Combining raster-scanning XRF and XRD with DFXM for the study of biominerals

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Biominerals are hierarchical materials found throughout nature in which a combination of inorganic mineral and organic template form a highly-ordered structure in both crystallography and habit [1, 2]. This control has evolved to produce materials whose properties are optimised for particular functions. One example is fish otoliths, which are calcified growths from the inner ear of Teleost fish. Otoliths are deposited in sequential layers over the fish's entire lifetime and are not resorbed, making them a biological archive of the individual's life history. They are composed of calcium carbonate, typically in the aragonite polymorph, arranged in prisms whose long axis is aligned with the growth axis, pointing from the centre toward the outside. These prisms are described in literature as continuous, and optical and SEM imagery support this description [3]. The optical appearance of the otolith typically alternates along the growth axis between translucent and opaque; opaque zones represent fast growth during summer periods while translucent zones represent slower winter growth.

The present work illustrates the combination of online complementary techniques combined with DFXM to study fish otoliths from the millimetric full-object scale to the sub-micrometric. Using a set of compound refractive lenses, the incident beam was focused to 5x5 μm^2 at the sample. This spot was raster scanned with simultaneous XRD and XRF data collection to produce maps of the macroscopic samples. These maps guided the selection of locations for DFXM analysis. A correlation of otolith opacity crystal domain size was observed. Elemental content shows partial correlation. The observed larger crystal domains during winter growth is consistent with a lower rate of crystallization. Some prisms in the winter growth were examined in detail by DFXM, which revealed the daily growth marks. It was not possible to examine summer growth by DFXM due to the small domain size.

The ability of DFXM to probe the crystallographic properties of bulk biominerals with high resolution shows promise to reveal new aspects of biomineralization. The flexibility of the DFXM bench allowed the incorporation of on-line complementary techniques to improve both the quality and breadth of data collected.

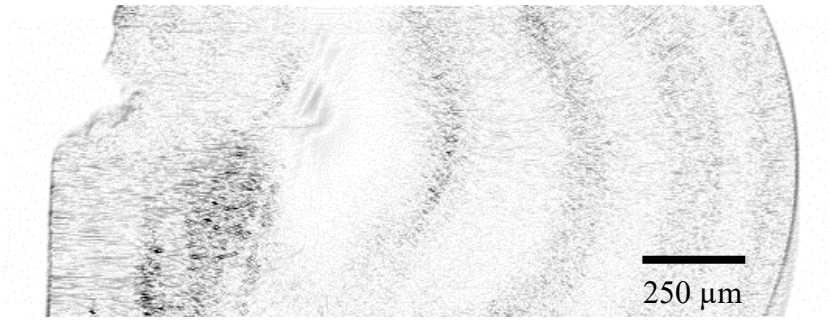

Figure 1: The standard deviation of the XRD pattern in a 2x2 pixel area illustrates the heterogeneity of crystal sizes. Low SD (white) indicates smaller crystal domains.

References

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