Paleoproteomics of fossil fish otoliths

The paleoproteomics is an emerging interdisciplinary field that draws from chemistry, molecular biology as much as paleontology and archaeology. Paleoproteomics is a study of ancient proteins that only rarely can be found embedded in biomineral structures (such as shells, tests, bones) of various organisms. Proteins have always been considered very prone to decomposition and thus unlikely to survive as high molecular mass components during secondary alteration (diagenesis). Time, temperature, burial environment and the biogeochemical composition of the skeleton may all influence how quickly proteins decay in fossils. Quite surprisingly, there is growing evidence of preservation of proteinaceous material in diverse fossils: the proteins stabilized by strong binding to the surface of the biomineral crystals were shown to be preserved in ca. 3.8 Ma eggshells or ca. 125-138 ka scleractinian coral skeletons. To date, the occurrence of protein residues in fossil otoliths was completely unexplored. Otoliths are biomineral structures with a calcium carbonate mineral phase growing through the lifetime of teleost fish and which form a part of the stato-acoustical organ, responsible the ability to hear and the sense of equilibrium. Otoliths are frequently found in the fossil record, including in the Mesozoic but are especially common in Cenozoic strata, and serve to interpret palaeobiodiversity of fish due to unique taxonomy-related morphology and in palaeoenvironmental interpretations owing to preservation of various isotope and geochemical environmental proxies in their mineral phase. Several proteins that play a role during biomineralization have been identified in modern fish otoliths. In our preliminary study (related to the previous project) we have isolated and identified a dozen or so proteins in Miocene otoliths (about 14 million years) whose structural and crystallographic features suggested pristine preservation. This discovery created an opportunity for groundbreaking research in three areas proposed in this project: (1) comparative studies of the sequences of modern and fossil proteins to determine possible evolutionary changes, (2) biomineralization function of the fossil proteins carried out in direct comparison with biomineralization activity of possibly homologous proteins isolated from most closely related modern fish, (3) comparative studies of the influence of fossil and experimentally altered proteins on calcium carbonate mineralization in different environmental conditions; this research is aimed at determining the possible influence of such proteins on characteristics of secondary precipitated minerals (tested hypothesis of the project). All three aspects of the proposed project are completely novel and are elaborated as the main research tasks of the project. The outcome of the project will open a new avenue for paleoproteomic research in paleontology and will significantly increase our knowledge about involvement of proteins in biomineralization and diagenetic processes.