ECHINODERM STABILIZATION ASSOCIATED WITH A PALEOKARST SURFACE AT THE MISSIPPIAN--PENNSYLVANIAN BOUNDARY IN TENNESSEE, U.S.A.

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ABSTRACT: Pennington Formation limestone deposits in Tennessee immediately underlie a paleokarst surface that straddles the Mississippian--Pennsylvanian unconformity. Vertic paleosols with significant gleying and coal seams overlie the paleokarst surface. This study quantifies the Fe loss associated with paleosol gleying and subsequent incorporation of Fe into echinoderm grains that underwent stabilization. Echinoderm grains immediately below the paleokarst surface have lower Mg and $\delta^{13}C$ values and higher Fe concentrations compared to echinoderm grains meters below the paleokarst surface. Additionally, echinoderm grains have variable $\delta^{13}C$ and invariant $\delta^{18}O$ values characteristic of alteration in a meteoric setting. Paleosols draping the paleokarst surface, and coal seams that were deposited immediately above the Mississippian--Pennsylvanian unconformity, provided ample organic matter that could have driven heterotrophic microbial activity. Additionally, the paleosols were an ample source of oxidized Fe that could have been used as a terminal electron acceptor by an anaerobic microbial community. Therefore, we suggest that Fe reduction transferred Fe from the paleosol to the limestone during meteoric stabilization of echinoderm grains. Fluid--rock modeling constrains the magnitude of Fe transfer that occurred during echinoderm stabilization. Stabilization can account for only a fraction (8 to 14%) of the total quantity of Fe lost from the gleyed paleosol, thus supporting the premise of continued transfer of Fe from the paleosol to limestone during burial diagenesis. Additionally, this study constrains the timescale associated with echinoderm stabilization, which was likely $\leq$ 12 ky. Finally, stabilization timescale is consistent with echinoderm alteration associated with organic diagenetic conditions, with elevated dissolved inorganic carbon in stabilizing pore fluids that were localized immediately below the paleokarst surface.