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ORIGINAL PAPER

Carbonate cements and grains in submarine fan sandstones—the Cergowa Beds (Oligocene, Carpathians of Poland) recorded by cathodoluminescence

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Abstract The cathodoluminescence (CL) observations with cold cathode, supplemented by reconnaissance scanning electron microscope analyses, bring new data on petrology, provenance and diagenesis of the Oligocene-age Cergowa sandstones from the Outer Carpathians (SE Poland). The sandstones represent a variety of mass gravity flow sediments deposited on a submarine fan, which now forms a lenticular lithosome—a part of the Menilite Beds–Krosno Beds suite important for the hydrocarbons industry. The most common components of the Cergowa sandstones observed under the CL are carbonates—cement and grains that are mainly represented by lithoclasts. Carbonate cement is represented by five generations: brown (Cb), orange (Co), yellow (Cy), zoned (Cz) and black (Ck). Pore-filling Cb and Co calcite cements are interpreted as genetically related to eo- and mesodiagenetic phases. The mesodiagenetic phase is characterised by randomly distributed relatively large monocrystalline-zoned rhombs of dolomite cement (Cz) and ankerite/ferroan dolomite (Ck). The telodiagenetic phase is represented by pore-filling yellow calcite (Cy) that crystallised under the influence of suboxic meteoric waters. Lithoclasts represent six microfacies of carbonate rocks eroded in the source area, i.e. microbreccia, tectonised immature calcarenite/wacke, microsparite, sparite, biomicrosparite/packstone and dolostone. Pronounced indentations of terrigenous sand grains into intraclasts of packstone/biomicrosparite, coupled with commonly present similar packstone-type matrix, suggest that a significant part of matrix resulted from compaction of soft biomicrosparite grains. Terrigenous grains bound by calcite cement are commonly corroded by acidic diagenetic fluids, and partial or even complete replacement of silicates by calcite and clay minerals is illustrated here by feldspar grains. Substantial carbonate cementation has resulted in both the significant hardness and abrasion resistance of the Cergowa sandstones as well giving rise to their very low porosity and permeability.

Keywords Cathodoluminescence · Diagenesis · Carbonate cements and lithoclasts · Carpathians · Cergowa sandstones

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Introduction

The Cergowa Beds are a part of the Oligocene-age succession of the Menilite Beds–Krosno Beds (Outer/Flysch Carpathians, Fig. 1) and are important for the hydrocarbon industry (Kotarba and Koltun 2006). The lenticular complex of deep marine Cergowa sandstones, underlain by, and embedded within a fine-grained succession dominated by bituminous Menilite Shales, hosts 'six hydrocarbon accumulations' (Dziadzio et al. 2006). A characteristic feature of the Cergowa Beds lithosome is the presence of organic matter with fragments of tree trunks present in its axial zone and abundant fine plant detritus disseminated in its marginal parts (the present authors' field observations). Where concentration of organic matter is high, coal interbeds are exposed. Moreover, the Cergowa sandstones are

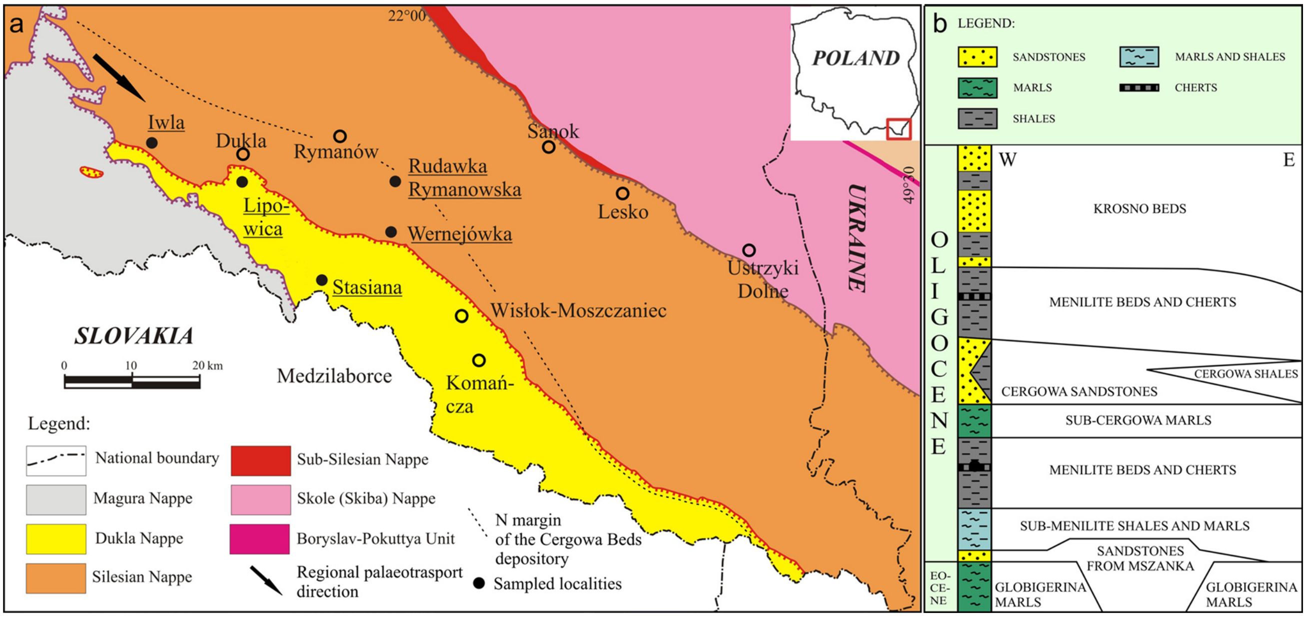

Fig. 1 **a** Schematic geological map of the Eastern Outer Carpathians of Poland showing the sampled localities of the Cergowa Beds sandstones (*underlined*; modified from Górecki 2013). Regional palaeotransport direction (*arrow*) and position of the depository northern margin are after Ślączka and Unrug (1976). **b** Lithostratigraphy of the succession containing the Cergowa Beds (sandstone and shale divisions) in the Dukla Tectonic Unit and the southern part of the Silesian Tectonic Unit (modified from Ślączka 1971; Ślączka et al. 2006)

considered as one of the most valuable industrial raw materials in the Polish Carpathians (Pszonka 2009; Pszonka and Wendorff 2014). Despite the economic importance of the Cergowa Beds sandstones, the knowledge of mineral composition and diagenetic features controlling their physical characteristics is rather general, dating back to the polarising microscope work by Peszat (1984). Therefore, in order to gain a better understanding of provenance, composition and diagenesis of the economically important Cergowa sandstones, cathodoluminescence (CL) was used in the course of this study and supplemented by reconnaissance SEM analyses.

CL imaging enables visualisation of the rock components that differ in luminescence colour and intensity, which in turn reflect variations in the concentration of activators, sensitisers, inhibitors or/and structural defects (Miller 1988). Moreover, CL imaging allows the detection of the diagenetic processes that cannot be distinguished by other methods. In the present study of deep marine sandstones of the Cergowa Beds, CL reveals previously unknown carbonate grains types plus diagenetic changes related to carbonates and feldspars, and these observations define the focus of this paper.

The visual CL colours of carbonates are mainly yellow, orange, red or brownish. Almost all luminescence in carbonates is caused by point defects in crystals and trace elements, which include activators such as: Mn^{2+}, REEs, sensitisers: Pb^{2+}, Ce^{3+} or inhibitors for instance: Fe^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+} (Adams and MacKenzie 1998; Machel 2000). The main activator and inhibitor are Mn^{2+} and Fe^{2+}, respectively. Higher concentration of Mn is probably responsible for self-quenching (Adams and MacKenzie 1998; Machel 2000). Fe-bearing carbonate minerals (ferroan dolomite, ankerite, siderite) show little or even a total absence of luminescence (Reed and Milliken 2003).

The CL emission of feldspars consists mainly of three broad emission bands: (1) blue (420–500 nm: substitution of Al^{3+} for Si^{4+}, Cu^{2+}, Ti^{3+} or association with an electron hole on an oxygen adjacent to a divalent impurity ion Si–O–…M^{2+}), (2) green (540–570 nm: Mn^{2+}) and (3) red (690–760 nm: Fe^{3+}) (Götze et al. 2000). Rare earth elements are also potential activators of CL in feldspars, with REE contents being usually higher in plagioclases than in K-feldspars (Götze et al. 1999). However, the rare earths rarely occur in sufficient amounts in natural feldspars to be CL activators (Marshall 1988). Apart from trace elements and structural defects in crystal lattices, the luminescence colour and intensity are controlled by specific physicochemical conditions of formation and alteration, which determine the temperature and rate of crystal growth, the crystal surface structure, the composition and chemical equilibrium of pore waters, changes in pH/Eh, organic matter content and presence of clay minerals (Adams and MacKenzie 1998; Machel 2000).

Taking into account that the carbonate components of the Cergowa sandstones constitute a considerable percentage of the rock (up to 46 % by volume), the aims of this study were to (1) document previously unidentified carbonate grains, thus broadening our knowledge of the source area composition; (2) identify the variety of carbonate cements, their temporal sequence and to show relations between such cements and the framework grains, as well as the features modifying rock porosity, and (3) suggest possible types and succession of the diagenetic phases.

Geological setting

The Cergowa Beds (Lower Oligocene) occur in two tectonic units of the eastern Outer Carpathians—the lithosome is situated within the Dukla Tectonic Unit in the SW, while its NE margin extends partway into the adjacent Silesian Tectonic Unit to the NE (Fig. 1a; Ślączka 1971; Ślączka and Unrug 1976; Cieszkowski et al. 1990). The lithosome occurs within the Menilite Beds made up of mudstones and menilite-type claystones with subordinate interbeds of sandstones and carbonates (Fig. 1b; Ślączka 1971; Ślączka and Unrug 1976; Dirnerová et al. 2012). It is lenticular in shape, up to 350 m thick and composed mainly of sandstones, which show low primary porosity and permeability (Ślączka 1970).

The Cergowa Beds originated as a deep marine fan deposited by a variety of mass gravity flows in the Dukla basin (Ślączka and Unrug 1976; Dirnerová et al. 2012), which at the turn of Eocene and Oligocene formed a trough isolated from the neighbouring depositional areas by ridges (Ślączka 1971). In general, the lithosome consists of two lithofacies, namely sandstones and sandstones interbedded with shales. Directional structures indicate prevailing palaeotransport direction to the SE, along the basin axis (Fig. 1a; Ślączka and Unrug 1976). Peszat (1984) suggested that the terrigenous detritus of the Cergowa Beds was derived from erosion of the Silesian Ridge located to the west of the depocentre, while some carbonate detritus probably originated from the coastal zone of the Ridge, in a low-energy shallow marine environment of a warm and dry climate. Grains of carbonate rocks constitute 14.6–45.9 % of the rock volume while the cement content, which is almost entirely carbonate in composition, ranges from 8.7 to 45.8 % (Peszat 1984). Based upon mineral composition, Peszat (1984) classified the Cergowa Beds' sandstones as lithic wackes; however, in subordinate cases, they plot on Pettijohn's classic discrimination diagram as lithic arenites (Pszonka 2009).

Methods

Samples of the Cergowa sandstones were collected from outcrops at five locations shown in Fig. 1a. Fifty uncovered, carbon-coated thin sections were prepared at the Cutting-Polishing Laboratory of the AGH University of Science and Technology in Kraków (Poland). The CL observations were carried out at the Institute of Geological Sciences, Jagiellonian University (Poland), on 40 thin sections (Table 1) using a CITL (UK) Mk 3A CL cold cathode luminescope attached to a Nikon Eclipse 50i polarising microscope. The applied voltage was 16–18 keV with an electron beam current of 700–800 µA. Luminescence images were captured using a Canon EOS 50D digital camera. Sixty-four chemical analyses undertaken on two thin sections were performed at the same laboratory with a FE-SEM HITACHI S-4700 microscope equipped with EDS NORAN Vantage system at an accelerating voltage of 20 keV, electron beam current of 10 µA, the spot-size of the electron beam was 5–6 µm and a working distance of 12 mm with backscattered electron detector (BSE).

Observations

CL images of carbonate cements

Carbonate cement occurs as sparite, and rarely microsparite, filling pore spaces and replacing some components of sandstones. Carbonate components in the Cergowa sandstones show orange, dark brown, brown, yellow and rarely red colour in CL images with two dominant colours. One type appears as brown to dark orange in colour (Cb called 'brown' throughout the text; Fig. 2a) and constitutes the main filling of the pore spaces. Another type is bright orange in colour (Co called 'orange' throughout the text; Fig. 2a), commonly forming tiny rims around pore spaces filled with brown carbonate, and also filling interboundary pores between brown sparite cement and partially or entirely filling pore spaces. When these two types of carbonate cement (Cb and Co) occur together, the boundaries between them range from sharp to diffuse. Sporadically, the carbonate cement reveals yellow and bright yellow colour in CL images (Cy called 'yellow' throughout the text; Fig. 2a). The nature of cements Cb and Co cannot be seen in plane-polarised and cross-polarised light. This type of cement partially fills out the remaining pore spaces, and representative examples of the SEM reconnaissance analyses show that it is composed mainly of calcite ('cc' in Fig. 3).

CL images of carbonate grains and grain–cement relations

Detrital carbonate grains reveal diverse luminescence intensities and colour ranges characteristic of carbonate minerals observed under CL (Machel 2000). One type of carbonate grain is microbreccia containing microsparite fragments that are brownish in CL, ranging from angular

Table 1 List of sampled locations, sample numbers and their reconnaissance EDS analyses

Location	Samples analysed by CL	EDS
IWLA	6/28/PI	
	28/356/PI	43
	35/441/PI	
	41/535/PI	
	50/422/PI	
	55/509/PI	
	63/636/PI	
	64/732/PI	
	66/808/PI	
	67/882/PI	
Rudawka rymanowska		
	A/15/RR	
	1/103/RR	
	8/177/RR	
	11/233/RR	
	13/283/RR	
	18/369/RR	
	47/915/RR	
	50/921/RR	
Lipowica		
	3/72/KL	
	4/71/KL	21
	15/121/KL	
	27/262/KL	
	28/266/KL	
	35/304/KL	
	38/312/KL	
	AD1/300/KL	
Wernejówka		
	4/PW	
	11/PW	
	14/PW	
	15/PW	
	17/PW	
	20/PW	
Stasiana		
	PJS/2p/1	
	PJS/4/6	
	PJS/8p/73	
	PJS/20p/195	
	PJS/24p/202	
	PJS/25p/205	
	PJS/33p/224	
	PJS/10A/58	

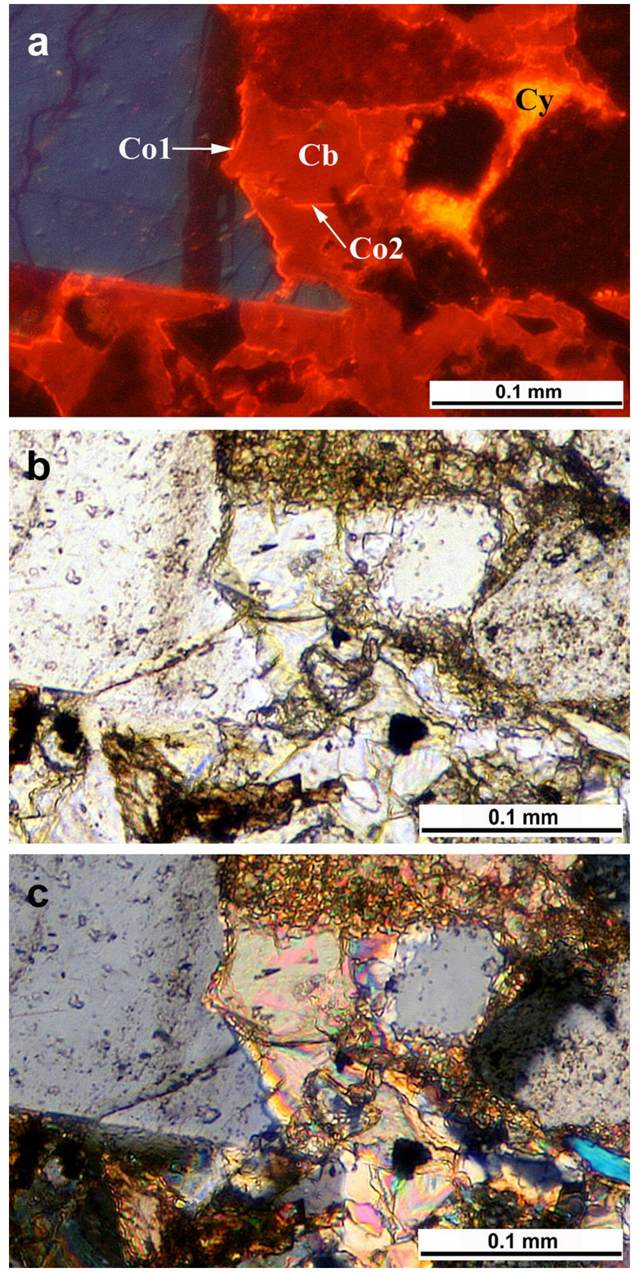

Fig. 2 Three types of carbonate cement and their space relations. Locality: Lipowica. **a** CL image suggestive of the genetic sequence: Cb *brown in colour* is the main type filling pore spaces and is the oldest generation, *orange* Co1 forms rims around pore spaces and fills interboundary pores Co2, and the youngest—*yellow* Cy—fills the remaining pore spaces. **b** The same as 2a but in PPL plane-polarised light. **c** The same as **a**, **b** but in XPL cross-polarised light

to subrounded and cemented with abundant orange sparite (Fig. 4a). These fragments contain carbonate-filled veinlets that do not extend through the cement and are oriented differently between fragments, thus testifying to their rotation prior to cementation of the source rock (Fig. 4a). In plane-polarised light, the microsparite fragments of the microbreccia exhibit a dusty appearance and poorly defined fuzzy outlines; the sparite cement is clear, and the carbonate-filled veinlets are invisible (Fig. 4b).

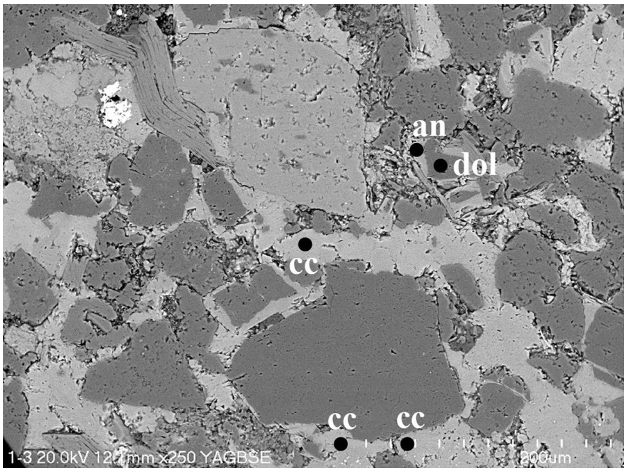

Fig. 3 SEM analytical results of cement (backscattered electron image): *cc* calcite, *an* ankerite/ferroan dolomite, *dol* dolomite. Locality: Stasiana

Another lithic grain type is calcarenite, and specifically wackestone (Fig. 4c–e). Such carbonate rock fragments are composed of subangular to rounded carbonate particles of very fine sand and coarse silt grade, which are supported by a matrix of micrite and microsparite (Fig. 4d, e). In PPL, the matrix has a dusty appearance, while very fine arenite subgrains are randomly oriented carbonate monocrystals (Fig. 4d). Carbonate veinlets cross the whole lithic grain, continuing through subgrains and matrix, and are only truncated by the grain boundary; therefore, they are a feature inherited from the source rock. Such veinlets are imperceptible in PL images and only revealed by cathodoluminescence (Fig. 4c–e).

The most common carbonate lithoclasts are brown, deep brown or just dull in CL (Fig. 5a), which in PL range in appearance from sparite to microsparite (Fig. 5b). They are massive and well rounded. However, some are subrounded fragments of larger grains broken up during transport and do not contain obvious tectonic microstructures (Fig. 5a, b).

Yet another carbonate microfacies is represented by poorly washed biosparite lithoclasts containing Foraminifera and fine carbonate grains (Fig. 5c), and displaying highly irregular outlines due to indentations caused by the surrounding terrigenous grains, as e.g. the quartz grains shown in Fig. 5e. There is no carbonate cement between the lithoclasts and the adjacent terrigenous grains. Such lithic grains are clearly much more obvious in CL images than in PL images (Fig. 5c–e). When observed in plane- and cross-polarised light, they appear very similar to the carbonate matrix of the Cergowa sandstone (Fig. 5d, e).

Striking CL images depicting rhomb-shaped crystals with concentric zoning, sporadically oscillatory, occur as either polycrystalline grains composed of rhombs (Fig. 6a, d) or solitary, randomly distributed monocrystals (Fig. 7a–c). The concentric zones consist of stripes of alternating darker (black to brown) and brighter (orange, red, yellow) luminescence, and some zones are clearly outlined (Fig. 6a) while some are fuzzy (Fig. 6d). Such concentric zones are undetectable under PPL and XPL (Fig. 6b, c, e, f). Generally, the rhomboidal outline (Scholle 1979; Scholle and Ulmer-Scholle 2003) coupled with sharply defined zonation and red CL colours (Machel 2000) are good criteria for recognition of dolomite crystals.

Rhombs that make up polycrystalline detrital grains of dolostone are truncated at grain boundaries (Fig. 6a, d). However, rhomb-shaped monocrystals not only occur as detrital constituents of the rock (Fig. 7c) but also form cement Cz (called 'zoned' throughout the text; Fig. 7a, b). Some occurrences of the latter are euhedral to subhedral and illustrate one of six types of dolomite cement identified and named 'subeuhedral' by Gawthorpe (1987). Such rhomboidal cement (Cz) occurs in the Cergowa sandstones as replacive overgrowths on carbonate grains (Fig. 7a) or as pore-filling sparite (Fig. 7b). The marginal parts of pore-filling dolosparite may be followed by non-luminescent cement Ck (called 'black' throughout the text; Fig. 7b). The reconnaissance SEM analyses of the Cergowa sandstones (Fig. 3) show rhomboidal dolomite (analytical point 'dol') with marginal zones replaced by ankerite/ferroan dolomite (analytical point 'an'). Theoretically, the non-luminescent cement could also be represented by silica, but the earlier data (Peszat 1984; confirmed by our observations) indicate that the Cergowa sandstones do not contain quartz cement, contrary to sandstones known from many other Carpathian units. Therefore, we conclude that the non-luminescence cement in Fig. 7b is Fe-rich carbonate (ankerite/ferroan dolomite) because iron is the main inhibitor of luminescence. Conversely, solitary rhombs that represent detrital grains are identifiable by abraded outlines truncating internal structures (Fig. 7c), both primary (e.g. constituent crystal surfaces) and secondary (e.g. carbonate-filled veinlets).

CL images of carbonate-replaced feldspars

Despite the fact that feldspars in the Cergowa sandstones constitute only 1.2–6.8 % of the rock volume (Peszat 1984), these mineral grains are one of the most striking components due to their distinct CL luminescence colours. K-feldspar exhibits blue luminescence while plagioclase, which occurs only as a subordinate type of feldspar, shows green and greenish-yellow luminescence.

Replacements of feldspars by carbonates are clearly seen in CL images as brown and orange colour zones, which appear mostly at marginal parts of feldspar grains,

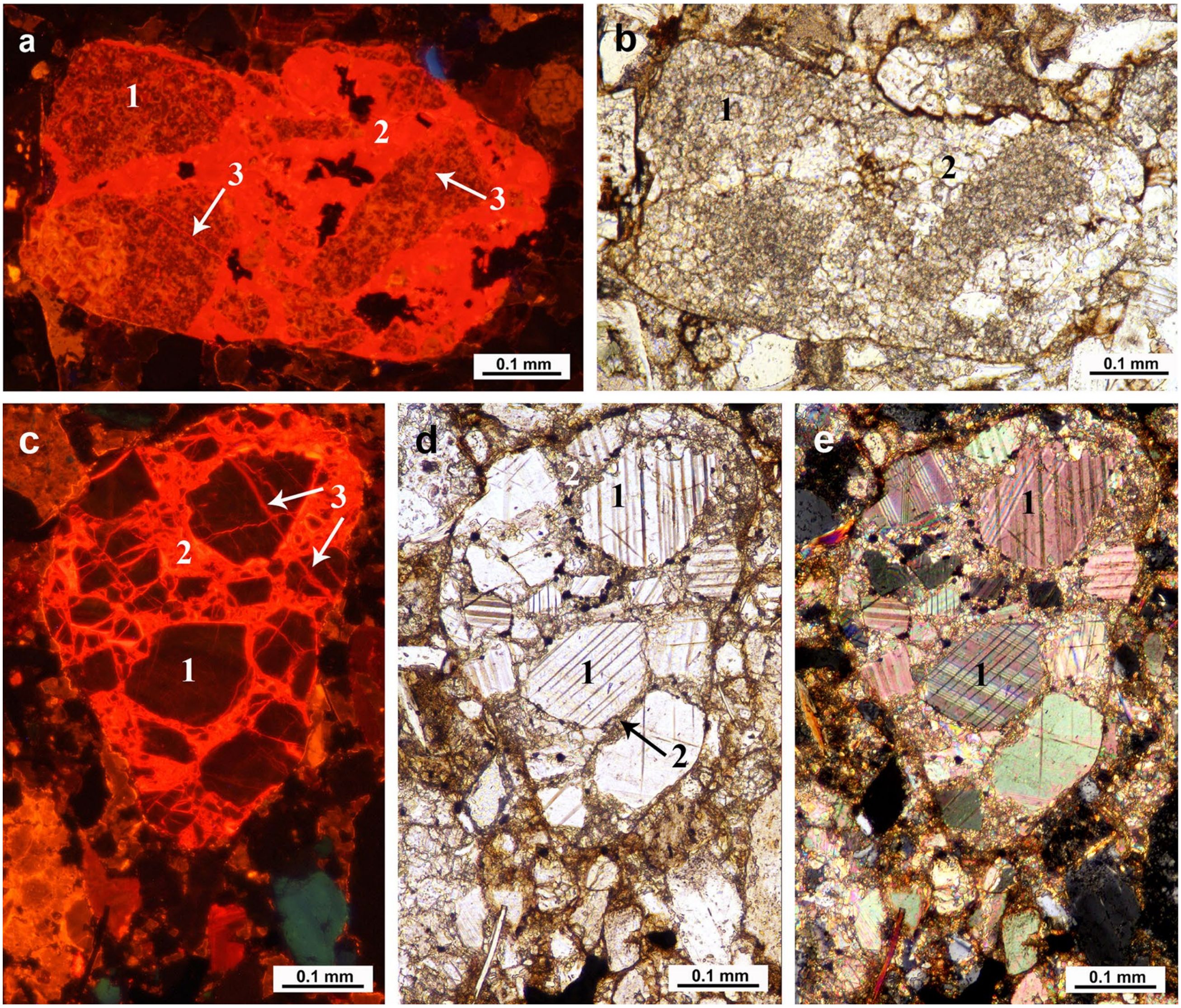

Fig. 4 Detrital carbonate grains in CL (**a**, **c**), in PPL plane-polarised light (**b**, **d**), and in XPL cross-polarised light (**e**). Locality **a**, **b**: Stasiana, locality **c**, **d**, **e**: Iwla. **a** Microbreccia: angular to subrounded microsparite fragments, *brownish in colour* (*1*) cemented by *orange sparite* (*2*). Note different orientation of pre-fragmentation carbonate veinlets (*3*) truncated by each microsparite fragment boundary. **b** The same as **a.** Microsparite fragments have dusty appearance (*1*) and sparite infill is clear (*2*). **c** Calcarenite/wackestone: subangular to rounded calcite grains of very fine sand and coarse silt grade (*1*) supported by matrix of micrite and microsparite (*2*—see **d**, **e** in PL). Note carbonate veinlets (*3*) crossing the lithic grain only, and truncated by the grain boundary, which are inherited from the source rock; they are revealed in CL image but invisible in PL images—compare **d**, **e**. **d** The same as **c**. Very fine calcarenite subgrains are randomly oriented carbonate monocrystals (*1*), while micrite and microsparite matrix has dusty appearance (*2*). **e** The same as **c**, **d**. XPL emphasising random orientation and twinning of subgrains/carbonate monocrystals (*1*)

with carbonate replacement areas also penetrating into feldspars along some cleavage planes and possibly fractures (Fig. 8a). Very highly advanced alteration results in patchy relics of feldspar ‘floating’ within carbonate (Fig. 8b), and complete replacement results in carbonate pseudomorphs (Fig. 8c). Total replacement of feldspars by carbonate is difficult to recognise in cathodoluminescence because no feldspar relics are visible. However, such replacements can be identified by comparison of CL, PPL and XPL images; the latter locally showing fuzzy relics of feldspar (Fig. 8e). PPL images do not display such features (Fig. 8d). On the other hand, images 8b–e may be interpreted alternatively as poikilotopic calcite cement overgrowths enveloping small feldspar grains.

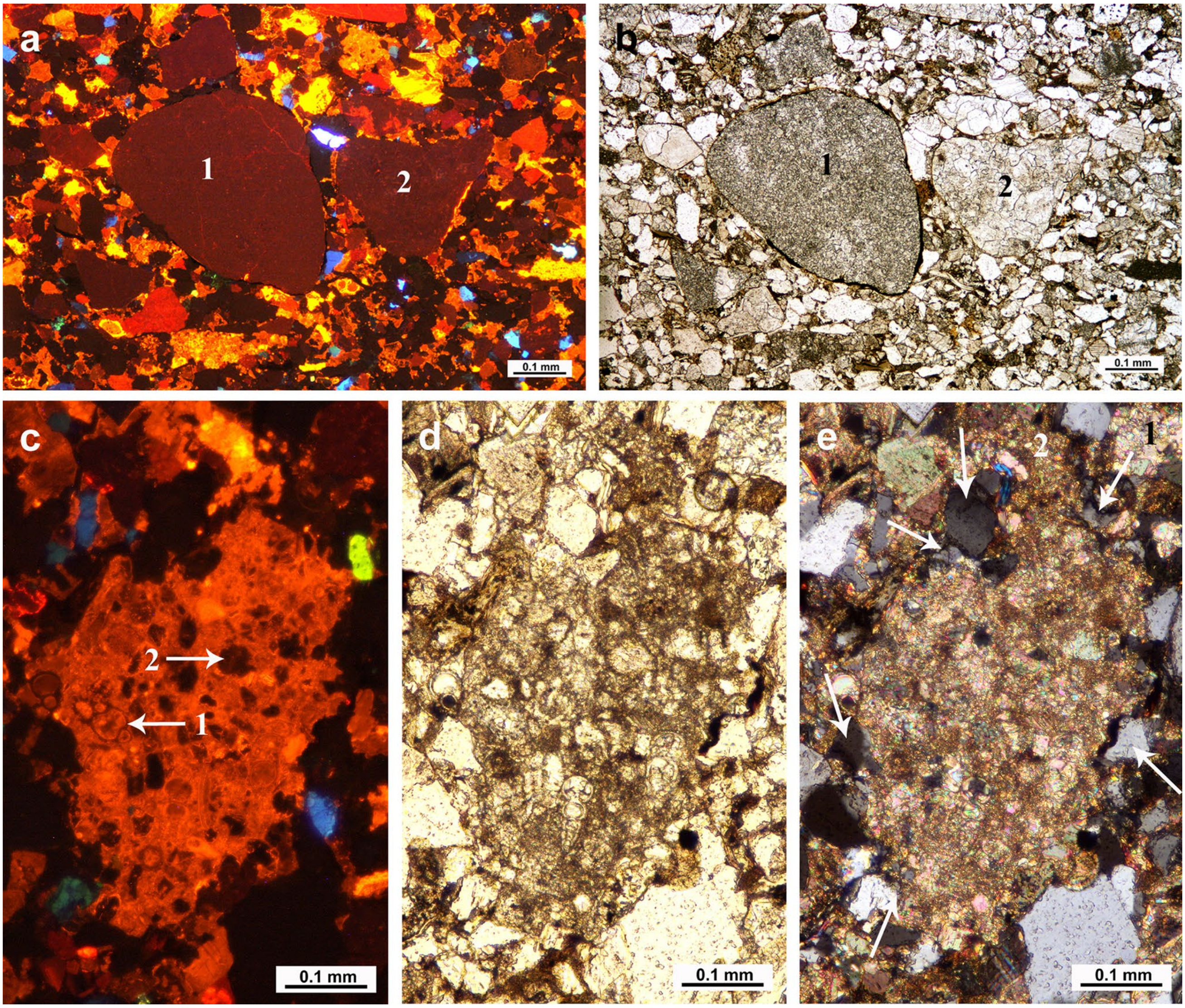

Fig. 5 Detrital carbonate grains in CL (**a**, **c**), in PPL plane-polarised light (**b**, **d**), and in XPL cross-polarised light (**e**). Locality: Iwla. **a** Limestone fragments: brown in colour, massive, without obvious tectonic microstructures. Note that one is well rounded (*1*) and other is a part of grain broken up during transport (*2*). **b** The same as **a**. Limestone fragments representing sparite (*1*) and microsparite (*2*). **c** Biomicsparite: rich in micrite matrix (wackestone) containing Foraminifera (*1*) and fine carbonate grains (*2*). **d** The same as **c**. Such grains are less clearly seen in PL images than in CL. **e** The same as **c**, **d**. Note the highly irregular outline due to indentations by the surrounding terrigenous grains (indicated by *arrows*) and marginal portions 'branching off' the lithoclast (*1*, *2*), evidently squeezed out during compaction. Such carbonate grains appear very similar to carbonate matrix seen elsewhere in the Cergowa sandstones

Interpretation and discussion

CL and SEM analyses of carbonates cements

The cathodoluminescence analysis of the Cergowa Beds sandstones provides evidence of several generations of carbonate cement that are unidentifiable using standard polarising microscopy. Five generations of carbonate cement are distinguished as follows: brown (Cb), orange (Co), yellow (Cy), zoned (Cz) and black/non-luminescent (Figs. 2, 6a, b).

The brown cement (Cb) represents the oldest generation, which crystallised in intergranular pore spaces and also replaced dissolved parts of detrital grains (Fig. 2). The younger, orange carbonate cement (Co), precipitated in the remaining pore spaces, within dissolved zones of contact between detrital grains and brown cement (Cb), and in interboundary pores between sparite crystals of brown cement (Fig. 2). Both generations of carbonate cements (Cb and Co) are represented by calcite (Fig. 3). These calcite cements may be assigned to eo- and/or mesodiagenesis (Table 2) because the Cb and Co represent two end

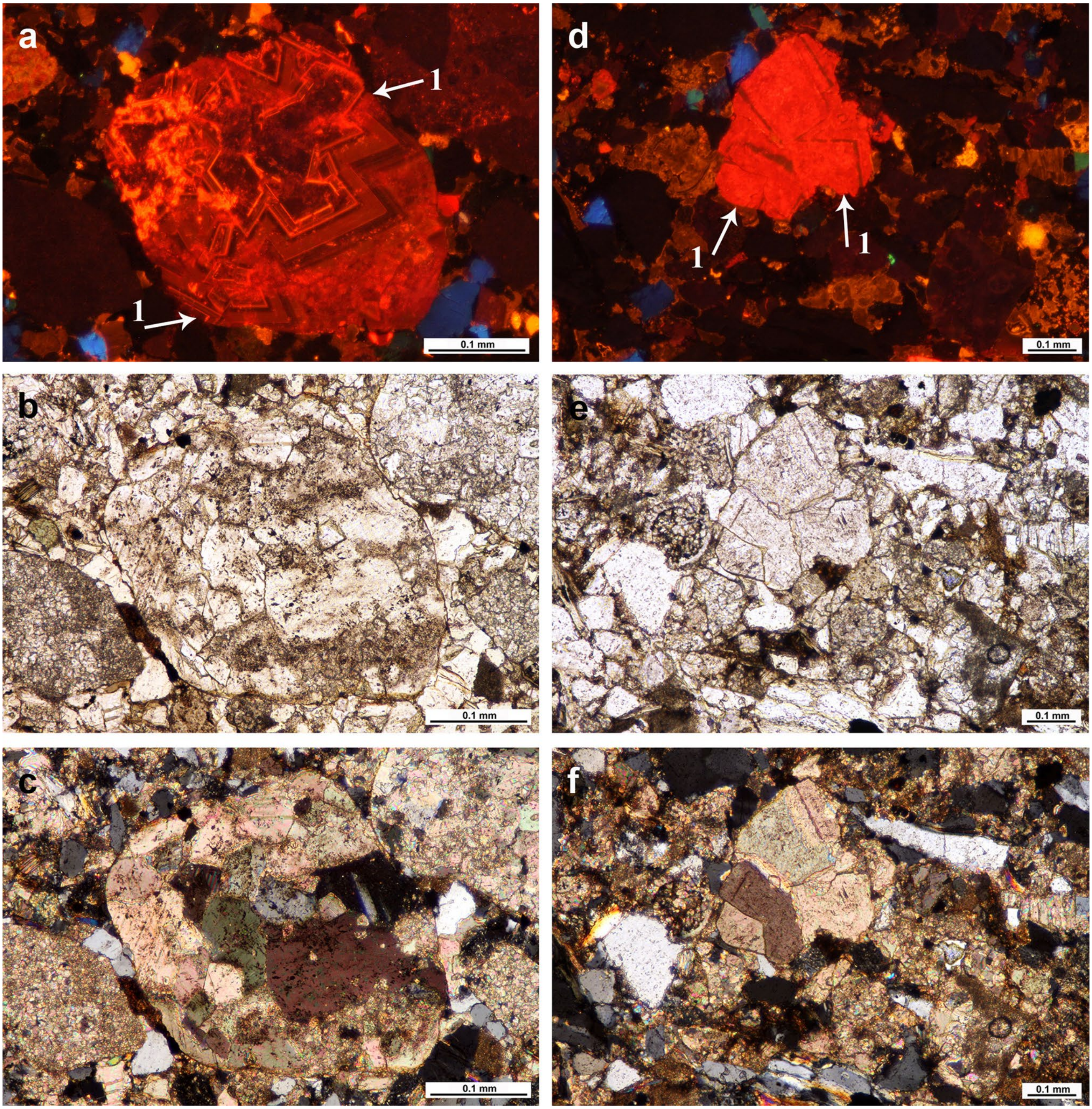

Fig. 6 Polycrystalline carbonate grains composed of rhombs in CL (**a**, **d**), in PPL plane-polarised light (**b**, **e**) and in XPL cross-polarised light (**c**, **f**). Locality **a**–**c**: Wernejówka, locality **d**–**f**: Stasiana. **a** Clearly defined euhedral concentric growth zones (which may indicate unimpeded crystal growth into what was once originally open porosity). *Arrows* indicate truncation of polycrystalline structure at the grain boundary. **b** The same as **a**. Concentric growth zones are not visible. **c** The same as **a**, **b**. Concentric growth zones are not visible. **d** Rhombs with indistinct concentric growth zones. *Arrows* indicate truncation of polycrystalline structure at the grain boundary. **e** The same as **d**. Concentric growth zones are not visible. **f** The same as **d**, **e**. Concentric growth zones are not visible

members of a broad spectrum of colour transitions that can be interpreted in terms of discrete diagenetic stages. In this context, Worden and Burley (2003) concluded that eogenetic cementation results in pore-filling cement fabrics composed of fine microspar crystals in quantities ≤40 %, whereas mesogenetic cementation is characterised by recrystallisation of pre-existing carbonate minerals/cement. However, in the Cergowa sandstones, the structural and textural features plus relationships between cement components observed under CL and PL lack the unequivocal clues

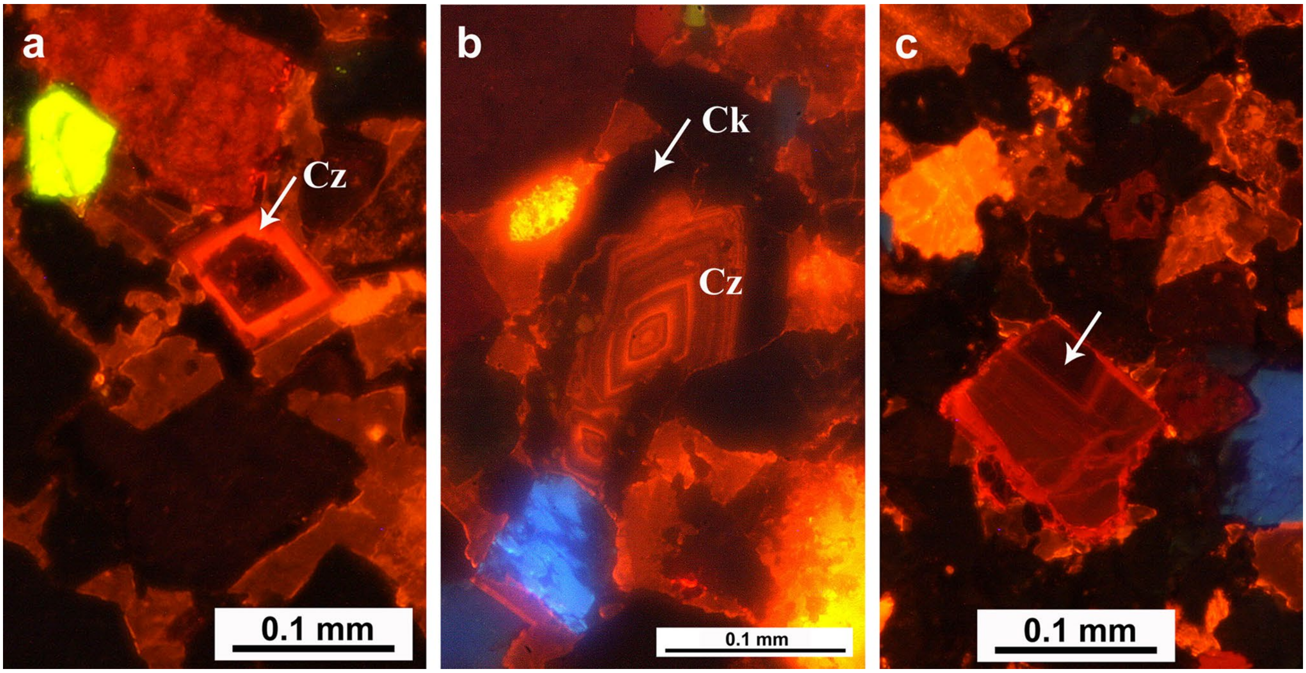

Fig. 7 Randomly distributed monocrystals of dolomite with concentric zones in CL (**a–c**). Locality **a**: Lipowica, locality **b**: Rudawka Rymanowska, locality **c**: Stasiana. **a** Replacive overgrowth Cz on carbonate grain. *Note*: Absence of truncation at grain boundary suggests its growth in situ and the *dusty dark centre* is a detrital carbonate grain overgrown by authigenic cement. Greenish grain (*upper left*) is apatite because it does not show the typical twinning and inclined extinction of a plagioclase. **b** Rhomboidal cement (Cz) occurring as pore filling, subsequently corroded by non-luminescent ankerite/ferroan dolomite (Ck). **c** Detrital dolomite grain (*arrowed*) identified by its abraded irregular outline that truncates the internal growth zones

helpful in resolving the problem of discrimination between eo- and mesodiagenesis. Therefore, we consider that eo- and mesodiagenetic stages merged into a relatively continuous diagenetic process. This suggestion seems plausible especially when taking the moderately deep marine environment of deposition into account. Namely, this setting should provide more stable conditions of early diagenesis than continental, coastal or shallow marine environments that are characterised by strong variations in meteoric waters composition. The latter factor is reflected in the cement features that enable the discrimination between eo- and mesodiagenesis (Horbury and Adams 1989; Machel 2000; Pahl and Sikorska 2004).

The brightest, yellow carbonate cement represents the youngest generation (Cy), which crystallised in pores that remained after precipitation of the preceding cement generations (Cb–Co; Fig. 2) and is represented by calcite, as shown by the preliminary SEM analyses (Fig. 3, analytical point 'cc'). Importantly, eo- and mesogenetic carbonate cements reduce the permeability of sandstone because they locally fill pores or preferentially block pore throats (Worden and Burley 2003). We suggest that for this reason, the quantity of the young yellow cement (Cy) in the Cergowa sandstones is much lower than that of the older Cb and Co cements. By comparison with these two earlier generations, the Cy luminescence colour may be related to a moderate increase in Mn concentration or lower contents of quenchers (e.g. Fe). According to Machel (2000), detectable luminescence occurs when Mn content in solid solution exceeds 10–20 ppm and total Fe amount is lower than 150 ppm; furthermore, 'Fe^{2+} commonly is considered to be the only quencher in natural carbonates, but Fe^{3+} and Ni^{2+} probably are important in at least some cases'. And further '… the interplay of Mn^{2+} and total Fe in determining the luminescence characteristics of natural carbonates is not well understood'. Taking all the above aspects into account and considering that meteoric waters are richer in Mn^{2+} than marine waters (Mozley 1989), we suggest that an influx of meteoric waters at the stage of formation of the Cy cement seems to be highly probable. In general, significant influence of meteoric waters is noted in publications at two extremes of diagenesis: the eo- and telodiagenetic stages (Morad 1998). Since the yellow carbonate cement (Cy) in the Cergowa sandstones represents the youngest generation (Fig. 2), therefore the meteoric waters infiltration in this case may only be related to telodiagenesis, not eodiagenesis (Table 2). Furthermore, if oil is present in pores, infiltration of meteoric waters causes its degradation, which increases the concentration of HCO_3^{2-} and results in precipitation of carbonate cements (Morad 1998). In the

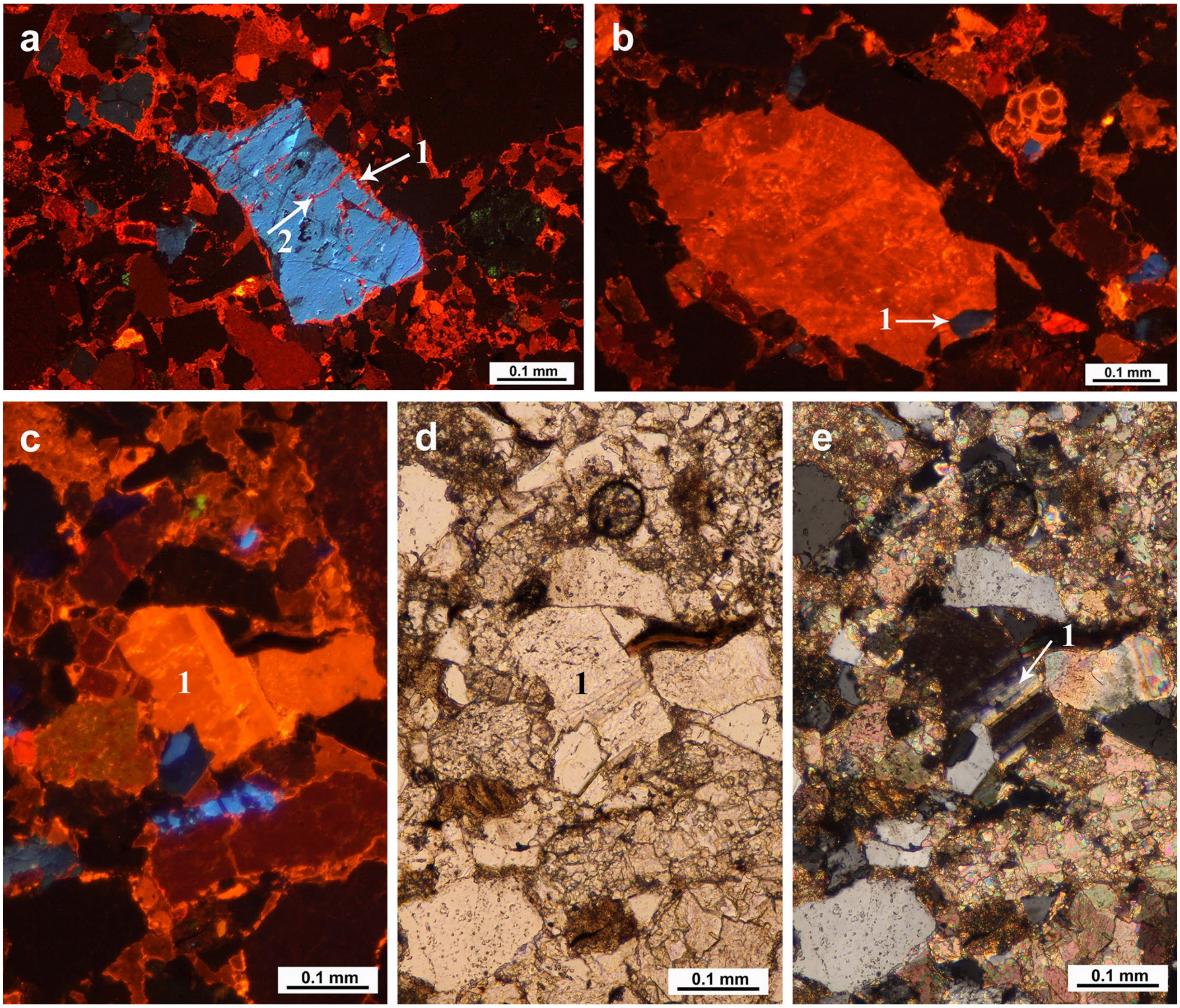

Fig. 8 Replacements of feldspars by carbonates in CL (**a**–**c**), in PPL plane-polarised light (**d**) in and XPL cross-polarised light (**e**). Locality **a** and **c**–**e**: Stasiana, locality **b**: Iwla. **a** Orange carbonate cement in marginal parts of feldspar grain (*1*) and along fissures (*2*) replaces *blue-luminescent* feldspar. **b** Very highly advanced alteration results in patchy relics of feldspar (*1*) 'floating' within carbonate. **c** Complete replacement results in carbonate pseudomorphs after detrital feldspar (*1*). **d** The same as **c**. **e** The same as **c**, **d**. Feldspar relics (*arrowed*) in carbonate pseudomorphs after detrital feldspar. Note that images **b**, **e** may be interpreted alternatively as poikilotopic calcite cement overgrowths enveloping small feldspar grains

Table 2 CL cement nomenclature, colour under CL, relative diagenetic stage and EDS determination of mineral phases in the analysed sandstones of the Cergowa Beds

Label	Colour	Diagenetic stages	EDS
Cb	Brown	Eodiagenesis, mesodiagenesis	Calcite (cc)
Co	Orange	Eodiagenetic, mesodiagenesis	Calcite (cc)
Cz	Zoned	Mesodiagenesis	Dolomite (dol)
Ck	Black	More advanced mesodiagenesis	Ankerite (an)
Cy	Yellow	Telodiagenesis	Calcite (cc)

Cergowa sandstones, both conditions are fulfilled, namely the rocks contain hydrocarbons manifested by natural oil seeps and the yellow carbonate cement originated under the influence of somewhat reduced meteoric waters. The effects of telodiagenesis can rarely be found in deeply buried successions but are often caused by incursion of meteoric waters at the stage of uplift and basin inversion (Worden and Morad 2009) and occur commonly in outcrops of sedimentary rocks (Worden and Burley 2003). In this context, the Cergowa sandstones are a part of the Outer

Carpathians flysch successions deposited in marine basins that experienced the final uplift pulse in Miocene, during the terminal stage of the Carpathian-Alpide orogenesis. In addition, all samples of the Cergowa sandstones discussed in this paper were collected in natural outcrops.

The zoned cement (Cz) is younger than brown and orange calcite cement, which is shown by truncation relations, e.g. in Fig. 7a. Marginal parts of pore-filling Cz cement are occasionally corroded and replaced by non-luminescent (black) ankerite/ferroan dolomite cement (Ck in Fig. 7b). Therefore, the generation Ck represents carbonate cement younger than Cz (Table 2). Conversely, the age relations between (Cy) and two other generations, i.e. zoned (Cz) and black (Ck), cannot be determined at this stage on the basis of their spatial relationships (which have not been observed), but may be deduced from the sequence of the diagenetic processes shown in Table 2.

Carbonate cement that crystallised at elevated temperatures is usually ferroan and, being dolomitic, consists of rhombs that often show zoned structure (Worden and Burley 2003). Increased temperatures promote carbonate cement crystallisation, which is associated with increased crystal size; therefore, one of the results of mesodiagenesis is a coarser grained crystal fabric. Morad (1998) considers that randomly distributed relatively large monocrystalline rhombs imply recrystallised carbonate cements. Worden and Burley (2003) state ‘late diagenetic carbonate crystals (usually ferroan dolomite) can also develop in the apparent absence of pre-existing carbonate minerals’. Hence, they crystallise directly from pore fluids. In this context, the observations presented in this paper enable the suggestion that the cement-forming dolomite rhombs in the Cergowa sandstones resulted from two independently operating diagenetic processes: (1) recrystallisation of the pre-existing carbonate components (Fig. 7a) and (2) pore-filling crystallisation out of the pore fluids without pre-existing carbonate minerals (Fig. 7b). Therefore, euhedral-to-subhedral rhombs of dolomite form replacive and pore-filling cements (Fig. 7a, b, respectively) sensu Gawthorpe (1987).

Several authors have demonstrated on the basis of geochemical studies that formation of ankerite cement, replacing eodiagenetic or earlier mesodiagenetic carbonate cement partially or even completely, occurs during mesodiagenesis (e.g. Boles 1978; Gawthorpe 1987; Taylor 1990; Morad 1998; Hendry et al. 2000). The same stage of diagenesis, which introduced ankerite/ferroan dolomite into the Cergowa Beds sandstones, is suggested here by relationship between Ck and the older (Cb and Co) cement generations. Reference to the equilibrium diagram published by Morad (1998) indicates that an increase of temperature between the time of crystallisation of cement Cz and its partial replacement by the ankeritic/ferroan dolomite cement Ck may be inferred.

Carbonate cement in sandstones may be derived from an internal source, i.e. from within the sandstone, and/or from external sources, i.e. from interbedded and juxtaposed beds as well as from the underlying fine-grained facies (Morad 1998). Several studies (e.g. Gawthorpe 1987; Morad 1998; Worden and Burley 2003) emphasised the influence of pore waters derived from the mudstone/siltstone complexes present in deeper parts of sedimentary successions upon the diagenesis of the overlying sandstones. Therefore, ‘fines’ are regarded as one of the most important sources of cement because in such conditions ‘pore waters tend to migrate from low-permeability to high-permeability rocks, such as from mudstone to sandstones’ (Worden and Burley 2003). Considering that the stratigraphic position of the Cergowa Beds lithosome is a lens within the shaly Menilite Beds (Fig. 1b), which include limestone and marl interbeds, it is likely to have played a role in the origin of the carbonate cements because of facies contrast and related porosity gradient at the interface between the two lithologies—a situation that could result in mass solute transfer (Morad 1998; Worden and Burley 2003). In this context, we suggest that migration of connate fluids from the low-permeability Menilite Beds into the overlying Cergowa sandstone complex with relatively low fluid pressure resulted in a decrease in partial pressure of CO_2 and therefore precipitation of intergranular carbonate cement, which occurred mainly during mesodiagenesis (Morad 1998).

CL analysis of carbonate grains

The cathodoluminescence analysis enabled the distinction of six previously unknown microfacies of grains that represent various carbonate rocks present in the source area of the Cergowa sandstones: microbreccia, calcarenite/wacke, microsparite, sparite, biomicrite and dolostone.

The source rock of the microbreccia was composed of microveined microsparite fragments cemented with sparite. The following features and cross-cutting relations seen in Fig. 4a support this interpretation: (1) carbonate veinlets extend only through the microsparite fragments are truncated by the fragments’ outlines and have different orientations, which implies they predate the first stage of fragmentation; (2) the sparry cement binding these fragments does not extend beyond the microbreccia grain outline resulting from transport-related abrasion subsequent to the second stage of fragmentation; therefore, it is a part of the microbreccia source rock. Consequently, such lithic grains are derived from erosion of microbreccia composed of sparite-cemented micro veined fragments of microsparite.

Low textural maturity of the calcarenite/wacke grains (Fig. 4c–e) suggests that their source rock resulted from short distance of transportation and rapid deposition of carbonate detritus. The subtle calcareous veinlets continuing through the whole grain (Fig. 4c) and twin bands resulting from deformation and strain (Fig. 4d, e) are suggested to be the features of a slightly tectonised immature calcarenite exposed to erosion in the source area.

The shapes of microsparite and sparite lithoclasts imply abrasion and occasional breakup of well-rounded grains during transport (Fig. 5a, b). They were derived from carbonate source rocks that did not undergo any significant tectonic deformation, as evidenced by the absence of obvious tectonic microstructures, in contrast to the grains shown in Fig. 4a, c.

The proportions of the biomicsparite components classify the rock as poorly washed biosparite. Deep indentations of terrigenous grains into the outlines of the biomicsparite grains are shown in Fig. 5c–e, coupled with the absence of cement between them suggest that the packstone lithoclasts were deposited as soft fragments. Therefore, they were probably derived from the carbonate shelf fringing the emergent source area. Thus, such lithoclasts may be considered as intraclasts redeposited from the littoral zone into the depths of the flysch basin. The above features coupled with a very close similarity of such intraclasts with the carbonate matrix observed in the Cergowa sandstones (Fig. 5d, e) suggest that what is commonly observed in these rocks as matrix may in fact represent biomicsparite (poorly washed biosparite) intraclasts squashed by compaction.

Polycrystalline dolomite grains with sharp or fuzzy concentric zones are composed of rhomboidal crystals (Fig. 6a, d). Truncation of the constituent crystals at subrounded-to-rounded grain boundaries implies a detrital origin of such grains involving erosion of dolostone at the source, transportation and abrasion prior to redeposition into the flysch basin. The absence of tectonic microstructures suggests that the source rock was undeformed. In general, concentrically zoned carbonates are considered to form under unstable conditions characterised by pronounced chemical variations of infiltrating meteoric waters that affect diffusion, precipitation and conditions of crystallisation (Machel 2000; Pahl and Sikorska 2004; Buijs and Goldstein 2012). Therefore, we suggest that in case of such tectonically intact dolomite grains composed of zoned rhombs (e.g. Fig. 6a, d) chemically unstable and possibly oscillating conditions existed during dolomitisation of a carbonate shelf complex adjacent to the Silesian Ridge that ultimately became the source rock of the Cergowa sandstones (Ślączka 1971). Variations in cation availability (e.g. Mn and Fe) arose due to changing redox potential as originally oxygenated meteoric waters became progressively reduced and more suboxic to anoxic. Repeated flushing and cycling of such pore waters resulted in multiple or oscillatory zoning of dolomites due to periodic changes in cation substitution. The zoned dolomite grains that occur as abraded or broken solitary rhomb fragments (Fig. 7c) may have resulted from disintegration of polycrystalline grains originally composed of rhomb-shaped dolomite during transport at the source area.

CL analysis of carbonate-replaced feldspars

Acidic pore waters, enriched with Ca^{2+} cations and with CO_3^{2-} anions, had a destructive effect on feldspars. Partial or total replacement of feldspar grains by calcite is a common diagenetic phenomenon in the Cergowa sandstones (Fig. 8a–c). The common calcite replacement of pre-existing feldspar is clearly visible in CL images. Exceptional are cases of extremely advanced replacement, when cross-polarised light images (Fig. 8e) are more useful in recognition of feldspar relics than CL observations.

The acidic environment favourable for feldspar dissolution in the Cergowa sandstones might have resulted from organic acids in the pore fluids (Hellmann et al. 2003), which could have been sourced from the underlying organic matter rich Menilite Beds that are known as a hydrocarbon source rock.

Conclusions

The cathodoluminescence observations on the Cergowa sandstones revealed many features with implications for provenance and diagenesis of these rocks. They are summarised below.

1. Five groups of carbonate cement are characteristic as follows: brown (Cb), orange (Co), yellow (Cy), zoned (Cz) and black (Ck); none are identifiable using standard polarising microscope.
2. Preliminary SEM analyses reveal that Cb, Co and Cy cement generations are calcite, while Cz generation represents dolomite and Ck ankerite/ferroan dolomite.
3. When dolomite and ankerite/ferroan dolomite occur together, ankerite/ferroan dolomite (Ck) forms replacements after the dolomite cement (Cz).
4. The most probable sequence of carbonate diagenetic phases responsible for the origin of Cb-Cz cements is (1) eo- and mesodiagenetic phase with pore-filling brown and orange luminescent calcite (Cb and Co), both forming in stable conditions, without a significant influence of meteoric waters; (2) mesodiagenetic phase with recrystallised cement appearing as randomly distributed relatively large monocrystalline dolomite rhombs (Cz); (3) more advanced mesodiagenetic stage represented by black ankerite ferroan/dolomite (Ck); (4) brightly luminescent cements (Cy) of telodiagenetic phase would indicate a suboxic setting with pore waters that underwent adequate reduction and decreasing redox potential (Eh) to permit Mn^{2+}

cation substitution for Ca^{2+} in the carbonate crystal lattice but insufficient redox potential/reducing conditions to permit Fe^{3+} reduction to Fe^{2+} (e.g. >~300 mv Eh where Fe^{3+} (ferric) is more stable). This would prevent any Fe^{2+} for Ca^{2+} lattice substitution and the associated diminished/quenching of the luminescent signal.

5. It is suggested that the stratigraphic position of the Cergowa Beds sandstone lithosome played a key role in the origin of the carbonate cements, as the interlayers of shales and marls in the underlying Menilite Beds may have supplied expelled connate waters to the overlaying strata.
6. Cathodoluminescence analysis distinguished six microfacies of grains representing various carbonate rocks exposed to erosion in the source area of the Cergowa sandstones located NW of the depositional basin. These are microbreccia, tectonised immature calcarenite/wacke, microsparite, and sparite, packstone and dolostone.
7. Despite the moderate intensity of the dissolution process, it was crucial for the sediment lithification by increasing the contact surface area between corroded grains and carbonate cement, which resulted in very strong cementation manifested by exceptionally high hardness, physical resistance and low porosity of the Cergowa sandstones.
8. Cathodoluminescence revealed other petrological features of the Cergowa sandstones, which the PL observations did not reveal, namely zonation in dolomite grains, the presence of distinct carbonate overgrowths and the origin of certain parts of the matrix by compression of soft pelitic carbonate rock fragments supplied from the source area.
9. Sparry calcite cements lack twinning bands suggesting a relatively low pressure during their crystallisation/recrystallisation. Preservation of soft pelitic packstone clasts with terrigenous sand grains imbedded into the individual fragments soft surface further supports this idea.
10. This study also demonstrates the difficulty of determining the nature of diagenetic changes by cold cathode CL alone. Without additional analytical techniques such as fluid inclusion analyses to elucidate cement palaeotemperatures and palaeosalinities or stable isotope analysis to ascertain possible fluid sources/environments or beam techniques for trace element chemical composition of cement zones this is extremely difficult. Such geochemical data are essential to the investigation of cement generations in order to pinpoint different stages during diagenesis.

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