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The role of microbial iron reduction in the formation of Proterozoic molar tooth structures

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ABSTRACT

Molar tooth structures are poorly understood early diagenetic, microspar-filled voids in clay-rich carbonate sediments. They are a common structure in sedimentary successions dating from 2600–720 Ma, but do not occur in rocks older or younger, with the exception of two isolated Ediacaran occurrences. Despite being locally volumetrically significant in carbonate rocks of this age, their formation and disappearance in the geological record remain enigmatic. Here we present iron isotope data, supported by carbon and oxygen isotopes, major and minor element concentrations, and total organic carbon and sulphur contents for 87 samples from units in ten different basins spanning ca. 1900–635 Ma. The iron isotope composition of molar tooth structures is almost always lighter (modal depletion of 2‰) than the carbonate or residue components in the host sediment. We interpret the isotopically light iron in molar tooth structures to have been produced by dissimilatory iron reduction utilising Fe-rich smectites and Fe-oxyhydroxides in the upper sediment column. The microbial conversion of smectite to illite results in a volume reduction of clay minerals (∼30%) while simultaneously increasing pore water alkalinity. When coupled with wave loading, this biogeochemical process is a viable mechanism to produce voids and subsequently precipitate carbonate minerals. The disappearance of molar tooth structures in the mid-Neoproterozoic is likely linked to a combination of a decrease in smectite abundance, a decline in the marine DIC reservoir, and an increase in the concentration of O_2 in shallow seawater.

1. Introduction

Molar tooth structures (MTS) are calcite-filled ribbons and blobs that occur in many Proterozoic marine carbonate successions (Fig. 1). They frequently deform bedding and occur as rip-up clasts, suggesting that they are early diagenetic features that formed prior to compaction. Most MTS are on the order of millimetres to centimetres in size but reach decimetres in rare cases. When observed under thin section, they are comprised of 5–15 μm equant calcite crystals (microspar) in a matrix of micrite and dolomicrite, fine quartz, feldspar, and clay (Pollock et al., 2006; Pratt, 1998; Furniss et al., 1998). Although they occur in a broad range of water depths, from near storm wave base to intertidal environments, MTS formed almost exclusively in clay-rich carbonates (Pratt, 1998; Bishop and Sumner, 2006; Shen et al., 2016). Significantly, MTS are essentially limited to stratigraphic units deposited between ca. 2600–720 Ma, and are most abundant in the late Paleoproterozoic to early Neoproterozoic, with only two isolated Ediacaran occurrences (Fig. 2). This temporal restriction implies that their occurrence is closely linked with unique paleoenvironmental conditions during this interval in Earth's history. Hence, both the appearance and disappearance of MTS are likely linked to major biogeochemical changes of Earth's surface environments.

First described in the 19th century (Bauerman, 1884), MTS have long been the subject of interest and debate. Many disparate explanations for their origin have been proposed, including *in situ* gas generation and escape (Furniss et al., 1998), microbial sulfate reduction and methanogenesis (Frank and Lyons, 1998; Shen et al., 2016), seismicity (Pratt, 1998), and wave-pumping (Bishop and Sumner, 2006). However, while each of these models addresses certain features of MTS, none of them explains all three key features: the mechanisms by which void spaces are created, the subsequent precipitation of microspar within these spaces, and their temporal restriction.

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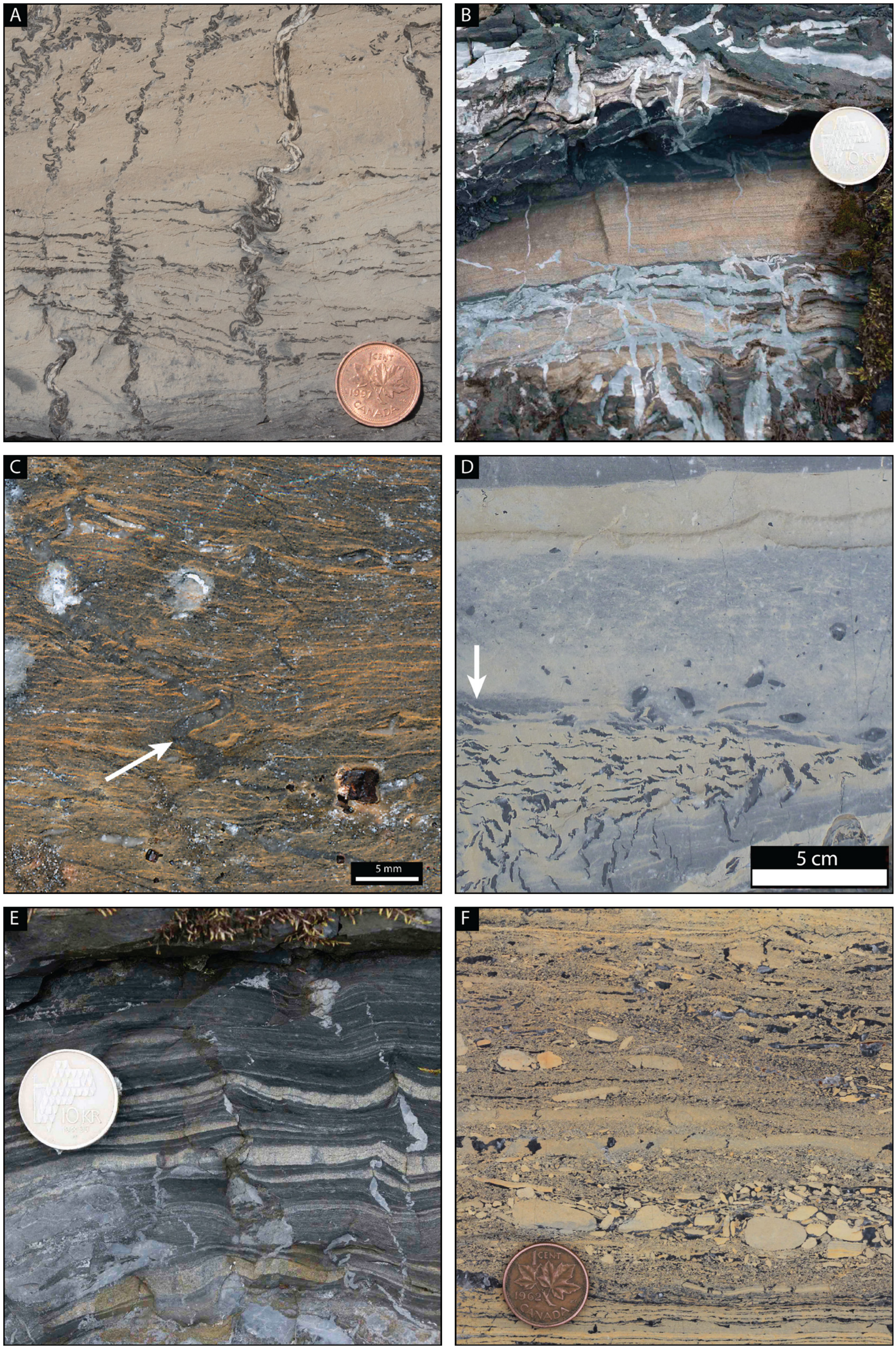

Fig. 1. A) Vertical ribbon MTS in the late Mesoproterozoic Victor Bay Formation, Arctic Canada. Canadian penny (19 mm) for scale. B) Vertical and horizontal ribbon MTS in the Båtsfjord Formation, Arctic Norway. Note the clear preference for formation in clay-rich micrite (dark grey) over buff weathering dolomicrite. 10 Kroner Norwegian coin for scale (24 mm). C) Ribbon MTS in the Keilberg Member of the Maieberg Formation, a Marinoan cap carbonate. D) Arrow points at a scour surface in carbonate outcrop of the Mesoproterozoic George Formation (Muskwa Assemblage, northeastern British Columbia, Canada), below which MTS are in place. Above the scour surface they have been reworked as rip-up clasts. E) MTS form prior to compaction of the sediment. This MTS in the Båtsfjord Formation shows clear evidence for deformation of bedding around it during compaction. F) Dark grey microspar infilling voids in an intraformational conglomerate in the Black Canyon Creek Formation, Yukon, Canada. MTS "blobs" also occur in some thin beds.