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Reflectance colourimetry as a method for estimating the approximate quantity of non-carbonate components in limestones: A case study in the Mokrá Quarry (Czech Republic)

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ABSTRACT

This paper demonstrates the applicability and usefulness of colourimetry as a fast and simple tool to assess the quality of limestones for cement and lime industry raw materials, a field where colourimetric measurements have not yet been applied. The results of the colourimetric analysis in a large sample set from the Mokrá Quarry in the Moravian Karst (NE from Brno, Czech Republic) and comparisons with the results obtained by other methods are presented here. The studied samples belong to two lithologically different series of strata: the Macocha Formation and the Líšeň Formation. Limestones of these formations differ in structure, the contents of their non-carbonate components and, therefore, in colour as well. The samples were prepared in four ways for the purposes of colourimetric measurements: i) unpolished bulk samples (fracture planes were measured), ii) polished sections, iii) powder in a plastic bag, and iv) uncovered powder. Each of these four ways led to different results, which were expressed using the CIE L*a*b* colour space. The L* (specific lightness) value gives an approximate estimate as to the amount of non-carbonate components. The specific lightness value can be used for assigning a sample to a lithostratigraphic member and, in many cases, possibly also to a correlation among members.

1. Introduction

Every geologist has presumably already encountered the problem of how to distinctively express the colour of an examined rock. Where the effort is collective, it may even spark disagreement. Non-uniform and rather subjective evaluation and description of rock colours can be partially remedied by using the Munsell system, with the Munsell Book of Colour (in all its variations) as a necessary tool. The eye is a reliable instrument for recognising differences in colour but not for precise measurement.

The colour of rocks can be measured scientifically with an appropriately constructed spectrometer. This issue has not yet been fully explored in geological literature, except in a handful of works that mainly deal with the evaluation of sediment or sedimentary rock, including stratigraphy (Wells et al., 2002; Hu et al., 2014), as well as educationally oriented works (Adderley et al., 2002; Ibáñez-Asensio et al., 2013; Cancelo-González et al., 2014). In addition to Earth science, colourimetry is used in many different fields such as archaeology (Oestmo, 2013; Ruiz and Pereira, 2014), restoration, painting and other art disciplines (Cochrane, 2014), the food industry (Sánchez-Zapata et al., 2011; García-Marino et al., 2013; Kljak et al., 2014) and medicine (Chang et al., 2012). Analyses are executed in two different colour spaces – CIE L*a*b* and CIE L*C*h (Viscarra Rossel et al., 2006; Korifi et al., 2013). Even mobile phones, equipped with a camera and software capable of characterising colour according to the parameters used by the Munsell or CIE (Gómez-Robledo et al., 2013) system, can conceivably be used for objective colour evaluation of rocks, soils, etc.

This paper summarises the data gathered by colorimetric measurement for a large collection of limestone samples that were studied for their chemical and mineralogical composition using the SP 62 spectrometer. The limestones were sampled from the Mokrá Quarry, which is located in the southern part of the Moravian Karst (Czech Republic) and divided into three parts, from which mined resources are used mostly in cement, dry plaster and mortar mixture manufacturing.

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2. Materials and methods

2.1. Samples

The subject of this research is a collection of 120 Devonian to Upper Carboniferous limestones from the southern part of the Moravian Karst (located south of Brno, Czech Republic). Lithostratigraphically, the Moravian Karst limestones are a part of two formations: the Macocha Formation and the Líšeň Formation (Dvořák et al., 1987; Hladil et al., 1999; Rez, 2010). The samples originate from all three divisions of the Mokrá Quarry. The Macocha Formation occurs in the central and western divisions of the Mokrá Quarry, while the Líšeň Formation is present in all three divisions of the quarry. Among the samples are massive limestones (typical for the Macocha Formation), nodular limestones (which occur mainly in the Líšeň Formation) and carbonate beds, which constitute a part of calciturbidites (found in the Líšeň Formation only). Limestones of different structures often differ in colour.

2.2. Obtaining the non-carbonate component of limestones

Limestone samples of an approximate weight of 400 g were dried, crushed and subsequently milled in a planetary ball mill. The powdered samples were then dissolved in 8% acetic acid, resulting in an insoluble (non-carbonate) residue needed for mineralogical study. The dissolution proceeded at laboratory temperature and lasted for approximately two months. The insoluble residue was filtered using a filtration paper.

2.3. Methods

2.3.1. Mineralogical and chemical study

Phase composition of the non-carbonate component, obtained by the described method above, from 25 structurally and stratigraphically different samples of limestone, was identified using powder X-ray diffraction. The analyses were made with the use of a Bruker D8 Advance diffractometer equipped with a copper tube ($\lambda_{K\alpha} = 0.15418$ nm) powered at 40 kV and 30 mA, a Ni filter, automatic divergence slits, and a 1–D position sensitive detector at the conventional Bragg–Brentano parafocusing $\Theta - \Theta$ reflecting geometry. The step size was 0.02°2θ, time per step was 188 s, angular range was 6–80°2θ and total scan time was 63 min 20 s. Zero background silicon wafers were used due to the small amount of samples being analysed. Data were processed using a Bruker AXS Diffrac plus, Topas 3 software, ICDD PDF 2 and a Bruker structure database. The quantitative phase analyses were made according to the Rietveld method using the fundamental parameters approach. The background was calculated by an eights order polynomial, and Lorentz polarisation was fixed at zero. The scale factor and the Lorentzian contribution to crystallite size were refined. The limestone samples were made into thin sections and examined by standard methods using a polarising microscope, focusing on the assessment of rock structure and the presence of non-carbonate components. Non-carbonate components were also studied using the JEOL 6490 LV electron microscope, and the EDX method was used to obtain data on the chemical composition of some of the non-carbonate minerals (mainly feldspars and phyllosilicates).

Prior to the measurements, 3 g of powder was placed in the centre of a circular polyethylene wafer and, using a roller of approximately 25 mm in diameter, the sample was compressed by hand pressure into a pellet, which was placed on the wafer in the measuring area of the instrument. A handheld X-ray fluorescence spectrometer Innov X Delta with a 4 W Rh anode and a 25 mm^2 silicon drift detector powered at 40 kV was used for the chemical composition analysis. Sample measurement time was always 180 s and over an irradiated area of 1 cm^2. In the "GEOCHEM" mode, relatively accurate quantitative determinations for the presence of Al, Si, P, S, K, Ca, Ti, Mn and Fe could be performed. The results of these analyses were corrected based on a set of standard

Table 1
Position of limestones of the Mokrá Quarry in standard colour spaces CIE L*a*b* and CIE L*C*h°.

		Macocha Formation				Líšeň Formation			
		FS	PS	P	PB	FS	PS	P	PB
L*	min.	34.82	38.46	83.31	85.59	25.09	26.51	62.14	67.75
	max.	63.10	51.65	93.17	94.01	56.88	48.60	89.39	90.54
	med.	47.81	45.44	87.60	89.57	34.85	35.80	76.59	80.12
a*	min.	0.60	0.54	0.48	0.33	−0.83	−0.12	0.12	0.18
	max.	5.08	5.08	1.38	1.17	4.04	2.97	2.39	1.96
	med.	1.00	1.01	0.67	0.56	0.70	0.63	1.60	1.22
b*	min.	2.95	2.97	3.41	2.87	0.71	0.40	4.09	3.17
	max.	17.13	14.43	10.81	9.35	16.88	11.01	12.21	10.35
	med.	4.58	4.49	4.69	3.76	2.82	2.62	7.63	6.00
C*	min.	3.01	3.03	3.48	2.91	0.74	0.47	4.15	3.21
	max.	17.87	15.21	10.90	9.43	16.99	11.40	12.29	10.42
	med.	4.68	4.66	4.75	3.80	2.89	2.71	7.86	6.17
h°	min.	73.47	70.49	78.75	66.68	68.43	57.33	74.58	73.00
	max.	83.94	84.81	86.37	87.21	106.82	93.05	88.71	87.56
	med.	77.38	77.03	81.53	81.19	76.76	75.65	78.72	78.92

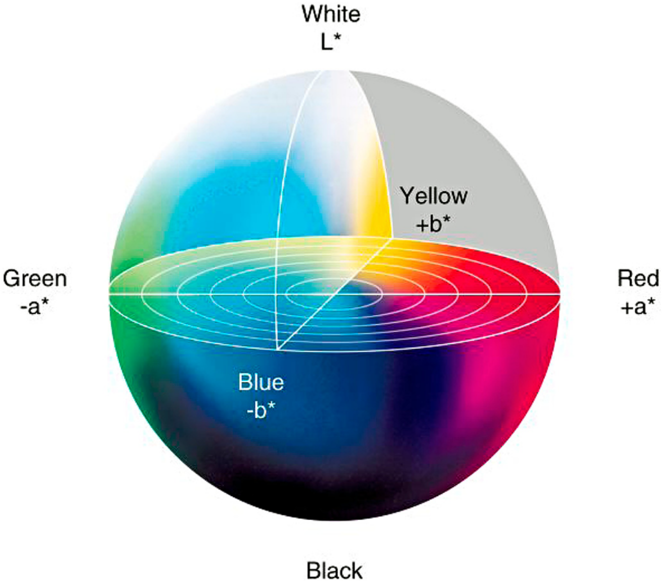

Fig. 1. Schematic drawing of a standard colour space CIE L*a*b* (Agudo et al., 2014). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

Table 2
The contents of selected elements in the main types of limestones and shales in the Mokrá Quarry (wt%; total iron content is expressed as Fe_2O_3; n = number of samples).

	Macocha Formation	Líšeň Formation	
	Limestone (n = 34)	Limestone (n = 53)	Shales (n = 13)
	Range	Range	Range
CaO	48.94–60.04	25.59–57.70	2.61–26.16
SiO_2	0.36–8.60	0.86–46.59	35.46–54.92
TiO_2	< 0.07–0.19	< 0.07–0.45	< 0.07–0.90
Al_2O_3	< 0.06–3.78	< 0.06–8.76	0.37–18.70
Fe_2O_3	0.05–0.39	0.10–3.87	0.40–5.92
MnO	< 0.01–0.03	< 0.01–0.46	< 0.01–0.46
K_2O	< 0.03–1.05	< 0.03–3.08	< 0.03–4.40
P_2O_5	< 0.07–1.41	< 0.07–4.01	< 0.07–0.99
S	< 0.03	< 0.03–0.66	< 0.03–1.78