Diagenesis of echinoderm skeletons: Constraints on paleoseawater Mg/Ca reconstructions

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ABSTRACT

One of the most profound environmental changes thought to be reflected in chemical composition of numerous geological archives is Mg/Ca ratio of the seawater, which has varied dramatically throughout the Phanerozoic. Echinoderms that today typically form high magnesium calcite skeletons are increasingly being utilized as a proxy for interpreting secular changes in seawater chemistry. However, accurate characterization of the diagenetic changes of their metastable high magnesium calcite skeletons is a prerequisite for assessing their original, major-element geochemical composition. Here we expand the existing models of diagenesis of echinoderm skeleton by integration of various analytical methods that up to now rarely have been used to assess the diagenetic changes of fossil echinoderms. We validated the preservation of a suite of differently preserved echinoderm ossicles, mostly crinoids, ranging in age from the Cambrian through Recent. In 13 of 99 fossil echinoderm ossicles we found well-preserved porous microstructure (stereom), non-luminescent behaviour or blotchy dark color in cathodoluminescence, and distinct nanostructural features (layered and nanocomposite structure). Moreover, in representatives of such preserved samples,

distribution of sulphates associated with organic matter is identical to those in Recent echinoderms. Only such ossicles, despite of local micrometer-scale diagenetic changes, were herein considered well-preserved, retaining their original major-element skeletal composition. By contrast, majority of samples show transformation to the stable low magnesium calcite that leads to obliteration of the primary geochemical and micro/nanostructural features and is accompanied with increase in cathodoluminescence emission intensity. Using only well-preserved fossil echinoderm samples, we found purely random variation in Mg/Ca in echinoderm skeletons through the observed time series; any periodicities in echinoderm skeletal Mg/Ca ratio which might be related to the secular transitions in calcite and aragonite seas were not confirmed. These findings suggest that, in contrast to some groups of organisms with relatively weak control over their biomineralization (such as algae, sponges, and bryozoans), in which polymorph mineralogies consistently changed according to the seawater type, application of fossil echinoderms, in particular crinoids, to seawater Mg/Ca reconstructions is unreliable. These data emphasize a key-role of physiological factors (the so-called vital effects) in echinoderm biomineralization.

Keywords: diagenesis; calcite; XANES; FESEM; CL; Mg/Ca.

1. Introduction

Evidence from fluid inclusions in primary marine halite shows that Mg/Ca ratio of seawater has varied between 1.0 and 5.2 throughout the Phanerozoic (e.g. Lowenstein et al., 2001; Horita et al., 2002). This secular oscillation in Mg/Ca ratio, that is thought to have been driven by global rates of ocean-crust formation, is considered a primary factor linking the synchronicity between secular changes in the polymorph of biogenic and abiogenic carbonate

mineralogies throughout the Phanerozoic (Hardie, 1996; Ries, 2010). It was proposed that a seawater Mg/Ca ratio of 2 separates the calcite ($\text{Mg/Ca} < 2$) and aragonite with high- Mg calcite ($\text{Mg/Ca} > 2$) nucleation fields (Lippmann, 1973; Folk, 1974). Thus, the intervals of low (<2) and high (>2) Mg/Ca ratio have been referred to as the calcite and aragonite seas, respectively (Sandberg, 1983; Hardie, 1996). However, recently Balthasar and Cusack (2015) showed experimentally that the proportions of CaCO_3 polymorphs should be quantified as a function of Mg/Ca and temperature. According to this work, calcite precipitation is inhibited under "aragonite sea" conditions only at temperatures above 20°C , whereas during "calcite sea" conditions, co-precipitation of aragonite and calcite can occur above 20°C . Consequently, the exclusive "calcite sea" scenarios would be rare in the geological past and constrained to temperatures below 20°C . Also several other previously published works question purely mechanistic understanding of factors affecting the observed patterns in Phanerozoic carbonate mineralogy and, in particular, the scale and magnitude of seawater Mg/Ca variation (e.g. Gaffin, 1987; Burton and Walter, 1987; Adabi, 2004; Lee and Morse, 2010; Bots et al., 2011). This shows that uncertainties introduced by assumptions invoked in the reconstructions still require reliable proxies to accurately reconstruct ancient Mg/Ca ratio of seawater. Among such proxies important role play biogenic carbonates.

Fossil echinoderms have long been disregarded in Mg/Ca seawater reconstructions. This is because echinoderm bio-calcite, that is formed via a highly controlled intracellular biomineralization process, differs in structure and biogeochemical composition from those of equivalent geologic or syntethic calcite (Okazaki, 1960; Märkel 1986). In particular, their skeletons are composed of mineral grains (20–100 nm in diameter) that are associated with an organic matter (Weiner and Addadi, 2011), and display high variation in MgCO_3 content (3–43.5 mole%) (e.g., Schroeder et al., 1969). Despite this, however, their skeletons are increasingly being used as a proxy of secular variations in Phanerozoic ocean chemistry (e.g.,

Dickson 1995, 2002, 2004; Ries, 2004, 2010; Hasiuk and Lohmann, 2010; Kroh and Nebelsick, 2010). For instance, depending on the author, fossil echinoderms are considered “reliable” (Dickson, 2002), “excellent” (Dickson, 2004) and “ideal” (Hasiuk and Lohmann, 2010) records of Phanerozoic seawater Mg/Ca ratio. However, reconstruction of the secular changes in Mg/Ca ratio of the ocean throughout the Phanerozoic relies on the accurate characterization of the extent of diagenetic alteration of fossil skeletons.

Abiotic or biotic high-Mg calcite (such as echinoderm biomineral) with more than ~12 mol% MgCO₃ is the most reactive and soluble carbonate polymorph (e.g., Plummer and Mackenzie, 1974; Walter and Morse, 1984; Bischoff et al., 1987). High-Mg calcite that becomes exposed to meteoric water rapidly (in about 10⁴ yr) loses all of its Mg (Land et al., 1967; Gavish and Friedman, 1969; Richter, 1974). Thus, it has long been accepted that high-Mg echinoderm calcite is virtually absent among pre-Holocene carbonates. Indeed, Weber and Raup (1968) in their analysis of 83 fossil echinoderm ossicles spanning a time interval from the Mississippian to Pleistocene, found only one echinoderm specimen from the Pleistocene with high-Mg calcite. However, as indicated by Bischoff et al. (1993) the diagenesis of Mg calcite might, under some circumstances, be accomplished without loss of Mg. Indeed, Mg-loss seems to be controlled by physical and chemical properties of the solid, such as carbonate ion positional or cation ordering, microstructural and surface defects, adhered small particles, or crystal size. In accordance with this, Dickson (1995, 2001a, 2002, 2004), in his seminal papers on fossil echinoderms, described numerous high-Mg calcite ossicles that have retained their original bulk chemistry, despite under-going micrometer-scale diagenetic changes. Furthermore, in the case of echinoderm skeleton, Dickson has questioned the paradigm that high-Mg calcite transforms to low-Mg calcite with perfect textural preservation and argued that microstructural variations can successfully be used to map the extent of diagenetic alternation. At the same time, however, the latter author admitted that microstructural criteria

to ascertain diagenetic change can be problematic (Dickson, 1995). For example, depletion of Mg may occur without textural change in Mg calcite foraminifera tests (Budd and Hiatt, 1993). As stated by Dickson (2001a), further work is obviously required before the diagenesis of echinoderm skeleton is properly understood. Indeed, it has been recently pointed out that the use of fossil echinoderms in the reconstruction of paleocean elemental chemistry can be limited because the accurate characterization of the diagenetic alteration of their skeletons is often hard to evaluate (e.g., Hasiuk and Lohmann, 2008a, b; Dickson, 2009). In particular, nanoscale structural and biogeochemical behaviour of echinoderm skeletons during diagenesis is unexplored.

In this paper we employed various analytical (micro/nanostructural, geochemical, cathodoluminescence) methods, that up to now rarely have been used to characterize diagenesis of fossil echinoderm biominerals, in order to provide new insights into structural and geochemical effects of diagenesis in fossil echinoderms from various stratigraphic intervals and rock types, and expand the existing model on diagenetic alteration of echinoderm skeleton. We also compiled published data on Mg/Ca ratio of well-preserved fossil echinoderms with results obtained from this study to further explore whether fossil echinoderms are indeed a good proxy for ancient seawater Mg/Ca reconstructions.

2. Materials and methods

2.1. Fossil and Recent samples

Materials examined consisted mostly of crinoid ossicles (details in Supplementary Appendix), which are stored at the following museums (institutional abbreviations in brackets): Faculty of Earth Sciences, University of Silesia (GIUS), Institute of Paleobiology, Polish Academy of

Sciences, Warsaw (ZPAL) and Natural History Museum, London (BMNH). Fossil localities from which investigated echinoderm ossicles were collected are described in the literature (see Table 1).

2.2. Preparatory techniques and equipments

Depending on the type of analysis various preparatory techniques were applied in this study and their brief descriptions are given below.

2.2.1. Structural analyses

Micro/nanostructural observations on fractured and carbon-coated skeletal fragments were performed using Field Emission Scanning Electron Microscope (FESEM) at the Institute of High Pressure Physics Unipress, Polish Academy of Sciences in Warsaw. The surfaces were lightly etched for up to about 90 seconds either in Mutvei's solution following described procedures (Schöne et al., 2005) or in 0.1% formic acid solution following Stolarski (2003). The sections were then rinsed in ultrapure water and air-dried. Additional observations on polished and carbon-coated skeletons were made with Scanning Electron Microscope (SEM) Philips XL-20 at the Institute of Paleobiology of the Polish Academy of Sciences in Warsaw (accelerating voltage = 25 kV, working distance = 34 mm).

2.2.2. Geochemical analyses

Spot elemental analyses on polished and carbon-coated samples (in some cases previously mounted in epoxy) were conducted using Energy Dispersive Spectroscopy (EDS) performed on a Scanning Electron Microscope Philips XL-20 coupled with the EDS detector ECON 6, system EDX-DX4i at the Institute of Paleobiology of the Polish Academy of Sciences in

Warsaw. The following conditions were used: accelerating voltage = 25 kV, a beam diameter ~5 μm . Each ossicle was analyzed on up to ~ 10 isolated spots on the stereom and up to ~ 5 spots on the cements. In every case, the area of each spot analysis was smaller than trabecular bar. The BSE detector of the Philips XL–20 microscope allowed the distinction between materials of lower *versus* higher atomic number.

Selected carbon-coated samples were also analyzed using Wavelength Dispersive Spectroscopy (WDS) performed on CAMECA SX100 electron microprobe at the Micro-Area Analysis Laboratory, Polish Geological Institute - National Research Institute in Warsaw. The following conditions were used: accelerating voltage 15 kV, beam current 5 nA for calcium and 20 nA for other elements, a beam diameter ~5 μm .

To determine both the oxidation state of sulphur and map of its spatial distribution, X-ray synchrotron fluorescence analysis was conducted on four polished samples representing different preservation type (Cuif et al., 2003). These analyses were performed with the scanning X-ray microscope (SXM) operating in the X-ray fluorescence mode at the X-ray Microscopy beamline ID21 of European Synchrotron Radiation Facility (Grenoble, France) following procedures described by Cuif et al. (2003; for details see also Gorzelak et al., 2013). The following conditions were used: a fixed exit double-crystal Si (111) monochromator with an energy resolution of $\Delta E/E=10^{-4}$, the Kirkpatrick-Baez mirror arrangement focussing the X-ray beam down to size of $0.3 \times 0.8 \mu\text{m}^2$ and HpGe detector placed at 90° scattering angle. μ -XRF 2D maps were obtained by point-by-point scanning of the sample across the focal point of the beam, with the exposure time of 100-300 ms per point. For a specific analysis of sulphur species, the X-ray beam was tuned to an energy level just above the K absorption edge of sulphur - referred to as the X-ray Absorption Near Edge Structure (XANES). The sulphate measurements were done using scanning the energy of the exciting beam across the sulphur absorption K-edge from 2.45 keV to 2.53 keV. Reference

spectra for disulfide bonds of standard compounds ((C-S-S-C) in cystine, H-S-C bonds in cysteine, C-S-C in methionine, and C-SO₄ in chondroitin sulfate) were also determined (see fig. 1a,b in Cuif et al. 2003). Spectra of S-reference compounds revealed that the amino acid cystine has a double peak around 2.473 keV, methionine and cysteine amino acid spectra display a single peak at 2.473 keV. The mineral sulphate (CaSO₄) and the sugar chondroitin sulphate both display main peaks at 2.4827 keV (see fig. 1a, b in Cuif et al., 2003).

2.2.3. Mineralogical analyses

X-ray diffraction analyses (XRD) and mineral composition of seven samples representing different preservation types were assessed with the aid of a Panalytical X'Pert PRO - PW 3040/60 X-ray diffractometer equipped with Cu K_{α1} source radiation ($\lambda=1.540598 \text{ \AA}$), Ni-Filter to reduce the K_β radiation and an X'Celerator detector at the Faculty of Earth Sciences, University of Silesia, Sosnowiec, Poland. The samples were ground manually using an agate mortar for 2 min. Subsequently, standard zero background Si sample holders with an internal cavity were filled with powder. In order to correct the peak positions on XRD pattern due to the sample displacement shift, small amount of pure NaCl powder was used as internal standard. Measurement parameters were: acceleration voltage: 40 kV; filament current: 40 mA; counting time: 300 s; goniometer settings: 2,5° - 65° 2 Θ ; step size: 0.01° 2 Θ .

Quantitative analysis of the collected data were carried out by means of the X'PERT HighScore Plus + Software using the newest ICSD database. The quantitative contents were calculated using the Rietveld Method.

2.2.4. Cathodoluminescence analyses

Polished and carbon-coated thin sections were examined with cathodoluminescence microscope equipped with a hot cathode integrated with UV-VIS spectrometer and linked to a

Kappa video camera for recording digital images, at the Institute of Paleobiology of the Polish Academy of Sciences in Warsaw. Integration times for CL-emission spectra of luminescent samples were commonly 15 s.

2.3. Statistical analyses

Mg/Ca data (either in a form of uncorrected ratio or recalculated as seawater Mg/Ca by using a partition coefficient $Mg/Ca_c = 0.3182(Mg/Ca_{sw})$ following Dickson (2004) and a partition function $Mg/Ca_c = 0.051(Mg/Ca_{sw})^{0.67}$ following Ries (2004)) were subjected to statistical tests (including Spearman's rank correlations for raw and detrended data (first differences), Mann Whitney and Monte Carlo permutation tests, and spectral analysis using Lomb periodogram) on PAST 3.0 (Hammer et al., 2001).

3. Results

3.1. Geochemistry and mineralogy

Five types of preservation can be conventionally distinguished in the investigated fossil material (Fig. 1; see Supplementary Tables 1-3): (i) low-magnesium calcium carbonate ossicles (< 4 mol % $MgCO_3$; see Supplementary Plates 1B₅, E₅; 2A₅, C₅-G₅; 3A₅-D₅; 4A₅-G₅; 5A₅, C₅-G₅; 6A₅-G₅; 7A₅, C₅-F₅; 10A₅, B₅, F₅, G₅; 11B₅-D₅, F₅, G₅; 12A₅-G₅; 13A₅-C₅; 15A₅-G₅; 16A₅-D₅; 17A₅, B₅); (ii) intermediate-magnesium calcium carbonate ossicles (ca. 4-7 mol % $MgCO_3$; Supplementary Plates 10C₅-E₅; 11A₅, E₅; 14A₅, B₅; 17F₅); (iii) high-magnesium calcium carbonate ossicles (> 7 mol % $MgCO_3$; Supplementary Plates 1A₅, C₅, D₅; 9A₅, B₅; 17C₅-E₅); (iv) dolomitized ossicles (Supplementary Plates 3E₅; 5B₅; 7B₅, G₅; 8A₅-D₅) and (v) silicified ossicles (Supplementary Plate 2B₅).

The first type predominates in the studied material. Mean bulk Mg content in these ossicles is variable (0.03-0.71 wt%, which corresponds to 0.11-2.9 mol % MgCO_3). Si, Al, Mn, Na, K, Cl, S and Fe were occasionally detected but their concentrations are rather low and close to the detection limits. Some differences in geochemical composition (in particular in Mg content) exist within individual ossicle as suggested by spot EDS and WDS analyses. For Mg, calculated standard deviations fell in the range 0.01 to 0.73 and the coefficients of variations (a normalized measure of dispersion of a probability distribution) ranged from 2.1 to 141.4 % (see Supplementary Tables 1-3). Chemical heterogeneity was also independently shown by non-uniform gray shade in BSE images in some ossicles (e.g. Fig. 1D₂₋₃; e.g., Supplementary Plates 2A₂₋₃, F₂₋₃; 6A₃, D₃; 7B₃; 13E₂₋₃). The interpretation of geochemical data from these ossicles is exceedingly difficult due to the inability to distinguish the stereom or its replacement from the cement infills. μ -XRF maps tuned to optimize sulphate-S at 2482.7 eV of selected specimen from the Kimmeridgian of Małogoszcz (Poland) preserved as low-Mg calcite showed that sulphates are distributed heterogeneously within the stereom trabeculae without any pattern (Fig. 2D). In CL-images, the samples commonly showed intense orange luminescence (Fig. 3I, J). The CL emission spectrum of an orange luminescing Mn^{2+} -activated showed emission maximum at about 615 nm (e.g., Fig. 4, Mn^{2+} activation in the Ca^{2+} position). XRD of these samples typically showed the presence of pure calcite (e.g. Fig. 5D, G).

The second type of preservation (i.e., intermediate-magnesium calcium carbonate ossicles) was only observed in some echinoderm ossicles from the Lower Jurassic (Pliensbachian) of Cheltenham (U.K.), Middle Jurassic (Bathonian and Callovian) clays of Gnaszyn and Łuków (Poland) and the Paleogene (Eocene) of Clapham (U.K.). Their mean Mg contents varied from 0.91 to 1.61 wt %, which correspond to 4.1-6.0 mol % MgCO_3 , and 0.04-0.064 (mol/mol) in Mg/Ca ratio (see Supplementary Tables 1-3). S, Mn, Na and Fe were

occasionally detected but their concentrations are very low and close to the detection limits. Differences in geochemical composition (in particular in Mg content) within the stereom of individual ossicle can be high as suggested by heterogeneity in BSE images and spot EDS analyses (Fig. 1A_{2-3,5}). For Mg, calculated standard deviation and coefficient of variations are up to 0.75 and 83.65 %, respectively. Distinct differences in geochemical composition (in Mg and Fe contents) were also observed between the stereom and interstereom deposits. EDS and WDS spot analyses revealed that the interstereom deposit is mostly ferroan calcite (enriched in Fe and depleted in Mg), calcium siderite or framboidal pyrite (see Supplementary Tables 1-3). Clear contrast in chemical composition is also visible in heterogeneous BSE images, i.e., the stereom regions appear darker, whereas interstereom deposits with elements with higher atomic numbers (such as iron) appear brighter (e.g. Fig. 1A). μ -XRF maps tuned to optimize sulphate-S at 2.4827 keV of selected specimen from the Bathonian of Gnaszyn preserved as intermediate-Mg calcite showed that the central regions of the stereom trabeculae contain higher levels of sulphates (Fig. 2B), a pattern that is also visible in Recent echinoderm skeletons (Fig. 2A). In CL-images, the samples are non-luminescent or show intrinsic dark blueish luminescence (Fig. 3C-E). XRD of these samples typically showed the presence of magnesium calcite; admixture of dolomite (if present) is small (~1 wt%) (Fig. 5E).

High-magnesium calcium carbonate ossicles were only documented in echinoderm ossicles from the Ordovician (Bobcaygeon Formation) of Brechin (Canada), Devonian (Eifelian) of Skały (Poland), Triassic (Carnian) of Cortina d'Ampezzo (Italy) and Miocene of Korytnica (Poland). Their mean Mg contents of 1.8 and 3.1 wt % correspond to 7.2-11.4 mol % MgCO_3 and 0.08-0.13 (mol/mol) in Mg/Ca ratio (see Supplementary Tables 1-3). Differences in Mg content within the stereom of individual ossicle are relatively small as suggested by homogeneity in BSE images and spot EDS analyses (e.g. Fig. 1B). For Mg, calculated standard deviations (0.2-0.84) and the coefficients of variations (12.0-36.36 %) are

not significant. However, in some well-preserved specimens distinct differences in geochemical composition (in particular in Mg and Fe contents) exist between the stereom and intersterom deposits. EDS and WDS spot analyses revealed that the intersterom deposit is ferroan calcite (enriched in Fe and depleted in Mg), framboidal pyrite or clay sediment. Clear contrast in geochemical composition was also visible in heterogeneous BSE images, i.e., the stereom regions appear darker, whereas intersterom deposits with elements with higher atomic numbers (such as iron) appear brighter (see Supplementary Plate 9A₃). The quality of preservation and diagenetic history are not uniform for the ossicles preserved as high-magnesium calcium carbonate. For instance, some ossicles (Fig. 1C) reveal black or dark gray spots commonly a few micrometers in diameter that are set randomly in larger pale gray background. Similar features have been observed in modern echinoid ossicles artificially heated to 300°C, which resulted in the development of small and irregular pores and the transformation of homogeneous Mg calcite stereom to a mixture of dolomite and calcite (Dickson, 2001b). Indeed, XRD of these samples showed the presence of magnesium calcite with high (up to about ~15 wt%) admixture of dolomite (Fig. 5A, F). In most cases, small size of the dolomite crystals and their mixture with the calcite did not allow for separate analysis with electron microprobe to be done, however, μ -XRF maps tuned to optimize sulphate-S at 2.4827 keV showed that sulphates are distributed heterogeneously within the ossicle without any pattern (Fig. 2C). In CL-images, the stereom show blotchy dark colors sometimes with luminescence brighter spots, whereas the cement is either orange or dark (due to Fe) (Fig. 3G, H).

Ossicles that underwent dolomitization were rarely documented (see Supplementary Tables 1-3; Fig. 5C). In these ossicles, Mg content reached up to ca. 12.7 wt%. A general feature observed in dolomitized ossicles was very low within-ossicle variations in Mg content

(standard deviations fell in the range of 0.1 to 2.2 and the coefficients of variations varied from 0.8 to 2.9 %).

A single ossicle (see Supplementary Plate 2B) from the Triassic material underwent silicification. The mean Si concentration was ca. 37 wt %; however this value is probably underestimated due to the carbon coating. Geochemical variations within this ossicle were rather small as suggested by homogeneity in BSE images and spot EDS analyses.

3.2. *Micro/nanostructure*

Although, external morphology (such as crenulation pattern) is well-preserved in nearly all studied echinoderm ossicles, the stereom structure was largely destroyed. In the case of dolomitized and silicified crinoid ossicles or those preserved as low-magnesium calcium carbonate, the distinction between the stereom microstructure from the cement infills was not possible in the studied material (e.g. Fig. 1D; Supplementary Plates 5A₁₋₄; 6G₁₋₄). In these ossicles, small round or angular pores commonly a few micrometers in diameter frequently occur (black dots in Fig. 1D; Supplementary Plates 2E₃; 8A₃; 12B₃). Only occasionally, relicts of primary shape of stereom morphology can be observed (e.g., Supplementary Plate 7A₃). However, the stereom trabeculae are not sharp or well-readily visible in these ossicles, which suggest that their internal structure was changed. Well-preserved stereom structure was mostly documented in crinoid ossicles preserved as high to intermediated calcium carbonate (Fig. 1A, B). In transverse sections of these columnals, two distinct microstructural regions can be observed: petaloid regions made of regular meshwork of galleried type stereom (*sensu* Smith 1980) and interpetaloid areas composed of denser and thicker stereom. Occasionally, the stereom structure of these ossicles after slight acidic etching revealed relicts of primary layered structure on the fractured surfaces (Fig. 6C-H; see e.g., Supplementary Plates 10D₃; 11C₃, E₃; 16C₃).

A bimodality of the state of preservation between crinoid ossicles with preserved stereom and those without preserved stereom is also visible at the nanoscale structural level. In the former ones, tightly aggregated semicircular nanograins ca. 100 nm in diameter are observed (e.g., Fig. 7C-H; see e.g., Supplementary Plate 9A₄, B₄; 10C₄, E₄). In other studied ossicles, nanograins are usually not preserved (Fig. 7I, J). Only occasionally, such ossicles, in which relicts of primary shape of stereom morphology are preserved, reveal hardly visible nanograins (see e.g., Supplementary Plates 4D₄, G₄; 5B₄; 7A₄). However, they commonly occur as isolated nanograins that are generally not tightly aggregated. In majority of poorly preserved ossicles, however, typical nanograins are not observed at all. In these ossicles, only plain surfaces, secondary fractures or small pores are visible at the nanoscale.

4. Discussion

4.1. General remarks on diagenesis of studied echinoderm skeletons

From the results presented above it is clear that the examined ossicles were altered along different diagenetic pathways (Fig. 8).

4.1.1. Well-preserved ossicles

The best preserved echinoderm ossicles are reported from localities with co-occurring aragonitic (metastable CaCO₃ polymorph) fossils such as ammonites and gastropods (e.g., Gedl et al., 2003; Manecki and Tarkowski, 1987). The ossicles seem to be not significantly altered by diagenesis as suggested by nanoscale structural features (relicts of layered stereom structure and nanograins) that are nearly identical to those observed in present-day crinoids (see Gorzelak et al., 2013). The stereom of these ossicles, after extensive acidic etching, has revealed relicts of layered structure on the fractured surfaces (Fig. 6C-F). This implies that a

sub-microscale removal of organic components as well as transfers of ions were limited. Furthermore, fine scale geochemical mappings of crinoid ossicle from Gnaszyn (NanoSims microprobe, see Stolarski et al., 2009, fig. 2) compared with μ -XRF maps tuned to optimize sulphate-S (Fig. 2B) show that the high Mg concentration in the central region of stereom bars coincides with the distribution of sulphates (most probably associated with sulphated polysaccharides). The exceptional preservation of these ossicles can be also explained by their preservation in clays and subsequent infilling of their stereom pores with ferroan calcite cement (Stolarski et al., 2009). However, in contrast with high-magnesium calcite skeletons of extant, tropical echinoderms, these fossil ossicles are mainly preserved as intermediate-magnesium calcite and contain only ca. 5 mol% of MgCO_3 . This low Mg content may be either due to one or a combination of several factors (that could be interconnected) including: 1) low Mg/Ca seawater ratio of the Jurassic “calcitic sea”, 2) low temperature of the Middle Jurassic epicontinental sea (9.2-13.1°C according to Marynowski et al. (2007) or 7.4-10.1°C according to Wierzbowski and Joachimski (2007), or other factors such as: decrease of salinity, physiological effects or less probably depletion of Mg due to nanoscale diagenetic changes. Likewise crinoid ossicles from Gnaszyn (Poland) (Fig. 7C, D) and echinoderm ossicles from the Miocene clays in Korytnica (Poland) also co-occur with numerous originally aragonitic (metastable CaCO_3 polymorph) fossils (such as gastropods and corals e.g., Złotnik, 2003; Stolarski and Mazur, 2005). All these ossicles have preserved nanoscale structural features (relicts of layered stereom structure and nanograins) and seem to be not significantly altered by diagenesis. The exceptional preservation of these ossicles can be also explained by their rapid burial and sealing in clays

Another preservation pattern represents fossil ossicles with high-magnesium calcium carbonate mineralogy. They display most of micro- (stereom structure) and nanoscale (nanograins) features that are observed in Recent echinoderm skeletons (cf. Fig. 2A; 3A-B;

6A, B; 7A, B; see also Gorzelak et al., 2013) hence they appear not to be significantly affected by diagenesis. This is explained by their preservation in mudstones and subsequent cementation of their stereom pores with ferroan calcite that is known to seal off the skeleton from diagenetic fluids (e.g., Dickson, 2004; Stolarski et al., 2009). However, the stereom of these ossicles, even after extensive acidic etching, rarely revealed a distinct layered structure on the fractured surfaces as observed in Recent echinoderms (Gorzelak et al., 2011b; 2014b). This suggests that a sub-microscale removal of organic components and subsequent internal dissolution-precipitation reaction with some transfer of ions took place as suggested by μ -XRF maps and CL-images.

4.1.2. Poorly preserved ossicles

Most ossicles studied herein underwent transformation to a more stable low-magnesium calcium carbonate without fine-scale textural preservation. This is the most common diagenetic transformation of echinoderm ossicles (Weber, 1969). According to Brand (1990) early cementation of the stroma and subsequent alternation to a more stable low-magnesium calcite generally obliterates original microstructure and mineralogy/geochemistry of echinoderm skeleton. Recrystallization of primary high-magnesium calcite commonly proceeds from ion transfer over a distance of tens of microns (Dickson, 2001a). This transformation generally leads to increase in Fe and Mn and decrease in Na, Sr and Mg (Brand, 1990). It is accomplished with complete textural alternation of the stereom, which leads to the formation of many secondary pores (dissolution cavities) up to a few micrometers in diameter (e.g., fig. 5 in Brand, 1990; fig. 6, 7 in Dickson, 2001a). Comparable pores were observed in modern echinoderm ossicles artificially transformed by heating (fig. 6, 7 in Dickson, 2001b). Examined ossicles display similar pores and do not reveal micro- (stereom shape and its layered structure) and nanoscale (nanograins) features that are observed in

Recent echinoderm skeleton (e.g. Fig. 1D; 6I, J; 7J). Although these ossicles cannot be used as a proxy for the original, major-element chemistry of echinoderm skeleton, they appear to be useful indicators of the degree of diagenetic alteration and provide insights into the diagenetic changes that occur at various structural levels (see below).

4.1.3. Dolomitized ossicles

A few examined ossicles from the Triassic of Poland were completely dolomitized. Dolomitization involved mostly ossicles from Kamyce and Piekary Śląskie in Silesia of Poland. Some ossicles from Tarnów Opolski (Karchowice Beds) and Wojkowice (Lower Gogolin Beds) in Silesia as well as from Brudzów in Holy Cross Mountains (Ceratites Beds) were also dolomitized, although the crinoid ossicles from these localities are predominantly preserved as low-magnesium calcium carbonate. Dolomitization of some of these Triassic sediments with crinoids was extensively discussed in the literature but the accurate mechanism of this process is still unclear. In general, depending on the author, dolomitization of these sediments occurred during different phases of diagenesis mainly through the mixing of meteoric and seawaters, infiltration of porewaters rich in magnesium or hydrothermal activity (reviewed in Pawłowska, 1982, 1985; Bodzioch, 2005). The morpho-chemical changes in crinoid ossicles that take place during the dolomitization were described for example by Brand (1990). According to this author dolomitization proceeded in fluid-controlled systems in the presence of mixed waters that completely obliterate original microstructure and geochemistry of crinoid ossicles. For the ossicles examined in the present study, the cementation and alteration from metastable high-magnesium to low-magnesium calcite preceded the general phase of dolomitization as suggested by complete obliteration of primary micro/nanostructures.

4.1.4. *Silicified ossicles*

A single ossicle from Wolica locality in Holy Cross Mountains, Poland (Wellenkalk Beds) is silicified. Silification of echinoderm ossicles has not been frequently described in the literature (e.g., Maliva and Siever, 1988). It has been argued that silification of calcitic fossils involves dissolution of skeleton with simultaneous efflux of the dissolved calcium and carbonate ions, and the influx of silica into the solution and its precipitation. This process commonly occurs during bacterial oxidation of organic matter under aerobic conditions which lead to the CO₂ increase in pore waters and consequently decrease in local pH where CaCO₃ dissolves and silica precipitates. This replacement mechanism may occur either simultaneously, when the growth of the silica phase exerts pressure across the silica-carbonate contact or separately, when the silica precipitates in pores formed by earlier dissolution of the skeleton. The second mechanisms of replacement most likely occurred in the single ossicle examined here as there is no evidence of inclusions of unreplaced stereom or “ghosts” of the stereom microstructure. Examined ossicle probably underwent microstructure-uncontrolled replacement (*sensu* Maliva and Siever, 1988) in which chalcedony fibres are oriented independently of the stereom microstructure (Maliva and Siever, 1988).

4.2. *Nanoscale behaviour of echinoderm skeleton during diagenesis*

From the results presented above it seems that nanostructural variations can be used to map the extent of diagenetic alternation of echinoderm skeletons. The skeletons that are not significantly affected by diagenesis commonly display nanocomposite structure that is almost identical to those observed in modern echinoderm skeleton. By contrast, the skeletons that are clearly affected by diagenesis do not reveal nanograins. The obliteration of nanograins is contemporaneous with obliteration of the microstructural features (such as the overall porous stereom shape and its layered structure) and is likely due to advanced organic components'

degradation and subsequent nanoscale secondary precipitation reaction as suggested by μ -XRF maps (Fig. 2). This is consistent with recent data showing that artificial calcination processes leading to the removal of organic components alter the nanogranular structures of echinoid spine making their structures more homogenous (Seto et al., 2012).

Although, our data suggest that nanostructural variations can indeed be a useful indicator of the level and intensity of diagenetic change of echinoderm skeletons, such interpretations solely based on nanoscale structural observations should be treated with caution. Although nanocomposite structure - consistent with the model of crystallization by particle attachment from amorphous calcium carbonate (ACC) precursors (e.g., Gong et al., 2012) - is widespread in biogenic carbonates, it may occur also in synthetic and geologic environments. For example, polymer stabilization of the amorphous phase and formation of nanocluster domains were observed in various CaCO_3 precipitation experiments (Gower, 2008, for review). In geological context, precipitation of secondary (diagenetic) carbonates in an aqueous solution in the presence of organic additives may also lead to the formation of nanogranular textures (Stolarski and Mazur, 2005).

4.3. Transformation types of echinoderm skeleton

Based on our and previously published literature data, general diagenetic pathways of the echinoderm biomineral transformation could be proposed. In Fig. 8 we expanded Dickson's (2001a) model of the diagenetic changes of the stereom by taking into account both micro/nanostructural patterns (stereom microstructure, growth layering, and nanograins), CL observations and evaluating the qualitative elemental distribution of sulphates that were likely associated with organic components (such as sulphated polysaccharides).

Among several preservational types of echinoderm skeleton, four main styles of preservation that are diagrammatically shown in Fig. 8 are the most common. Clearly, this

model is highly simplified in which a variety of other preservation types (e.g., where the stereom meshes are filled with non-carbonate cements or sediments) were not included. Each transformation types are briefly described below.

4.3.1. Type '0' transformation (Fig. 8D)

This type of transformation applies to the ossicles that were rapidly buried, sealed in clays and encased in ferroan calcite cements, which prevented extensive diagenetic fluid influx and thus minimize their diagenetic change. The stereom trabeculae of such ossicles are well defined and clearly distinguishable from the cement infills (e.g. Fig. 1A). Lack of significant internal change of the stereom trabeculae was evidenced by lack of any secondary pores (Fig. 6C-F), μ -XRF maps showing distinct distribution of sulphates (Fig. 2D) that are comparable to those obtained from Recent crinoids (Fig. 2A) and preserved primary nanocomposite structure (Fig. 7C-F). However, some minor (nanometer-scale) internal change could have occurred as suggested by the presence of indistinct relicts of primary banding structure (Fig. 6C-F). This type of preservation is probably typical for the ossicles that were primary composed of low or intermediate-Mg calcite that is less reactive and less soluble than high-Mg calcite. In CL-images, the stereom is either non-luminescent or shows dark blue intrinsic luminescence whereas the cement is Mn^{2+} -activated (orange) or dark (due to Fe^{2+} as an inhibitor) (Fig. 3C-F).

4.3.2. Type '1' transformation (Fig. 8E)

This type of transformation was initially described by Dickson (2001a). Of material investigated herein, the ossicles from Skały (Poland) and Cortina d'Ampezzo (Poland) underwent similar type of transformation. According to Dickson (2001a) this transformation was probably catalyzed by internal water from the stereom leading to only minor, within-

stereom transfer of ions as suggested by the well defined general outline of stereom trabeculae that is clearly distinguishable from the cement infills (mostly ferroan calcite) (see also Fig. 1B). Internal texture of the stereom trabeculae of such ossicles possesses mottled appearance due to the presence of numerous pores and small size of dolomite crystals (both up to about few micrometers) that are intimately mixed with calcite. Internal change of the stereom trabeculae was also herein evidenced by ‘noisy’ character of μ -XRF maps which show extremely heterogeneous distribution of sulphates without any pattern (Fig. 2C). At the nanoscale structural level, nanograins are sometimes preserved though they are not distinct (Fig. 7G). According to Dickson (2001a), despite these micrometer-scale changes, such ossicles retained their original high-Mg calcitic bulk chemical composition, which is in agreement with our data. In CL-images, the stereom show blotchy dark colors sometimes with luminescent brighter spots (microdolomites cf. plate 4c in Richter et al., 2003) whereas the cement is either orange (Mn^{2+} activator) or dark (due to Fe) (Fig. 3G, H).

4.3.3. Type ‘2’ transformation (Fig. 8F)

This type of transformation, that involves both stereom and infills, has been thoroughly described by Dickson (2001a). Of material investigated herein, some ossicles from Cortina d’Ampezzo (Italy), Skaly (Poland) and Brechin (Canada) underwent similar type of transformation. The stereom that underwent this type of transformation has largely lost its primary meshwork-like appearance (Fig. 1D). The texture of such ossicles is composed of irregularly shaped dolomite crystals (about 20 μm) that are set in non-ferroan calcite with numerous pores indicating that transfer of ions occurred over distances of tens of microns (Fig. 6H; 7H). According to Dickson (2001a), such ossicles have the same bulk composition as the ossicles that underwent type ‘1’ transformation. However, due to non-recognizable

stereom in these ossicles, they cannot be used as proxies for their original bulk chemical composition.

4.3.4. Type '3' transformation (Fig. 8G, H)

This type of transformation is probably the most common type found in the fossil record.

Both primary geochemical (specific distribution of sulphates) and micro/nanostructural features (stereom structure, growth layering, nanograins) of the skeletons are obliterated to various extent (e.g. Fig. 1D; 6I, J; 7I, J; Fig. 8G, H). Alternation of the stereom with cement to a single monocrystal of stable low-Mg calcite leads to the formation of many secondary pores (dissolution cavities) up to a few micrometers in diameter (e.g., fig. 5 in Brand, 1990; fig. 6, 7 in Dickson, 2001a) and redistribution of ions, such as increase of Fe and Mn, and decrease of Mg, Sr, Na. In CL-images, the samples show intense orange to violet luminescence (Fig. 3I, J).

4.4. Integrated model of diagenetic changes of fossil echinoderm skeleton

As stressed above, magnesium calcitic skeletons of echinoderms are prone to significant diagenetic alternations. It has been argued that high-Mg calcite with over 8.5 mol% MgCO_3 is even more soluble than aragonite in normal Mg/Ca ratio of seawater (Berner, 1975; Haese et al., 2014). Furthermore, echinoderm biomineral is more likely to dissolve than other carbonate biominerals because of its highly porous structure, thus high surface areas (kinetic effect). Therefore the first diagenetic transformation of various carbonate skeletons in the sediment affects high-Mg calcitic skeletons (such as porous stereom of echinoderms).

Echinoderm skeleton may be transformed along different diagenetic pathways depending on its primary Mg contents, type of sediment in which it was buried, diagenetic fluid residence' time and its chemical composition, temperature conditions, and many other factors

that cannot be included in the present model. However, our and other published data show that similar diagenetic patterns occur repeatedly in different stratigraphic intervals and rock types and allow some generalizations to be made.

Echinoderm biominerals if rapidly buried to anoxic conditions that commonly occur a few centimeters below the sediment, in the presence of Fe could be encased in ferroan calcite cements, which prevented extensive diagenetic fluid influx. Such skeletons may undergo closed-system diagenesis (e.g., Richter et al., 2003) and commonly retain their original bulk major-chemical composition. Initially, internal diagenetic changes occur via biochemical degradation of intrastereom organic matrix (IOM *sensu* Weiner, 1985). During this process, the layered structure of the stereom interpreted as the alternations of mineral and organic-enriched layers (see Dubois, 1991) could be at least partly obscured due to the microscale internal dissolution-precipitation reaction. In the next steps, these internal changes of the stereom could further proceed (e.g., by thermal influence) leading to the stabilization of primary high-Mg calcite into the mixture of irregularly shaped microdolomite crystals that are set in non-ferroan calcite. The nanocomposite structure of such ossicles, despite these minor internal changes, is still preserved, though it is not as distinct as in recent echinoderm skeleton. In the final step, the stereom structure may largely lose its primary meshwork-like appearance due to the further growth of dolomite crystals.

On the other hand, echinoderm biominerals if not relatively rapidly buried in the sediment commonly undergo early diagenesis in the oxic conditions by epitaxial cementation of stereom pores and biochemical degradation of intrastereom organic matrix (IOM). Subsequently, if the skeleton is buried, it is prone to further open-system diagenetic alternation including transformation to low-Mg calcite. This process completely obliterates micro/nanostructure and biogeochemical properties of echinoderm skeleton which shows a

massive monocrystalline behavior and rhombohedral cleavage faces on the broken surfaces. Lately, other diagenetic transformations may occur such as dolomitization or silification.

4.5. Reassessing the applicability of echinoderm skeletons in paleoseawater Mg/Ca reconstructions

It has been argued that skeletal Mg/Ca and polymorph mineralogies of anatomically simple organisms (some bryozoans, corals, sponges and algae) consistently changed following secular changes in seawater geochemistry (Stanley, 2008). Likewise, in the case of echinoderms, many authors (e.g., Dickson, 1995, 2002, 2004; Ries, 2004; Hasiuk and Lohmann, 2010) suggested that the skeletal Mg/Ca ratio of well-preserved fossil echinoderms can be used in the reconstructions of Mg/Ca ratio in seawater up to the Phanerozoic. Nevertheless, the minimum and maximum Mg/Ca ratio for well-preserved fossil echinoderms derived from paleotropical or paleosubtropical settings from published (Dickson, 2004) and our own data (either in a form of uncorrected ratio or recalculated as seawater Mg/Ca by using a partition coefficient $Mg/Ca_c = 0.3182(Mg/Ca_{sw})$ and a power partition function $Mg/Ca_c = 0.051(Mg/Ca_{sw})^{0.67}$) from the calcite and aragonite seas clearly overlap (Fig. 9, 11A). Furthermore, after splitting and averaging (per locality) Dickson's (2004) and our own data into two different data sets (calcite and aragonite seas), a non-significant difference between median echinoderm Mg/Ca ratio can be observed (Fig. 11A). This strongly suggests a purely random variation in Mg/Ca determined from fossil echinoderm data through the time series. Indeed, our spectral analysis for echinoderm Mg/Ca ratio does not reveal any significant periodicities, which might be related to the putative ~150 My oscillations in calcite and aragonite seas driven by changes in spreading rates along mid-ocean ridges (Hardie, 1996) (Fig. 10). In particular, the strongest peak was found at a frequency of 0.01069

cycles/my, which corresponds to a period of 93.5 my. This peak does not reach the white noise line for a significance level of $p = 0.05$. Likewise, the next substantial peak, found at a frequency of 0.0037276 cycles/my. (=268.3 my.), also does not reach the white noise line for a significance level of $p = 0.05$.

To further test reliability and accuracy of fossil echinoderm data for oceanic Mg/Ca reconstruction we also compared data between seawater Mg/Ca inferred from Hardie's curve (1996) and seawater Mg/Ca determined from data on well-preserved fossil echinoderms employing a partition coefficient ($Mg/Ca_c = 0.3182(Mg/Ca_{sw})$). The results (Fig. 11B,C) show no significant correlation either for raw (Spearman rank order correlation coefficient $P = 0.2039$, $p = 0.29801$) and detrended data (Spearman rank order correlation coefficient $P = 0.2777$, $p = 0.16071$). Likewise, there is no significant correlation ($p >> 0.05$) when employing uncorrected echinoderm Mg/Ca ratio or echinoderm Mg/Ca ratio recalculated using a power partition function ($Mg/Ca_c = 0.051(Mg/Ca_{sw})^{0.67}$). Overall, these data suggest that the skeletal Mg/Ca of fossil echinoderms is not a robust proxy for paleoseawater Mg/Ca reconstruction. This is consistent with geochemical data obtained from the skeletons of Recent echinoderms, in which significant variation in Mg content (3.0 to 43.5 mol% $MgCO_3$) is observed that is related to physiological (vital) and/or environmental factors (Weber, 1969, 1973; Roux et al., 1995; Ebert, 2007; Borremans et al., 2009; Hermans et al., 2010). Although different authors (Dickson, 2002; Ries, 2004; Hasiuk and Lohmann, 2010) proposed to use various corrections for "physiological" and temperature effects, their studies were based on a limited number of specimens (and commonly using only one species of echinoids). Those algorithms are, however, species-specific (though intra-species variations may also occur; see Ries, 2004) thus applications of a single algorithm to all echinoderms (especially to the fossil groups) is unwarranted. Furthermore, other environmental (including salinity, pH) and biological (e.g., variations in growth rates=kinetic effect) factors that are known to influence Mg content in

Recent echinoderms (e.g., Borremans et al., 2009) have not been yet incorporated into the proposed algorithms. Therefore, making a reliable reconstruction of elemental contents of past oceans, even based on well-preserved fossil echinoderm skeletons, is questionable.

5. Conclusions

Echinoderm skeletons that underwent transformation to a low-magnesium calcium carbonate phase possess completely obliterated primary geochemical pattern (distinct distribution of sulphates) and micro/nanostructure (stereom structure, growth layering, nanograins).

Diagenetic changes that affect the internal stereom structure are initially coupled with organic phase removal, leading to the obliteration of the primary layered and nanogranular structure of echinoderm biomineral. Echinoderm ossicles with preserved stereom structure without any major signs of internal change display nearly all geochemical (i.e., specific distribution of sulphates) and micro/nanostructural details (stereom structure, relicts of growth layering, nanograins) which are comparable to those observed in Recent skeletons. Compilation of published data with those obtained from this study suggest that fossil echinoderms, even if exceptionally preserved, cannot be used as a reliable proxy in seawater Mg/Ca reconstructions.

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Figure and Table captions

Table 1. Localities from which investigated echinoderm ossicles were collected.

Sampling site	Age	Reference
Purujosa, Spain	Leonian (Middle Cambrian)	Gorzelak and Zamora, 2013
Brechin, Canada	Katian (Upper Ordovician)	Gorzelak and Zamora, 2016
Skały, Poland	Eifelian (Middle Devonian)	Gorzelak et al., 2014a
Clattering Sike, U.K	Visean, Lower Carboniferous	Dickson, 2004
Gębice and Wolica, Poland	Anisian, Middle Triassic	Salamon, 2003
Silesian localities (Nakło Śląskie, Sławków, Milowice-Czeladź, Kamyce, Piekary Śląskie, Ząbkowice Będzińskie, Strzelce Opolskie, Tarnów Opolski), Poland	Anisian, Middle Triassic	Hagdorn and Głuchowski, 1993; Hagdorn et al., 1996; Zatoń et al., 2008a
Brudzów, Poland	Ladinian, Middle Triassic	Salamon et al., 2008
Cortina d'Ampezzo, Italy	Carnian, Upper Triassic	Nützel and Geiger, 2006
Cheltenham, U.K.	Piensbachian, Lower Jurassic	Simms, 2003
Kawodrza, Poland	Bajocian, Middle Jurassic	Majewski, 1997
Lincolnshire, U.K.	Bajocian, Middle Jurassic	Ashton, 1980
Gnaszyn, Poland	Bathonian, Middle Jurassic	Majewski, 1997
Łuków, Poland	Callovian, Middle Jurassic	Salamon, 2008b
Zalas, Poland	Callovian and Oxfordian, Middle Jurassic	Radwańska, 2005
Jarcenay, France	Oxfordian, Upper Jurassic	Dickson, 2004
Ogrodzieniec, Poland	Oxfordian and Kimmeridgian, Upper Jurassic	Zatoń et al., 2008b
Julianka, Poland	Kimmeridgian, Upper Jurassic	Gorzelak and Salamon, 2009
Małogoszcz, Poland	Kimmeridgian, Upper Jurassic	Kutek et al., 1992
Owadów, Poland	Tithonian, Upper Jurassic	Salamon et al., 2006
Wąwał, Poland	Valanginian, Lower Cretaceous	Salamon, 2009
Glanów, Poland	Cenomanian and Turonian, Upper Cretaceous	Salamon et al., 2009
Jakubowice, Poland	Turonian, Upper Cretaceous	Salamon and Gorzelak, 2010
Słupia Nadbrzeżna-Wesołówka, Poland	Coniacian, Upper Cretaceous	Walaszczyk, 1992
Lipnik, Poland	Santonian, Upper Cretaceous	Remin, 2004
Kornica, Poland	Santonian and Maastrichtian, Upper Cretaceous	Alexandrowicz and Radwan, 1983
Clapham, U.K	Eocene, Paleogene	Dickson, 2004
Korytnica, Poland	Miocene, Neogene	Gorzelak et al., 2011a
NE Suruga Bay (depth:140 m), Japan	Recent	Gorzelak et al., 2012, 2013
Shima Spur, off Kii Peninsula (depth: 805-852 m), Japan	Recent	Gorzelak et al., 2012, 2013
West end of Great Bahama Island (depth:402 m), North Atlantic Ocean	Recent	Gorzelak et al., 2012, 2013

Fig. 1. Examples of BSE images of different preservational types. (A) Type 0 transformation (Early Jurassic (Pliensbachian) *Isocrinus* sp. (BMNH E 14634)), (B) Type 1 transformation (Early Carboniferous (Visean) *Anematocrinus* sp. (BMNH E 70952)), C) Type 2 transformation (Late Triassic (Carnian) *Isocrinus tyrolensis* (ZPALV.42c/T/8.1)), (D) Type 3

transformation (Middle Triassic (Anisian) *Dadocrinus* sp. (GIUS 7-516)). s=stereom; c=cement; d=dolomite inclusions; arrows=pores. [2-column fitting image].

Fig. 2. μ -XRF maps of the crinoid ossicles tuned to optimize sulphate-S at 2.4827 keV showing sequential increase of diagenetic change from original sulphate content and distribution. (A) Columnal stereom of recent crinoid *Neocrinus decorus* (ZPALV.42c/R/3.1) having the higher concentrations of sulphur in the inner stereom, (B) Columnal stereom of Middle Jurassic (Bathonian) *Balanocrinus berchteni* (ZPALV.42c/J/1.1) with preserved original sulphate content and distribution, (C) Columnal stereom of Late Triassic (Carnian) *Isocrinus tyrolensis* (ZPALV.42c/T/8.1) with depleted and faded sulphate content and distribution, (D) Columnal stereom of Late Jurassic (Kimmeridgian) *Millericrinida* indet. (ZPALV.42c/J/10.1) with completely depleted and faded sulphate content and distribution in stereom (higher concentration in ossicle lumen (upper-right)). Number of counts on the right. [2-column fitting image].

Fig. 3. Examples of CL-images of the crinoid ossicles showing sequential increase of Mn-activated orange luminescence in step with increase of diagenetic change. (A) Columnal stereom of recent crinoid *Metacrinus rotundus* (ZPALV.42c/R/1.1-3), some parts display dark blueish intrinsic luminescence, (B) Columnal stereom of recent crinoid *Metacrinus rotundus* (ZPALV.42c/R/1.104) with some intrinsic luminescent pinkish spots (arrow), (C) Columnal stereom of Middle Jurassic (Bathonian) *Balanocrinus berchteni* (ZPALV.42c/J/1.1) with dark blueish intrinsic luminescence and some brighter orange spots (arrows), (D) Columnal stereom of Middle Jurassic (Bathonian) *Balanocrinus berchteni* (ZPALV.42c/J/1.1) with blueish intrinsic luminescence and brighter calcite cement infilling, (E) Columnal stereom of Early Jurassic (Pliensbachian) *Isocrinus* sp. (E 14634) with hardly visible blotchy dark colors

sometimes with luminescent brighter spots (arrow) and non-luminescent ferroan calcite cement, (F) Columnal stereom of Paleogene (Eocene) *Balanocrinus* sp. (BMNH E 68144) with hardly visible blotchy dark colors and non-luminescent ferroan calcite cement, (G) Columnal stereom of the Middle Devonian (Eifelian) *Ammonicrinus* sp. (ZPALV.42D/1) with hardly visible blotchy dark colors contacting (dotted line) luminescent brighter area (arrows), (H) Columnal stereom of Late Triassic (Carnian) *Isocrinus tyrolensis* (ZPALV.42c/T/8.1) with blotchy dark colors sometimes with luminescent brighter spots (microdolomites), (I) Columnal stereom of Middle Triassic (Anisian) *Dadocrinus* sp. (GIUS 7-516) with intense orange luminescence, (J) Columnal stereom of Late Jurassic (Kimmeridgian) *Millericrinida* indet. (ZPALV.42c/J/10.1) with intense purple luminescence. [1.5 column fitting image].

Fig. 4. Example of the CL-activated UV-VIS spectrum of the crinoid ossicle of *Dadocrinus* sp. (GIUS 7-516) from the Middle Triassic (Anisian) showing Mn emission maximum at 615 nm. [1.5 column fitting image].

Fig. 5. XRD diffraction patterns of seven samples representing different preservation types, (A) *Ammonicrinus* sp., Middle Devonian (Eifelian); Poland, (B) *Isocrinus* sp.; Middle Jurassic (Bajocian), Poland, (C) *Dadocrinus* sp., Middle Triassic (Anisian), Poland, (D) *Isocrinus* sp., Upper Jurassic (Kimmeridgian), Poland, (e) *Isocrinus* sp., Lower Jurassic (Pliensbachian), (F) *Torynocrinus* sp., Upper Triassic (Carnian), Italy; U.K., (G) *Isocrinus* sp., Middle Jurassic (Bajocian), U.K. Main reflections of calcite, dolomite and NaCl standard (h) are indicated in the range of 24.5 to 34.5°2 θ . [1.5 column fitting image].

Fig. 6. Examples of FESEM micrographs of the crinoid stereom revealed by slight acidic etching on fractured surfaces showing sequential increase of diagenetic change from original

microstructural features, (A) Recent crinoid *Hypalocrinus naresianus* (ZPALV.42c/R/xx) with lamination microstructure, (B) Recent crinoid *Metacrinus rotundus* (ZPALV.42c/R/1.1-3) with lamination microstructure, (C) Middle Jurassic (Bathonian) crinoid *Balanocrinus berchteni* (ZPALV.42c/J/1.2) with preserved relicts of lamination microstructure, (D) Middle Jurassic (Bathonian) crinoid *Balanocrinus berchteni* (ZPALV.42c/J/1.2) with preserved relicts of lamination microstructure, (E) Columnal stereom of Early Jurassic (Pliensbachian) *Isocrinus* sp. (BMNH E 14634) with preserved relicts of lamination microstructure, (F) Columnal stereom of Paleogene (Eocene) *Balanocrinus* sp. (E 68144) with preserved relicts of lamination microstructure, (G) Columnal stereom of Middle Devonian (Eifelian) *Ammonocrinus* sp. (ZPALV.42D/1) with preserved relicts of lamination microstructure, (H) Columnal stereom of Late Triassic (Carnian) *Isocrinus tyrolensis* (ZPALV.42c/T/8.1) with altered lamination microstructure and microdolomite inclusion (arrow), (I) Middle Triassic (Anisian) *Dadocrinus* sp. (GIUS 7-516) with completely altered lamination microstructure, (J) Columnal stereom of Late Jurassic (Kimmeridgian) Millericrinida indet. (ZPALV.42c/J/10.1) with completely altered lamination microstructure. [1.5-column fitting image].

Fig. 7. Examples of FESEM micrographs showing sequential increase of diagenetic change from original nanostructural features of the crinoid stereom, (A) Recent crinoid *Metacrinus rotundus* (ZPALV.42c/R/1.1-3) with nanograins, (B) Recent crinoid *Hypalocrinus naresianus* (ZPALV.42c/R/xx) with nanograins, (C) Middle Jurassic (Bathonian) crinoid *Balanocrinus berchteni* (ZPALV.42c/J/1.2) with preserved nanograins, (dD) Middle Jurassic (Bathonian) crinoid *Balanocrinus berchteni* (ZPALV.42c/J/1.2) with preserved nanograins, (E) Early Jurassic (Pliensbachian) *Isocrinus* sp. (E 14634) with preserved relicts of nanograins, (F) Paleogene (Eocene) *Balanocrinus* sp. (E 68144) with partly faded nanograins, (G) Middle

Devonian (Eifelian) *Ammonocrinus* sp. (ZPALV.42D/1) with partly faded nanograins, (H) Late Triassic (Carnian) *Isocrinus tyrolensis* (ZPALV.42c/T/8.1) with completely faded nanograins and microdolomite inclusion (arrow), (I) Middle Triassic (Anisian) *Dadocrinus* sp. (GIUS 7-516) with completely altered nanograins, (J) Columnal stereom of Late Jurassic (Kimmeridgian) Millericrinida indet. (ZPALV.42c/J/10.1) with completely altered nanostructure. [1.5-column fitting image].

Fig. 8. The sequential steps in transformation of echinoderm Mg calcite showing different preservational types, (A) Initial original Mg calcite skeleton, (B) Mg calcite skeleton rapidly buried in the sediment, (C) Mg calcite skeleton with epitaxial cement, (D) Type 0 transformation, Mg calcite skeleton with ferroan calcite cement, (E) Type 1 transformation, stereom composed of small dolomite crystals (dark gray spots) set in calcite matrix (pale gray) both with small pores, (F) Type 2 transformation, faded stereom microstructure due to the growth of the large dolomite crystals (dark gray areas) set in calcite matrix (pale gray) both with small pores, (G) Type 3 transformation, recrystallized skeleton with obliterated stereom microstructure, (H) Advanced Type 3 transformation, recrystallized skeleton with obliterated stereom microstructure with secondary dissolution cavities. For more explanation see text. [2-column fitting image].

Fig. 9. Global trends in seawater Mg/Ca ratio (slightly modified after Stanley, 2008). Circles and stars are Mg concentration data for fossil echinoderm samples recalculated as seawater Mg/Ca by using a partition coefficient ($Mg/Ca_C = 0.3182(Mg/Ca_{sw})$), green circles, after Dickson 2004; black stars, our own data) and a power partition function ($Mg/Ca_C = 0.051(Mg/Ca_{sw})^{0.67}$, red circles, after Ries 2004; white stars, our own data). Red circles and white stars have been shifted 2My younger for clarity. An arrow indicates Mg/Ca ratio

obtained from Bathonian crinoids which came from sediments deposited in cold water (~10 °C) settings (see Stolarski et al., 2009), therefore these ossicles were not taken into account for further statistical analyses. Blue and red areas below the time scale indicate the extent of traditional aragonite- and calcite-sea intervals, with question marks indicating periods of uncertain aragonite-calcite sea status (after Porter, 2010). [1.5-column fitting image]

Fig. 10. Power spectrum computed with the Lomb periodogram method and detrending showing the highest peak with its frequency, power value, and probability that the peak could occur from random data. The $p = 0.01$ and 0.05 significance levels ('white noise lines' shown as dashed lines) are found at spectral power values of 8.631 and 6.996, respectively. The frequency axis is in units of cycles per million years. [1-column fitting image]

Fig. 11. Box-plot showing a non-significant difference between median echinoderm Mg/Ca ratios from calcite and aragonite seas (A), Correlations for raw (B) and detrended data (C) between seawater Mg/Ca inferred from Hardie curve (1996) and seawater Mg/Ca determined from data on fossil echinoderms (Dickson, 2004 and this study) employing a partition coefficient ($Mg/Ca_c = 0.3182(Mg/Ca_{sw})$). S_p rs=Spearman rank order correlation coefficient $p = p$ values. [2-column fitting image]

A **B** **C** **D**