



Magnetic Freeze Casting Inspired by Nature

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Bioinspired Materials are synthetic materials that mimic one or more aspects of the design, function, or properties of natural biological materials. Many structural biological materials, such as abalone nacre and bone (below), have evolved exceptional mechanical properties, a product of their intricate microstructural organization (right).

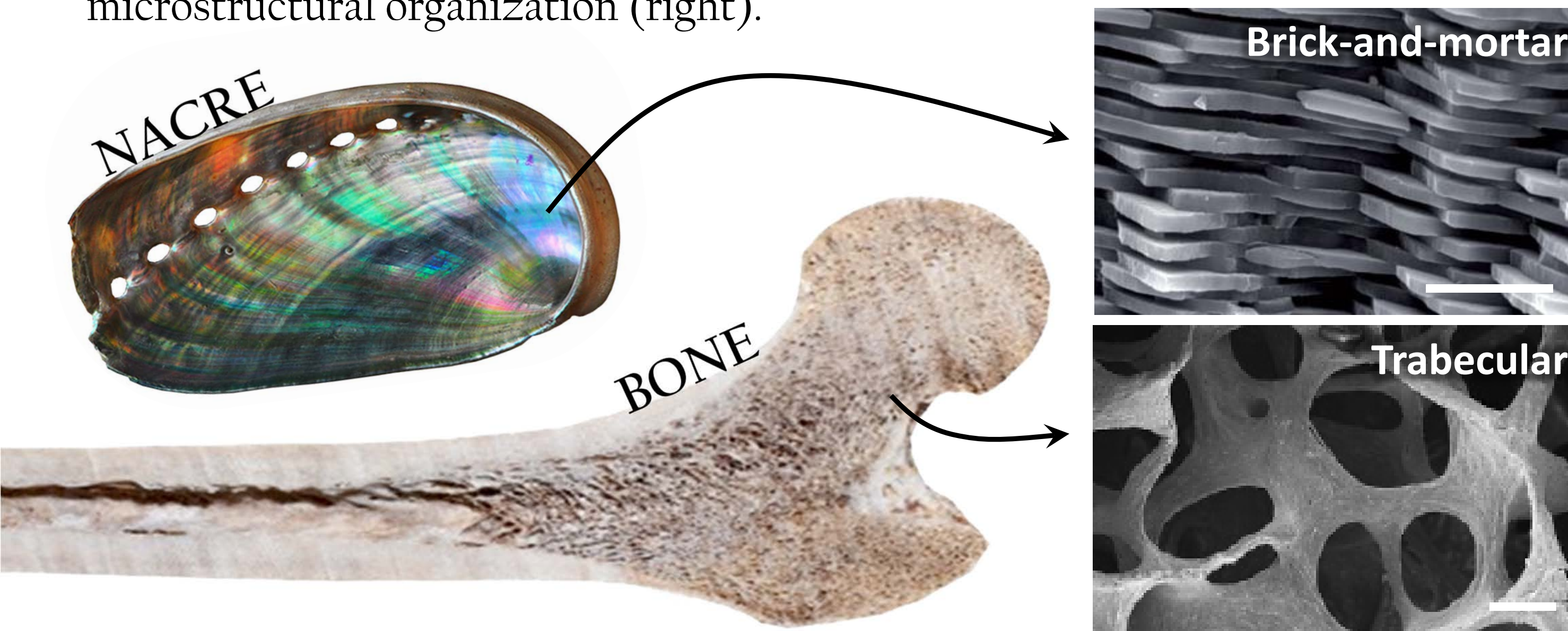


Fig. 1. Images of abalone nacre and bone. The scale bars are 5 μm (top) and 250 μm (bottom).

Freeze Casting is a convenient materials processing route to form ceramic scaffolds with controllable microstructures that mimic nacre and bone. It is a physical process in which a liquid slurry, composed of ceramic particles dispersed in a solvent (e.g., water), is directionally frozen, then lyophilized to remove the frozen solvent, and sintered to partially densify and strengthen the porous constructs (right). During freezing, the ceramic particles are pushed between and trapped within the growing lamellar ice crystals. After lyophilization, the resulting pores are direct replicas of the frozen ice crystals. Intricate microstructural features, such as the pore morphology, wall thickness, surface roughness and inter-lamellar bridging, can be controlled by altering the slurry properties or freezing conditions (below). An inherent drawback of conventional freeze-cast scaffolds is their lack of strength and stiffness transverse to the direction of ice growth. The innovation of magnetic field aligned freeze casting allows microstructural features to be aligned in multiple directions, enhancing the mechanical properties of freeze-cast scaffolds transverse to the ice growth direction.

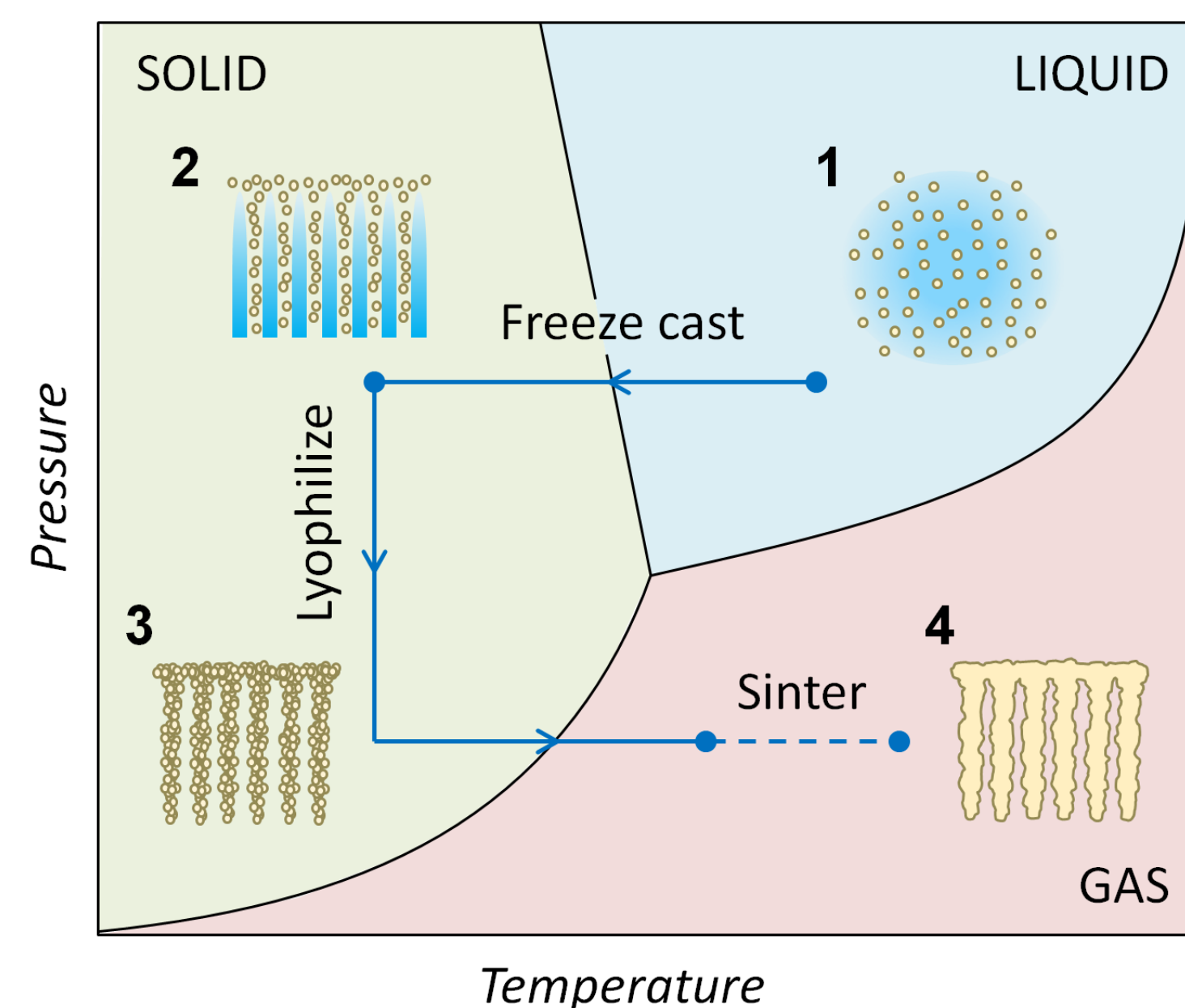


Fig. 2. Phase diagram of water showing the path of processing steps involved in freeze casting ceramics: (1) slurry preparation and mixing; (2) freeze casting; (3) lyophilizing; (4) sintering.

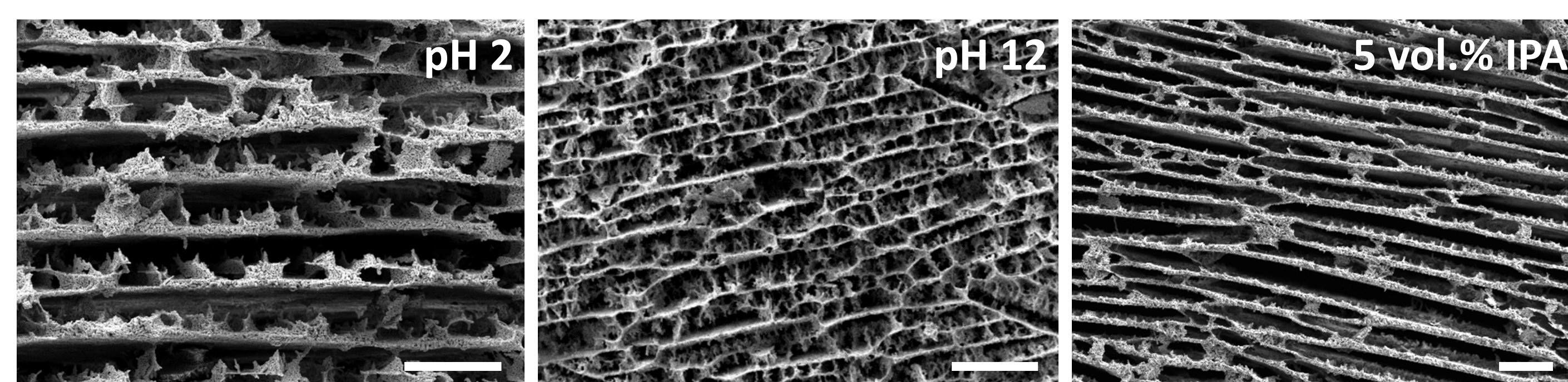


Fig. 3. Scanning electron micrographs of TiO₂ scaffolds (-85% porosity) freeze cast in different conditions: (Left) Acidic solution adjusted with HCl (pH 2); (Middle) Basic solution adjusted with NaOH (pH 12); (Right) Isopropanol solution (5 vol.% IPA). The scale bars are 100 μm.



Spiraling Ceramics

(right) that mimic the spiraling structure of the narwhal tusk (above) were fabricated by the innovation of magnetic field aligned freeze casting.

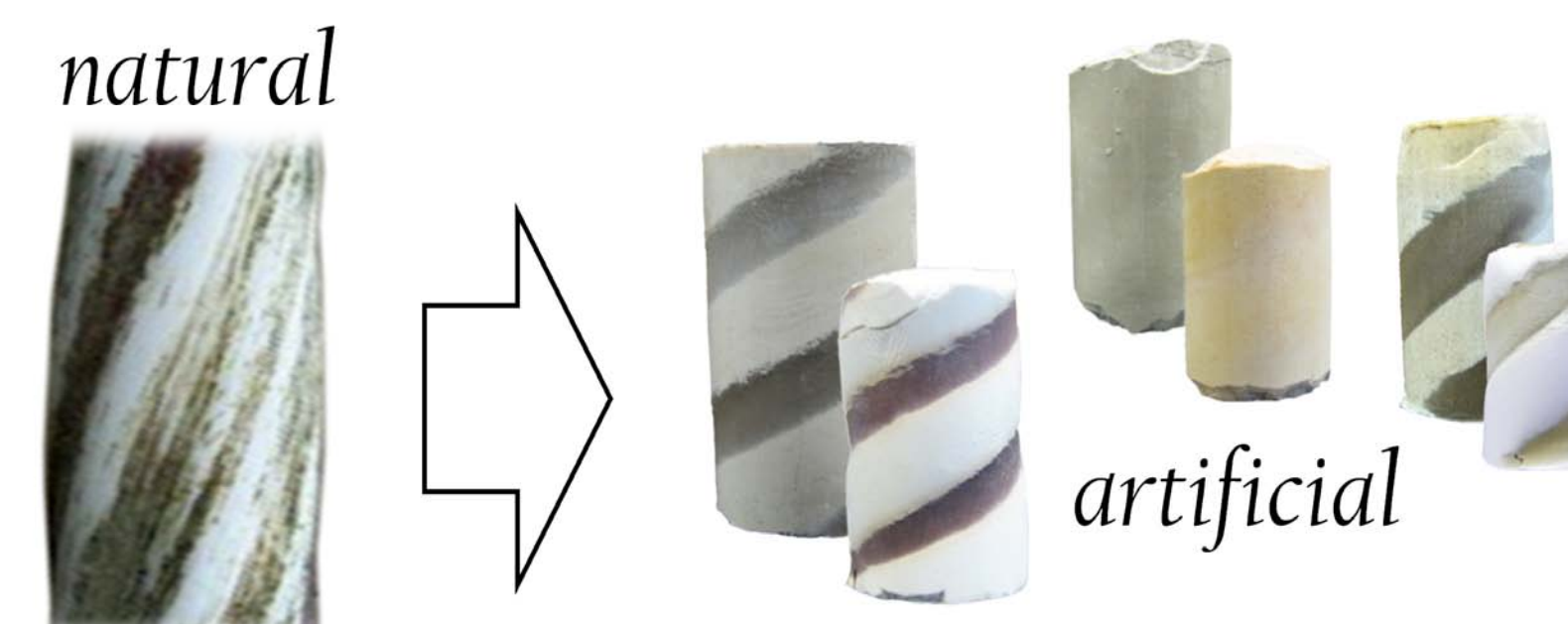


Fig. 4. (Top) Image of a narwhal tusk showing its spiraling structure. (Middle, right) Images of a natural spiraling narwhal tusk and artificial spiraling ceramic scaffolds. (Bottom) Images of several male narwhals.

Magnetic Field Aligned Freeze Casting

is a novel method to fabricate porous, anisotropic ceramic scaffolds with a hierarchy of architectural alignment in multiple directions. A weak rotating magnetic field applied normal to the ice growth direction in a uniaxial freeze apparatus (below) allowed the manipulation of magnetic nanoparticles (Fe₃O₄) to create composite ceramic scaffolds with different pore morphologies aligned in multiple directions: (1) ice growth direction; (2) magnetic flux path.

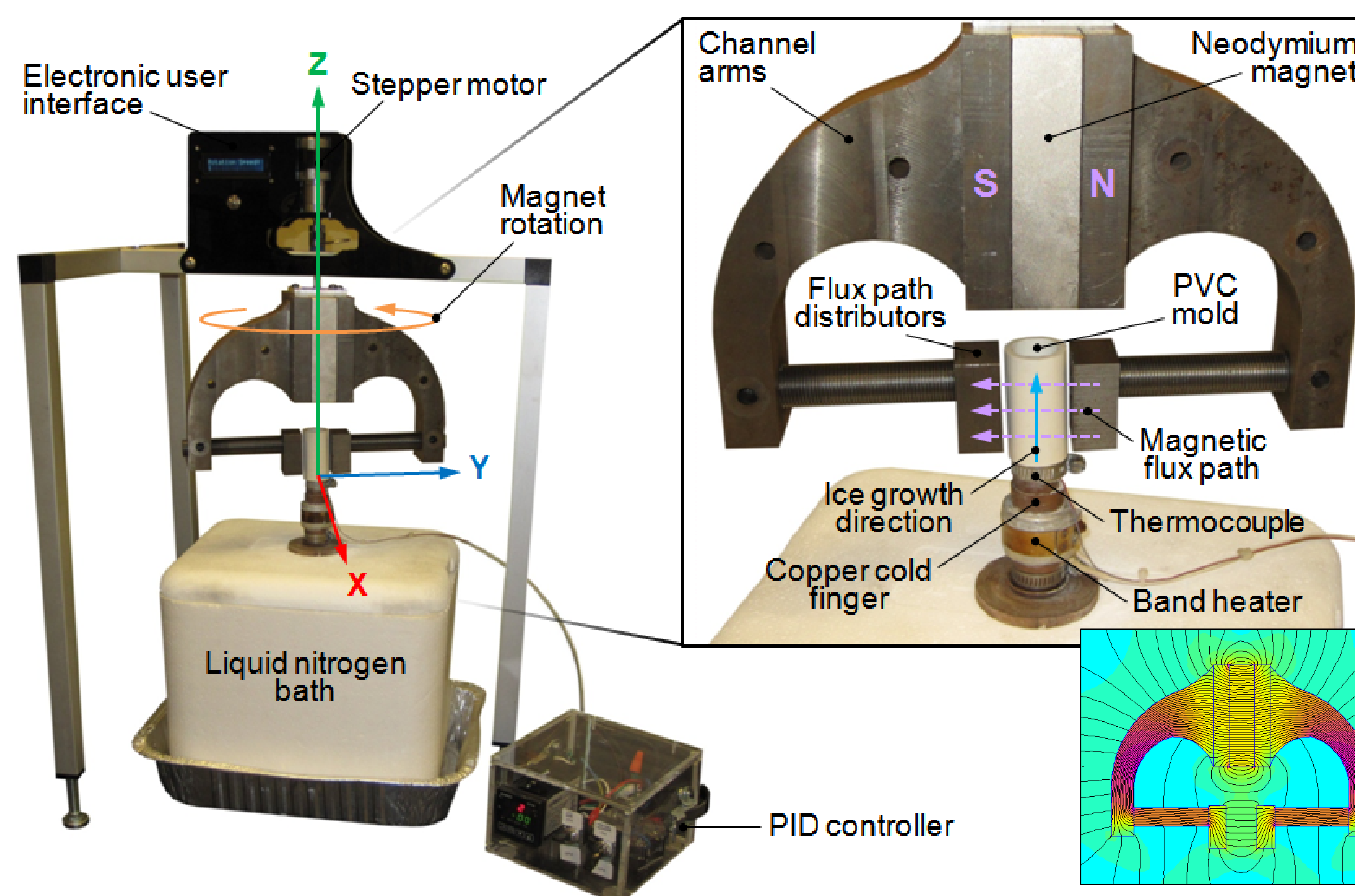


Fig. 5. Image of the magnetic freeze casting setup, illustrating the magnet rotation, ice growth and magnetic flux path directions. Inset (bottom, right): finite element model showing the magnetic flux path and density distributions through the permanent magnet apparatus.

Microstructural Alignment and biphasic material properties induced by magnetic fields are controlled by changing the field strength, orientation and rotation speed. Different nonmagnetic host ceramics (e.g., TiO₂ or ZrO₂) show varying structural alignment and separation of phases (below).

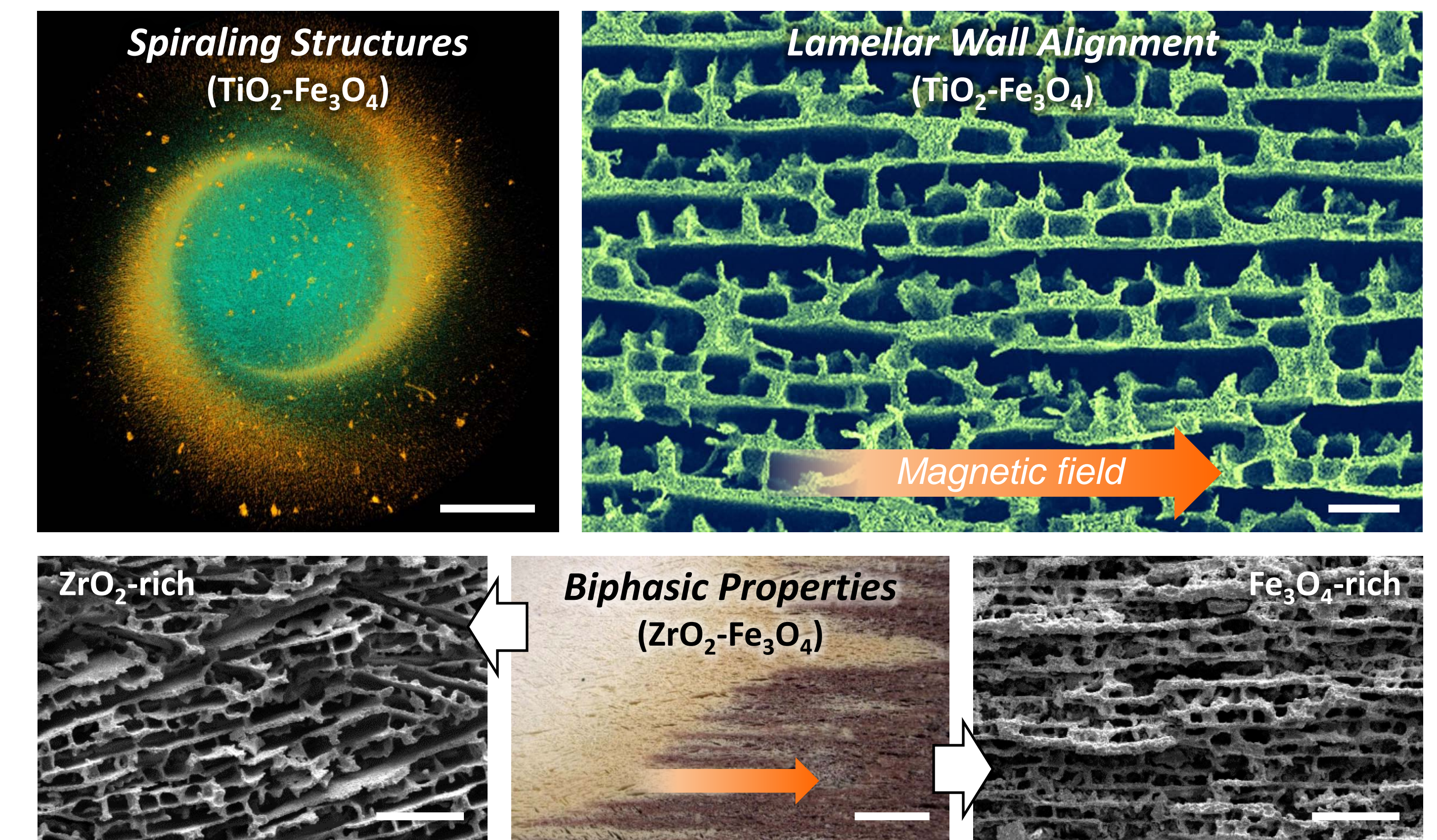


Fig. 6. (Top, left) Micro-computed tomography image of a TiO₂-Fe₃O₄ scaffold created by the alignment of Fe₃O₄ nanoparticles to a rotating magnetic field (0.12 T, 0.05 rpm). The Ti- and Fe-rich phases appear cyan and orange, respectively. (Top, right) Scanning electron microscopy image of a TiO₂-Fe₃O₄ scaffold showing the alignment of lamellar walls to a static magnetic field (0.12 T). (Bottom) Images of a ZrO₂-Fe₃O₄ scaffold with biphasic material properties caused by the separation Fe₃O₄ (left) and ZrO₂ (right) particles by a static magnetic field (0.12 T). For all images, the ice growth direction is out of the page. The scale bars are 4 mm (top, left), 25 μm (top, right), 500 μm (bottom, middle), and 50 μm (bottom, left and right).

Enhanced Mechanical Performance is a product of the microstructural alignment of lamellar walls parallel to the magnetic field and ice growth. In the magnetic field direction, the compressive strength and stiffness of the TiO₂-Fe₃O₄ scaffolds is more than doubled (below).

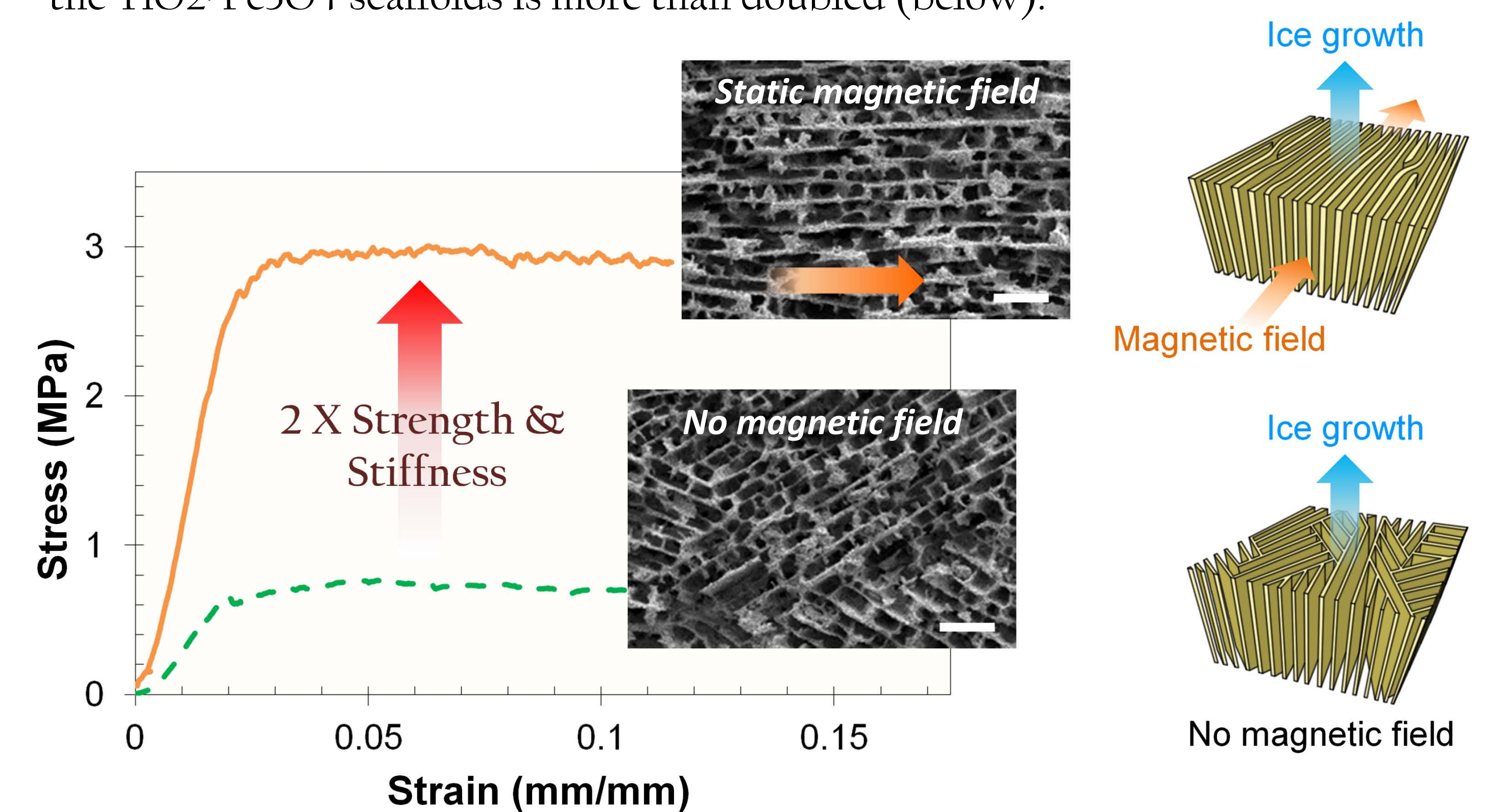


Fig. 7. (Left) Stress-strain curves comparing TiO₂-Fe₃O₄ scaffolds made with a static magnetic field and no magnetic field. (Right) Schematics of the lamellar wall alignment. The scale bars are 50 μm.

Further reading:

Porter M.M., McKittrick J., Meyers M.A. (2013). 'Biomimetic Materials by Freeze Casting.' *JOM*. (in press) <http://dx.doi.org/10.1007/s11837-013-0606-3>
 Porter M.M., Yeh M., Strawson J., Goehring T., Lujan S., Siripasopon P., Meyers M.A., McKittrick J. (2012). 'Magnetic freeze casting inspired by nature.' *Materials Science and Engineering: A*. 556: 741-750. <http://dx.doi.org/10.1016/j.msea.2012.07.058>