

## **Spectroscopic characterization of sodium uptake in fish otoliths**

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Otoliths develop incrementally and are inert. Their elemental composition can vary throughout life due to extrinsic (environmental) and intrinsic (biological) factors. Elements can be incorporated into the otolith through three proposed methods: 1) substitution for Ca during crystallization, 2) becoming trapped in the crystal lattice, or 3) being bound to the organic matrix. Na is a typical, highly regulated component of otoliths, that has been proposed to be incorporated through the second method and resides in the interstitial spaces in the crystal lattice. The substitution of Ca<sup>2+</sup> by Na<sup>+</sup> would however result in a charge imbalance, which would either require a coupled substitution involving a trivalent ion, the protonation of a carbonyl-group, or the formation of a phase, structurally distinguished from the aragonite structure. To better understand the mode of Na incorporation into otoliths, we investigated its chemical distribution at the atomic- and nanoscale using Transmission Electron Microscopy (TEM) and Atom Probe Tomography (APT). For this purpose, lapilli otoliths from freshwater catfish were analysed from the Red River, Manitoba, Canada. Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) line scans were used to identify areas with sodium concentrations in the ppm range. These areas, with an average value of 2600 ppm, occurred closer to the nucleus of the otolith. Next, an ion mill section was extracted and thinned to electron transparency for subsequent TEM examinations. The latter studies revealed that Na is clustered in discrete nano-size domains within the aragonite matrix of the otolith. To confirm the occurrence of Na clusters and to visualize them three-dimensionally, samples were prepared with a Focused Ion Beam (FIB) and analysed subsequently with APT. Contrary to TEM, APT can not only resolve the distribution of Na but also that of the organic material within the otolith. In this regard, the APT studies confirmed the occurrence of Na clusters but also indicated that these occur in the organic material and in the mineralized crystal structure. These results suggest that the charge balance problem is mitigated through clustering Na in nanosize domains throughout the organic and inorganic areas of the otolith.