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# Parametric Chemistry

## Reverse Engineering Biomaterial Composites for Additive Manufacturing of Bio-cement Structures across Scales

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**ABSTRACT:** Motivated by the need to develop novel renewable and biocompatible composites for complex macro-scale structures, and inspired by natural shell, insect cuticles, and plant cell walls, we have developed a multi-material, robotic 3D printing platform and associated computational techniques that leverage the concepts of parametric chemistry and tunable hierarchical structuring for the additive manufacturing of hierarchical biomaterials, in meter-scale forms, with complex geometries. To do so, we have designed and engineered a bio-cement composite using natural and abundant polymers such as chitosan and cellulose. After assessing the chemical, mechanical, and optical properties of this prototypical bio-composite, we utilized these results as inputs to modulate our computational design and robotic fabrication platforms. Doing so has taken us closer to our goal of true fabrication information modelling (FIM), which integrates atomistic material properties to inform large-scale digital fabrication.

### 1 INTRODUCTION

Natural biopolymers—such as chitosan and cellulose—are widely abundant in Nature and exhibit extraordinary mechanical properties, especially when combined with organic and inorganic substances (Fernandez & Ingber, 2013; Mogas-Soldevila *et al.*, 2014; Vincent, 2012). However, architects, designers and engineers have yet to establish the methods by which to reconfigure these biopolymers into useful composites across functional length-scales that match—and even transcend—the properties of traditional building materials (Fernandez & Ingber, 2012).

Motivated by the need, and inspired by the opportunities associated with the development of renewable and biocompatible composites for the generation of complex large-scale structures, we have developed a novel bio-composite that can be digitally tuned and fabricated using a previously developed platform—*Water-Based Digital Fabrication (WDF) Platform* (Duro-Royo *et al.* 2015a; Duro-Royo *et al.* 2014)—designed to enable designers and manufacturers to digitally design and fabricate hierarchical large-scale bio-composite architectures (Figure 3).

### 2 MATERIAL ECOLOGY

#### 2.1 *Material Ecology*

The concept of a *Material Ecology* promotes the conceptualization of holistic products, characterized by property gradients and multi-functionality. Like the constructs it enables, its processes are just as seamless: *Material Ecology* considers computational design, digital fabrication, synthetic biology, environmental science, and the material itself as inseparable and harmonized dimensions of design (Oxman, 2011). *Material Ecology's* intimate relationship between design and biology proposes a shift from *consuming* Nature as a geological resource to *editing* it as a biological one.

#### 2.2 *Fabrication-Information Modeling*

The *Water-Based Digital Fabrication* platform (WBDF) has recently been developed by The Mediated Matter Group at the MIT Media Lab to enable multilateral additive manufacturing of hierarchical biomaterial structures across scales, using a robotic platform (Duro-Royo *et al.* 2015a; Duro-Royo *et al.* 2014). The development of this enabling technology has furthered our research into Material Ecology (Oxman, 2013) through Fabrication Information Modeling (FIM) (Duro-Royo *et al.*, 2015b; Duro-

Royo & Oxman, 2015). FIM is a computational environment designed to enable real-time sensing and physical feedback across digital and physical domains, thereby allowing for complete integration between form-finding, digital fabrication, and material computation across virtual and physical domains.

The WDF platform consists of a custom extrusion system attached to a multi-axis robotic arm, for which have programmed real-time feedback capabilities (Duro-Royo *et al.* 2015a). Designs are computationally driven and robotically informed, incorporating nozzle speed, robotic motion paths, nozzle sizes, air pressure, and distance from the substrate to tune mechanical and optical properties of extruded substrates at sub-millimeter tolerances, including weight and height, (Duro-Royo *et al.* 2015a). The platform is configured to deposit water-based materials such as polysaccharide blends, clays and cements, as well as various colloids in 2.5 dimensions (*i.e.* X, Y and sectional height).

Novel bio-composites developed by our team are inspired by natural shell structures—integrating organic and inorganic materials—derived from our previous research into composite hierarchical constructs (Mogas-Soldevila, Duro-Royo, *et al.* 2015). The resulting properties of digitally deposited and structured materials will inform further design and development associated with the WDF, enabling extended extrusion capabilities, as well as novel biological integration within the fabrication platform.

### 2.3 Learning from Nature

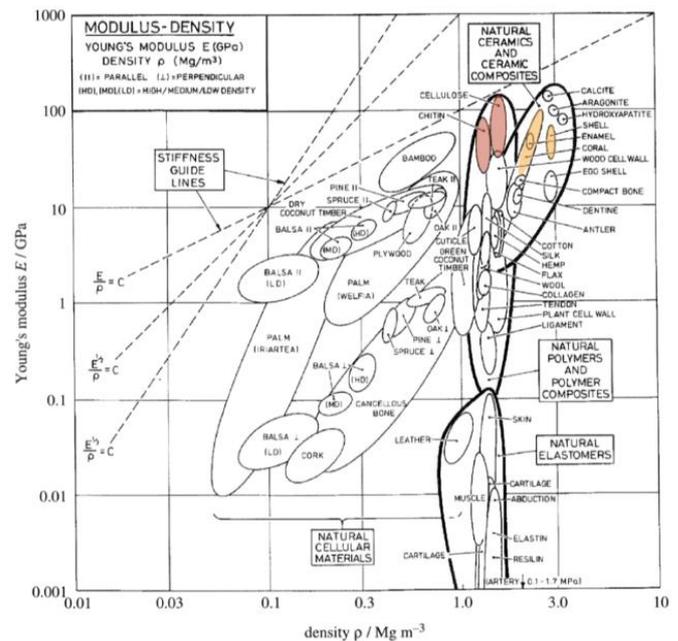
Over millions of years of evolution, organisms have meticulously reconfigured the materials they create in response to various environmental stimuli by modulating molecular self-assembly, chemistry, geometry, and three-dimensional conformation (Vincent 2012). Resulting materials exhibit extraordinary mechanical properties endowed by their hierarchical organization and functionally graded features (Ashby *et al.* 1995; Wegst *et al.* 2014). Importantly, the process of growth often requires a simple chemical palette of universal building blocks, maximal energy conservation, molecular self-assembly, and hierarchical structures to generate environmentally-driven optimization and self-healing (Wegst *et al.* 2014). Shell is one such evolutionary tactic for growing a multifunctional shelter that provides extraordinary structural stability, protection from the elements, and thermal comfort—by using simple materials and fabrication strategies (Li *et al.*, 2008).

### 2.4 Novel bio-cement design

Unlike natural materials, synthetic materials generally off-gas toxic fumes; are non-biodegradable;

consume large amounts of energy in manufacturing, maintenance, and disposal; have homogeneous properties across scales; and do not benefit from—or react—to the environment (Fernandez & Ingber 2012). Engineers have yet to create high-performance bio-composites with the strength and stability of traditional man-made materials (Fernandez & Ingber 2012). Bio-cement composites discussed in this paper utilize a chitosan-cellulose backbone with organic and inorganic additives. The synthesis of these structural biomaterials is a promising step toward large-scale digital manufacturing of economically viable, nontoxic, biocompatible, and biodegradable products and parts.

Specifically, we have reverse-engineered and reconfigured the chemicals and compounds that make up most natural shells, adding them to cellulose-chitosan blends. The goal is to endow a novel bio-cement with precise material properties that perform differently at multiple scales, with locally tailored characteristics for desired global outcomes. To do so, we have digitally designed and synthesized various blends of cellulose, chitosan, cornstarch, pectin and calcium carbonate to elicit specific mechanical and optical properties by varying their proportional chemistry and the fabrication strategies implemented to structure and construct them.



**Figure 1** – The material properties of our composite building blocks perform similarly to man-made technical materials.

### 2.5 Biomaterials background

Natural biopolymers such as chitosan and cellulose are abundant, biocompatible, biodegradable, and nontoxic—making them appealing as stock materials for use in additive manufacturing of sustainable products (Tran *et al.* 2013).

**Chitosan** is a natural biopolymer found in the shells of crustaceans such as shrimp and lobster. It is the second most abundant natural polysaccharide on the planet, after cellulose (Dawsey 1994). **Cellulose** is a natural biopolymer found predominantly in the plant kingdom, and is structured as a long chain of linked sugar molecules, which give wood its stiffness. It is also the main structural component of plant cell walls and a building block for textiles (Augustine 1990) (**Figure 3a, b**).

**Calcium carbonate** is widely used in the pharmaceutical, agricultural, construction, and paper industries. It comes mainly from powdered marble and limestone, but is also found in mollusk shells and stony corals (Cho *et al.* 2016). Importantly, calcium carbonate can endow a very strong material with a high stiffness-to-weight ratio (Ofem, Umar, & Muhammed 2015), which—in Nature—allows for the formation of lightweight, easy to carry shells. Applied on a larger scale, calcium carbonate can enable significant reductions in the mass of structures, which can allow for smaller and lighter supports, formal freedom, precise and purposeful geometric patterning, and low embodied energy (Mo *et al.* 2016).

**Pectin** is a carbohydrate in the skin and core of fruit that acts as structural ‘glue’, holding cell walls together. In solution, pectin can form a fibrous network that traps liquid and sets upon cooling. When combined with acid and sugar, pectin can form a hydrogel (Lopez-Sanchez *et al.* 2016). In layering our bio-cement on top of pectin films, a mechanical bond counteracts the bio-cement’s propensity for contraction and curling. In a favorable proportion, its elasticity dominates the bio-cement’s rigidity and strength, thereby increasing control over both the local and global shape of large bio-cement pieces. Furthermore, pectin’s translucency allows it to act as skin in patches.

**Cornstarch** is a powder made by pulverizing corn grains after soaking and removal of the embryo and outer covering (Crawford *et al.* 2013). Cornstarch is used here as a shear-thickening liquid, which gives the bio-cement, added rigidity and cohesion.

## 2.6 Research motivation

By specifically reconfiguring the chemical properties and mechanical hierarchies of natural shells, we have optimized the *tunability* of novel bio-cements within our customized additive manufacturing platform (WDF) (Duro-Royo *et al.* 2015a; Duro-Royo *et al.* 2014). In doing so, we demonstrate the capacity for hierarchical biomaterial design thereby obtaining both structurally- and aesthetically rich constructs. Hence, we have implemented a nano-to-macro control system for biomaterial blends, and integrated results from

mechanical testing within our computational environment. In this way, we can embed local control of extrusion thickness and material distribution for precise global structural requirements.

This research has enabled the design and fabrication of large-scale architectural structures that demonstrate: (1) differentiated optical qualities and mechanical behavior within a single material system, (2) lightweight structures, and (3) complete biodegradability. Work-in-progress explores the potential for biological augmentation within the structure.

## 3 MATERIALS AND METHODS

### 3.1 Bio-cement preparation

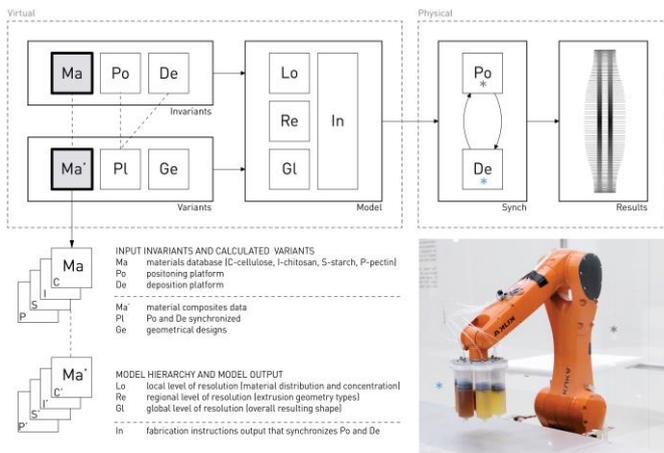
A solution of 4-10% cornstarch (w/v) (VWR, Radnor, PA) is heated to 95°C for 20 minutes while stirring vigorously with a magnetic stirrer. The temperature is then lowered to 78°C, at which point 8-22.5% chitosan (w/v) (85% de-acetylated VWR, Radnor, PA) is added to the mixture. The temperature of the solution is then lowered to 37°C, and acetic acid is added in a ratio of 2 parts chitosan to 1-part acetic acid (v/v). At this point, 1-15% calcium carbonate (w/v) is stirred in while folding vigorously to avoid rapid expansion. Finally, 40-70% cellulose (v/v) is added in small amounts to get an extremely viscous hydrogel.

### 3.2 Computational design

Line patterns are elaborated in 2.5 dimensions within a putative computer-aided design environment (Rhinoceros3D®) and its parametric modeling tool (Grasshopper®). Here, toolpath instructions are seamlessly sent to fabrication agents by embedding geometries with abundant meta-data, corresponding to nozzle size, direction, and height, as well as mechanical pressure and positioning speed. Further detail can be found in (Duro-Royo *et al.* 2015a).

### 3.3 Robotic fabrication parameters

The WDF fabrication platform is able to integrate both pneumatic extrusion of materials and precise positioning of a nozzle in space via a custom virtual interface (Duro-Royo *et al.* 2015a). In order to smoothly deposit material structures, the robotic interface distributes serial-based signals and valve response delays to inform the custom extrusion system. Simultaneously, an Ethernet-enabled data stream locates feedback for the existing robotic arm system (Duro-Royo *et al.* 2015a).



**Figure 2** – Workflow diagram of the WDF platform showing how a materials database delivers instructions to hardware components (graphics extended and adapted from Duro-Royo et al. (2015a)).

### 3.4 Material testing methods

An Instron mechanical tester with a load capacity of 20,000 lbs (10,000 kg, 100 kN) at a speed of 35 mm/min is used to measure the tensile strength of 12 material samples, each with a unique proportion of organic and inorganic ingredients. An extensometer is placed on each 19.05 mm x 127 mm x 12.7 mm sample to measure the deformation of the material under the stress of tensile testing. Material samples are prepared by printing material blends, which are cured on the substrate at room temperature, and cut to shape with a laser-cutter.

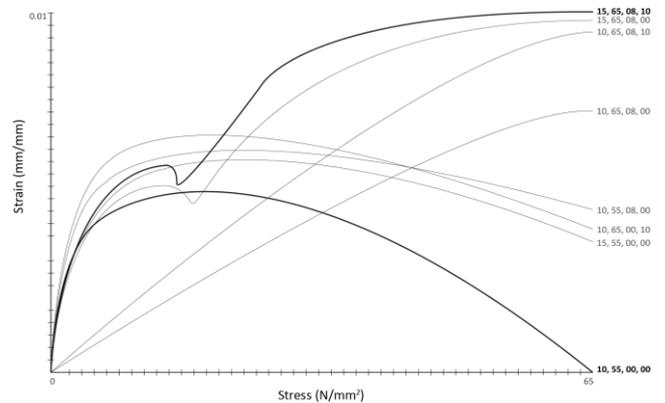
## 4 RESULTS AND DISCUSSION

This work integrates multiple disciplines to realize large-scale design and fabrication with biomaterials. Coined “Parametric Chemistry”, aspects of materials science and engineering, architecture, physics, biology, mathematical modeling, and chemistry are utilized to parametrically tune the chemical components and fabrication methods for various bio-cement composites.

We have digitally fabricated our material blends at various scales using the WDF platform, which allows for 2.5D deposition of water-based materials in hierarchical structures. In this case, we have layered multiple materials, oriented in a semi-parallel or semi-perpendicular fashion, to control local-to-global mechanical properties (**Figure 3**). Such geometric patterning has been configured to either enhance or compensate for mechanical and optical properties of the bio-cement material blends described below.

### 4.1 Material characterization

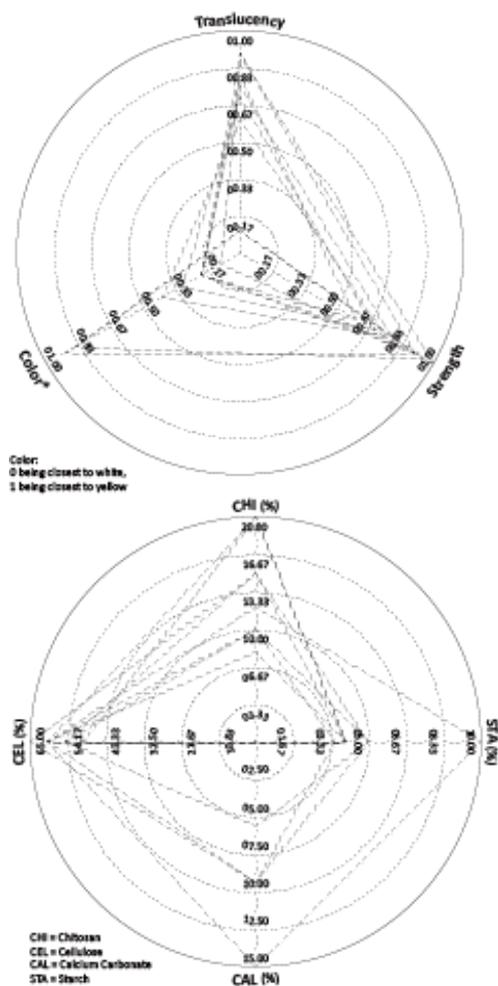
We have identified a direct relationship between the mechanical properties of our prototypical bio-cement and the relative proportions of cellulose, chitosan, calcium carbonate, and starch. By observing the controlled layering of organic and inorganic materials found in natural shells, we have been able to tailor material properties as well as drying durations of constructs to particular local and global needs through chemical interactions and fiber alignments.



**Figure 3** – Initial medium-scale results and mechanical testing. Ultimate tensile strength results from testing all material compositions in strips using an Instron load cell.

A high proportion of **cellulose** (40-70% v/v) provides the material with additional mechanical strength; likely due to the distributing of cellulose fibers contributing to an increase in anisotropy. Adding cellulose to the solution turns it into a more viscous, quick-drying hydrogel. Material tests of intricate geometry printed using this material show little-to-no spreading on the substrate. The hydrogel is squeezed through a ~1.0mm nozzle with 40-90 psi of air pressure, resulting in an ability to print at a higher resolution. Increasing the amount of cellulose relative to the amount of chitosan results in a whiter, slightly translucent material. Conversely, the speed at which the robotic arm is programmed to move decreases with increasing amounts of cellulose; because the printed geometries stick together so well such that turning corners and making curves drags the material out of place.

A greater proportion of **chitosan** (8-22.5% w/v) results in a global increase in both strength and elasticity. A high ratio of chitosan relative to cellulose and starch makes the material more golden-brown in color and opaque. However, this ratio also results in a more viscous hydrogel that does not keep its shape well when printed, thereby reducing our ability to print at high resolutions. Conversely, the robotic arm could move at a higher speed because the hydrogel does not stick together as well, nor does it dry as quickly.



**Figure 4** – Initial results and mechanical testing. Color is indicated from 0 to 1 being 0 closest to white and 1 closest to yellow.

Increasing the amount of **calcium carbonate** (1-10% w/v) yields a lighter weight material with the same or improved mechanical strength; a whiter, more translucent color; faster drying time; and added stiffness. The hydrogel also becomes much lighter—likely due to chemical reactions with the acetic acid—and holds its shape very well. This allows for a high printing resolution (~1.0mm), but again necessitates a slower printing speed and more air pressure (40-90psi). Adding calcium carbonate also results in a higher pH (4-7.3), which may create a more hospitable environment for bacteria and other organisms.

Finally, increasing the amount of **cornstarch** (4-10% w/v) results in added stiffness as well as a whiter color and slightly more translucency. We have also empirically determined that the use of **pectin** can dominate the bio-cements rigidity and endow the material with more flexibility.

#### 4.2 Initial results and material behavior testing

We have analyzed material behavior in eight geometric lattices with selected varying material compositions (**Figure 3**). Geometric design, amount of layers, and printing nozzle size is kept constant for every lattice, while pressure and speed are varied

depending on material's shear stress and flow once deposited. We have described in **Figure 3** material composition of each lattice as well as its effects in terms of color, translucency and strength. In **Figure 3**, we display stress-strain behavior curves of mechanically tested material strips similar to end extended from the blends used for lattice printing.

We have found that **calcium carbonate** is a determining factor in both the strength and stiffness of the material. We observed a higher ultimate tensile strength in materials with greater concentrations of **chitosan**; whereas, increased stiffness can be largely attributed to a higher concentration of **starch**. Alternatively, a higher concentration of **cellulose** added both strength and a higher elastic modulus to the composite most likely because of its fibrous structure (**Figure 4**). It is important to note that potential interactions between materials were not further analyzed here.

It should also be noted that the bio-cement was crosslinked with acetic acid to form a hydrogel, which then dried at room temperature after being deposited in 2.5 dimensions from the WDFP. Both heat and humidity led to embrittlement and large contractile deformations in the material, respectively. Further curing, crosslinking, and deprotonating experiments will be conducted. Regardless of the material composition, a thicker line weight and an increase in layer count can result in increased mechanical strength and rigidity. Similarly, more complex geometrical features could be used to compensate for the contractions of the material as it dries, as well as a strengthening agent. Printing successive layers in opposite orientations could endow the material with additional resistance to lateral forces. We have tried some of these strategies in a large construct described in **Figure 5**.

#### 4.3 Large-scale results

We have designed and manufactured a large proof-of-concept construct with differentiated geometric and material distribution to respond to varied structural behavior along its construction. The deposition of materials has been done with the WDFP in subsequent layers of cured multi-material colloids. Specifically, a base layer of pectin (35% w/v) (**BASE**), acetic acid (15% v/v), and glycerin (2% v/v) has been coarsely deposited and left to dry to accommodate subsequent hierarchical extrusions (**Figure 5**).

The first lattice-like layer (**LI**) consists of vertical and horizontal bio-cement extrusions. Vertical extrusions are performed with differential pressure to ensure a rigidity gradient with maximal material content toward the top and bottom of the construct. Doing so will—in the future—allow us to compose connections to the ground and the top of an architectural pavilion crowning. At the construct's center, additional flexibility has been achieved by layering

less material amounts and higher polymer concentrations to allow the piece to accommodate an arch-like configuration (**Figure 5**). The horizontal bio-cement extrusions in the first layer (*L1*) also follow a pressure gradient, with a maximum at the edges. The same strategy has been applied in the final and external layer, layer five (*L5*), in order to accommodate for deformation in the center of the construct.

## 5 CONCLUSIONS AND FUTURE WORK

Motivated by the need to synthesize renewable and biocompatible composites to generate complex macro-scale structures, we have developed a 3D printing platform and associated computational techniques that leverage parametric chemistry and tunable hierarchical structuring to produce meter-scale forms with complex geometries. As demonstrated through mechanical tests of material properties and components, and using a wide array of tunable bio-composites, we have enabled precise control over the shape and properties of 3D printed constructs.

Coined “Parametric Chemistry”, this approach and related workflow allow for the design of structure-function relationships in bio-composite materials across length scales. We have demonstrated our techniques in the context of medium-to-large-scale lattices, resulting in robust yet lightweight structures. Moreover, we have demonstrated control over 3D folding of large-scale structural members by guiding 2.5D material deposition and stiffness distribution of materials while curing.

By differentially configuring nozzle pressure, nozzle radius, and robotic arm speed, we compensate for weaknesses that appear in various bio-cements and augment additional mechanical and optical properties. Our progress will inform future work toward designing and digitally fabricating biomaterial structures at an architectural scale. Thus, the next iteration of the WDF platform will include improved extrusion capabilities and real-time feedback to and from robotic positioning and digital deposition.

Furthermore, our natural bio-cements have been configured to contain and control living micro-organisms in large-scale biomaterial structures, which, in turn, will enable temporal control over shape and material properties via bio-mineralization, microbial digestion, tissue formation, and ambient sensing.

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**Figure 5** – Experimental results. **a)** Fabrication parameters and material composition data within a large-scale construct. **b)** Local and global-scale behavior.

Meanwhile, layers two (*L2*) and four (*L4*) consist of thick, bio-cement members that span the length of the panel. Additionally, these layers contain added horizontal extrusions of pectin to ensure flexibility of the cross ribs and provide longitudinal, arch-like behavior, as displayed in **Figure 5**. Layer three (*L3*) contains a combination of pectin and bio-cement in its horizontal lines. The center of the construct is expected to achieve maximal folding in longitudinal and transversal directions, so its material composition is kept as flexible as possible. *L3* also contains vertical bio-cement extrusions, with a pressure gradient for differential rigidity from the extremes towards the center.

Differential extrusion thickness is achieved by incrementally varying air pressure from 40 to 80 PSI through a 1 mm nozzle. Qualitative observations on the behavior of the fully cured, large-scale construct, displayed in **Figure 5**, confirm the capacity for flexibility and rigidity templating enabled by our multi-material system in the WDFP.

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