GEOLOGY

Early plant organics increased global terrestrial mud deposition through enhanced flocculation

Sarah S. Zeichner[1]*, Justin Nghiem[1], Michael P. Lamb[1], Nina Takashima[1], Jan de Leeuw[1], Vamsi Ganti[2,3], Woodward W. Fischer[1]

An irreversible increase in alluvial mudrock occurred with the Ordovician-Silurian evolution of bryophytes, challenging a paradigm that deep-rooted plants were responsible for this landscape shift. We tested the idea that increased primary production and plant organics promoted aggregation of clay into flocs in rivers and facilitated mud deposition on floodplains. In experiments, we observed that clay readily flocculated for organic and clay concentrations common to modern rivers, yielding settling velocities three orders of magnitude larger than those without organics. Using a transport model, we found that flocculation substantially increased mud deposition, resulting in muddier floodplains. Thus, organic-induced flocculation may have been more critical than deep-rooted plants in the proliferation of muddy floodplains.

The Paleozoic evolution and proliferation of terrestrial plants has been connected with changes in soil and atmospheric chemistry and increased land primary productivity and organic carbon deposition (*1*). Correspondingly, the stratigraphic record contains a major first-order change in the construction of river floodplain deposits (*2*). A recent study quantified an Ordovician-Silurian increase in alluvial mudrock—that is, siliciclastic rock consisting of at least 50% mud-sized particles—which occurred concurrently with the evolution of early plants (Fig. 1A) (*3*). However, these data presented an apparent paradox. One explanation could be that the proliferation of plants led to mud production, yet the sedimentary record contains abundant mudrock throughout Earth's history, albeit in marine paleoenvironments before early Paleozoic time (*4*). Further, this increase in alluvial mudrock predated the evolution of large rooted plants and forests (Fig. 1A) (*3*, *5*). Early plants were small in size (~1 cm tall; inset of Fig. 1A) and lacked the deep rooting (*1*) that was likely necessary for floodplain binding through rooting and flow baffling (*6*). We hypothesized that these plants instead could have increased mudrock prevalence through a molecular mechanism: The rise in terrestrial organic material associated with early plants would drive mud flocculation in rivers and, in consequence, enhance mud settling and deposition on river floodplains. Plant polymers are not uniquely capable of binding sediment—previous work demonstrated the presence of sedimentary structures built by pre-Silurian terrestrial microbiota (*7*). However, the proliferation of early plants dramatically increased the productivity of the land surface and thereby the flux of organic polymers in terrestrial environments—both the polymers produced directly by the plants themselves as well as those generated and further modified by the rich associated microbial communities (*1*, *5*).

Flocculation is the process of binding of individual particles into larger aggregates called "flocs" (Fig. 1B) and is known to promote the deposition of clay and silt (i.e., mud) within estuarine and marine environments (*8*). Flocculation can substantially increase mud settling velocities (*9*), and growing evidence suggests that mud flocculation occurs in modern rivers (*10*) (Fig. 1B). Therefore, an increase in the ability to flocculate fluvial sediment has the potential to cause a major rise in alluvial mud deposition rates.

Flocculation in freshwater is associated with the presence of organics (*9*) because they—particularly polymers—facilitate particle binding interactions (*11*). Laboratory studies found that combinations of primary particles and polymers could lead to variable levels of flocculation (*9*, *12*). However, these studies did not directly measure the effect of polymer-clay combinations on floc settling velocity. Evidence for widespread flocculation in natural rivers came from an analysis of suspended sediment concentration-depth profiles, which showed systematically larger settling velocities compared with theoretical expectations for sediment smaller than 40 μm in diameter (*10*). Thus, flocculation appears to be a primary control on mud settling in modern fluvial environments, but the specific roles of organic matter in driving flocculation in rivers have remained unclear.

We conducted 83 flume experiments with distinct combinations of model organic polymers (xanthan gum and guar gum) and clay minerals (smectite and kaolinite) (inset of Fig. 2A) to quantify the role of organic material in determining mud settling rates in freshwater rivers (*13*). The experiments had constant turbulent Reynolds numbers, volumetric sediment concentrations of ~0.1 g/liter, and low ionic strength, similar to natural rivers (table S1) (*13*). Although these abiotic variables can also affect flocculation, particularly in marine and estuarine settings (*12*), our goal was to isolate the effect of organics on freshwater flocculation. We performed experiments in a fixed-volume stirred-batch reactor within a light-sensitive box (inset of Fig. 2A). For each experiment, we mixed specific proportions of clay and organic polymer, fully suspended the sediment in the water, and then captured time-lapse photographs of suspended sediment once the turbulent mixing was stopped. We calibrated the time-series absorbance data to derive sediment concentration (fig. S2) and regressed the concentration data on time to calculate settling velocities (Fig. 2A) (*13*).

We observed that organic polymers had a substantial, varied, and nonlinear effect on clay flocculation and settling velocity. All experiments with organic polymers formed visible flocs (fig. S1), which settled significantly faster than primary unflocculated clay particles [primary particle median diameter (D_{50}) = 1 μm; settling velocity ($w_{s,\mathrm{unflocculated}}$) = 2.205×10^{-6} m/s; p = 0.004] (Fig. 2B) (*13*). Generally, floc settling velocities increased with organic concentrations (table S2) (*13*). Guar gum was a more effective flocculant compared with xanthan gum (p = 0.004), likely because of its charge and branched structure, which increased the number of possible cross-links between clays and organics. Together, guar gum and smectite formed the largest flocs with the fastest settling velocities ($w_s \sim 10^{-3}$ m/s; p = 0.001) (Fig. 2B), even when mixed with kaolinite. Additional particle-tracking experiments using humic acids and kaolinite also yielded readily observable flocs and settling velocities of ~1×10^{-3} m/s—albeit at much higher sediment concentrations (*13*). Settling velocities from our floc experiments deviated substantially from Stokes' settling velocity predictions (*14*) for clay primary particles by up to three orders of magnitude (Fig. 2, B and C) and instead yielded velocities expected for medium to coarse silt [diameter (D) = 20 to 63 μm].

Our experimental results were consistent with data from previous experiments that characterized freshwater flocculation for similar combinations of clay with organic polymers, and they demonstrated, both qualitatively and quantitatively (Fig. 2C) (*9*, *15*), the optimal conditions for flocculation (Fig. 2B). The results also agreed with previous measurements of freshwater floc settling velocities from activated sludge (*16*) and natural sediment from rivers (Fig. 2C) (*16*–*19*). In particular, the guar-smectite experiments produced settling velocities consistent with those estimated in rivers by inversion of suspended sediment concentration-depth profiles (Fig. 2, B and C) (*10*).

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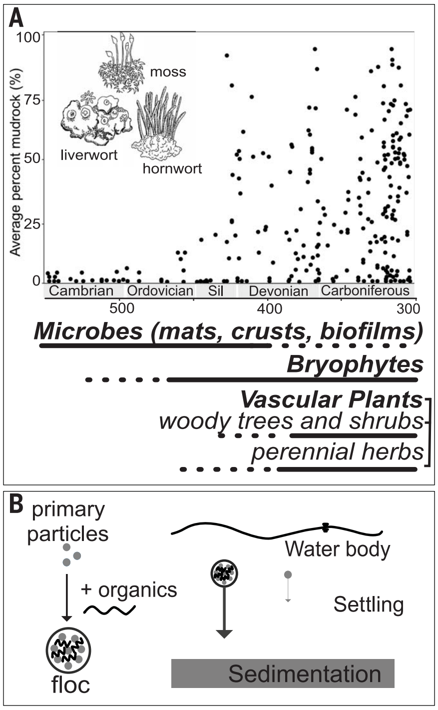

Fig. 1. Mudrock abundance, plant evolution, and flocculation. (**A**) Average percent mudrock for alluvial deposits over time, adapted from (*3*), shown alongside ranges of key evolutionary events in early plant evolution (*1*). The amount of alluvial mudrock increased with proliferation of early diverging plant lineages (e.g., bryophytes, including liverworts, hornworts, and mosses). Solid lines indicate the ranges for landscape occupation of different biological groups derived from the fossil record, whereas dashed lines indicate intervals of lesser occupational importance. Sil, Silurian. (**B**) Organic polymers (black squiggles) can bind primary clay particles (gray dots) together into flocs (black circles), which increases their settling velocities and sedimentation rates. The size of the arrow indicates increased settling velocities driven by larger particle aggregate size upon flocculation.

The mineralogical and organic materials found in rivers can be more complex than those that we simulated in our experiments. However, we found that interactions between clays with charged interlayers and charged branched polymers can produce settling velocities like those observed in rivers ($w_s \sim 10^{-4}$ to 10^{-3} m/s) (*10*), even if we added other clays like kaolinite to the mixture. Experiments without organics or with low organic concentrations did not produce enhanced settling velocities (Fig. 2B and fig. S1); these conditions are atypical for modern rivers. Likewise, the presence of silt common to rivers would further increase floc settling velocities compared with those measured in our experiments (*20*). Although we used idealized, chemically well-defined polymers, these polymers have comparable structures and functional groups to a range of plant-derived materials (*13*), including those found in modern plant cell walls (*21*), and are thought to have remained relatively consistent throughout plant evolution (*22*). This similarity supported the notion that organics play an important role in mud sediment transport in rivers, and vice versa.

We used a one-dimensional (1D) advection-settling analytical model to study the effect of organic-driven flocculation on overbank floodplain deposition, scaled roughly after the Mississippi River (Fig. 3) (*13*) as an example of the deep channeled, low-gradient single-threaded rivers common before and after the Silurian period (*23*). Model results showed systematically higher mud abundance relative to that of sand across the floodplain width in a flocculated scenario compared with an unflocculated scenario (26% mud for flocculated compared with 15% for unflocculated near the channel; Fig. 3C). For the flocculated case, we assumed that particles with $D < 20$ μm settled at a rate of 0.34 mm/s (Fig. 3B), similar to observations from rivers (*10*, *13*). Mud abundances in the flocculated case exceeded 50%—the definition of mudrock—everywhere beyond ~80 m of the channel edge. Both scenarios predicted predominantly mud deposition beyond ~200 m of the channel because this is beyond the advection-settling length for sand in our model (Fig. 3C) (*13*). Notably, flocculation also caused twofold-higher mud deposition rates at kilometer-scale distances from the channel (Fig. 3D). These model results can be generalized to any river system by changing the overbank water discharge, sediment concentration, and the sediment size distribution (fig. S4) (*13*). Although changing parameter values affected the mud deposition rate and the transition location from sandstone to mudrock, the general result of flocculation resulting in muddier overbank deposition held for all scenarios (*13*).

Our results have substantial implications for the proliferation of fluvial mudrock. The model predicted that flocculation results in muddier channel banks (Fig. 3C), which can increase bank cohesion and reduce the channel lateral migration rates (*24*). Slower lateral migration rates, in turn, limit the width of sandy channel-belt deposits (*25*). Furthermore, muddier channel-proximal deposits can cause channel narrowing, restrict braiding, and decrease channel sinuosity (*24*), all of which limit the extent of sandy channel-belt deposits. When this deposition pattern is spatially superposed over time as channels aggrade and migrate laterally, these feedbacks should produce overall muddier floodplains than predicted by our simple model that lacked channel dynamics. At the larger basin scale, increased rates of mud deposition kilometers from the channel owing to flocculation (Fig. 3D) will make mud preservation overall

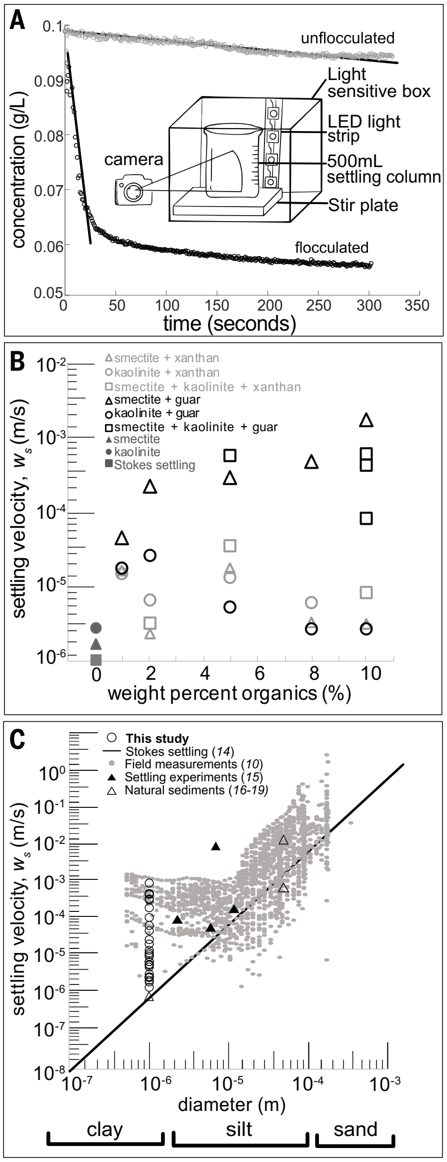

Fig. 2. Experimental results. (**A**) Suspended sediment concentration as a function of time from an example experiment with smectite control (gray) compared with an experiment of 5 wt % guar gum with smectite (black). Floc settling velocity was determined from the rate of concentration change over time, as shown by the fit black line (*13*). The inset shows the experimental setup. LED, light-emitting diode. (**B**) Settling velocities measured from our experiments as a function of weight percent organics for different combinations of clays and organics compared with the Stokes' settling rate for primary (unflocculated) particles (*14*). (**C**) Settling velocities from our experiments and previous work as a function of primary particle diameter and the Stokes' prediction for unflocculated particles (*14*). Previous studies include settling experiments with clay and organic polymers comparable to our experiments (*15*), experiments with natural sediments (*16*–*19*), and settling velocities from modern rivers inverted from concentration-depth profiles (*10*).

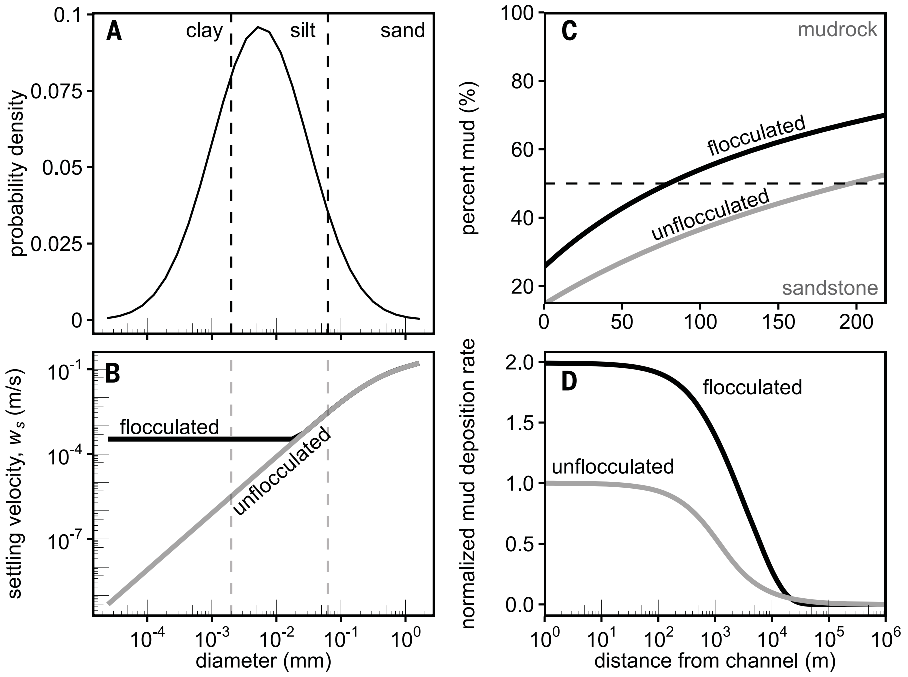

Fig. 3. Floodplain sediment transport model. (**A**) Grain-size distribution of sediment supplied from the channel onto the floodplain, approximately scaled after the Mississippi River (*13*). (**B**) Settling velocities used in the model for flocculated and unflocculated scenarios. (**C**) Results for the percentage of mud in the proximal floodplain, classified as mudrock and sandstone. (**D**) Mud deposition rate as a function of distance from the channel, normalized by the rate at the channel edge for the unflocculated case.

more likely, with lower chances of reworking by fluvial or aeolian processes (fig. S3) (*13*, *26*). In addition, the rates of lateral migration relative to channel switching, or avulsion, determine the stacking pattern and preservation of channel-belt sandstone bodies (*25*). Thus, slower lateral migration rates not only reduce the extent of individual sandstone bodies but also shift the alluvial architecture to a pattern characterized by mudrock with isolated sandstone bodies (fig. S3) (*13*, *25*). By contrast, the architecture of Precambrian alluvial deposits is characterized by laterally extensive sandstone bodies with substantial amalgamation and low mudrock preservation (*3*, *27*–*29*)—features indicative of high rates of channel lateral migration, relative to channel avulsion (*26*).

Our experiments illustrate how plant-associated organics can cause flocculation and substantially increase the settling velocity of mud in freshwater rivers, resulting in muddier floodplains. This coupling between organic carbon and mud transport and deposition has important implications for carbon cycling and sequestration. The proliferation of early land plants in terrestrial ecosystems during the Ordovician and Silurian periods increased the amount of primary production and the burial flux of organic material by at least an order of magnitude (*30*). This increase in the amount of organic matter in terrestrial environments would have generated a diverse suite of polymeric molecules, both through direct synthesis from plants as well as the microbial communities that thrive on plant-derived organic matter (*31*). Together, all these polysaccharides would drive the binding of fine sediment particles. Thus, a natural correlate of a plant-driven flocculation mechanism would have been an increase in organic carbon content in fluvial deposits associated with the increase in mudrock in those deposits. Although only a few examples are suitable for comparison, and total organic carbon (TOC) might be lower on average in older rocks owing to preservation biases, existing geochemical data supported the idea that pre-Ordovician rivers had lower TOC contents and thus relatively less effective mud flocculation (and sandier floodplains). Proterozoic alluvial rocks with low mudrock abundances have commensurately low TOC (e.g., Nonesuch Formation, which has <1% alluvial mudrock and <1% TOC) (*32*). By contrast, alluvial rocks postdating the evolution of land plants have both greater mudrock abundances and greater TOC concentrations within those mudrocks (e.g., lower Carboniferous Hørybreen/Mormien Formation, which has up to 28% mudrock and 11 to 30% TOC) (*3*, *33*). These trends are consistent with the hypothesis that plant proliferation, with its commensurate rise in primary production and terrestrial organic carbon fluxes, could have contributed substantially to the abrupt and irreversible early Paleozoic increase in alluvial mudrocks (*3*). Likewise, the processes of flocculation and enhanced settling of mud onto floodplains outlined an efficacious mechanism for organic carbon burial in ancient and modern alluvial systems.

REFERENCES AND NOTES

1. C. K. Boyce, J.-E. Lee, *Annu. Rev. Earth Planet. Sci.* **45**, 61–87 (2017).
2. D. Long, in *Fluvial Sedimentology—Memoir 5*, A. D. Miall Ed. (Canadian Society of Petroleum Geologists, 1978), pp. 313–341.
3. W. J. McMahon, N. S. Davies, *Science* **359**, 1022–1024 (2018).
4. N. S. Davies, M. R. Gibling, *Earth Sci. Rev.* **98**, 171–200 (2010).
5. W. W. Fischer, *Science* **359**, 994–995 (2018).
6. R. Hadley, "Influence of riparian vegetation on channel shape, northeastern Arizona" (Geological Survey Professional Paper 424–C, U.S. Government Printing Office, 1961), pp. 30–31.
7. S. McMahon, J. Parnell, *J. Geol. Soc. London* **175**, 716–720 (2018).
8. F. Maggi, thesis, Delft University of Technology (2005).
9. G. Zhang, H. Yin, Z. Lei, A. H. Reed, Y. Furukawa, *J. Geophys. Res. Oceans* **118**, 3473–3489 (2013).
10. M. P. Lamb *et al.*, *Nat. Geosci.* **13**, 566–570 (2020).
11. E. R. Sholkovitz, *Geochim. Cosmochim. Acta* **40**, 831–845 (1976).
12. Y. Furukawa, A. H. Reed, G. Zhang, *Geochem. Trans.* **15**, 1–9 (2014).
13. See supplementary materials.
14. G. G. Stokes, *Trans. Cambridge Philos. Soc.* **9**, 8–106 (1851).
15. X. L. Tan, G. P. Zhang, H. Yin, A. H. Reed, Y. Furukawa, *Int. J. Sediment Res.* **27**, 473–485 (2012).
16. J. Námer, J. J. Ganczarczyk, *Water Res.* **27**, 1285–1294 (1993).
17. W. Lick, H. Huang, R. Jepsen, *J. Geophys. Res.* **98**, 10279 (1993).
18. Q. Q. Shang, H. W. Fang, H. M. Zhao, G. J. He, Z. H. Cui, *Int. J. Sediment Res.* **29**, 471–480 (2014).
19. V. Wendling *et al.*, *J. Soils Sediments* **15**, 1991–2003 (2015).
20. D. Tran, K. Strom, *Cont. Shelf Res.* **138**, 81–94 (2017).
21. M. Pauly, K. Keegstra, *Curr. Opin. Plant Biol.* **13**, 305–312 (2010).
22. Z. A. Popper, *Curr. Opin. Plant Biol.* **11**, 286–292 (2008).
23. V. Ganti, A. C. Whittaker, M. P. Lamb, W. W. Fischer, *Proc. Natl. Acad. Sci. U.S.A.* **116**, 11652–11657 (2019).
24. M. G. A. Lapôtre, A. Ielpi, M. P. Lamb, R. M. E. Williams, A. H. Knoll, *J. Geophys. Res. Earth Surf.* **124**, 2757–2777 (2019).
25. D. J. Jerolmack, D. Mohrig, *Geology* **35**, 463–466 (2007).
26. V. Ganti, E. A. Hajek, K. Leary, K. M. Straub, C. Paola, *Geophys. Res. Lett.* **47**, 1–10 (2020).
27. D. Winston, in *Fluvial Sedimentology—Memoir 5*, A. D. Miall, Ed. (Canadian Society of Petroleum Geologists, 1978), pp. 343–359.
28. E. Cotter, in *Fluvial Sedimentology—Memoir 5*, A. D. Miall, Ed. (Canadian Society of Petroleum Geologists, 1978), pp. 361–383.
29. A. Ielpi *et al.*, *Sediment. Geol.* **372**, 140–172 (2018).
30. D. Edwards, L. Cherns, J. A. Raven, *Palaeontology* **58**, 803–837 (2015).
31. M. V. Cheshire, *J. Soil Sci.* **28**, 1–10 (1977).
32. J. R. Hatch, G. B. Morey, *Am. Assoc. Pet. Geol. Bull.* **69**, 1208–1216 (1985).
33. E. Dallmann *et al.*, in *Lithostratigraphic Lexicon of Svalbard: Review and Recommendations for Nomenclature Use: Upper Palaeozoic to Quaternary Bedrock*, W. K. Dallman, Ed. (Norsk Polarinstitutt, 2004), pp. 29–65.
34. S. S. Zeichner, J. Nghiem, M. P. Lamb, N. Takashima, J. de Leeuw, V. Ganti, W. W. Fischer, szeichner/Flocs-Code-and-Models: flocs1.1. Zenodo (2020); https://doi.org/10.5281/zenodo.4033293.

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SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/371/6528/526/suppl/DC1
Materials and Methods
Figs. S1 to S4
Tables S1 and S2
References (*35*–*50*)

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What matters for mudrocks

Rock such as slate and shale, which form from mud, suddenly start appearing in the geologic record around 450 million years ago. Their appearance at about the same time as certain plants seems to implicate plant roots in the formation of these ubiquitous rocks. Zeichner *et al.* found a different route for creating the flocculation required for mudrock. Using analog experiments, the authors found that organic matter from plants alone was sufficient for the formation of flocs––aggregates of small silt and clay particles––which are required to deposit mudrock. This observation could explain the appearance of these rocks in places where the plants did not have deep roots.

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