Sedimentary Geology 243-244 (2012) 17–32

Contents lists available at SciVerse ScienceDirect

Sedimentary Geology

journal homepage: www.elsevier.com/locate/sedgeo

# An organodiagenetic model for Marinoan-age cap carbonates

P.R. Gammon *

*Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, Canada K1A 0E8*
*Department of Earth Sciences, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6*

ARTICLE INFO

*Article history:*
Received 22 July 2011
Received in revised form 30 November 2011
Accepted 5 December 2011
Available online 13 December 2011

*Keywords:*
Cap carbonate
Paragenesis
Fluid overpressure
Marinoan
Neoproterozoic
Organodiagenetic

ABSTRACT

The Nuccaleena Formation cap carbonate is the global stratotype for the Marinoan glaciation and Ediacaran GSSP, a designation that emphasises the importance of cap carbonates to our current understanding of global Neoproterozoic biogeochemistry, sedimentology and stratigraphy. However, to date there is no agreed depositional model for cap carbonates, and there remains minimal detailed paragenetic data for developing process based depositional models. Here an early diagenetic "organodiagenetic" dolomite cementation model for Marinoan cap carbonate formation is hypothesised and explored. It is demonstrated how this process-based model can explain the three main atypical sedimentary structures that are the basis for correlation of Marinoan-age cap carbonates; giant tepee-like structures, sheet veins and tubestones. These features are interpreted to be products of fluid overpressure deformation induced by organodiagenetic expansive cementation. Giant tepee-like structures, the hallmark of Marinoan cap carbonates, conform to a simple structural analysis that is consistent with the predicted stress field induced by expansive cementation-driven fluid overpressure. The undeformed to highly deformed gradient of deformation features in cap carbonates is consistent with the range of rheologies in a shallowly buried cementing carbonate. Modification of matrix textures and bedding surfaces also conforms to the range of expected textures within this model. Overall, it is hypothesised that the aggradational, condensed section architecture of cap carbonates was the primary control over the generation of these atypical sedimentary features. The available paragenetic analysis suggests that the geochemical data, particularly the C-isotopic data, can be reinterpreted as supportive of the organodiagenetic model, and that the Neoproterozoic ocean was perhaps similar to that of today. The proposed model indicates that the current criteria for the placement of the Ediacaran GSSP are non-unique and potentially non-isochronous. Perhaps the most important aspect of this model is that it is testable, and is a call for focused research on the much-overlooked paragenesis of cap carbonates.



## 1. Introduction

The only Global Stratotype and Point (GSSP or "golden spike") yet determined for the Precambrian is situated in Enorama Gorge at the base of the Nuccaleena Formation, a dolostone cap carbonate in the Adelaidean succession (Knoll et al., 2006). This dolostone overlies Elatina Formation diamictites that have been interpreted as glacial in origin (Lemon and Gostin, 1990; Eyles et al., 2007). The inferred global correlatives of this succession are now termed "Marinoan-age" after the local name for the Adelaidean glacial succession.

The definition of the GSSP was based on five criteria: 1) the negative carbon isotopic signature of cap carbonates (Fig. 3 of Knoll et al., 2006); 2) the texture of the cap carbonates, in particular the highly unusual, large tepee-like structures found in Marinoan-age cap carbonates (Fig. 2 of Knoll et al., 2006); 3) radiometric dating, to an age of ~635 Ma, of cap carbonates distal to the Nuccaleena Formation, which lacks suitable material for dating in this portion of the succession; 4) a dolomitic mineralogy; and 5) a thin, sheet-like geometry (e.g. Lemon and Gostin, 1990; James et al., 2001; McKirdy et al., 2001; Hoffman et al., 2007). The last two criteria portray basic attributes shared with many other Precambrian sediments demonstrably not of Marinoan-age, and hence form a basic framework for Marinoan-age cap carbonates rather than diagnostic attributes. The first two criteria are intimately linked litho- and chemostratigraphic correlations, since the isotopic measurements are from the same matrix that formed the tepee structures. The third criterion is essentially non-diagnostic and dependent on criteria 1 and 2 since the radiometric dating is linked to the GSSP through lithostratigraphic correlation using the first two criteria. This linkage is best demonstrated by two radiometric dates, one from immediately above the Sturtian diamictite of the Adelaidean succession (Kendall et al., 2006), and one from a nearby diamictite–cap carbonate succession in Tasmania that has been lithostratigraphically correlated to the Nuccaleena Formation (the Grassy Group, Calver et al., 2004). Both of these ages, particularly the latter, are more consistent with the Marinoan glaciation being significantly younger, perhaps ~580 Ma, rather than the 635 Ma age

* Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, Canada K1A 0E8. Tel.: +1 613 995 4909; fax: +1 613 992 0190.
*E-mail address:* pgammon@nrcan.gc.ca.

0037-0738/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.sedgeo.2011.12.004

indicated by radiometric dates from distal successions (i.e. perhaps more equivalent to what is termed the Gaskiers glaciation). Overall, the summation by Fairchild and Kennedy (2007) that radiometric dating is yet to resolve the temporal correlations of the different Neoproterozoic glaciations still applies.

Criterion 1 above is non-unique due to the abundance of negative carbonate C-isotopic values reported from strata above and below inferred glacial diamictites (e.g. the "Trezona" anomaly, Halverson et al., 2005). Furthermore, the original C-isotopic trend identified by Hoffman et al. (1998b) has now been falsified (Kennedy et al., 1998; McKirdy et al., 2001; Halverson et al., 2005). Hence a negative C-isotopic signature is not of itself a unique identifier (Melezhik et al., 2001; Halverson et al., 2005), and hence can only represent a supporting line of evidence. This leaves criterion 2 as by far the strongest basis for correlation of Marinoan-age cap carbonates, particularly the highly atypical tepee-like structures with associated sheet veining. This means that the significance of the GSSP and its inferred correlatives is reliant on the assumption that the processes that formed these atypical sedimentary structures were globally synchronous.

This paper extends the detailed paragenetic analysis of Gammon et al. (in press) to rationalise and explain how expansive dolomite cementation is all that is required to explain the diagnostic features of Marinoan-age cap carbonates, particularly the giant tepee-like structures, sheet veins and "tubestones", the three main atypical sedimentary structures used for identifying Marinoan-age cap carbonates. As such the paper addresses the essential lithostratigraphic criteria 1 and 2 above. Both available data and space constraints do not permit an exhaustive explanation of all cap carbonate features, although extending the proposed model to other features should be a fruitful line of research. The paper concludes with remarks on the significance of the model, should it be proven correct. The paper also notes unresolved questions for cap carbonates, along with potential methods for resolving these issues.

Gammon et al. (in press) and this paper are confined to the dolostones that comprise the basal cap carbonates (i.e. cap carbonates sensu stricto), rather than the whole package of dolomitic and calcitic carbonates that overly some glacial diamictites. Some authors prefer to package some or all of the overlying calcitic limestones as part of the cap carbonate (e.g. Hoffman and Schrag, 2002; Halverson et al., 2005; Knoll et al., 2006). However, the relationship of overlying calcitic limestones to the dolostone cap carbonates remains unclear for three reasons: 1) many successions, including the Adelaidean, do not have calcitic limestones overlying the dolostone cap carbonates, and hence correlations to the global stratotype and Marinoan-age are necessarily based upon the features exhibited by the dolostones; 2) unconformities of unknown significance separate the overlying calcitic limestones from the dolostone cap carbonates in all localities where sufficiently detailed stratigraphic information is known (e.g. James et al., 2001); and 3) the calcitic limestones commonly exhibit different features to those of the dolostone cap carbonates, which infer different processes (e.g. altered aragonitic fans are commonly reported and giant tepee-like structures are absent from these limestones, James et al., 2001; Hoffman and Schrag, 2002). From both a temporal (unconformity) and a sedimentary process perspective it remains unclear if these limestones should be coupled to or decoupled from dolostone cap carbonate deposition. Hence this paper erects a process-based model for Marinoan-age cap carbonates sensu stricto, with the diagnostic features as documented by Knoll et al. (2006) of dolomite; thin, planar geometry; atypical sedimentary structures; and negative C-isotopic values.

## 2. Previous cap carbonate models

There has been little detailed research into the when, where and how cap dolomites precipitated, although there is a general consensus that most of the carbonate was precipitated "early", although what different authors imply by "early" is obviously an important question. Mechanisms generally claim carbonate supersaturation leading to rapid carbonate precipitation: 1) at the sediment–water interface from seawater (Williams, 1979; Hoffman et al., 1998b); 2) in the oceanic mixed layer (Roberts, 1976; Aitken, 1991; Fairchild, 1993; Kaufman and Knoll, 1995); 3) on the seafloor in association with growth of atypical tepee structures (von der Borch, 1976; Kennedy, 1996; James et al., 2001; Kennedy et al., 2001; Jiang et al., 2003); and/or 4) as an early diagenetic cement (Kennedy, 1996; Jiang et al., 2003).

Points 1 and 2 have been used to infer that first order controls over precipitation were processes such-as enhanced Neoproterozoic continental erosion and input of Ca and Mg to seawater (Tucker, 1982; Kaufman et al., 1993; Kaufman and Knoll, 1995; Jacobsen and Kaufman, 1999); an increase in the reductive flux of iron and $CO_2$ from volcanic and hydrothermal sources into the oceans (Kauffman et al., 1991; Derry et al., 1992; Kennedy et al., 1998); and a warm, seasonal climate (Williams, 1979). Such claims are currently non-testable hypotheses since many of these processes cannot yet be deciphered from the sedimentary record. Furthermore, virtually all of these processes will have occurred at multiple times throughout earth history, and hence do not easily explain the rarity of the atypical sedimentary structures of Marinoan-age cap carbonates. More importantly, virtually all of these studies lack any detailed paragenetic–geochemical analysis that addresses issues critical to dolomite precipitation, and hence the reliability of the proposed solution remains questionable; e.g. redox, pH, carbonate alkalinity, and magnesium, calcium, iron, and sulphate concentrations are all critical to dolomite precipitation (e.g. Folk and Land, 1975; Baker and Kastner, 1981; Tucker, 1982; Baker and Burns, 1985; Compton and Siever, 1986; Morrow and Ricketts, 1988; Slaughter and Hill, 1991; Lumsden et al., 1995; Budd, 1997; Machel, 1997; Mazzullo, 2000).

The difficulty in determining water chemistry at the time of cap carbonate precipitation has led to the current interpretation of cap carbonates as essentially by-products of the global biogeochemical cycles implicit within paleoclimatic models for Neoproterozoic glaciations; e.g. Snowball Earth Hypothesis and an earlier version, now resurrected, Slushball Earth Hypothesis (Harland, 1964; Harland and Rudwick, 1964; Hoffman et al., 1998b; Fairchild and Kennedy, 2007); the Clathrate Hypothesis (Kennedy et al., 2001; Jiang et al., 2003); and the Plume Hypothesis (Shields, 2005). As currently formulated all of these hypotheses rely on the absolute value and secular changes in C-isotopic signatures as an accurate indicator of global biogeochemical processes. For cap carbonates they all infer high atmospheric and surface water $pCO_2$ led to a highly carbonate-supersaturated surface ocean. Some global climate models indicate that the required $pCO_2$ states are attainable (e.g. Ridgwell et al., 2003), and that these could generate the negative cap carbonate C-isotopic signature (Fairchild and Kennedy, 2007). To empirically test this proposition requires a paragenetic understanding that isolates which component (or components) within a cap carbonate is (are) an accurate proxy for surface water chemistry. In general appropriate empirical testing has not been accomplished. Instead, most authors use cap carbonate matrix dolomite, with or without chemical screening, as a surface water proxy (Fairchild and Kennedy, 2007). In contrast, the only detailed paragenetic study of cap carbonates to date has concluded that matrix dolomite of the global stratotype (Nuccaleena Formation) is early diagenetic in origin and unlikely to represent surface waters (Gammon et al., 2005; Gammon et al., in press).

Overall, the lack of progress on cap carbonate precipitation mechanisms led Fairchild and Kennedy (2007) to state in their summary of the Neoproterozoic record (p 901): "The origin of the cap carbonate and its possible relation to changes in the carbon cycle during deglaciation are still open. At issue are the origin and mechanisms capable of producing the negative carbon isotope values common in each section, duration of cap carbonate deposition, unusual sedimentary structures, timing with respect to glacigenic deposits, and stratigraphic relations at basin margins." This paper extends the Gammon et al. (in press) resolution of these questions to Marinoan-age cap carbonates globally.