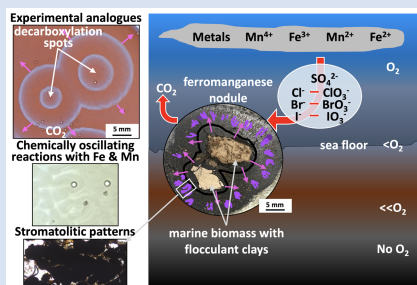


Abiotic chemically oscillating reactions make patterns in deep-sea ferromanganese nodules and crusts

D. Papineau^{1*}, H. Xu¹, Y. Qu¹, S. Liu¹, K. Ta¹, X. Peng¹



Ferromanganese deposits in deep-sea sediments, including both ferromanganese nodules (FMN) and ferromanganese crusts (FMC) are mineralised spheroids of metalliferous oxides that have been attributed to hydrogenetic and diagenetic processes. While ferromanganese deposits are volumetrically dominated by stromatolitic patterns, these have been left unexplained by specific processes. Here, we show that deep-sea FMN and FMC represent mineralised fractal objects, spanning five orders of magnitude in size, and they have self-similar patterns of circular concentricity, radial alignment, spheroidal twins, compositional gradients and stromatolitic-type arborescences. We also show that the same self-similar patterns are produced by abiotic chemically oscillating reactions (COR) performed with different carboxylic acids and iron and manga-

nese compounds with out-of-equilibrium oxidation states. Compositionally, dendritic arborescences and stromatolitic columns in ferromanganese deposits consist of manganese oxides and organic matter (OM) with some directly occurring onto calcitic forams. Spectra show that OM in stromatolitic columns contains slightly fewer carboxyl groups and more C=C bonds compared to the more functionalised OM in the intercolumnar space. The new observations point to a major role for pattern-forming COR during the abiotic decomposition of biomass, which is how patterns in FMN and FMC are likely produced.

Received 3 December 2024 | Accepted 9 June 2025 | Published 28 July 2025

Introduction

Deep-sea FMN are sub-spheroidal objects, with one or more distinct nuclei encircled by manganese (Mn) and iron (Fe) oxide minerals, that occur on the sea floor worldwide. Their nuclei are often fossil-bearing and the presence of chemolithotrophic bacteria suggests potential biological influences (Molari *et al.*, 2020; Hein *et al.*, 2023). In comparison, FMC commonly form on deep-sea hardgrounds, like rock outcrops (Josso *et al.*, 2021, and both FMN and FMC contain stromatolitic patterns with rhythmic laminations reminiscent of Milankovitch cycles (Han *et al.*, 2003; Josso *et al.*, 2021). Both also contain abundant elements critical for the transition towards greener sources of energy, making them attractive for deep-sea mining (Hein *et al.*, 2023). Prevailing hypotheses suggest origins possibly controlled by microbial metabolisms, hydrogenetic precipitation in seawater, hydrothermal fluids, slow accretion onto nuclei, and porewater diagenetic processes (Dekov *et al.*, 2003; Li *et al.*, 2021; Machida *et al.*, 2021; Hein *et al.*, 2023; Yang *et al.*, 2024). However, the exact mechanism of pattern formation in FMN and FMC remains elusive. This contribution aims to compare patterns and substances in FMN and FMC with those from geochemically relevant COR experiments. Characteristic patterns and substances of COR have already been successfully compared with those of botryoidal minerals, concretions, agate geodes, granules, and rosettes (Papineau *et al.*, 2021, 2024, 2025); therefore, COR are relevant for understanding the abiotic origin of various spheroidal objects forming during sedimentary diagenesis.

Materials and methods

The ferromanganese deposit samples of FMN and FMC came from the Indian and Pacific oceans and have representative patterns and sizes (Fig. 1a, Table S-1). Petrography was performed on polished thin sections by polarising microscopy and by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). Targets with OM were analysed using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). COR were performed according to the classical recipe with 6 ml of a strong acid (sulphuric acid (H₂SO₄) [0.33 M]) mixed with a strong oxidiser (sodium bromate (NaBrO₃) [1 M]), 1 ml of carboxylic acids (malonic acid (C₃H₄O₄) [1 M]), 0.5 ml of sodium bromide (NaBr) [1 M], and 1ml of the redox indicator ferroin (phenanthroline ferrous sulphate [0.025 M]). In this work, these COR were also performed with added 1 ml α-ketoglutarate (C₅H₄O₅) [1 M], 1 ml potassium permanganate (KMnO₄) [0.1 M] and 1 ml manganese sulphate (MnSO₄) [0.1 M]. COR experiments were done inside a 10 cm diameter glass Petri dish, filmed with a charged-coupled device camera, and directly compared with patterns in FMN and FMC (see more details on methods in Supplementary Information).

Fractal Patterns in Deep-Sea Ferromanganese Deposits

Deep-sea FMN typically preserve concentric laminations and multiple nuclei (Xu *et al.*, 2020) with radially aligned Mn oxide patterns, akin to those made by dendritic minerals

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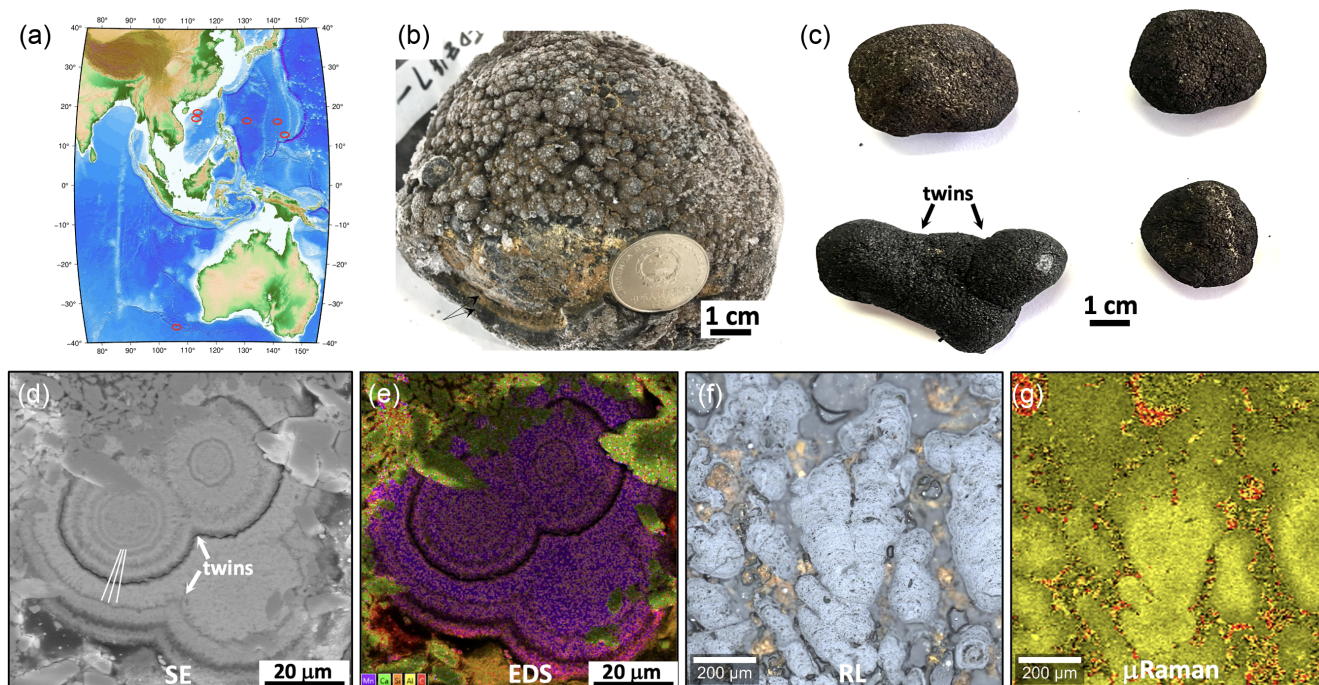


Figure 1 (a) Bathymetric map of sample collection sites (in red). (b) dm-sized sub-spheroidal FMN with circularly concentric layers (arrows) and cm- and mm-sized botryoids (FDZ187-NO4). (c) cm-sized FMN with multiple spheroidal twins (JLBC01). (d) μm-sized circularly concentric rosettes with spheroidal twins (arrows) and radially aligned patterns (lines) (SY165). (e) EDS map showing gradients of Mn and C. (f) Arborescent microdigitate stromatolites (MDS) of Mn oxide in FMC (SY314). (g) Raman image of panel (e) showing more functionalised (red) and sp²-hybridised carbon (yellow) OM. RL: reflected light, SE: secondary electron.

(Machida *et al.*, 2021). A range of twinned and circularly concentric patterns are discernible in FMN, and they span five orders of magnitude in size, ranging from tens of micrometres (also known as micro-nodules in Dekov *et al.*, 2003 and Xu *et al.*, 2020) to several decimetres (Fig. 1b–d). In FMN, common patterns include circular concentricity and compositional gradients of C and Mn (Figs. 1e, 2a), spheroidal twins (Figs. 1c,d, 2b,c), and radial alignment (Figs. 1d, 2b,d), all of which are akin to patterns in botryoidal minerals and agate geodes, where they have been described as fractal patterns (Varkouhi and Papineau, 2023; Papineau, 2024).

FMN and FMC also commonly contain arborescent and stromatolitic patterns (Figs. 1e, 2e,f), akin to dendrites, *Frutexitis* (a microscopic dubiofossil of uncertain biological origin and akin to macroscopic dendrites) and MDS (micrometre to millimetre size columnar branching stromatolites). In fact, deep-sea ferromanganese deposits appear volumetrically dominated by MDS patterns, such as in the abyss of the Pacific (Akai *et al.*, 2013; Yang *et al.*, 2024), Atlantic (Josso *et al.*, 2021), Indian (Fig. 1b; van Dongen *et al.*, 2014), Arctic oceans (Kim *et al.*, 2023) and of the Philippine and South China Seas (Fig. 1c–f; Xu *et al.*, 2020). In the hadal, such as the Mariana Trench, MDS patterns occur in FMN (Li *et al.*, 2021) and *Frutexitis* occur inside concretionary zeolite (Peng *et al.*, 2020). However, MDS from the geological record fundamentally differ because they are composed of carbonate minerals and attributed to photosynthetic microbial activity, and therefore occurrences of MDS patterns in the light-deprived abyssal and hadal ferromanganese deposits pose an enduring enigma. Yet, MDS and botryoidal patterns in FMN have been described by mathematical fractals because of their self-similarity at many size scales (Akai *et al.*, 2013), which appears critical in understanding the possible abiotic origin of some Precambrian stromatolites (Grotzinger and Rothman, 1996). For instance, Proterozoic MDS display millimetre-sized finger-like columns, sometimes with laminations of botryoidal and diagenetic minerals thought

to have mixed abiotic and microbial origins (Goodwin and Papineau, 2022; Yang *et al.*, 2022).

Comparisons of Patterns Between COR and Ferromanganese Deposits

In the classical COR (*i.e.* the Belousov–Zhabotinsky (B–Z) reaction), decarboxylation (*i.e.* the removal of –COOH groups from organic molecules) of C₃H₄O₄ takes place in the presence of H₂SO₄, NaBrO₃ and NaBr, when this process is self-catalyzed by ferroin (Zaikin and Zhabotinsky, 1970). Notably, this out-of-equilibrium mixture, containing Br⁵⁺ and Br[–], spontaneously initiates periodic oscillations manifested as self-similar patterns of radially expanding circularly concentric rings with colour gradients (Fig. 2a). Circular twins form when rings merge during radial diffusion (Fig. 2b,c; Papineau, 2024), akin to the above described patterns in FMN (Fig. 2a–c). Periodic oscillations can also arise in COR performed with Mn compounds (Briggs and Rauscher, 1973; Belmonte *et al.*, 1997); however, the patterns of Mn-based COR are not well documented.

New COR experiments performed with other carboxylic acids and out-of-equilibrium Mn compounds with different oxidation states, namely KMnO₄ and MnSO₄, produce stromatolitic and arborescent patterns (Fig. 2d–h). COR with these Mn⁷⁺ and Mn²⁺ compounds produce stromatolitic patterns with knobby edges and colour gradients (Fig. 2d), domal patterns with fine laminations (Fig. 2e), knobby columns like MDS (Fig. 2f), equidistant to branching lines (Fig. 2g) and arborescences with tapered branches (Fig. 2h). All these patterns (Fig. S–1) occur in FMN and FMC (Fig. 1, 2), and can occur directly on calcitic foraminifera (Fig. 2e,f), coralline algae (Xu *et al.*, 2020), or as dendritic to *Frutexitis*-like patterns (Fig. 2g,h). Hence, COR produce at least ten qualitatively distinct types of self-similar patterns like those in ferromanganese deposits, which suggest the involvement of

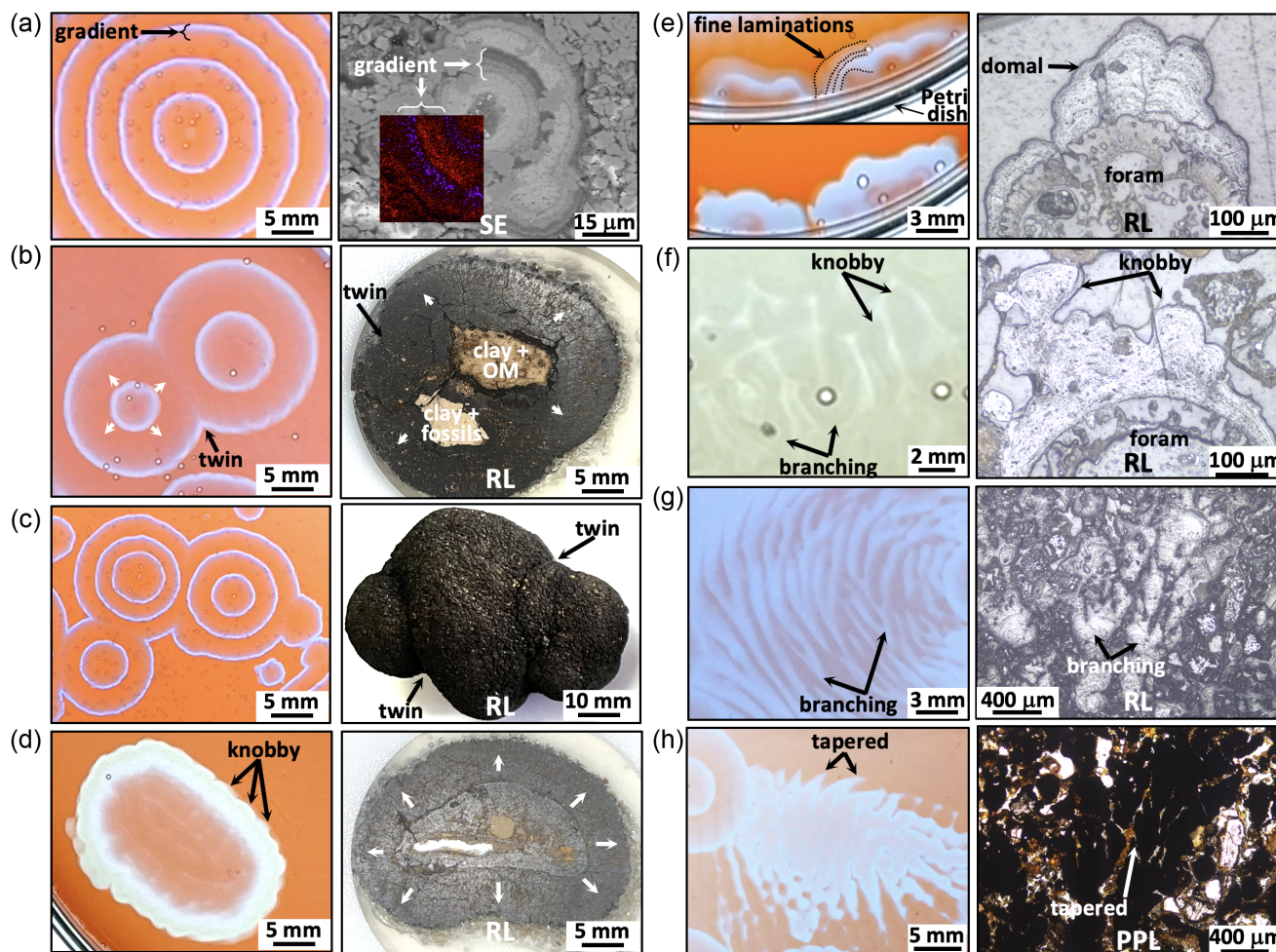


Figure 2 Comparison of patterns between COR (left columns) and FMN (right columns). (a) Circularly concentric rings with colour gradients. Inset shows EDS map overlays for C (red) and Mn (purple). (b) Double twin and radial geometry (white arrows). (c) Multiple twins. (d) Sub-circular pattern with knobby edges. (e) Finely laminated domal stromatolitic pattern. (f) Knobby stromatolitic pattern. (g) Equidistant to branching linear pattern. (h) Arborescent pattern with tapered branches. (b) and (d) show FMN with nuclei of clay with OM and fossils. Reactants for COR are the classical B-Z reaction except for (d), (e) and (f), where MnSO_4 and KMnO_4 are added, and for (g) where α -keto-glutarate is added. PPL: plane polarised light.

COR in their formation. The COR model also suggests that stromatolite patterns in FMN and FMC are abiotic, supporting long held views that abiotic processes likely produced some patterns in ancient stromatolites (Grotzinger and Rothman, 1996).

Differences in time scales and spatial representation between COR and ferromanganese deposits need to be considered and contrasted to support the comparisons established in this work. Firstly, to experimentally produce COR patterns within a reasonable time span, solutions of reactants are prepared using elevated concentrations compared to natural concentrations in deep-sea environments where ferromanganese deposits form. It has been argued that lower reactant concentrations would produce COR patterns at a slower rate because the duration of intermediate steps in chemical reactions is directly proportional to the concentration of reactants (Belmonte *et al.*, 1997). Secondly, the spatial representation of COR as two-dimensional films of aqueous solutions can be legitimately extrapolated to three dimensions, because this is commonly done in geology with two-dimensional petrographic images in thin sections linked back to three-dimensional rock samples. Hence, the self-repeating patterns in COR have dimensions and geometries like those in ferromanganese deposits (Fig. 2), which points to similar processes regulating their formation

(Varkouhi and Papineau, 2023; Papineau *et al.*, 2025). Therefore, it is argued that comparisons between the patterns in COR experiments and ferromanganese deposits are justified, well-supported, novel and informative.

Comparisons of Substances Between COR and Ferromanganese Deposits

Malonic acid is a reactant that enables COR to proceed over minutes time scales, and it represents a simple dicarboxylic acid common in lifeforms. Carboxylic acids, in general, are widespread in lifeforms and have a wide range of biochemical functions, such as in metabolic pathways, amino acids and phospholipids. Other carboxylic acids, such as α -ketoglutarate and succinate, can produce B-Z patterns in COR experiments (Fig. 2g; Papineau *et al.*, 2021). In deep-sea sediments, a significant source of carboxylic acids is decaying biomass raining down from the water column. Although not enriched in ferromanganese deposits, OM preserved in stromatolitic columns has more sp^2 -hybridised carbon than OM in the intercolumnar space, which is more functionalised as indicated by Raman spectroscopy (Fig. 1f–g). In fact, the Raman spectra of OM within MDS of Mn oxides grown on calcitic foraminifera (Fig. 3a–d)

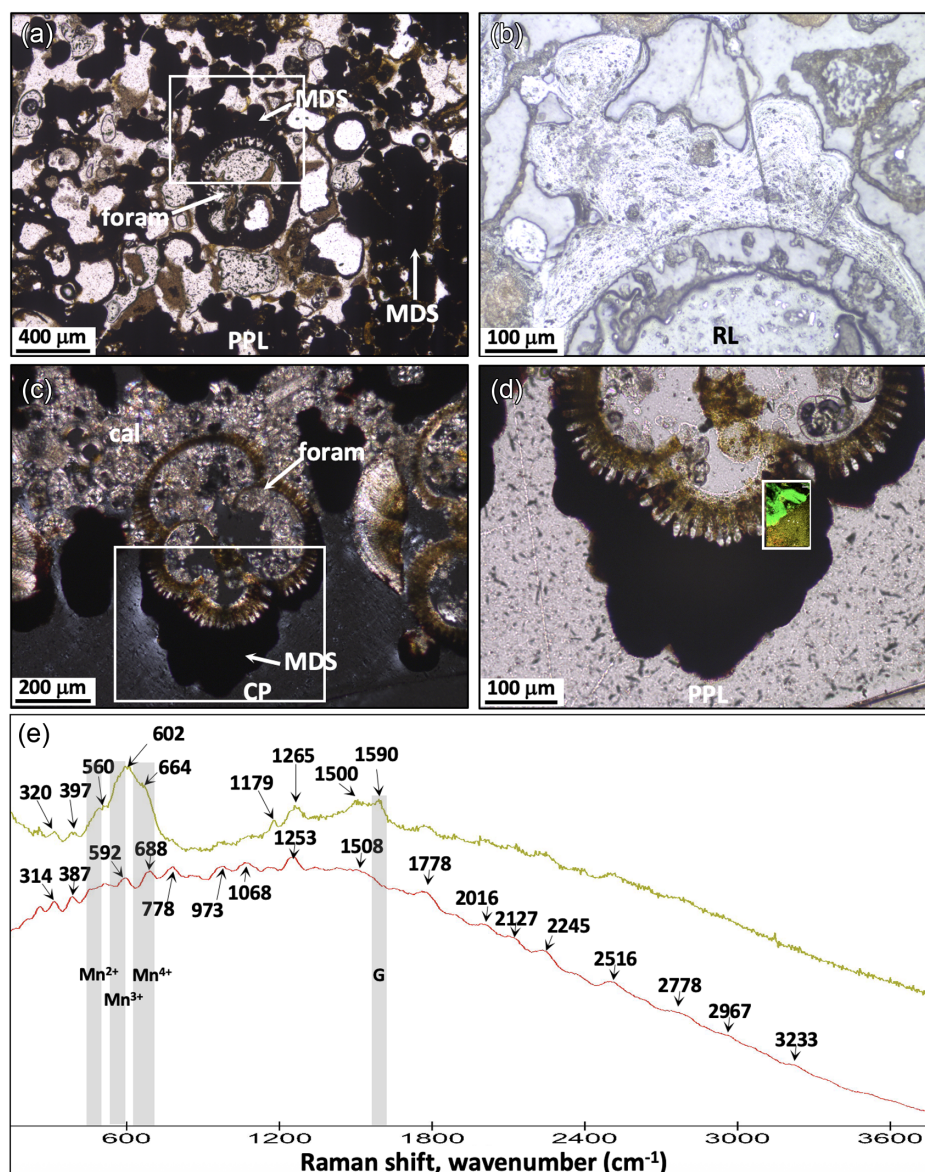


Figure 3 Fossil-bound MDS in FMC (SY314). (a) Foram with brown OM and coated with black multifurcate MDS. (b) Details of fine laminations in MDS. (c) Calcite-rich region with a foram coated with MDS. (d) MDS with location of Raman image in overlay (green: calcite, yellow: sp²-hybridised carbon in OM). (e) Raman spectra of more functionalized OM (red) in foram and sp²-hybridised carbon in OM (yellow) in MDS. The G-band and Mn oxide oxidation states bands (after Bernardini *et al.*, 2020) are highlighted. CP: cross polarised light.

have a well resolved G-peak at 1590 cm⁻¹, which indicates a higher abundance of sp²-hybridised C=C bonds. In contrast, this peak is absent in the Raman spectra of OM preserved in stromatolite intercolumns and in calcite, although the latter has other, more prominent peaks, including at 1179 cm⁻¹, 1778 cm⁻¹, 2516 cm⁻¹, 2778 cm⁻¹, 2967 cm⁻¹, and 3233 cm⁻¹ (Fig. 3e). These peaks can be assigned to various organic molecular vibrational modes.

XPS spectra from those distinct locations—stromatolite column and intercolumnar space—independently confirm slightly different levels of C=O/O=C=O bonds between the two types of OM (Fig. S-2d). This is attributable to slightly higher levels of carboxyl in OM from the intercolumnar space. Therefore, OM in stromatolitic Mn oxide columns is shown by XPS observations to have a slightly lower proportion of O=C=O bonds and by Raman spectra to have higher levels of C=C bonds. In brief, OM in stromatolitic Mn oxide columns preserves more defunctionalised OM

from primary biomass, which is thus interpreted to have experienced more metal-catalysed, redox-based decomposition and decarboxylation, compared to OM in stromatolite intercolumns.

A novelty in the COR experiments performed in this work is the inclusion of Mn oxide compounds with out-of-equilibrium oxidation states in addition to the ferroin catalyst usually used in COR. This means that these modified COR experiments contain the same dominant transition metal catalysts, each with an analogous range of oxidation states as those found in minerals from FMN. In fact, common minerals in FMN include Mn oxides (todorokite, vernadite, asbolane, etc.), Fe oxides (goethite, hematite, etc.), and accessory barite, pyrite, calcite, carbonate fluorapatite and clays (Zhong *et al.*, 2017). Raman spectra in the stromatolitic columns exhibit a broad peak with Mn oxides of variable oxidation states, including Mn²⁺ near 560 cm⁻¹, Mn³⁺ near 602 cm⁻¹, and Mn⁴⁺ near 664 cm⁻¹ (Fig. 3e; Bernardini *et al.*, 2020). In addition, XPS

spectra at the Mn_{2p} and Mn_{3s} edges independently confirm the presence of mixed Mn^{3+} and Mn^{4+} in the stromatolitic columns (Fig. S-2g–h; Ilton *et al.*, 2016). Furthermore, the XPS spectra at the Fe_{2p} edge show the presence of oxide phases with both Fe^{3+} and Fe^{2+} (Fig. S-2i). Spectroscopic observations therefore demonstrate that both Mn and Fe have variable oxidation states in the metalliferous stromatolitic columns of ferromanganese deposits. In deep-sea FMN, it can thus be argued that the redox-variable Fe and Mn contribute to the catalysis of abiotic decarboxylation of marine biomass, analogously to Fe and Mn catalysed COR (Papineau *et al.*, 2021) and to abiotic oxidative decarboxylation reactions with ferrous iron catalysts (Muchowska *et al.*, 2019). As petrographic observations show some metalliferous stromatolites occur directly over foraminifera or other microfossils, the source of the carboxylic acid for the inferred COR in deep-sea FMN and FMC is inferred to be a combination of marine microorganisms, dead marine biomass, animal excrements and OM flocculated onto clays (Fig. 4). Hence, pattern comparisons between COR and ferromanganese deposits are well justified and solidly established, as based on observations that they represent fractal objects with self-similar patterns and composed of similar comparable substances.

Influences of Environmental Conditions on FMN and FMC

Subsurface sea floor redox conditions during early diagenesis are thought to influence the formation of FMN (Wegorzewski and Kuhn, 2014; Hein *et al.*, 2023). Microorganisms performing Fe and Mn oxidation and reduction occur in FMN (Xu *et al.*, 2020), and while they play a significant role in deep-sea Mn biogeochemical cycling (Molari *et al.*, 2020), these bacteria are not known to mediate the formation of stromatolites or nodules (Akai *et al.*, 2013), which suggests a possible opportunistic presence in ferromanganese deposits. Besides, organic geochemical analyses suggest the formation of FMN is likely abiotic (van Dongen *et al.*, 2014). During the abiotic decomposition of biomass by compounds such as sulphate, oxidised halogens and redox sensitive metals (*e.g.*, Fe and Mn) are suggested to spontaneously produce patterned objects on sea floor sediments and rock outcrops (Fig. 4). Under redox gradients in sea floor sediments, COR are expected to occur when this combination of reactants spontaneously reacts with carboxylic acids of biological origin, which can explain why FMN and FMC may contain teeth, bones and microfossils. FMN cores can also be composed of clays

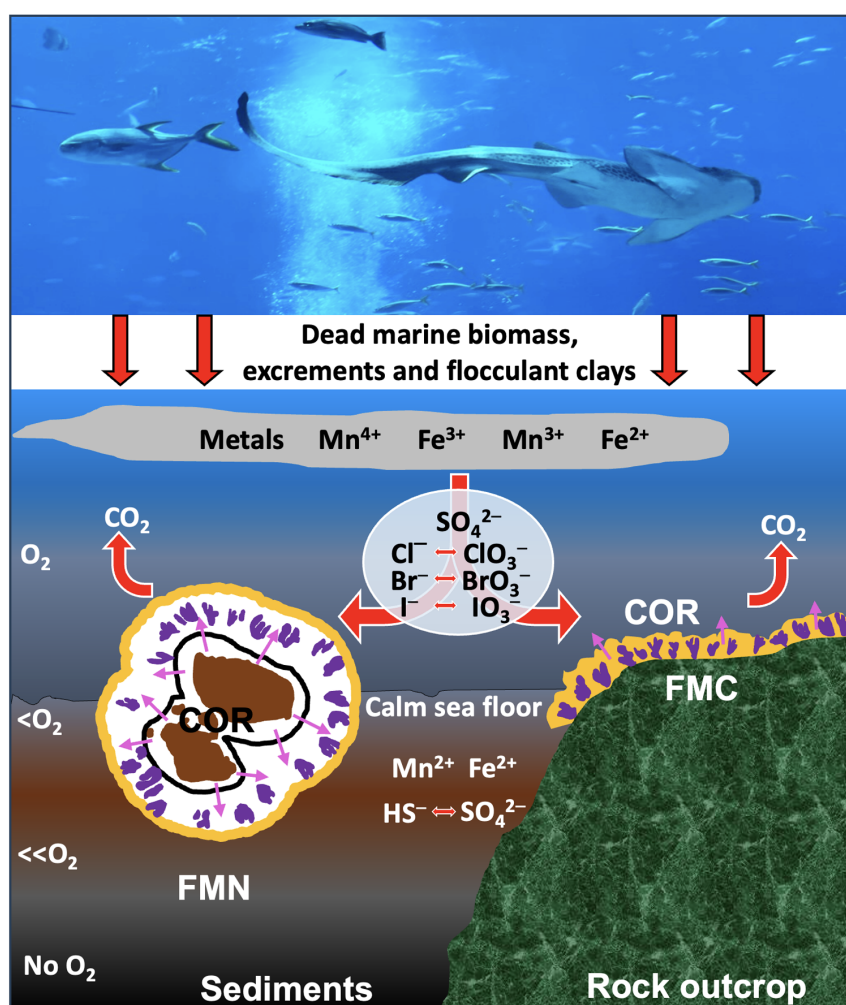


Figure 4 Interpreted formation of FMN and FMC on the sea floor. Botryoidal crust (yellow) is formed by diffusion growth (pink arrows) of radially aligned MDS (purple). FMN are concentrically centred (black line) on one or more variably sized nuclei, possibly flocculated onto clays (brown), while FMC form on hardgrounds volcanic rock outcrops. For both FMN and FMC, marine biomass is derived from the water column, which fuels pattern-forming COR using common reactants in seawater and metals from hydrothermal sources. COR in redox gradients produce ferromanganese oxides and decarboxylate biomass.

onto which OM flocculates in the water column. Hence, biological remains on the sea floor provide fuel for slow abiotic decarboxylation reactions, which then lead to the formation of patterns in FMN and FMC when other COR reactants are available. Importantly and more broadly, ferromanganese deposits do not necessarily require biomass as a source of carboxylic acids; COR could also occur with abiotically synthesised carboxylic acids, such as from Fischer–Tropsch synthesis (Fu *et al.*, 2008; McCollom, 2016). Therefore, while FMN and FMC can represent indirect signs of life when they contain fossils and microorganisms, it is conceivable that they could also form during abiotic carbon cycling of abiotic carboxylic acids.

Conclusions

The formation of circular and stromatolitic patterns in FMN and FMC is elegantly explained by the abiotic COR model. COR with added Mn compounds display the same self-similar patterns as in ferromanganese deposits, including circular concentricity, compositional gradients, spheroidal twins, radial orientation, stromatolites and arborescences. Spectra of OM in deep-sea FMN show higher levels of sp^2 -hybridised carbon in OM inside stromatolitic columns compared to the more functionalised OM in the intercolumnar space. Spectra also show Mn and Fe have highly variable oxidation states in FMN, comparable to the new pattern-forming COR experiments with Fe and Mn documented here. It is thus inferred that abiotic COR participate in the formation of fractal patterns in FMN and FMC from deep-sea environments where both have a purported diagenetic and hydrogenetic origin.

The formation of FMN and FMC on the sea floor likely depends on the availability of carboxylic acids, metal catalysts, halogens, sulphate, as well as redox gradients. Broader implications of abiotic stromatolite pattern formation by COR include possible roles for COR in the formation of MDS in the Precambrian geological record and of concretionary objects in modern shallow marine, lacustrine and evaporative environments. The deep-sea biogeochemical cycle of Mn and other metals in FMN thus appears intimately linked to abiotic carbon cycling. The COR model sheds some light on the multifaceted problem of distinguishing biosignatures from abiotic signatures, including in stromatolites, and possibly in prebiotic-like processes potentially before the origin of life.

Acknowledgements

We thank the crews of the R/V Tansuoyihao (cruises TS07–1, TS14, TS29–3), R/V Tansuoerhao (cruise TS2–2), and R/V Senhaiyihao (cruise 2021) and the pilots of Jiaolong, Shenhaiyongshi, and Fendouzhe manned submersibles. We thank Ms. Shuang Liu for assistance collecting XPS analyses. We also thank Fanghui Wang of the Theoretical and Computational Chemistry Team from Scientific Compass, Shiyanjia Lab (www.shiyanjia.com) for XPS spectral corrections. The National Key Research and Development Program of China (Grant No. 2022YFC2805400). DP acknowledges a PiFi fellowship from the Chinese Academy of Sciences. We also acknowledge the following sources of funding: the IDSSE (Grant No. E572070101), the CAS (Grant No. E51X070102), ISTC Program of Hainan Province (GHYF2024009), and the NSFC (Grant No. 42372229).

Editor: Andreas Kappler

Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2524>.



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Cite this letter as: Papineau, D., Xu, H., Qu, Y., Liu, S., Ta, K., Peng, X. (2025) Abiotic chemically oscillating reactions make patterns in deep-sea ferromanganese nodules and crusts. *Geochem. Persp. Let.* 35, 55–61. <https://doi.org/10.7185/geochemlet.2524>

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