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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.

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 (Mg/Ca < 2) and aragonite with high-Mg calcite (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

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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)

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 synthetic 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 mol%) (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.

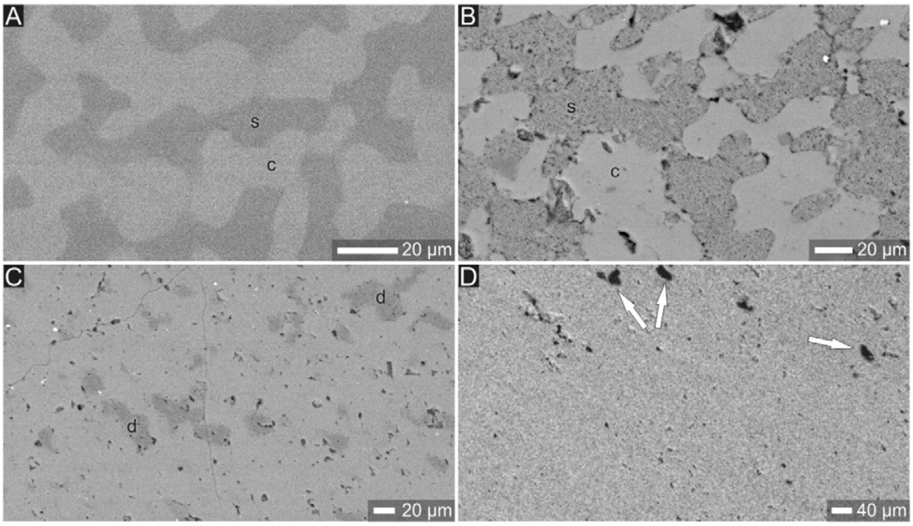

Fig. 1. Examples of BSE images of different preservational types. (A) Type 0 transformation (Early Jurassic (Pliensbachian) *Isocrinus* sp. (BMNH E 14634)), (B) Type 1 transformation (Early Carboniferous (Visean) *Anematocrinus* sp. (BMNH E 70952)), C) Type 2 transformation (Late Triassic (Carnian) *Isocrinus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