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## The many lives of calcium carbonate

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Standfirst

Fiona C. Meldrum and Helmut Cölfen chalk up some of the myriad forms and uses of calcium carbonate to burnish a 'dull' reputation.

For those working with materials that are magnetic, superconducting, heat-resistant or that may even glow in the dark, the mention of calcium carbonate seldom elicits much excitement. Yet, it is one of the most abundant minerals on earth (constituting 4% of the earth's crust), and is encountered every day, for example as limestone, seashells, the base material of medicinal tablets, limescale in boilers, and glossy paper coatings. With its low cost, low toxicity and mild basicity calcium carbonate is of huge industrial importance. It can be ground up and used as fillers in plastics and paints, to increase the heat resistance and durability of plastics, or as a component of agricultural lime and animal feeds. Where more sophisticated properties are required – such as in the production of high gloss papers – calcium carbonate must be reprecipitated from solution. This process enables control over the size and shape of the crystals and requires an understanding of crystal nucleation and growth mechanisms.

Fortuitously, calcium carbonate is the favourite lab-rat for those of us interested in crystallisation processes. In contrast to most inorganic compounds whose polymorphs are specific to the reaction conditions, all three anhydrous polymorphs of calcium carbonate can form in a single reaction solution. This affords a unique opportunity to learn about polymorph control, an important skill in crystallisation. Calcite, the thermodynamically stable polymorph under ambient conditions, also forms as large crystals that cleave to expose pristine, planar surfaces (pictured). Much of our current understanding of crystal growth mechanisms has therefore come from *in situ* atomic force microscopy studies of calcite growth, which ideally requires planar surfaces.<sup>1</sup>

That invertebrates use calcium carbonate as their biomineral-of-choice has provided a wealth of knowledge about its formation and properties. Under biological control, the brittle, rhombohedral calcite single crystals generated in the lab become tough, fracture-resistant materials with complex, sponge-like morphologies and curved surfaces as found in sea urchin spines. These morphologies challenge our preconceptions about crystalline materials, but once shown what is possible, we often find that these biogenic strategies can be readily translated to synthetic systems. Calcite single crystals with non-crystallographic morphologies are easily formed by growing crystals within mould templates,<sup>2</sup> and toughness can be readily enhanced by co-precipitating calcite crystals with organic additives that become incorporated within the crystal lattice.<sup>3</sup> Biomineralisation studies, in which amorphous calcium carbonate (ACC) was observed to be a precursor to calcite in sea urchin embryos<sup>4</sup>, have inspired decades of research into the formation, structure and transformation of this ubiquitous phase. Biomineralization also offers one of the ultimate examples of polymorph control, as exemplified by molluscs that can switch between calcite and the metastable polymorph aragonite with perfect fidelity.<sup>5</sup>

Despite its diversity of form and function, there are situations where calcium carbonate can be a curse. Its decarbonisation during the production of cement – which is the compound most-used by

humanity after water – leads to massive CO<sub>2</sub> emissions.<sup>8</sup> And as a principal component of the limescale formed when water is heated, calcium carbonate causes huge damage and decreases the efficiency of many industrial and domestic processes. Although chemical inhibitors exist, they cannot fully prevent mescale formation.<sup>9</sup> Non-chemical treatments have therefore been explored, where the first US patent for an electromagnetic field (EMF) water-treatment device was issued as far back as 1873.<sup>10</sup>

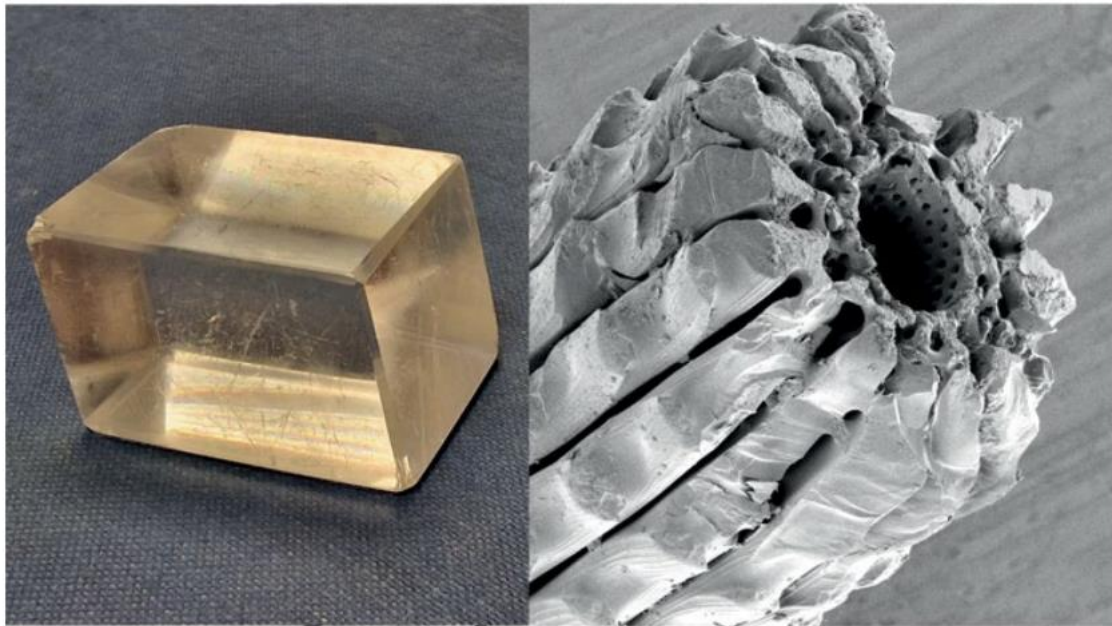
However, the advantages of calcium carbonate massively outweigh the disadvantages. This is exemplified by the potential role of calcium carbonate in building a sustainable future. Self-healing concrete incorporates CaCO<sub>3</sub>-producing bacterial spores, along with appropriate nutrients, which lie dormant until cracks form. Their exposure to water and air triggers the formation of calcium carbonate, which closes the crack and increases the lifetime of the building.<sup>6</sup> Climate change is one of the greatest challenges currently facing humanity, with anthropogenic carbon dioxide being the principal cause of rising temperatures. As the most abundant carbonate mineral, calcium carbonate is already a significant carbon sink, and is being explored as a means of storing CO<sub>2</sub>. For example, flue gas containing CO<sub>2</sub> can be reacted with solid high-calcium industrial waste to generate a calcium carbonate cement.<sup>7</sup>

So, is it justified to describe calcium carbonate as dull? Absolutely not! Despite the periodic table encompassing over 90 metals, no other compound is quite the same.

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**Figure.** The many faces of calcium carbonate. Left: single crystal of geological calcite. Right: cross-section through a sea urchin spine, which is also a single crystal of calcite