Giving some tooth to Precambrian carbonates and the tales they tell about ancient oceans

Timothy W. Lyons[1], Chenyi Tu[1], and Leanne Hancock[1]

[1]Department of Earth and Planetary Sciences, University of California, Riverside, 92507 U.S.A. (timothy.lyons@ucr.edu)

Enigmatic is a word that often comes up in discussions about Proterozoic molar tooth carbonate structures (MTS). But when unusual features such as these are common in rocks of a particular age, there is almost always an important message waiting to be discovered. In this case, the observed temporal patterns for MTS likely track first-order trends in evolving compositions in the oceans during Earth's middle history when CO_2 in the atmosphere and carbonate saturation in the ocean were high but declining and oxygen (O_2) in the ocean-atmosphere system was on the rise. A new paper by Tang et al. (this volume) gives us a new way to think about MTS origins, and nested within their model are wide ranging implicit and explicit linkages to Earth surface evolution as life was becoming more complex in a slow march toward the world we know today.

The best part of preparing a commentary on a paper written by others is the license to add two more cents about the big picture of the authors' work, often by providing some additional context and another perspective. The authors carry the responsibility of developing rigorous often complex narratives through the standard meter of methods, models, results, and discussions. And if they are lucky, they have left themselves enough space to hammer hard on what famous carbonate geologist Bob Ginsburg used to refer to as the 'so what'—what does it mean, and why should we care? It is hard to imagine a part of the Precambrian stratigraphic record more deserving of those questions than molar tooth structure: planar to complexly folded, preferentially or randomly oriented sheets of diagenetic microcrystalline calcite (often described as ribbons in 2D) occurring within clayey calcitic and dolomitic host rocks formed in shallow marine settings.

That's a mouth full, and this nuts-and-bolts description belies the elegance of what those crenulated calcitic cracks might be telling us, if we are smart enough to figure it. Limited to a specific window in time but found throughout the world during that temporal slice, MTS has captured the attention of generations of scientists seeking to explain their origins and the secrets they hold about oceans and atmospheres hundreds of millions to billions of years ago. Tang et al. take another important step in that journey with entirely new ways to imagine how these features formed and what they might mean.

Hilary Bauerman first described these features in 1885 from outcrops in northwest Montana and adjacent parts of Canada and coined the term MTS because of general similarities to the ridges on the molar teeth of elephants, although MTS are highly varied and often far more complex in their morphologies. More importantly, despite the bio-morphological parallel, MTS are certainly not fossils of any sort. No matter, the name has stuck, and so has the search for their paleoenvironmental messages. A comprehensive discussion of the related decades of research is sadly beyond our space allowance, but happily there are wonderful reviews already available (e.g., Kriscautzky et al., 2022).

There are a few things that fans of MTS seem to agree on. They are unquestionably interesting and puzzling. There are varying morphologies and differing uses of the term in the literature when described from their many occurrences, but the details above (sheets of diagenetic, void-filling calcite in an argillaceous matrix) emerge most consistently. We could also find agreement about their very early formation, perhaps in the upper centimeters to tens of centimeters of burial. Imagine formation in a stiff but not yet lithified mud. Figure 1 is our take on a paragenetic sequence for early formation in the Mesoproterozoic Belt Supergroup in Montana based on some of the most spectacular MTS anywhere. This is just one example, but these fabrics and mechanistic inferences extend partly or entirely to other locations, with early diagenetic formation as the umbrella theme.

Another point of harmony is that these features, while widespread across the globe, have a specific time range of occurrence, and it is that observation that is perhaps most tantalizing and telling—as we think about the 'so what.' Figure 2 (after Kriscautzky et al., 2022) is a timeline assembled from an extensive literature spanning the many known occurrences. These temporal tracings reveal something quite remarkable, that the ocean was primed to produce MTS almost exclusively during the Proterozoic, and the Meso- and Neoproterozoic in particular.

Most MTS researchers would also agree that formation occurred via cracks that filled quickly with essentially pure microcrystalline calcite, but that's where the roads start to diverge. There are many views on how these cracks formed and how they filled so quickly and with a fabric so nontraditional for carbonate cements—that is, uniform microspar (a mass of uniformly sized calcite grains on the order of 10 µm across) rather than needle-like crystals growing inward from the wall giving way to coarser sparry calcite in the void center.

A popular model for crack formation, and something that Tang et al. and we agree on, invokes gas expansion/escape as the driver (e.g., Furniss et al., 1998, who generated MTS-like crack morphologies via CO_2 during experiments with yeast but with relevance to other gases, such as methane). Among other models is the notion of cracking and fluid pumping under the influence of wave loading at shallow marine sites (Bishop et al., 2006) rather than by gas, and possibly in phase with volume changes during clay transformations (Hodgskiss et al., 2018). As a decidedly different end member, Pratt (1998) invoked sediment deformation by earthquake shaking.

The pathways by which such rapid and atypical cements filled those voids also spawn discussions and debates with far-reaching implications. These exchanges include localized controls on alkalinity and thus carbonate mineral saturation, such as the importance of alkalinity production by mineral transformations and microbial reactions, or decreases in pore-water concentrations of ions that can inhibit precipitation (a central theme in Tang et al. that we will come back to). Other likely factors are overall high levels of saturation in the global ocean at this time and wave pumping of pore waters that facilitated rapid influx of Ca^{2+} and alkalinity from seawater while flushing out inhibiting ions. Of course all of these possibilities depend on the first-order properties of the local and global ocean, which should leave you asking why MTS was confined to a long but particular chapter of Earth history. What, specifically, was going on during the Meso- and Neoproterozoic that was so different than the times before and after?

Other temporal knobs that tuned the world for MTS certainly include the lack of bioturbation during the Proterozoic, which would have otherwise overprinted early cracks and fills. Life's ability to mix sediment deeply and pervasively came long after, in the Silurian or even later (Tarhan et al., 2015). Further, water depth would influence confining pressure and gas release, perhaps explaining why MTS is sometimes concentrated in the upper parts of shallowing-upward cycles. The initiation of abundant shallow water carbonates during the Proterozoic could also be key, but these are not uniquely Proterozoic features, so that is not the whole story.

Carbonate mineral saturation must have been a key lever. In general, the Proterozoic was a time of elevated atmospheric CO_2 compared to times following, ultimately because of lower early solar luminosity. Through feedbacks, lower insolation results in higher CO_2 modulated by rates of weathering on continents and the seafloor, so that CO_2 was high early and has dropped since (reviewed in Krissansen-Totton et al., 2018). Continental weathering would have brought alkalinity to the ocean and bolstered carbonate saturation, and these impacts decreased over time in phase with a brightening sun and corresponding secular decrease in atmospheric CO_2 and coupled marine dissolved inorganic carbon (DIC; e.g., Bartley and Kah, 2004). We can imagine the Meso- and Neoproterozoic lying within a particular sweet spot, where saturation was high enough to foster seafloor cementation at intermediate levels, producing semi-cohesive mud that could crack easily rather than solid hardground that would not. At the same time, high enough levels of calcite saturation, perhaps enhanced by local biological and mineralogical reactions, would have favored the rapid precipitation essential to filling the cracks quickly before they closed by compaction, while also explaining the unusual microspar cement fabric.

Carbonate saturation through time is a complex interplay of Ca^{2+} availability, alkalinity, and pH (Krissansen-Totton et al., 2018), a cocktail that is far beyond the space permitted here. But we can envisage an Archean with relatively scarce shallow marine settings for tectonic reasons. Carbonate saturation was likely very high during those pre-MTS times (Grotzinger and Knoll, 1999) due in part to inhibited carbonate precipitation under high levels of dissolved iron in the oceans. This throttle on precipitation might have limited the abundance of fine-grained carbonate sediments of the types that later hosted MTS—until those inhibitors were minimized (Sumner and Grotzinger, 1996). Could MTS times reflect an ocean optimized through a balance of carbonate saturation that allowed for both early but partial cementation of a muddy seafloor—a precondition for MTS formation—yet also rapid filling of cracks formed in those stiff muds by gases?

We hinted up top at the likelihood that MTS were tracking some big trends, and clearly among them is evolving carbonate mineral saturation paced by co-evolving solar luminosity and concomitantly declining CO_2 in the atmosphere and DIC in the ocean. A final nail in the MTS coffin may have been driven by the early Paleozoic proliferation of carbonate biomineralization. Tang et al. remind us, however, that MTS relationships to early biospheric oxygenation also deserve attention.

It is almost certain that the Proterozoic deep ocean, like that of the Archean, was mostly O_2-free and loaded with dissolved iron (Planavsky et al., 2011; Poulton and Canfield, 2011). Because iron is a kinetic inhibitor of carbonate mineral precipitation (e.g., Sumner and Grotzinger, 1996), removal of that dissolved iron might have triggered carbonate precipitation in the ancient water column (the "whitings" of Tang et al.), and oxidation via O_2 is one of the best ways to do that.

Could the result have been the muddy hosts of MTS along with the rapid precipitation of crack-filling calcite? Tang et al. think so—and thereby link the delicate balances nested implicitly in MTS to marine oxygenation.

The details of the authors' story are complicated. That's not a surprise—these are unusual features with lots of thematic threads running through their stories. Their clever spin begins with the idea that even the very shallow parts of the ocean during this critical time lacked oxygen and contained iron. A lot of people would agree that marine oxygen was still mostly low during the mid and even late Proterozoic (e.g., Planavsky et al., 2014; Hardisty et al., 2017; Liu et al., 2021; Wang et al., 2022). We are among that group. But whether the surface ocean was mostly O_2-free and iron-rich (ferruginous) at very shallow depths beneath a still O_2-lean atmosphere is something many have debated (reviewed in Lyons et al., 2021).

The authors assume fundamentally that molar tooth formed in this time window in response to an Earth surface going through a sea change from a world without oxygen to one with lots, and this middle chapter was one of decidedly intermediate character with much of the ocean lacking O_2. They are not alone in this view, nor is the idea that there may have been episodes of higher oxygenation (Diamond et al., 2018; Zhang et al., 2018; reviewed in Lyons et al., 2021) against that backdrop and, more generally, dynamic redox even in shallow waters (Hardisty et al., 2017). The authors invoke sporadic oxygenation to explain the stratigraphic distribution of MTS they observed and give us geochemical data (trends for iodine and cerium anomalies) that generally jibe with that argument, although the signals are small. We might expect subtle responses if O_2 shifts were short-lived and relatively small. Even slight oxygenation could remove iron and permit mud formation in the water column, along with incipient cementation of that accumulated mud. These muddy deposits, Tang et al. tell us, were the subsequently cracked substrates of MTS left only partially consolidated thanks in part to the weak-acid generating potential of O_2-utilizing bacteria. Here too is a delicate balance between controls that favor and disfavor carbonate mineral formation.

An added consideration is that organic matter that would have supported microbial activity is often in very short supply in MTS-hosting rocks, raising questions about the importance of purported connections to microbial reactions. Also, the role of cyanobacterial photosynthesis (local CO_2 drawdown and concomitant increases in the carbonate saturation state) imagined by Tang et al. for further facilitation of mud formation in the water column (their "whitings") should be reconciled with the possibility that water-column-dwelling (planktonic) cyanobacteria may not have evolved or become important until fairly late in the Proterozoic (Sánchez-Baracaldo et al., 2022). More generally, the arguments of Tang et al. can be distilled down to a combination of generally high carbonate saturation (per discussions above) and loss of iron inhibitors via periods of deeper oxygen penetration that presumably catalyzed the rapid precipitation of the microspar cement that filled the MTS void. At the risk of further muddying the waters, however, there are data that show high iron levels in MTS carbonate fill (Frank et al., 1997), suggesting that iron removal may not have been an essential prerequisite, or that iron was low enough in general, relative to the earlier Archean ocean, to have had little consequence for carbonate formation. Another possibility is that partial cementation of the host sediments occurred under low Proterozoic iron levels without oxygenation, while leaving O_2 as a possible trigger for the rapid cementation of the cracks (MTS) that formed in those muds. It's hard to know.

There are a lot of inferences here, but the Tang et al. model does check a lot of boxes. The final variable in the equation, however, lies with the specifics of crack formation. The authors, like many researchers before them (e.g., Shen et al., 2016), invoke methane accumulation. There is no doubt that methane can accumulate in sediments and lead to sediment disturbance, just ask anyone who has collected a sediment core of modern organic-rich mud, capped it, and come back latter to an expanded, disturbed mess. Methane can leave behind fingerprints of its past presence, most notably carbonate minerals that form from the ^{13}C-heavy DIC left behind following microbial formation of ^{12}C-rich methane from CO_2—rather than from decomposition of organic material, the other key pathway. At the other extreme, carbonate rocks formed in methanic systems can also show extreme, diagnostic ^{12}C richness stemming from methane oxidation in the sediments. The authors' isotopic claims in this regard are subtle but are certainly not inconsistent MTS formation linked to methane.

Imagining methane's place in MTS formation is particularly interesting from the standpoint of broad-scale paleoenvironmental messages. Generally low sulfate (SO_4^{2-}) and oxygen in the ocean is a terrific way of preserving methane, because both are key oxidants in methanotrophy (microbial methane oxidation), such as biological destruction via anaerobic oxidation (AOM) coupled to sulfate reduction. In addition to promoting preservation, low oxygen and sulfate are also gateways to high methane production because methanogenesis is an anaerobic biological process and because substantial amounts of organic matter suitable for microbial methane production can be lost to aerobic microbes and those making a living by sulfate reduction. In the competitive battle for degradable organic material defined by pathway-specific energy yields, aerobes and sulfate reducers generally win over methanogens.

There are plenty of pitches in the literature for low sulfate in the Meso- and Neoproterozoic ocean (Fig. 2, e.g., Kah et al., 2004; Fakhraee et al., 2019). Marine sulfate levels are controlled principally by oxidative weathering of sulfide minerals on land, which should have turned on in earnest during the Great Oxidation Event at ca. 2.3-2.4 billion years ago, long before the apex of MTS formation. But the sinks are also vital, and efficient pyrite formation and burial in the still widely anoxic and iron-rich ocean and underlying sediments must have drawn that reservoir down with great success. All of these pieces of first-order biospheric relevance could have conspired to make high methane in sediments during the Meso- and Neoproterozoic, even if it was not high in the atmosphere (Olson et al., 2016).

It may be a coincidence, but occurrences of MTS drop off precipitously around 800 million years ago (Fig. 2), when O_2 likely rose appreciably in the ocean and atmosphere (reviewed in Lyons et al., 2021), and sulfate may have risen as well. Both steps up would have made methane accumulation harder, although sulfate and O_2 may have declined again and remained highly dynamic into the Paleozoic (e.g., Loyd et al, 2012; He et al., 2019; Lyons et al., 2021). What's more, the Archean was if anything more methane-friendly, yet it was devoid of MTS (Catling and Zahnle, 2020), so it alone cannot explain the limited temporal distribution of MTS. It must have been a combination of factors. In this regard, it is worth also mentioning that phosphate in the ocean almost certainly increased during the late Neoproterozoic (Reinhard et al., 2017) as MTS was on the decline, and it too is known to have an inhibiting effect on carbonate precipitation (Roest-Ellis et al., 2020).

Confounding things further, MTS often lacks the geochemical signposts of methane's former presence—in $\delta^{13}C$ records in particular (e.g., Frank and Lyons, 1998). The suggestion is that the methane formed elsewhere, perhaps in deeper layers richer in organic matter, and that it migrated in but was not oxidized appreciably at the site of crack formation perhaps because of generally low O_2 and sulfate conditions in the surface ocean. Or maybe the methane, if actually involved, was flushed out or simply escaped into the overlying water before the crack filled with calcite.

If we add up the score, it is easy to argue that these peculiar little microspar-filled cracks may very well count among our best evidence for high CO_2 in the atmosphere and concomitant high levels of carbonate saturation in the ocean during Earth's middle history. Through these connections, they are among the smoking guns for CO_2's role in early climate warming at a time noted for long stretches without major glaciation despite the faint sun. MTS could also be on the list of evidence for at least episodic decreases in dissolved marine iron in the shallow ocean, indicative of growing but perhaps dynamic O_2 concentrations in the early ocean and atmosphere, as Tang et al. have suggested. Such possibilities carry tons of relevance for our understanding of the controls on evolution of the earliest eukaryotes and even animals in those same waters. Despite all the interest, there is still little agreement about the full swath of mechanistic pieces and how they lined up when controlling MTS formation, and there may not be a single correct model. But we can all agree that sorting out those details and their biggest take-home lessons about Earth's early environments is a laudable goal with high marks on the 'so what' test.

References

Bartley, J. K., & Kah, L. C. (2004). Marine carbon reservoir, C_{org}-C_{carb} coupling, and the evolution of the Proterozoic carbon cycle. *Geology*, *32*(2), 129–132. https://doi.org/10.1130/G19939.1

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*(5), 1069–1082. https://doi.org/10.1111/j.1365-3091.2006.00802.x

Catling, D.C., & Zahnle, K.J. (2020). The Archean atmosphere. *Science advances*, *6*(9), eaax1420. https://doi.org/10.1126/sciadv.aax1420

Diamond, C.W., Planavsky, N.J., Wang, C., & Lyons, T.W. (2018). What the ~1.4 Ga Xiamaling Formation can and cannot tell us about the mid-Proterozoic ocean. *Geobiology*, *16*(3), 219–236. https://doi.org/10.1111/gbi.12282

Fakhraee, M., Hancisse, O., Canfield, D. E., Crowe, S. A., & Katsev, S. (2019). Proterozoic seawater sulfate scarcity and the evolution of ocean–atmosphere chemistry. *Nature Geoscience*, *12*(5), 375–380. https://doi.org/10.1038/s41561-019-0351-5

Frank, T. D., & Lyons, T. W. (1998). "Molar-tooth" structures: A geochemical perspective on a Proterozoic enigma. *Geology*, *26*(8), 683–686. https://doi.org/10.1130/0091-7613(1998)026<0683:MTSAGP>2.3.CO;2

Frank, T.D., Lyons, T.W., & Lohmann, K.C. (1997). Isotopic evidence for the paleoenvironmental evolution of the Mesoproterozoic Helena Formation, Belt Supergroup, Montana, USA. *Geochimica et Cosmochimica Acta*, *61*(23), 5023–5041. https://doi.org/10.1016/S0016-7037(97)80341-9

Furniss, G., Rittel, 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*(1), 104–114. https://doi.org/10.2110/jsr.68.104

Grotzinger, J.P., & Knoll, A.H. (1999). Stromatolites in Precambrian carbonates: evolutionary mileposts or environmental dipsticks? *Annual Review of Earth and Planetary Sciences*, *27*(1), 313–358. https://doi.org/10.1146/annurev.earth.27.1.313

Hardisty, D. S., Lu, Z., Bekker, A., Diamond, C. W., Gill, B. C., Jiang, G., et al. (2017). Perspectives on Proterozoic surface ocean redox from iodine contents in ancient and recent carbonate. *Earth and Planetary Science Letters*, *463*, 159–170. https://doi.org/10.1016/j.epsl.2017.01.032

He, T., Zhu, M., Mills, B.J., Wynn, P.M., Zhuravlev, A.Y., Tostevin, R., et al. (2019). Possible links between extreme oxygen perturbations and the Cambrian radiation of animals. *Nature Geoscience*, *12*(6), 468–474. https://doi.org/10.1038/s41561-019-0357-z

Hodgskiss, M. S., Kunzmann, M., Poirier, A., & Halverson, G. P. (2018). The role of microbial iron reduction in the formation of Proterozoic molar tooth structures. *Earth and Planetary Science Letters*, *482*, 1–11. https://doi.org/10.1016/j.epsl.2017.10.037

Kah, L. C., Lyons, T. W., & Frank, T. D. (2004). Low marine sulphate and protracted oxygenation of the Proterozoic biosphere. *Nature*, *431*(7010), 834–838. https://doi.org/10.1038/nature02974

Kriscautzky, A., Kah, L. C., & Bartley, J. K. (2022). Molar-Tooth Structure as a window into the deposition and diagenesis of Precambrian carbonate. *Annual Review of Earth and Planetary Sciences*, *50*(1), 205–230. https://doi.org/10.1146/annurev-earth-031621-080804

Krissansen-Totton, J., Arney, G.N., & Catling, D.C. (2018). Constraining the climate and ocean pH of the early Earth with a geological carbon cycle model. *Proceedings of the National Academy of Sciences*, *115*(16), 4105–4110. https://doi.org/10.1073/pnas.1721296115

Liu, X. M., Kah, L. C., Knoll, A. H., Cui, H., Wang, C., Bekker, A., & Hazen, R. M. (2021). A persistently low level of atmospheric oxygen in Earth's middle age. *Nature Communications*, *12*(1), 1–7. https://doi.org/10.1038/s41467-020-20484-7

Loyd, S.J., Marenco, P.J., Hagadorn, J.W., Lyons, T.W., Kaufman, A.J., Sour-Tovar, F., et al. (2012). Sustained low marine sulfate concentrations from the Neoproterozoic to the Cambrian: Insights from carbonates of northwestern Mexico and eastern California. *Earth and Planetary Science Letters*, *339*, 79–94. https://doi.org/10.1016/j.epsl.2012.05.032

Lyons, T. W., Diamond, C. W., Planavsky, N. J., Reinhard, C. T., & Li, C. (2021). Oxygenation, life, and the planetary system during Earth's middle history: An overview. *Astrobiology*, *21*(8), 906–923. https://doi.org/10.1089/ast.2020.2418

Olson, S.L., Reinhard, C.T., & Lyons, T.W. (2016). Limited role for methane in the mid-Proterozoic greenhouse. *Proceedings of the National Academy of Sciences*, *113*(41), 11447–11452. https://doi.org/10.1073/pnas.1608549113

Planavsky, N. J., McGoldrick, P., Scott, C. T., Li, C., Reinhard, C. T., Kelly, A. E., et al. (2011). Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature*, *477*(7365), 448–451. https://doi.org/10.1038/nature10327

Planavsky, N. J., Reinhard, C. T., Wang, X., Thomson, D., McGoldrick, P., Rainbird, R. H., et al. (2014). Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. *Science*, *346*(6209), 635–638. https://doi.org/10.1126/science.1258410

Poulton, S. W., & Canfield, D. E. (2011). Ferruginous conditions: A dominant feature of the ocean through Earth's history. *Elements*, *7*(2), 107–112. https://doi.org/10.2113/gselements.7.2.107

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. *The Geological Society of America Bulletin*, *110*(8), 1028–1045. https://doi.org/10.1130/0016-7606(1998)110<1028:MTSIPC>2.3.CO;2

Reinhard, C.T., Planavsky, N.J., Gill, B.C., Ozaki, K., Robbins, L.J., Lyons, T.W., et al. (2017). Evolution of the global phosphorus cycle. *Nature*, *541*(7637), 386–389. https://doi.org/10.1038/nature20772

Roest-Ellis, S., Strauss, J.V., & Tosca, N.J. (2021). Experimental constraints on nonskeletal $CaCO_3$ precipitation from Proterozoic seawater. *Geology*, *49*(5), 561–565. https://doi.org/10.1130/G48044.1

Sánchez-Baracaldo, P., Bianchini, G., Wilson, J.D., & Knoll, A.H. (2022). Cyanobacteria and biogeochemical cycles through Earth history. *Trends in Microbiology*, *30*(2), 143–157. https://doi.org/10.1016/j.tim.2021.05.008

Shen, B., Dong, L., Xiao, S., Lang, X., Huang, K., Peng, Y., et al. (2016). Molar tooth carbonates and benthic methane fluxes in Proterozoic oceans. *Nature Communications*, *7*(1), 1–6. https://doi.org/10.1038/ncomms10317

Sumner, D. Y., & Grotzinger, J. P. (1996). Were kinetics of Archean calcium carbonate precipitation related to oxygen concentration? *Geology*, *24*(2), 119–122. https://doi.org/10.1130/0091-7613(1996)024<0119:WKOACC>2.3.CO;2

Tarhan, L.G., Droser, M.L., Planavsky, N.J., & Johnston, D.T. (2015). Protracted development of bioturbation through the early Palaeozoic Era. *Nature Geoscience*, *8*(11), 865–869. https://doi.org/10.1038/ngeo2537

Wang, C., Lechte, M. A., Reinhard, C. T., Asael, D., Cole, D. B., Halverson, G. P., et al. (2022). Strong evidence for a weakly oxygenated ocean–atmosphere system during the Proterozoic. *Proceedings of the National Academy of Sciences*, *119*(6), e2116101119. https://doi.org/10.1073/pnas.2116101119

Zhang, K., Zhu, X., Wood, R. A., Shi, Y., Gao, Z., & Poulton, S. W. (2018). Oxygenation of the Mesoproterozoic ocean and the evolution of complex eukaryotes. *Nature Geoscience*, *11*(5), 345–350. https://doi.org/10.1038/s41561-018-0111-y

Figure.

Figure 1. Field and petrographic features of MTS, Helena Formation, Mesoproterozoic Belt Supergroup, Montana. (a) Sketch and two thin section images showing compactional draping of laminae around MTS (pink coloring in the image on the right is a stain specific to calcite). MTS is stained, but the dolomite host is not. (b) Sketch and photos of lag deposits related to erosion of MTS-bearing sediments showing incorporation of reworked clasts of host dolomite and MTS ribbons in lag. Field photo from the Helena Formation, Logan Pass, Glacier National Park, Montana. (c) Sketch, field, and thin section images of calcitic 'halos' around MTS ribbons from an outcrop at Logan Pass. *This a-c sequence captures the steps of formation and evidence for very early origins (shallow burial) of MTS*: (i) cracks form by gas expansion in partially cemented stiff mud; (ii) cracks fill rapidly by microspar (calcitic) cement, with invasion of cement into surrounding host sediment along margins of cracks; (iii) penetrating fluids subsequently dolomitize the original $CaCO_3$ host muds without replacing the more strongly calcite-cemented crack fills and halos; (iv) currents erode early formed ribbons and replacive dolomite, leaving behind lags; and (v) continued compaction of partially lithified muds results in draping around stiffer, early cemented ribbons.
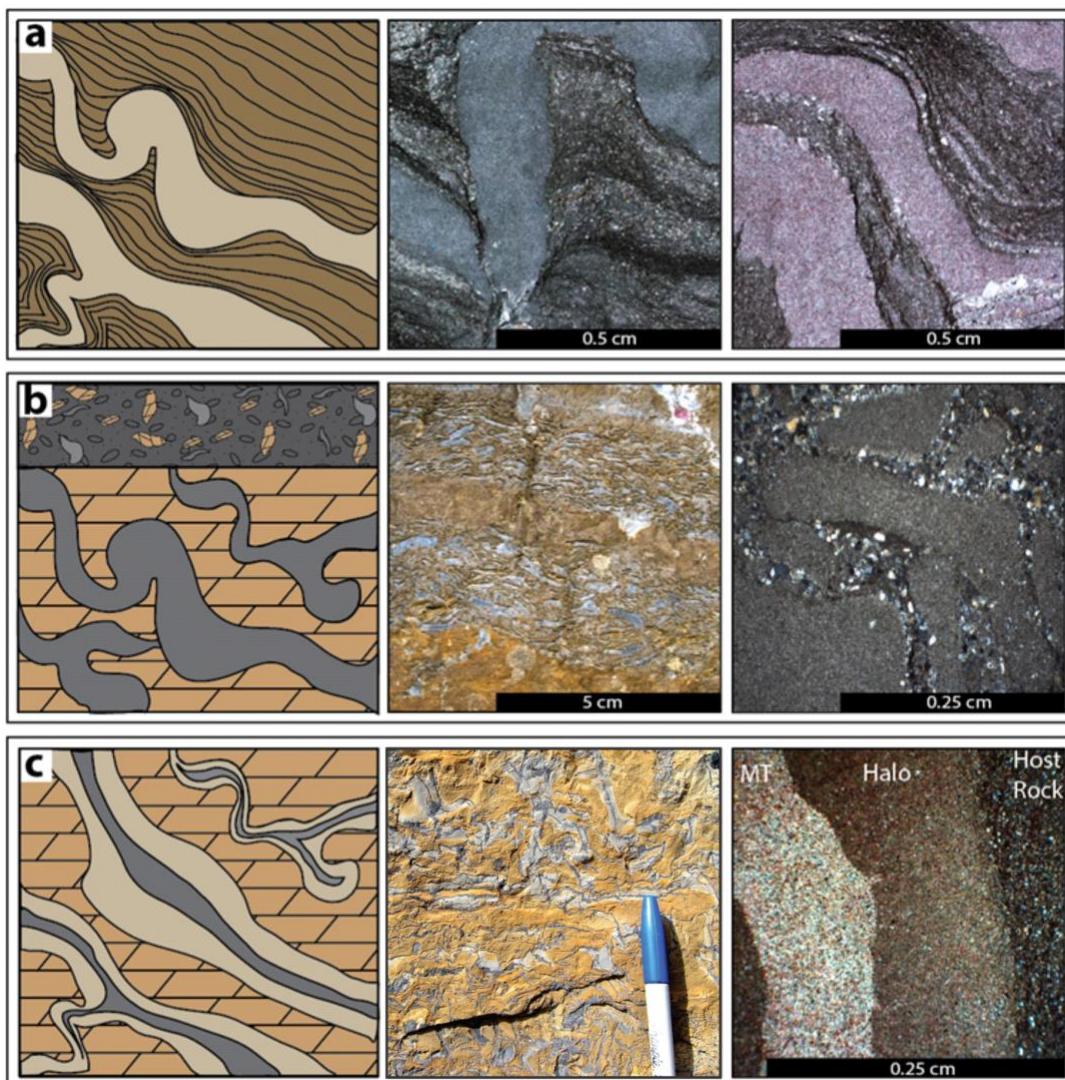
Figure 2. Temporal distribution of MTS (modified from Kriscautzky et al., 2022) and estimates for evolving marine sulfate concentrations (modified from Fakhraee et al., 2019, additional sulfate constraints from Crowe et al., 2014, and Blättler et al., 2018). Note that stratigraphic successions are binned into 200 My intervals, and vertical dashed lines mark the approximate timing of the Great Oxidation Event and the Neoproterozoic Oxidation Event.