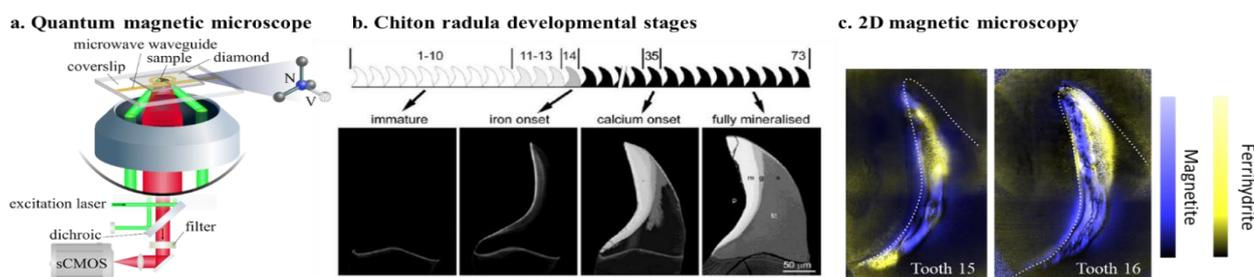


Quantum Magnetic Microscopy: A new view on iron-based biomineralisation

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Magnetic imaging technology is generally characterized by spatial and temporal resolution; but criteria such as sensitivity, field disturbance, sample damage, field of view, cost, and ease of use, are critical for broad applicability, which ultimately drives the future development of our understanding of magnetism in advanced materials and applications. Electron and X-ray magnetic microscopy techniques can provide high spatial resolution down to a few nanometres, but are time-consuming, and require expensive and complex apparatus, careful sample preparation often requiring dehydration, and a high vacuum environment. Magnetic force microscopy is commonly used to characterise magnetic materials, but is inherently slow and not suited to imaging fragile magnetisation states due to its invasive magnetic tip. Magneto-optical Kerr Effect microscopy, on the other hand, is non-invasive, but requires materials that exhibit a strong Kerr response, which severely restricts its application in biology. Here we introduce a new magnetic microscopy platform, quantum magnetic microscopy (QMM) that exploits atomic sized defect centres in diamond for nanoscale magnetic sensing and imaging. By engineering 2D near surface arrays of nitrogen-vacancy (NV) centres into diamond, we have demonstrated how this technology can be applied to image the ferromagnetic¹, paramagnetic² and superparamagnetic³ properties of nanoscale materials. In this work, we apply this technology to elucidate the principles governing controlled iron nucleation and mineralisation in an important biological system, see Fig.1.



Chitons, a specialised class of marine mollusc, are known to mineralise their own teeth under ambient conditions by sequestering iron from their surroundings, and directing its assembly into biogenic magnetite. Importantly, studies have shown that this form of magnetite is the hardest biomineral reported to date⁴. This system therefore provides a unique opportunity to understand the biological design principles behind lightweight, durable, wear-resistant magnetic materials. Hence, the chiton system has attracted considerable interest and has been studied through many conventional imaging approaches. Electron microscopy^{5, 6} and atomic probe tomography⁷ are two stand out examples of techniques that can capture species-specific information with nanoscale spatial resolution. Unfortunately, the field of view of these types of systems is limited to hundreds of nm², preventing large scale mapping of the entire tooth section. Moreover, significant time and money is spent/lost with these techniques searching for regions of interest where mineral phase transformation is occurring, making for a 'needle-in-a-hay-stack' problem. X-ray fluorescence, on the other hand, provides elemental mapping capabilities over wide fields of view using synchrotron irradiation, however this approach suffers from poor spatial resolution (typically 2-5µm) and limited specificity in terms of the iron oxide species. In this work, we demonstrate how QMM can be used to map the distribution of ferrihydrite and magnetite within thin histological slices of chiton teeth with diffraction limited spatial resolution of 300 nm at fields of view that cover the entire tooth. The magnetic images enable rapid identification of regions of magnetic phase transformations within the tooth; and since the magnetic imaging technique is optical and non-destructive, these maps can be correlated back to the overall tooth structure. We will discuss how this technology can be applied more generally in the field of biology to characterise and monitor magnetic signals.

Figure 1: Quantum magnetic microscopy (QMM). a, Schematic of the QMM setup. b, chiton radula describing the various stages of mineralisation. c, Spatial mapping of magnetite (blue) and ferrihydrite (yellow) regions of partially mineralised chiton teeth #15 and #16 from *A. hirtosa*.

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