Mineralogical and cathodoluminescence characteristics of Ca-rich kutnohorite from the Úrkút Mn-carbonate mineralization, Hungary

M. Polgári^{1,*}, B. Bajnóczi¹, V. Kovács Kis², J. Götze³, G. Dobosi¹, M. Tóth¹ and T. Vigh⁴

 ¹ Institute for Geochemical Research, Hungarian Academy of Sciences, H-1112, Budapest, Budaörsi út 45, Hungary
 ² Research Institute for Technical Physics and Materials Science, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 49, Hungary

³ Department of Mineralogy, TU Bergakademie Freiberg, Brennhausgasse 14, D-09596 Freiberg, Germany
 ⁴ Mangán Ltd., H-8409 Úrkút, Hungary

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ABSTRACT

Kutnohorite with moderate and bright orange-red cathodoluminescence (CL) was studied by CL microscopy and spectroscopy. This mineral was found in fossiliferous concretions composed mainly of rhodochrosite from the Mn-carbonate mineralization at Úrkút, Hungary. The CL microscopy reveals that kutnohorite occurs as impregnations, layers and veinlets. X-ray diffraction, infrared spectroscopy and electron microprobe studies indicate that the luminescent kutnohorite has excess Ca (72.9–80.0 mol.% CaCO₃, 16.3–20.5 mol.% MnCO₃, 3.3–5.6 mol.% MgCO₃ and 0.0–0.5 mol.% FeCO₃). Transmission electron microscopy shows that the luminescent carbonate has a dolomite-type structure, with modulated and mosaic microstructures. The CL spectra of this Ca-rich kutnohorite have a single emission band at 630 nm that is characteristic of Mn^{2+} substitution in the structure. Our results provide evidence for moderate-to-bright cathodoluminescence of Mn-rich natural carbonates even at 8–10 wt.% Mn and up to 2400 ppm Fe. The self-quenching of Mn appears incomplete in the case of Ca-rich kutnohorite from Úrkút.

Keywords: kutnohorite, kutnahorite[†], rhodochrosite, cathodoluminescence, spectroscopy, PIXE, TEM, Úrkút, Hungary.

Introduction

CATHODOLUMINESCENCE microscopy is a technique routinely used in sedimentary petrology for the study of carbonate rocks and their diagenetic history (Marshall, 1988; Machel, 2000). Aside from the texture revealed by cathodoluminescence (CL) microscopy, the (quantitative) CL spectroscopy combined with trace element determinations (e.g. particle-induced X-ray emission – PIXE) can provide further information about the activator elements in carbonates regarding their coordination and ionic charge (Richter *et al.*, 2003; Gaft *et al.*, 2005). Much work has been done on the CL characteristics of the most important and abundant carbonate minerals such as calcite, dolomite and aragonite. Other less common carbonate species have received little attention using either CL microscopy or spectroscopy. There are some studies which deal with magnesite (Spötl, 1991; El Ali *et al.*, 1993), smithsonite (Götte and Richter, 2004) and rhodochrosite (Gaft *et al.*, 2005).

It is generally accepted that the Mn^{2+} ion (3d⁵) and most trivalent rare-earth elements (*REE*) (4f) are the most important activators of extrinsic CL in carbonate minerals, while Fe²⁺ is a quencher of

^{*} E-mail: polgari@geochem.hu

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[†] According to the IMA CNMNC the official name is kutnohorite, but kutnahorite is also widely used.

CL (e.g. Marshall, 1988; Machel, 2000). Using the Quantitative High Resolution Spectral analysis of CL (QHRS-CL) the lower activation limit of Mn^{2+} in calcite (yellow-orange CL) and dolomite (yellow to red CL) has been extended to <1 ppm (Habermann *et al.*, 1998, 1999; Gillhaus *et al.*, 2001). A dull-blue CL emission, possibly caused by lattice defects and imperfections, has been reported for carbonates with no or only minor traces of impurities (intrinsic luminescence, e.g. Machel *et al.*, 1991).

The CL spectra of calcite usually display one emission peak and studies have reported various wavelengths from 580 to 640 nm; mostly 605-620 nm for this peak (El Ali et al., 1993; Richter et al., 2003). Dolomite can also show single-band CL spectra at ~660 nm, but two peaks are much more characteristic. The Mn²⁺ ion can occupy Ca^{2+} -sites (A sites) as well as Mg^{2+} -sites (B sites) in dolomite and this phenomenon produces two overlapping broad bands in the CL spectra (El Ali et al., 1993; Gillhaus et al., 2000, 2001). The emission peak of red luminescent dolomites at 640-670 nm is related to Mn substitution in the Mg-site, as is the case for the ~655 nm peak for Mn^{2+} in magnesite (El Ali *et* al., 1993; Spötl, 1991) and the ~660 nm peak in smithsonite (Götte and Richter, 2004), due to the similar ionic radii and metal-oxygen bond lengths of their structures (Marshall, 1988). In yelloworange dolomites, subtraction of the 640-670 nm emission band reveals the 565-595 nm peak for Mn²⁺ at the Ca-site (El Ali et al., 1993; Gillhaus et al., 2000, 2001).

Habermann et al. (1998, 1999) developed a quantification method for Mn with OHRS-CL (<10 ppm) for Fe-poor calcite using the peak height of the Mn emission band in the CL spectra correlated with the Mn content determined by PIXE (>10 ppm Mn). The application of Mn quantification to dolomite is complicated by the two overlapping bands in the emission spectra. Gillhaus et al. (2000) distinguished red and yellow luminescent dolomites with different relations of the two broad bands: using the peak-height as a criterion, a linear correlation for Mn between 20-1000 ppm was detected, which corresponds to the same correlation found by Habermann et al. (1998, 1999) for calcite. By integrating peak areas, rather than peak heights, a very good correlation between Mn content and CL intensity in Fe-poor dolomite with <3000 ppm Mn was obtained (Gillhaus et al., 2001). Similar results were found for other carbonates by Götte and Richter (2004).

Although it is well known that Mn is the most important CL activator in carbonates, the CL method is rarely applied in the petrological investigation of Mn-carbonate mineralization, due to the widely acknowledged effect of concentration-quenching or self-quenching. The decrease in CL intensity (self-quenching) occurs at large activator (Mn) concentrations, when the average space between activator ions becomes smaller and instead of being emitted as luminescence, the excitation energy is transferred from the absorbing activator ion to neighbouring similar ions (Marshall, 1988). Critical concentrations of 500-1000 ppm were documented for the start of self-quenching for Mn²⁺-activated CL in calcite (Mason, 1987; Mason and Mariano, 1990; El Ali et al., 1993; Habermann et al., 2000). However, comprehensive knowledge of the luminescence behaviour of Mn-rich (>1 wt.% Mn) carbonates (manganocalcite, kutnohorite, rhodochrosite) does not exist. The possible limit of concentration extinction is not known. Walker et al. (1989) found that rhodochrosite with 46.0 wt.% Mn and 1.0 wt.% Fe was virtually non-luminescent. However, luminescent rhodochrosite, was reported by Gorobets et al. (1978) and Gaft et al. (1981, 2005), which seems to indicate incomplete self-quenching for Mn²⁺ and support for the suggestion of Machel et al. (1991) that luminescence up to that of the large Mn concentrations may occur.

We found a brightly to moderately luminescent carbonate with 8-10 wt.% Mn in some rhodochrosite concretions containing fossil fish collected from the Úrkút Manganese Mine, Hungary. Powder X-ray diffraction (XRD) revealed that this carbonate was kutnohorite. Kutnohorite is a dolomite-type double carbonate with the general formula CaMn(CO₃)₂ (hexagonal, space group $R\bar{3}$ (Frondel and Bauer, 1955; Farkas et al., 1988). It is often cited without any structural or chemical characterization as Mn-rich calcite occurring as a rare mineral in hydrothermal, metamorphosed and sedimentary sequences (e.g. Ozturk and Frakes, 1995; Gutzmer and Beukes, 1996, 1998; Fan et al., 1999; Hein et al., 1999; Krajewsky et al., 2001; Large et al., 2001; Burke and Kemp, 2002; Nyame et al., 2003). In this paper we report the CL microscopic and spectroscopic properties of kutnohorite for the first time. The aims of our study were to characterize the structure of the luminescent carbonate and determine the possible causes of CL. In addition to conventional powder XRD, infrared (IR) spectroscopy, EMPA and CL spectroscopy were used to characterize emission centres and their structural position. Transmission electron microscopy (TEM) was used for the structural characterization.

Materials and methods

Three concretions were collected from the Úrkút Manganese Mine, which is situated in the Trans-Danubian Central Range in Hungary (Fig. 1). Samples H1, H3 and H4 were collected from shaft No. III level +186 (archive numbers of the samples at the Institute for Geochemical Research, Budapest are PM144/H1, PM144/H3 and PM144/H4). The geology and mineralogy of the Úrkút manganese deposit is described by Polgári (2001) and Polgári *et al.* (1991, 2000, 2004, 2005*a*,*b*).

The brown and pinkish elliptical concretions are 30-50 cm in size (Fig. 2*a*). The very finegrained samples contain parts with different colours and show coarser breccia-like microlayers, signs of infiltration and microfractures (Fig. 2b-d, Table 1). Occasionally, veinlets a few millimetres thick cut the matrix of the concretions (Fig. 2*d*).

Bulk samples were analysed by powder XRD. A Philips 1730 X-ray diffractometer with a graphite crystal monochromator and Cu- $K\alpha$ radiation was used and continuous scans were run from 3–70°20 at 45 kV and 35 mA, with a scan speed of 0.02°20/s. Fragments of the luminescent veinlet from sample H4 were also analysed separately using a slower scan speed.

Separate samples of the luminescent veinlet and its adjacent matrix from sample H4 were examined by IR spectroscopy. Measurements between 400 and 4000 cm⁻¹ were carried out with a Bruker Equinox type Fourier transform infrared (FTIR) spectrometer with 2 cm⁻¹ resolution. The KBr pastille method was used with ~1 mg of samples and ~200 mg KBr.

Quantitative EMP measurements of carbonates were performed on carbon-coated rock chips and thin sections using a JEOL Superprobe 733 EMP equipped with an Oxford INCA 2000 energydispersive X-ray spectrometer (EDS). The analytical conditions were 15 kV accelerating voltage, 5 nA beam current and a counting time of 50 s. Calcite, dolomite, siderite and spessartine (for Mn) standards were used for calibration. An alternative calibration using wollastonite, MgO, hematite and spessartine standards gave practically the same results. All analyses were made using a fast scanning mode at different magnifications to prevent carbonate decomposition under the electron beam and in the case of very fine scale heterogeneities to produce an average value for the analysed area.

Cathodoluminescence examinations were initially performed on polished rock chips using a Reliotron 'cold-cathode' microscope operated at 5-7 kV accelerating voltage and 0.5 to 0.9 mA current. Additionally, carbon-coated thin sections were studied using a 'hot-cathode' CL microscope HC1-LM (see Neuser, 1995) operated at 14 kV acceleration voltage and a current density of ~10 μ A/mm². Luminescence images were captured on-line during CL operations by means of an adapted digital video-



FIG. 1. Location of the Úrkút Manganese Mine in Hungary (central Europe).

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FIG. 2. Macroscopic appearance of the Mn-carbonate concretions. Carbonate concretion with fish fossil (*a*: sample H1). The very fine-grained samples contain parts different in colour (*b*: sample H1) and show coarser debris-like microlayers (*c*: sample H3) with a greater content of microfossils. Signs of infiltration, microfractures and, rarely, veinlets (*d*: sample H4) occur. For the chemical composition of the different parts see Table 1.

camera (KAPPA 961-1138 CF 20 DXC) with cooling stage. Cathodoluminescence spectra in the wavelength range 300-900 nm were

recorded with an Acton Research SP-2356 digital triple-grating spectrograph with a Princeton Spec-10 400/B/XP CCD detector

TABLE 1. Chemical composition (wt.%) of the different parts of the concretions (data are averages of four EMP analyses made on an area 100 μ m × 100 μ m for 100 s; for occurrence see Fig. 2).

Sample code and part	SiO_2	TiO ₂	Al_2O_3	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5
H1, part 1 (Fig. 2b)	0.16	0.00	0.09	0.32	40.65	0.23	12.85	0.31	0.03	8.72
H1, part 2	0.65	0.09	0.40	0.32	42.92	1.05	10.19	0.12	0.06	0.34
H1, part 3	1.81	0.01	0.75	0.16	32.41	2.01	19.43	0.06	0.01	0.37
H3, part 1 (Fig. 2c)	1.22	0.04	0.31	0.24	33.82	1.76	18.49	0.08	0.03	0.19
H3, part 2	29.43	0.13	2.60	2.24	23.49	12.29	2.80	0.11	0.62	0.08
H3, part 3	11.25	0.08	1.01	0.55	33.36	6.36	10.27	0.13	0.22	0.13
H4, part 1 (Fig. 2d)	1.57	0.05	4.65	0.19	43.52	1.69	5.16	0.21	0.06	0.46
H4, part 2	0.92	0.05	1.18	0.23	40.70	1.23	11.21	0.08	0.13	0.32
H4, part 3 (veinlet)	0.17	0.03	0.11	0.20	11.21	1.25	39.89	0.05	0.00	0.00

attached to the CL microscope by a silica-glass fibre guide. The spectra were measured under standardized conditions (wavelength calibration using Hg lamp, spot width 30 μ m). To prevent any falsification of the CL spectra due to electron bombardment, all spectra were taken on non-irradiated sample spots.

For the TEM study, a fragment of the luminescent veinlet from sample H4 was gently crushed in ethanol and a drop of the resulting suspension was placed onto a carbon-Cu grid. The selected area electron diffraction (SAED) patterns and TEM images were obtained using a Philips CM20 TEM operating at 200 keV. The grain compositions were measured using a NORAN EDS.

Results

Mineralogy and chemistry

Rhodochrosite (3.67-3.66 Å, 2.85-2.84 Å, 2.39 Å, 2.18 Å, 2.00 Å, 1.83 Å, ASTM 86-0173 for rhodochrosite, syn) and kutnohorite <math>(3.80-3.79 Å, 2.99 Å, 2.79 Å, 2.46 Å, 2.23-2.26 Å, 2.07 Å, 1.87 Å, 1.84 Å, ASTM 19-0234 for kutnohorite, calcic) can be identified as the main components in the XRD patterns of the bulk concretions (Fig. 3). Sharp peaks are



FIG. 3. (a) XRD patterns of the bulk concretions and (b) the separated veinlet of sample H4.

characteristic for kutnohorite, while rhodochrosite shows slight peak broadening. Some smectite and hydroxylapatite were also detected, the latter mostly in the core of sample H1. The main component of the veinlet from sample H4 proved to be Ca-rich kutnohorite, beside which the most intense peaks of rhodochrosite also appear (Fig. 3*b*), which is inferred to be derived from the adjacent matrix of the concretion.

Back-scattered electron (BSE) images revealed that the bulk material of the concretions is an intimate mixture of two $10-100 \mu m$ phases (Fig. 4). Irregularly-shaped light and dark patches alternate in the samples; the sizes of the patches as well as the proportion of the two phases change from site to site (Fig. 4a-d). At lower magnification, the dark veinlet in sample H4 exhibits an apparently homogeneous appearance (Fig. 4e); however, crystals with feather-like compositional patterns are seen at higher magnification (Fig. 4f). The light phase in the BSE images is a Mn-rich carbonate (45.5-49.5 wt.%MnO, Table 2) with a small Ca and Mg content (4.1-7.0 wt.% CaO and 0.8-1.0 wt.% MgO) identified as rhodochrosite with $81.2-87.5 \text{ mol.}\% \text{ MnCO}_3$. The dark phase (in patches and the veinlet in sample H4) is Ca-rich with significantly less Mn than the light phase (38.1-40.5 wt.% CaO, 10.2-12.5 wt.% MnO and 1.2-2.7 wt.% MgO, Table 2). This dark carbonate is kutnohorite with an excess of Ca ($72.9-80.0 \text{ mol.}\% \text{ CaCO}_3$, $16.3-20.5 \text{ mol.}\% \text{ MnCO}_3$, $3.3-7.4 \text{ mol.}\% \text{ MgCO}_3$). Light zones in the feather-like pattern of the kutnohorite veinlet (Fig. 4f) have ~1 wt.\% more MnO and 1.6 wt.% less CaO than the darker zones. The FeO contents of kutnohorite and rhodochrosite are 0.0-0.3 and 0.1-0.3 wt.%, respectively.

Mid-IR spectra of the separated parts of sample H4 confirm the different chemical composition of the two carbonate phases (Fig. 5). The matrix of the concretion is mainly composed of rhodochrosite with vibration bands v2 at 865 cm⁻¹ and v4 at 725 cm⁻¹. Vibration bands (v2 at 872 cm⁻¹ and v4 at 717 cm⁻¹) for the dominant carbonate of the veinlet are shifted towards higher and lower frequencies, respectively, compared with rhodochrosite spectra and indicate a Ca-dominant



FIG. 4. BSE images showing the texture of the concretions. (*a*,*b*) Sample H1 with dark phase (kutnohorite) and light phase (rhodochrosite). (*c*) Dark kutnohorite displacing light rhodochrosite in sample H3. (*d*) Matrix of sample H4. (*e*,*f*) Kutnohorite veinlet in sample H4 at higher magnification showing a feather-like compositional pattern.

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remainder were acquire	d by point	measureme	ents).									
		Oxide (wt.%)		7	Atom fracti	on (a.p.f.u.	(- Carbonate	: (mol.%) -	
Sample code and part	CaO	MnO	MgO	FeO	Са	Mn	Mg	Fe	$CaCO_3$	MnCO ₃	MgCO ₃	FeCO ₃
Kutnohorite (dark phase of	n BSE ima	ges, Fig. 4)										
H1, part 2	39.10	11.95	1.95	0.05	1.524	0.368	0.106	0.002	76.20	18.40	5.30	0.10
H1, part 3	37.03	12.35	2.71	0.32	1.457	0.384	0.148	0.010	72.85	19.20	7.40	0.50
H3, part 1	38.36	12.47	2.03	0.00	1.503	0.386	0.111	0.000	75.15	19.30	5.55	0.00
H4, part 2	38.14	13.26	1.71	0.26	1.490	0.409	0.093	0.008	74.50	20.45	4.65	0.40
H4, part 3 (veinlet) (4)	39.89	11.21	1.25	0.20	1.575	0.350	0.069	0.006	78.75	17.50	3.45	0.30
H4, part 3 (veinlet) (10)	39.51	10.26	1.34	0.24	1.591	0.326	0.075	0.007	79.55	16.30	3.75	0.35
H4, part 3 (veinlet) (7)	40.51	10.51	1.21	0.18	1.600	0.328	0.066	0.005	80.00	16.40	3.30	0.25
H4, matrix (3)	37.95	12.38	1.43	0.31	1.519	0.392	0.080	0.010	75.95	19.60	4.00	0.50
Average	38.81	11.80	1.70	0.20	1.532	0.368	0.094	0.006	76.62	18.39	4.68	0.30
Rhodochrosite (light phase	on BSE ir	nages, Fig.	4)									
H1, part 2	4.16	49.55	0.88	0.27	0.186	1.750	0.055	0.009	9.30	87.50	2.75	0.45
H1, part 3	4.13	49.48	0.96	0.22	0.184	1.748	0.060	0.008	9.20	87.40	3.00	0.40
H3, part 1	4.92	48.84	0.64	0.05	0.221	1.737	0.040	0.002	11.05	86.85	2.00	0.10
H4, part 2	7.04	45.54	0.91	0.06	0.317	1.623	0.057	0.002	15.85	81.15	2.85	0.10
H4, matrix (4)	5.38	45.53	0.84	0.26	0.254	1.681	0.055	0.009	12.70	84.05	2.75	0.45
Average	5.13	47.69	0.85	0.17	0.232	1.708	0.053	0.006	11.52	85.39	2.67	0.30

TABLE 2. Chemical composition of the carbonate phases in the concretions determined by EMP analysis (number of analyses are indicated in parentheses; the



FIG. 5. IR absorbance spectra for sample H4. The vibrational bands v3, v2 and v4, characteristic of carbonates, are indicated between 1800 and 500 cm⁻¹. The veinlet contains a Ca-Mn carbonate (Ca-kutnohorite) with some MnCO₃ (rhodochrosite), while its adjacent matrix is mainly composed of rhodochrosite.

carbonate, according to Böttcher et al. (1992, 1993).

Cathodoluminescence microscopy and spectroscopy

Our samples show moderate and bright orange-red luminescence in the form of layers, infiltration-like textures and veinlets (Fig. 6). In the matrix of the concretions, areas with moderate and bright CL can be observed alongside non-luminescent areas (Fig. 6b,d,f). Veinlets in sample H4 exhibit moderate red-brownish CL (Fig. 6f,h). The crystals in the veinlets do not show zoning, only slight inhomogeneity, but their rims have brighter orange CL. The borders of the veinlets show an outer part with moderate red-brown CL and an inner part with bright orange-red CL (Fig. 6f,h).

The CL spectra of the luminescent phases, in both the matrix and veinlets of the concretions, show one emission peak at 629–636 nm (Fig. 7), without any visible shoulder. No difference in the position of this peak is observed in the spectra of moderately and brightly luminescent areas and only the peak intensities vary, at 3500–15000 counts. The spectra of the areas with moderate CL have lower intensities than that of the brightly luminescent areas. The veinlets with moderate CL show higher spectral intensity than their bright margin.

According to the mineralogical (XRD) and textural (EMPA) studies the moderately and brightly luminescent carbonate phase with a 630 nm emission peak is kutnohorite. The nonluminescent phase in the matrix is rhodochrosite.

TEM study

A small fragment of the luminescent veinlet from concretion H4 was investigated by TEM in order to determine whether or not the excess Ca measured by EMPA with respect to a stoichiometric CaMn(CO₃)₂ is related to submicroscopic domains of calcite that cannot be resolved by EMPA. Both monocrystalline parts (grains) and polycrystalline aggregates were identified within the analysed sample.

A 110*- c^* SAED pattern in Fig. 8*a* shows a 5.4 Å periodicity along c^* , which indicates that

FIG. 6 (facing page). Polarized light and 'hot-cathode' CL micrographs of the Mn-carbonate concretions. (a,b) Layered material with CL of different intensity in sample H1. (c,d) Moderately and brightly luminescent areas in sample H3. (e,f) Homogeneously luminescent carbonate veinlet and partly luminescent matrix in sample H4 (m: moderate CL, b: bright CL). (g,h) Luminescent carbonate veinlet with brighter rim in sample H4.

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FIG. 7. CL spectra of the luminescent carbonate phases (matrix and veinlet) in the concretions. All the experimental spectra are uniformly characterized by one emission band with a maximum at ~630 nm.

the grain has a dolomite-type double-carbonate structure. This supports the XRD results. The d values of polycrystalline aggregates measured from SAED patterns (Fig. 8b) are close to those

of a calcite-type single-carbonate structure. However, the missing diffraction rings with respect to the dolomite structure (at 5.4 Å, 4.1 Å, 2.75 Å and 2.6 Å, JCPDS #84-1291)



FIG. 8. Images of the luminescent veinlet in sample H4. (a) 110*-c* SAED pattern of a dolomite-type doublecarbonate grain. (b) SAED pattern of a polycrystalline aggregate. (c) Bright-field image of a grain with single crystal-type SAED pattern. The strongly changing contrast on a 10 nm scale is due either to bending of the individual domains or a high defect density. (d) Bright-field and (e) dark-field images of a polycrystalline aggregate. The darkfield image was made with the diffraction arc at 2.9 Å corresponding to the (104), the most intense, reflection. The bright field image shows the bent, mosaic microstructure and the corresponding dark-field image shows the sizes and distribution of domains within the aggregate.

have low intensities (<2%). This observation may be explained by an incomplete random orientation of the polycrystalline aggregates. Bright- and dark-field images of individual grains and the polycrystalline aggregates show an irregularly undulating and mosaic microstructure (Fig. 8c-e). The patches of strong contrast may arise from strain (bending) of individual domains or, alternatively, be due to a high defect density. The domain size is a few tens of nanometres.

The chemical compositions of the individual crystals and polycrystalline aggregates were also measured (EDS). All measurements give a very similar composition, with no significant difference between the grains and polycrystalline aggregates. The cation proportions (40 at.% Ca, 8–10 at.% Mn, 2 at.% Mg) are consistent with the EMPA data.

Discussion

The luminescent carbonate in the Úrkút Mncarbonate concretions is kutnohorite, characterized by a considerable excess of Ca. The compositional variation of kutnohorites extends from Fe-Mg-rich varieties to Ca-rich varieties (see Fig. 9, data in Table 3). In nature, Cadeficient (Frondel and Bauer, 1955) and Caexcessive (Gabrielson and Sundius, 1966) nonstoichiometric kutnohorites are known to occur (Reeder, 1983, Table 3). Kutnohorite with



FIG. 9. Chemical composition of kutnohorite from Úrkút and from other occurrences on the CaMn(CO₃)₂-CaMg(CO₃)₂-CaFe(CO₃)₂ ternary diagram (modified after Vassileva *et al.*, 2003). Legend – filled circle: Úrkút, Hungary; open circles: other occurrences. For localities and data, see Table 3.

elevated Ca content (>60 mol.% CaCO₃) compared to its standard composition was also described from Långban (Sweden; Gabrielson and Sundius, 1966), Levane, Upper Valdarno (Italy; Bini and Menchetti, 1985), Fujikura (Japan; Tanida and Kitamura, 1982) and Kremikovtsi (Bulgaria; Vassileva *et al.*, 2003) (Table 3, Fig. 9). While XRD indicates one phase in the Úrkút kutnohorite, EMPA data revealed microscale heterogeneity in the veinlet type, which seems to be a common feature in kutnohorites (Žak and Povondra, 1981; Barber and Khan, 1987).

Two structural models for excess-Ca dolomite have been proposed. Reeder (2000) found excess-Ca dolomites with a mixed proportion of Ca and Mg in both structural sites, while Drits et al. (2005) described dolomites with Ca in the A positions and mixed Ca and Mg cations in the *B* layers. Both types show 'c'-type superstructure reflections in SAED due to ordering in the basal layers (Reeder, 1992). The SAED patterns of the Úrkút kutnohorite veinlet, however, show only 'a'- and 'b'-type reflections characteristic of the dolomite structure. No 'c'- or 'd'-type reflections, the latter resulting from periodic stacking defects (Reeder, 1992), were observed. Modulations, striations and ribbon microstructures, which appear in, and seem to be typical of, Ca-rich dolomite in pre-Holocene sediments (e.g. Reeder, 1992) and which also occur in kutnohorite from the type locality (Barber and Khan, 1987), were not detected. Úrkút kutnohorite is a heterogeneous material with mosaic microstructure in which the mis-orientation of the sub-microscopic domains or crystallites is sometimes very slight, which resembles the Holocene dolomite and high-Mg calcite reported by Reeder (1981, 1992).

The Mn²⁺ ion has an ionic radius between those of Ca^{2+} and Mg^{2+} (Reeder, 1983). As a result it can, theoretically, occupy both Ca(A) and Mg(B)sites in the dolomite structure. The Mn substitutes in the A site and has a strong preference for the B site of dolomite (e.g. Lumsen and Lloyd, 1984). However, such ordering may be true only for small Mn concentrations and may not apply to kutnohorite (Peacor et al., 1987). Large concentrations of Mn may only have a slight tendency to order and so highly-disordered kutnohorite can also form (Peacor et al., 1987). In nature, disordered as well as ordered kutnohorite can exist; Peacor et al. (1987) reported almost completely disordered and largely ordered kutnohorites with similar (near stoichiometric)

Sample no.	CaCO ₃	MnCO ₃	MgCO ₃	FeCO ₃	Locality	References
1	54.46	22.94	19.34	3.26	Ribnitsa, Bulgaria	Vassileva et al. (2003)
2	53.03	26.20	14.64	6.13	Ribnitsa, Bulgaria	Kolkovski et al. (1980)
3	51.13	20.12	19.01	9.74	Ruen, Bulgaria	Dragov (1965)
4*	49.00	23.55	13.60	13.85	Martinovo, Bulgaria	Dragov and Neykov (1991)
5	51.50	42.00	5.77	0.73	Franklin, New Jersey, USA	Frondel and Bauer (1955)
6	51.00	35.85	10.12	3.03	Kutna Hora, Czech Republic	Trdlička (1963)
7	51.22	23.73	12.42	12.63	Kutna Hora, Czech Republic	Trdlička (1963)
8	47.45	34.75	11.30	6.50	Chvaletice, Czech Republic	Žak and Povondra (1981)
6	48.53	24.90	24.81	1.76	Ryûjima, Japan	Tsusue (1967)
10	74.00	19.00	7.00	Ι	Långban, Sweden	Gabrielson and Sundius (1966)
11*	66.95	26.35	6.50	0.20	Levane, Upper Valdarno, Italy	Bini and Menchetti (1985)
12	64.03	31.06	4.12	0.79	Fujikura, Japan	Tanida and Kitamura (1982)
13	68.86	25.37	5.36	0.41	Kremikovtsi, Bulgaria	Vassileva et al. (2003)
14*	49.00	49.60	1.10	0.30	Bald Knob, North Carolina, USA	Peacor et al. (1987)
15*	48.00	47.70	1.30	1.20	Sterling, New Jersey, USA	Peacor et al. (1987)
16^{*}	60.70	35.10	2.50	0.80	Sterling, New Jersey, USA	Peacor et al. (1987)
17*	76.62	18.39	4.68	0.30	Úrkút, Hungary	Recent study
* FMD data						
LIVIE Uata						

TABLE 3. Chemical composition (mol.%) of kutnohorite from a range of occurrences (after Vassileva at el., 2003).

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chemical compositions. The large Ca excess in the Úrkút kutnohorite suggests that some Ca occupies the *B* site; however, the site preference of Mn is not clear (only *B* site or both *A* and *B* sites).

The CL spectra of non-stoichiometric dolomite characteristically have two peaks. El Ali et al. (1993) documented a small variability of K_D values ($K_D = Mn_{Mg \, site}^{2+}/Mn_{Ca \, site}^{2+}$) between 2.7 and 5.4 compared with those of stoichiometric dolomites ($K_D = 1.8-24.0$). This observation suggests that if excess Ca is incorporated into the structure, it is possible for significant Mn²⁺ to substitute at the Ca site, i.e. there is significant cation disorder. According to the dolomite-type structure of kutnohorite, a composite luminescence band consisting of emission bands of Mn²⁺ in A and B positions, respectively, can be expected. However, the CL spectra of Úrkút kutnohorite consistently have a single emission band at ~630 nm, with differences observed only in peak intensities. Similar spectra with a single peak at ~630 nm have been reported for dolomite with calcite domains and Mg-calcite with magnesite clusters (Habermann et al., 1996, 2000; Habermann, 2002). Our XRD and TEM studies show that Úrkút kutnohorite is monophase and its CL spectra more closely resemble those of red luminescent dolomites, where only one peak appears due to Mn substituting for Mg.

The position of the Mn²⁺-activated emission band in the CL spectra of kutnohorite can be explained by Crystal Field Theory. As the Mn²⁺ ions (3d⁵) are very sensitive to their immediate environment, changes in the average bond length between oxygen and the metal ions cause wavelength shifts in the luminescence emission of carbonates. There is a linear correlation between the wavelength of the luminescence and the metal-oxygen (M-O) distance in the thermoluminescence and ionoluminescence spectra of carbonates (Calderón et al., 1996; Calvo de Castillo et al., 2006). The same happens in cathodoluminescence: the CL emission shifts to shorter wavelengths as the bond-length increases. In an ordered stoichiometric dolomite the M(Mg)-O distance in B position is 2.084 Å resulting in a ~660 nm peak for the Mn^{2+} activated CL, whereas the M(Ca)-O distance in A position is 2.38 Å causing a luminescence band at ~575 nm (Walker et al., 1989; El Ali et al., 1993; Calderón et al., 1996).

The emission band in the CL spectra of the Úrkút kutnohorite has a longer wavelength than

the Mn^{2+} -activated emission of the A (Ca) site of dolomite or, indeed, of calcite (Ca-O distance: 2.36 Å). Furthermore, due to the probable mixed Ca-Mn composition, its CL band should have a shorter wavelength than that of any luminescent pure Mn-bearing carbonate (rhodochrosite with Mn–O distance: 2.19 Å). This is supported by our preliminary CL data from rhodochrosite with dull orange luminescence in other Úrkút samples. which has an emission band maximum at ~635-640 nm. However, it remains undecided as to whether or not the CL spectra of the kutnohorite have a single emission band or, due to a quite similar Ca-Mn occupation of A and B positions, it is composed of two peaks with nearly identical wavelengths. In the latter case it is not possible to distinguish the two emission bands and it is also difficult to determine at which site Mn causes luminescence or shows self-quenching.

For self-quenching, the absolute concentration of the activator elements, and therefore the distance between Mn²⁺ ions, seems to be a critical factor. Marfunin (1979) pointed out that the maximum CL intensity often occurs at ~0.1-1% concentration level of the activator ion and at greater concentrations the self-quenching is dominant. Machel et al. (1991) suggested that bright Mn²⁺-activated CL extends up to ~5 wt.% Mn (log Mn = 4.7). At greater Mn concentrations, dull luminescence exists due to self-quenching, probably up to the rhodochrosite composition (48 wt.% Mn, $\log Mn = 5.68$). This suggestion is strongly supported by the excess-Ca kutnohorite from Úrkút, which shows moderate-bright cathodoluminescence at 8.2-10.3 wt.% Mn concentration $(\log Mn = 4.9 - 5.0, Fig. 10)$. Our data are close to the luminescent manganocalcite (11.5 wt.% Mn, 0.5 wt.% Fe) described by Walker et al. (1989) (Fig. 10). The Fe content (up to 2400 ppm, log Fe = 3.4), determined in the Úrkút kutnohorite, could also partially influence its luminescent character with some Fe-quenching.

In summary, the moderate- and bright-orange luminescent carbonate in the Mn-carbonate concretions from Úrkút is identified as kutnohorite with considerable Ca excess (average composition: Ca_{1.53}Mn_{0.37}Mg_{0.09}Fe_{0.01}), which appears in the form of layers, infiltrations and veinlets. The TEM results show that the luminescent carbonate is a single-phase mineral with dolomite-like structure and an undulating-mosaic microstructure. The CL spectra of Úrkút kutnohorite show a single-peak pattern with a maximum at ~630 nm due to Mn²⁺ activation. Úrkút kutnohorite is a



FIG. 10. CL behaviour of carbonates as a function of Mn vs. Fe concentration (ppm on logarithmic scale) (modified after Machel *et al.*, 1991). The Úrkút kutnohorite samples support the theory that intensive luminescence can exist up to 10 wt.% Mn and 2400 ppm Fe concentrations (log Mn = 5, log Fe = 3.4). Legend – open circles: kutnohorite in concretion H1; filled circles: kutnohorite in concretion H4; grey square: mangano-calcite with 11.5 wt.% Mn and 0.5 wt.% Fe (Walker *et al.*, 1989).

natural example which supports the earlier assumption that Mn does not show complete self-quenching in carbonates at $\sim 8-10$ wt.% Mn concentrations, with up to 2400 ppm Fe.

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