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Quantifying trace element uptake in megafaunal avian eggshells

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Megafaunal avian eggshells are effective for both paleoclimate and chronological reconstruction in the archaeological and fossil records due to 1) a stable low-Mg calcite composition suitable for light stable isotope- and dating methods, 2) common occurrence in terrestrial sequences, and 3) useful paleoenvironmental proxy records [1]. Recent work has shown eggshells can be an accurate uranium-thorium (U-Th) dating material and possibly a provenience tool via strontium (Sr) isotopes [2, 3], and other trace-elemental proxies are under development. Since trace-elements may be incorporated from primary and/or secondary processes, we aim to evaluate the mechanisms and rates of secondary elemental uptake in avian eggshells. *In vivo* experiments immerse modern ostrich and emu eggshell fragments into sediment mixtures saturated with pH-neutral solutions containing ~5 ppm of 17 elements to mimic "soils" hosting pore waters with a dissolved leachate. Measurements of pristine eggshell fragments provide a baseline for elemental compositions after immersion in the solution-saturated "soils". Eggshell fragments are sequentially removed from the enriched solutions at known intervals since immersion and measured by laser ablation (LA) inductively coupled plasma mass spectrometry (ICP-MS) to characterize the spatial patterns of newly acquired elements. Elemental patterns show incorporation of U very shortly after deposition into the "soil", on the order of months, while Th is not detectable. This provides a valuable validation of the assumption that U uptake is rapid and Th in ancient eggshells is primarily due to radiogenic ingrowth, with minimal unsupported Th. Other elements record the primary composition of the modern un-immersed eggshell (e.g., Sr) and can be added secondarily during immersion, indicating their measurement in ancient samples represents a mixture of primary and secondary signals. Some elements closely track eggshell microstructures and patterns may be explained by diffusive uptake. For these elements, we determine diffusivity constants and compare to other studies of trace elements in biominerals.

[1] Niespolo et al. (2020) QSR 230, 106142; [2] Sharp et al. (2019) QSR 219, 263-276; [3] Stewart et al. (2020) PNAS 117, 6453-6462