Available online at www.sciencedirect.com
ScienceDirect
Gondwana Research 12 (2007) 566–570
www.elsevier.com/locate/gr

GR Letter

Tomographic study of Paleoproterozoic carbonates as key to understanding the formation of molar-tooth structure

Darrel G.F. Long

Department of Earth Sciences, Laurentian University, Sudbury, Ontario, Canada P3E 2C6

Received 21 September 2006; received in revised form 16 January 2007; accepted 14 February 2007
Available online 28 February 2007

Abstract

X-ray computed tomographic studies of relatively pure Paleoproterozoic limestones from the George Formation, Muskwa Assemblage, northern British Columbia, Canada indicate that molar-tooth structures developed along linked fractures in gel-like semi-plastic carbonate mud, with a high organic content. Where pore fluid and/or gas pressures matched confining loads, MT blobs developed. Where pressure exceeded loads, cracks propagated into adjacent semi-elastic sediment and were rapidly filled by clusters of uniform, equant, microcrystalline carbonate. Where abundant carbonate was not precipitated, incipient cracks and sheets collapsed leaving residual trains of microcrystalline carbonate with similar density to the molar-tooth carbonate. Tomographic studies show that the density of calcite domains within petrographically uniform sheets of MT void-filling calcite is uneven, suggesting that precipitation was not instantaneous, but was propagated from discrete centres.

It is here suggested that carbonate production and sediment rheology were both strongly influenced by organic matter. During early sea-floor diagenesis microcrystalline carbonate precipitated within organic-rich sediment with high water content, possibly within decomposing mats of microbial extracellular polymeric substances (EPS). When pore pressures in the host sediment increased in response to cyclic loading by long-period waves, pore fluids containing EPS were injected into newly created fractures, allowing rapid precipitation of molar-tooth carbonate. Because tomographic studies allow detailed resolution of minor density differences, they provide a useful method of evaluating structures in relatively uniform carbonate rocks of any age.
© 2007 International Association for Gondwana Research. Published by Elsevier B.V. All rights reserved.

Keywords: Paleoproterozoic; Carbonates; Tomography; Diagenesis; Cyclic loading by storms

1. Introduction

Molar-tooth structures are early diagenetic features of enigmatic origin that appear to be largely restricted to fine-grained Proterozoic carbonates deposited in mid- to upper-ramp settings. The term was first used in the geological literature by Bauerman (1885) to describe structures "resembling the markings on the molar-tooth of an elephant" in carbonates of the Belt Supergroup, near the Canada–USA border. This group of structures includes predominantly downward-tapered, vertical to inclined, micro-crystalline carbonate-filled crack-like structures, which in many examples appear to be ptygmatically folded and/or fractured due to early compaction (Fig. 1). Sub-horizontal sheets and spherical forms (blobs) are less common. All show signs of compaction, in both cross-section and plan view. Some resemble extensional vein arrays and parts of ductile shear zones that have been modified by compaction and thinning (c.f. Maltmam, 1994; Brothers et al., 1996; Grimm and Orange, 1997).

The fill of molar-tooth structures is characterized by pure, uniform, equant, polygonal, blocky calcite spar 5–15 μm in diameter (Fig. 2). These crystals lack typical cement features and in some cases show evidence of injected sediment fill (Pratt, 1998) or internal fluid flow (Bishop et al., 2006; Bishop and Sumner, 2006). Associated host carbonates are typically characterized by wavy to crenulate lamination, suggestive of microbial mat development.

The development of molar-tooth structures seems to be largely restricted to the interval between 1900 and 550 Ma (Pratt, 1998; James et al., 1998; Shields, 2002), with two examples (in siliciclastic mudstone) from the Archean (Bishop et al., 2006; Bishop and Sumner, 2006). The major decline in abundance

E-mail address: dlong@laurentian.ca.

1342-937X/$ - see front matter © 2007 International Association for Gondwana Research. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.gr.2007.02.004

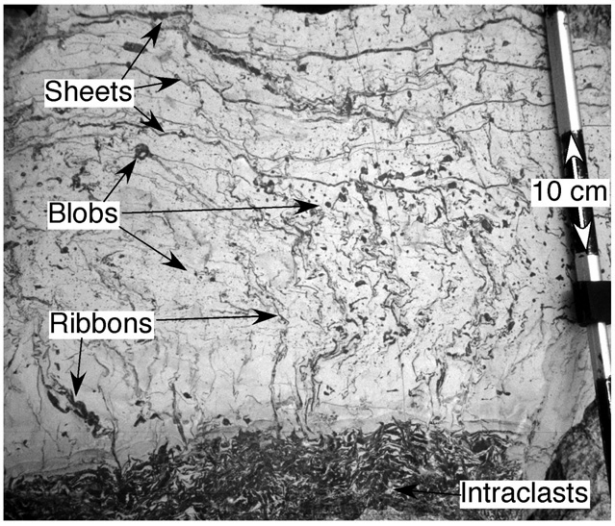


Fig. 1. Molar-tooth structures in lime mudstone (calcilutite) in the George Fm (~ 1.6 Ga), northern British Columbia.

appears to coincide with a major shift in the strontium-isotope record at ~750 Ma, well before the advent of extensive reworking of sediments by metazoans. Shields (2002) indicates that this may reflect a decrease in $CaCO_3$ concentrations in the world ocean, combined with a possible increase in the concentration of precipitation inhibitors.

Since the discovery of molar-tooth structures 1885, numerous theories have been proposed to explain the origin of molar-tooth structures, none of which are universally accepted. Smith (1968) and O'Connor (1972) suggested that they reflect calcite replacement of algal structures. Eby (1977) preferred calcite replacement of evaporitic structures. Horodyski (1983) proposed biogenic precipitation within syneresis cracks. Furniss et al. (1998), and Frank and Lyons (1998), evoked rapid carbonate precipitation in gas-generated voids and expansion cracks. Gellatly and Winston (1998) and Pollock et al. (2006) suggested this in combination with rapid replacement of a vaterite ($CaCO_3$) precursor by micritic calcite in an organic-rich alkaline setting. Qiao Song et al. (1994), Fairchild et al. (1997), Pratt (1998, 2001), Qiao and Gao (2000), and others have indicated that crack generation is directly related to seismic activity. Pratt (1998, 2001) claimed that seismic pumping may have triggered physical injection of particulate carbonate into these voids, and hence implied that molar-tooth carbonate is primarily a chemical sediment, not a cement. The seismic argument suggests that the cracks were generated by cyclic loading, a process which also occurs due to the passage of long-period marine waves, and hence molar-tooth structures could be storm-induced (Fairchild et al., 1997; Long, 2001; Bishop et al., 2006). This may explain the predominance of these structures in ramp settings above storm wave-base and their common association with hummocky cross-stratified beds (James et al., 1998; Long, 2001; Sherman et al., 2001; Bishop et al., 2006). An alternate model (Marshall and Anglin, 2004) suggested that these structures were produced by explosive CO_2 clathrate destabilization within tens of metres of the sediment/water interface, at water depths well in excess of 100 m and temperatures below 10 °C. Whatever the mechanism of formation of molar-tooth carbonate, both the rheology of the host strata and the void-forming process play a role in influencing the final morphology of the structure (Pollock et al., 2006). A common problem in all models is the question of interconnectedness of the initial cracks, both for passage of fluids and/or gas, and for direct connection of pores to sea-water.

2. Tomographic study

X-ray computed tomography (CT) allows three-dimensional analysis of differences in rock composition based on minor contrasts in X-ray attenuation. These differences are due largely to the density and composition of the material examined (Mees et al., 2003). Although the 3D geometry could be approximated using a series of slabs, this method is time-consuming, and considerable material is lost at saw cuts, reducing the amount of information available. CT scanners offer a rapid method of determining the distribution of minerals in three-dimensional solids, provided there is sufficient density difference between phases. CT scanners have previously been used for the study of three-dimensional aspects of sedimentary structures, joints and pores in siliciclastic mudstones and sandstones (Boespflug et al., 1995; Duliu, 1999; Briggs et al., 2002; Flisch and Becker, 2003). They have also been used to determine skeletal density of corals (Bosscher, 1993; Carlson et al., 2003) and echinoderms (Stock and Veis, 2003). In these studies compaction, carbonate content and grain size have all been shown to directly affect tomographic intensity. A comprehensive review of the theory of computed axial tomography has been presented by Duliu (1999).

2.1. Method

The medical CT scanner used in this study is located at the INRS-ETE facility in Quebec City. It can detect density differ-

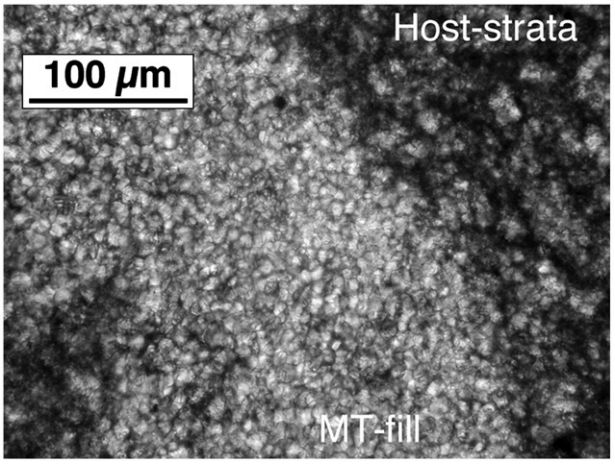


Fig. 2. Thin section view (in PPL) of tightly packed, uniform, equant calcite crystals forming the fill of a molar-tooth structure (left). Dark area in top right is the host sediment that contains clusters of crystals of similar size and form. Note irregular reticulate network of dark organic-rich material surrounding patches of calcite and minor quartz in the host strata. Organic material is not preserved in the MT fill.

ences of as little as 0.1% on a sub-millimeter scale. In this study thin (>8 cm) and thick (8–30 cm) samples of well developed molar-tooth (MT) carbonate, preserved in horizontal sheets, sub-vertical ribbons and as isolated blobs, were examined within samples of relatively pure limestone from the late Paleproterozoic George Formation, Muskwa Assemblage, northern British Columbia, Canada (Long et al., 1999; Long and Pratt, 2000; Pratt and Long, 2001). Tomographic datasets, collected at 1 mm spacing were processed using OsiriX software, to generate two- and three-dimensional images. Data were recorded in Hounsfield Units (HU). These represent 0.1% of the difference in the X-ray attenuation coefficient of water (HU=0) and air (HU=−1000).

2.2. Results

Although both MT structures and adjacent matrix are dominated by calcite, the higher purity and compact packing of the MT fill means that it has a greater density (by 100 to 300 HU) than the surrounding organic-rich carbonate matrix. Problems were encountered with slabs thicker than 8 cm, due to refraction and attenuation of X-rays. Examination of thick (0.5–1 cm) sub-vertical MT ribbons indicates a local depression of HU values on the margins of structures, supporting the hypothesis that at least part of the carbonate fill was derived or transferred from the adjacent host strata (Fig. 3 left). Similar density depressions of ~ 20 HU units were noted around blobs (Fig. 3 right).

Examination of samples dominated by blobs indicates that these are typically irregular flattened oblate spheroids rather than spherical bodies (Figs. 3 left, 4). As such they resemble gas bubbles in marine clays, which appear to grow by fracturing adjacent sediment or reopening existing fractures (Boudreau et al., 2005). Closely spaced blobs appear to be linked by necks containing carbonate with intermediate density, suggesting interconnectivity of pore systems prior to precipitation of the microcrystalline carbonate within these structures. These are not visible in thin sections of these samples. Within thin sheet and vein-type MT carbonate bodies, density changes are apparent along strike by differences in HU intensity, suggesting that crystallization (or recrystallization of a carbonate precursor)

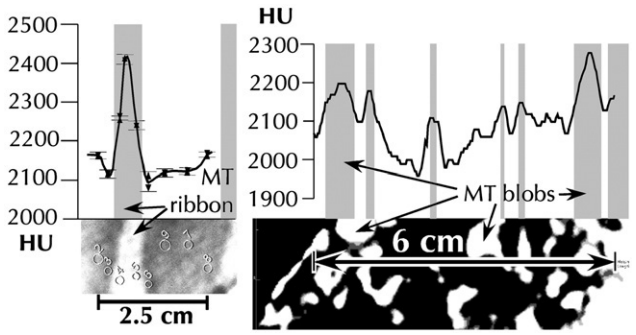


Fig. 3. Left: density profile across thick MT ribbon. Right: traverse through a series of MT blobs. The OsiriX reconstructions at the base of the figures show matrix as dark areas and higher density MT carbonate as light areas.

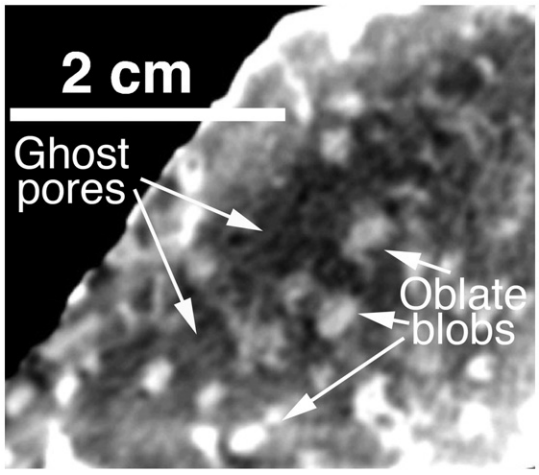


Fig. 4. Transverse density map of MT blobs (white) at 2099 HU, showing non-spherical nature of blobs, and ghost-like network of interconnected pores (thin white lines). Resolution is limited by the voxel size (observation volume) of the CT scanner.

was initiated at numerous local centres within crack systems, rather than being uniform (Fig. 5).

3. Interpretation

Tomographic studies of molar-tooth structures in Paleoproterozoic limestones of the George Formation demonstrate that these structures formed in a system of interconnected pores and fractures that may have been enhanced by cyclic loading due to long period waves (Seed and Rhaman, 1978). This confirms that observations on molar-tooth carbonates in Archean siliciclastic mudstones by Bishop et al. (2006) can be applied to similar structures in a carbonate host. Given that organic material is so common in the limestone host rock, where it is preserved as anastomosing sheets of carbonaceous material, encapsulating

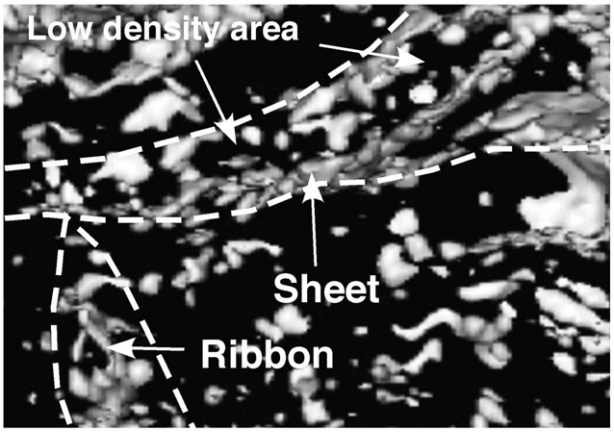


Fig. 5. Part of a 3D view, created in OsiriX, showing irregular distribution of higher density areas within selected continuous horizontal MT sheets and sub-vertical ribbons. In this reconstruction light areas have a density of 2100 HU or more. MT structures appear as continuous forms in OsiriX reconstructions at a slightly lower density, indicating lateral density changes within individual MT structures. Light areas outside the designated fields include blobs and high-density areas within other sheets and ribbons. Field of view is ~ 8 cm.

isolated 5–15 μm diameter carbonate crystals (Fig. 2, top right), formation of molar-tooth structures must have occurred below the sediment surface in an oxygen-starved situation. Molar-tooth structures in the George Formation do not contain remnant pyrite (as do some Archean and Mesoproterozoic examples), hence formation may have occurred within the nitrate reduction zone, where the concentration of dissolved oxygen is below 0.5 mL O_2 (L H_2)$^{-1}$, rather than the underlying sulphate reduction zone where anerobic bacteria can survive (Hesse, 1990). Dysaerobic bacteria could have survived within the pore spaces under these conditions. It is possible that when the sediment was undisturbed by cyclic loading, carbonate crystallization occurred within microbial extracellular polymeric substances (EPS). These are known to coat modern bryophytes and cyanobacteria, and are present in most earth-surface environments (Turner and Jones, 2005).

Studies of the physical character of modern carbonate mud in Florida by Briggs et al. (2002) indicate that bulk density of carbonate mud increases rapidly from around 1.5 to 1.75 g/cm^3 in the upper 5 cm of the sediment column, then increases more slowly, to 1.8 g/cm^3 in the next 30 cm. Gradual compaction of sediment could give rise to local concentration of fluids (and gas) within larger pores to create space for blob-like molar-tooth structures. Cyclic loading by waves during storms (or seismic events) would have increased pore pressure due to partial fabric collapse (Seed and Rhaman, 1978). Transient lateral changes in pore pressure, developed as the wave-induced compression front moved across and through the sediment, would have encouraged accumulation of gas and fluids containing EPS in larger pores, that would subsequently expand and propagate into cracks (c.f. Boudreau et al., 2005; Pollock et al., 2006). Concentration of carbonate-saturated EPS bearing fluids into fractures and blobs may have been followed by rapid precipitation of equant microspar around crystal nuclei in the EPS to form the uniform fill of the molar-tooth structures in the George Formation. As carbon isotope studies of molar-tooth carbonates consistently demonstrate similarity to contemporaneous limestones a direct link between pore-water and seawater is implied, which is consistent with wave induced pumping (Bishop et al., 2006). Fluid flow was concentrated through open fractures, causing rapid nucleation of calcite cores. Collapse of unfilled structures following storm-induced cyclic loading may have left a ghostly trace of conduits between blobs and sheets (Fig. 4), which are not visible using conventional microscopy.

Formation of molar-tooth carbonate in the carbonate reduction zone is not likely because carbonate becomes an oxidant and methanogenesis occurs (Hesse, 1990). This would produce a strong negative C isotope signature that is not apparent in any study of molar-tooth carbonates to date.

4. Conclusions

Tomographic analysis provides a rapid non-destructive method of examining MT structures *in situ*. This study has demonstrated that density differences between MT carbonate and the host carbonate is sufficient to allow 3D imaging. This has provided for the first time clear evidence that MT voids were interconnected at the time of formation. It illustrates that some MT voids collapsed early, before being filled with 5–15 μm scale calcite. In addition it is shown that MT void-filling calcite domains are slightly irregular in composition, which has important implications for the mechanisms of spar formation.

Medical CT scanners do not appear to be able to distinguish multiple layering within thick MT veins, so the technique does not entirely replace three-dimensional reconstructions based on serial sectioning or grinding. As the method allows recognition of very small differences in bulk density it is an ideal method for determining the 3D geometry of ancient carbonate rocks, and may allow better understanding of the organization of mineral grains and pores within other enigmatic structures.

Acknowledgements

This research was funded through an NSERC Discovery grant to the author. I thank Bernard Long for introducing me to the wonders of CT scanning, and Don Winston, Brian Pratt, Graham Shields, Meng Xianghu and many other participants in IGCP 447 for continuing discussions on the enigma of MT carbonates. I thank James Bishop, Elizabeth Turner and Rajat Mazumder for their constructive reviews of this paper.

References

Bauerman, H., 1885. Report on the geology of the country near the forty-ninth parallel of north latitude west of the Rocky Mountains. Report of Progress 1882–1884, Part B. Geological Survey of Canada, pp. 1–42.

Bishop, J.W., Sumner, D.Y., 2006. Molar tooth structures of the Neoarchean Monteville Formation, Transvaal Supergroup, South Africa: I. constraints on microcrystalline $CaCO_3$ precipitation. Sedimentology 53, 1049–1068.

Bishop, J.W., Sumner, D.Y., Huerta, N.J., 2006. Molar tooth structures of the Neoarchean Monteville Formation, Transvaal Supergroup, South Africa: II. a wave-induced fluid flow model. Sedimentology 53, 1069–1082.

Boespflug, X., Long, B., Occhietti, S., 1995. Cat-scan in marine stratigraphy: a quantitative approach. Marine Geology 122, 281–301.

Bosscher, H., 1993. Computerized tomography and skeletal density of coral skeleton. Coral Reefs 12, 97–103.

Boudreau, B.P., Algar, C., Johnson, B.D., Croudance, I., Reed, A., Furukawa, Y., Dorgan, K.M., Jumars, P.A., Grader, A.S., Gardiner, B.S., 2005. Bubble growth and rise in soft sediments. Geology 33, 517–520.

Briggs, K.B., Williams, K.L., Jackson, D.R., Jones, C.D., Ivakin, A.N., Orsi, T.H., 2002. Fine-scale sedimentary structure: implications for acoustic remote sensing. Marine Geology 182, 141–159.

Brothers, R.J., Kemp, A.E.S., Maltman, A.J., 1996. Mechanical development of vein structures due to the passage of earthquake waves through poorly-consolidated sediments. Tectonophysics 260, 227–244.

Carlson, W.D., Rowe, T., Ketcham, R.A., Colbert, M.W., 2003. Application of high-resolution X-ray computed tomography in petrology, meteorics and paleontology. In: Mees, F., Swennen, R., Van Geet, M., Jacobs, P. (Eds.), Applications of X-ray computed tomography in the geosciences. Special Publication, vol. 215. Geological Society, London, pp. 7–22.

Duliu, O.G., 1999. Computer axial tomography in geosciences: an overview. Earth Science Reviews 48, 265–281.

Eby, D.E., 1977. Sedimentation and early diagenesis within eastern portions of the "middle Belt carbonate interval" (Helena Formation, Belt Supergroup, Precambrian Y), western Montana. PhD thesis, State University of New York, Stoney Brook, N.Y.

Fairchild, I.J., Einsele, G., Song, T., 1997. Possible seismic origin of molar tooth structures in Neoproterozoic carbonate ramp deposits, north China. Sedimentology 44, 611–636.

Flisch, A., Becker, A., 2003. Industrial X-ray computed tomography studies lake sediment drill cores. In: Mees, F., Swennen, R., Van Geet, M., Jacobs, P. (Eds.), Applications of X-ray computed tomography in the geosciences. Special Publication, vol. 215. Geological Society, London, pp. 205–212.

Frank, T.D., Lyons, T.W., 1998. "Molar-Tooth" structures: a geochemical perspective on a Proterozoic enigma. Geology 26, 683–686.

Furniss, G., Rittle, J.F., Winston, D., 1998. Gas bubble and expansion crack origin of "molar tooth" calcite structures in the Middle Proterozoic Belt Supergroup, Western Montana. Journal of Sedimentary Research 68, 104–114.

Gellatly, A.M., Winston, D., 1998. Is "molar-tooth" calcite in the Helena Formation (middle Proterozoic Belt Supergroup, Montana) inverted vaterite? Geological Society of America, Abstracts with Programs 30 (7), 333.

Grimm, K.A., Orange, D.L., 1997. Synsedimentary fracturing, fluid migration, and subaqueous mass wasting: intrastratal microfractured zones in laminated diatomaceous sediments, Miocene Monterey Formation, California, U.S.A. Journal of Sedimentary Research 67, 601–613.

Hesse, R., 1990. Early diagenetic pore water/sediment interaction: modern offshore basins. In: McIlreath, I.A., Morrow, D.W. (Eds.), Diagenesis. Reprint series, vol. 4. Geoscience Canada, pp. 227–316.

Horodyski, R.J., 1983. Sedimentary geology and stromatolites of the Mesoproterozoic Belt Supergroup, Glacier National Park, Montana. Precambrian Research 20, 391–425.

James, N.P., Narbonne, G.M., Sherman, A.G., 1998. Molar-tooth carbonates: shallow subtidal facies of the mid-late Proterozoic. Journal of Sedimentary Research 68, 716–722.

Long, D.G.F., 2001. Molar tooth structures: enigmatic microbially influenced structures in Proterozoic carbonates. In: Wortmann, U.G., Funk, H. (Eds.), Abstracts and Programme, International Association of Sedimentologists, 21 st Meeting, Davos, Switzerland, 3–5 Sept, p. 181.

Long, D.G.F., Pratt, B.R., 2000. Mesoproterozoic evolution of Northeastern British Columbia. In: Cook, F., Erdmer, P., (compilers), Slave-Northern Cordilleran Lithospheric Evolution (SNORCLE) Transect and Cordilleran Workshop Meeting, University of Calgary, Lithoprobe Report, 72, 91–92.

Long, D.G.F., Devaney, J.R., Pratt, B.R., 1999. Tectonostratigraphic framework of the Mesoproterozoic Muskwa assemblage, Northern British Columbia. In: Cook, F., and Erdmer, P., (compilers) Slave-Northern Cordilleran Lithospheric Evolution (SNORCLE) Transect and Cordilleran Workshop Meeting (March 5–7), University of Calgary, Lithoprobe Report 69, 112–119.

Maltmam, A., 1994. The geological deformation of sediments. Chapman and Hall, London, UK. 362 pp.

Marshall, D., Anglin, C.D., 2004. CO_2 clathrate destabilization: a new model of formation for molar tooth structures. Precambrian Research 129, 325–341.

Mees, F., Swennen, R., Van Geet, M., Jacobs, P., 2003. Applications of X-ray computed tomography in the geosciences. Special Publication, vol. 215. Geological Society, London.

O'Connor, M.P., 1972. Classification and environmental interpretation of the cryptalgal organosedimentary "molar-tooth" structure from the late Precambrian Belt–Purcell Supergroup. Journal of Geology 80, 592–610.

Pollock, M.D., Kah, L.C., Bartley, J.K., 2006. Morphology of molar-tooth structures in Precambrian carbonates: influence of substrate rheology and implications for genesis. Journal of Sedimentary Research 76, 310–323.

Pratt, B.R., 1998. Molar-tooth structure in Proterozoic carbonate rocks: Origin from synsedimentary earthquakes, and implications for the nature and evolution of basins and marine sediment. Bulletin, vol. 110. Geological Society of America, pp. 1028–1045.

Pratt, B.R., 2001. Oceanography, bathymetry and syndepositional tectonics of a Precambrian intracratonic basin: integrating sediments, storms, earthquakes and tsunamis in the Belt Supergroup (Helena Formation, ca. 1.45 Ga), western North America. Sedimentary Geology 141–142, 371–394.

Pratt, B.R., Long, D.G.F., 2001. Sedimentology and syndepositional tectonics of Cambrian strata, Muskwa Ranges, northern British Columbia. In: Lane, L.S. (Ed.), Geological Survey of Canada, Central Forelands NATMAP Project Workshop, Project and Abstracts, 2001. Calgary, Alberta, unpaginated.

Qiao, X., Gao, L., 2000. Earthquake events in Neoproterozoic and early Paleozoic and its relationship with supercontinental Rodinia in North China. Chinese Science Bulletin, vol. 45. Science Press, Beijing, China, pp. 931–935.

Qiao Song, T., Gao, L., Peng, Y., Li, H., Gao, M., Song, B., Zhang, Q., 1994. Seismic sequences in carbonate rocks by vibrational liquifaction. Acta Geologica Sinica (English Edition) 7, 243–265.

Seed, H.B., Rhaman, M.S., 1978. Wave-induced pore pressure in relation to ocean floor stability of cohesionless soils. Marine Geotechnology 3, 123–150.

Sherman, A.G., Narbonne, G.M., James, N.P., 2001. Anatomy of a cyclically packaged Mesoproterozoic carbonate ramp in northern Canada. Sedimentary Geology 139, 171–203.

Shields, Graham A., 2002. "Molar-tooth microspar": a chemical explanation for its disappearance ~ 750 Ma. Terra Nova 14, 108–113.

Smith, A.G., 1968. The origin and deformation of some "molar-tooth" structures in the Precambrian Belt–Purcell Supergroup. Journal of Geology 76, 426–443.

Stock, S.R., Veis, A., 2003. Preliminary microfocus X-ray computed tomography survey of echinoid fossil microstructure. In: Mees, F., Swennen, R., Van Geet, M., Jacobs, P. (Eds.), Applications of X-ray computed tomography in the geosciences. . Special Publication, vol. 215. Geological Society, London, pp. 225–235.

Turner, E.C., Jones, B., 2005. Microscopic calcite dendrites in cold-water tufa: implications for nucleation of micrite and cement. Sedimentology 52, 1043–1066.