



Chemical ghosts: Imaging geochemical-palaeobiological interactions throughout Earth history.

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Quantitative chemical analyses are rarely undertaken on fossil remains, despite the potentially valuable information that can be recovered on key geochemical-palaeobiological interactions. Trace metal biomarkers have shown that discrete elemental inventories can be identified and mapped in fossil organisms that correlate to specific anatomical structures and biosynthetic pathways. Infra-red mapping (FTIR) of organic functional groups also helps verify the identification of organometallic compounds that map within discrete biological structures. Additionally, Pyrolysis Gas Chromatography Mass Spectrometry (Py-GCMS) and Matrix Assisted Laser Desorption/Ionization (MALDI) mass spectrometry can further constrain the macromolecular composition and endogeneity of samples being mapped. Such elemental inventories and macromolecular data provides unique insight to specific biologic processes. Ideally such analyses measure and map the chemistry of tissue structures (shell, bone, tendon, skin, feather and other soft tissue) and most importantly the embedding rock matrix. Mapping fossils in situ helps place constraints on mass transfer between the embedding matrix (environment) and fossil (organism), aiding in distinguishing chemotaphonomic processes from original chemical zonation remnant from the organism itself. Conventional non-destructive analytical methods face serious problems in this case and most recent technological advances have been targeted at developing nanometer-scale rather than decimeter-scale capabilities. However, the development of Synchrotron Rapid Scanning X-ray Fluorescence (SRS-XRF) at the Stanford Synchrotron permits large specimens to be non-destructively analyzed (1-100 μm resolution) and imaged using major, minor and trace element concentrations. Fossil and extant samples are mounted in a purpose-built sample chamber held on a computerized x-y-z translational stage. For light-element XRF imaging, an X-ray-transparent $\sim 30\text{-}\mu\text{m}$ thick polyethylene film was placed on the sample chamber, and purged of air with He to minimize scattering and increase signal to the detector. X-ray Absorption Spectroscopy (XAS) constrains oxidation state and coordination chemistry of key elements (S, Ca, Cu, Zn, Sr, etc.), providing significant insight to the endogeneity of chemistry mapped to PPM sensitivity. The combination of precise, repeatable and quantitative techniques builds upon decades of research at synchrotron and lab-based facilities, shedding new light on the chemistry, taphonomy and evolution of life.