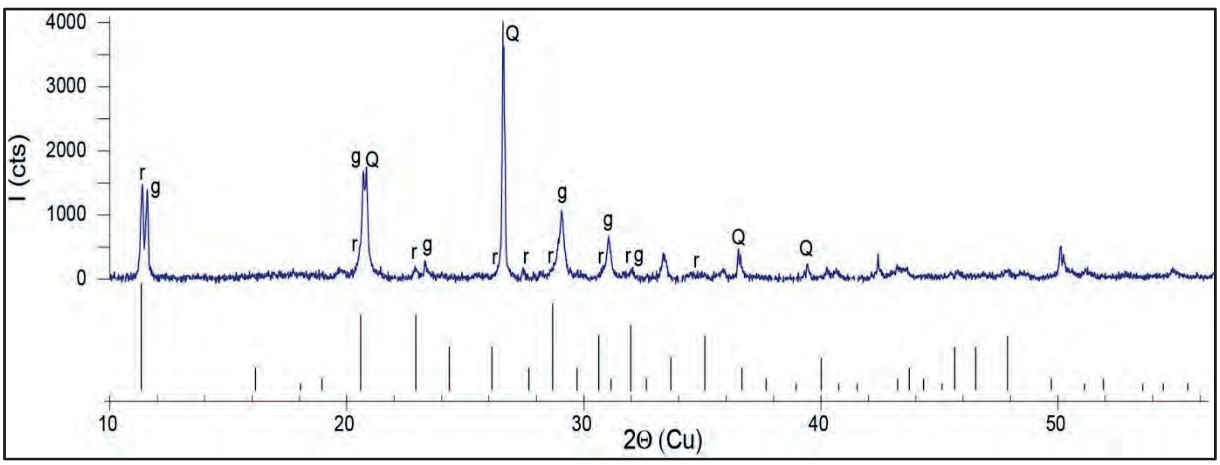

Figure 3: X-ray powder diffraction pattern for a sample containing rapidcreekite (r), gypsum (g), and quartz (Q) with the lines from the pattern of ROBERTS et al. (1986) for comparison.

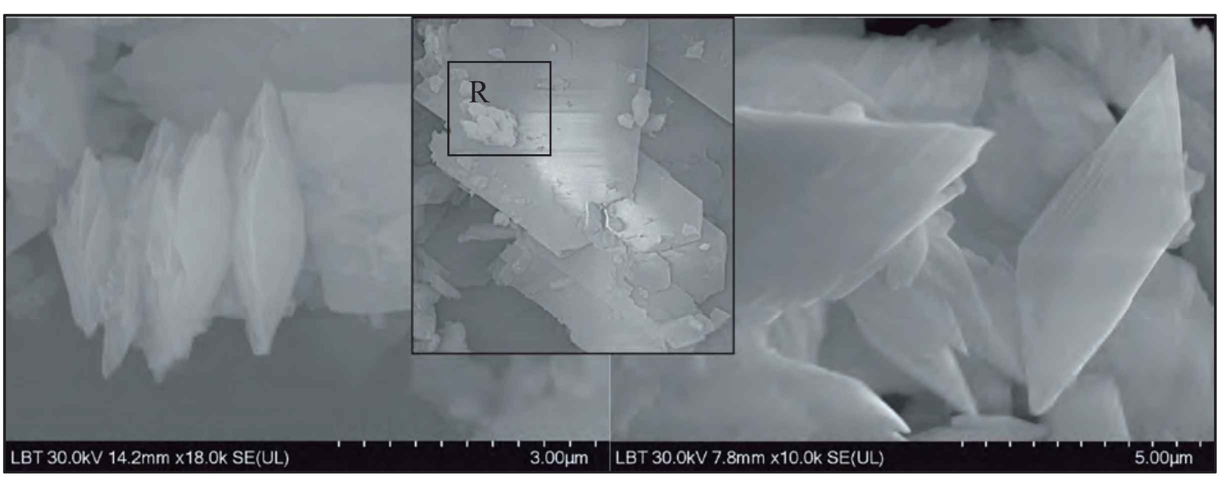

Figure 4: SEM images of rapidcreekite crystals (left) and monoclinic prisms originally of gypsum (right) with similar chemical (EDS) composition. Inset: gypsum crystals (ca. 10 µm long) with rapidcreekite crystals (R, 1µm).

5. Concluding remarks

The study of soil-like sediments from a short cave passage located in the Ponor karst plateau, NW Romania has uncovered a mineral association consisting of carbonates (calcite, Mg-calcite), calcium sulfates (gypsum, rapidcreekite), and phosphates (hydroxylapatite, brushite, and ardealite). The main focus of this study was the third occurrence of rapidcreekite in a karstic environment. Although not present as the main mineral in any of the samples analyzed, and with crystals very rarely over 2 µm in size - and as such posing various analytic inconveniences - its reflections present are consistent with the pattern obtained by ROBERTS et al. (1986) on crystals from the type locality. EDS analyses sustain our inference, the low phosphorus contents differentiating the crystals from ardealite, which has a somewhat similar diffraction pattern. The depositional environment is different from the two cave occurrences already published (ONAC et al. 2009, 2013 and ŽAK et al 2010), rapidcreekite forming in a passage filling in which it is directly associated only with calcite and gypsum, the carbonate being provided by the few drip points existent in the ceiling of the passage. Up to this point, the SEM and EDS data seem to suggest that rapidcreekite crystals are formed on the surface of existing gypsum aggregates as a secondary phase, and also probably replacing gypsum. Another peculiarity of the occurrence is the fact that in close vicinity (1 cm away), crusts and nodules very similar in appearance consist of calcium phosphates (brushite and minor ardealite), pointing to the presence of very localized sources of phosphorus and sulfur inside the passage sediments. The initial source of sulfur for the gypsum speleothem formation is most likely pyrite disseminated in the limestone host rocks.

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References

GABRIAN I., TĂMAŞ T., SAHY D., ONAC B.P. (2010). Ponor Plateau (South-Eastern Plopis Mountains). In Orăşeanu, I., Iurkievicz, A., editors: Karst Hydrogeology of Romania, Belvedere, Oradea, p. 325-328.

GUNTER R. (2020). Yukon phosphate Update 2020. https://www.mindat.org/article.php/3865/Yukon+Phosphate+Update+2020.

MOORE D.M. & REYNOLDS R.C., Jr. (1997). X-Ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd ed. Oxford: Oxford University Press, 378 pp.

ONAC B.P., SUMRALL J., TĂMAŞ T., POVARĂ I., KEARNS J., DÂRMICEANU V., VEREŞ D., LASCU, C. (2009). The relationship between cave minerals and hypogene speleogenesis along the Cerna valley (SW Romania). Acta Carsologica, 38,1, 27-39.

ONAC B.P., EFFENBERGER H., WYNN J.G., POVARĂ I. (2013). Rapidcreekite in the Sulfuric acid Weathering Environment of Diana Cave, Romania. American Mineralogist, 97,7, 1302-1309.

ROBERTS A.C., ANSELL H. G.; JONASSON I. R.; GRICE J.D. RAMIK R.A. (1986). Rapidcreekite, a new hydrated calcium sulfate-carbonate from the Rapid Creek area, Yukon Territory. Canadian Mineralogist, 24, 51-54.

ROBERTSON B.T. (1982). Occurrence of epigenetic phosphate minerals in a phosphatic iron formation, Yukon. Canadian Mineralogist, 20, 177-187.

ROBINSON G.W., VAN VELTHUIZEN J., ANSELL H.G., STURMAN B.D. (1992). Mineralogy of the Rapid Creek and Big Fish River area, Yukon Territory. Mineralogical Record, 23, 1-47.

ŽAK K., SKALA R., FILIPPI M., PLASIL J. (2010). Ikaite - little known mineral of iced caves: occurrence in seasonal cave ice formations of the Koda Cave (Bohemian Karst). Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, 18, 1, 109-115. (in Czech)