Chitinozoan contributions to unraveling the origin of rare earth element-enriched Upper Ordovician phosphorites in the eastern U.S.

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Abstract

The Upper Ordovician Maquoketa Group and equivalents in the eastern U.S. contain at least two major rare earth element (REE)-enriched phosphorite packages, the total endowment of each dwarfing currently mined REE resources. Our multiyear effort to unravel the complex history of these phosphorites is providing new insights, including illumination of the sequence of events that led to the multi-phased Late Ordovician mass extinction. We have utilized an integrated biochemostratigraphic approach to study an extensive number of surface and subsurface sections. Remarkably, the Upper Ordovician has yielded exceptionally well-preserved chitinozoan assemblages across the region. The linchpin section that reduces uncertainty about temporal correlation of the Upper Ordovician Appalachians and Cincinnati Arch in the east with those of the Midcontinent in the west is a continuous core drilled at Fort Wayne, Indiana, referred to as F688.

The Upper Ordovician succession in the F688 core consists of a mixture of shallow- and deep-water facies containing abundant and well-preserved zonally important taxa and displays diagnostic chemostratigraphic patterns. The Maquoketa Group in the core is 210 meters thick and spans several lithofacies that are assigned to five lithostratigraphic units (Kope, Waynesville, Liberty, Whitewater, and "Fort Atkinson" formations). Detailed benchtop examination of the core revealed multiple phosphatic intervals, rich brachiopod faunas, and multiple graptolitic horizons. Elemental analysis of the entire Maquoketa Group, using portable X-ray fluorescence, was conducted at 60 cm intervals and powders drilled from the same horizons for carbonate carbon isotope data have revealed the positions of the Kope, Waynesville, and Elkhorn δ13Ccarb excursions. The Fairview δ13Ccarb Excursion is absent from the F688 core, suggesting that part of the Maysvillian (and perhaps the uppermost Edenian) sedimentary record is missing. Twenty samples were digested in buffered formic acid yielding abundant, well-preserved, low-diversity conodont assemblages that clearly demarcate the position of the Ordovician-Silurian boundary within the core. Laboratory study of more than fifty palynological samples targeted graptolitic intervals and produced important new insights

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The chitinozoan assemblage in F688 is well-preserved, rich, and stratigraphically varied. The lower Katian Kope Formation contains *e.g. Belonechitina kjellstromi*, *Hercochitina downiei*, and *Clathrochitina* sp. nov., and the top of the unit can be calibrated with a graptolite assemblage suggestive of the *Geniculograptus pygmaeus* Zone (upper Edenian and lower Maysvillian regional stages; approximately uppermost lower Katian, upper Ka1 Stage Slice). Samples from the overlying Waynesville Formation have produced graptolites indicative of the upper *pygmaeus* to *Paraorthograptus manitoulinensis* zones (upper Maysvillian and lower Richmondian regional stages; middle Katian, Ka2 and Ka3 stage slices). Chitinozoans from the Waynesville Formation include long-ranging species such as *Belonechitina micracantha* and *Plectochitina spongiosa*, together with several new species of the genera *Tanuchitina* and *Hercochitina*. Higher in the core, the Liberty, Whitewater, and "Fort Atkinson" formations yielded chitinozoan species characteristic of the upper Katian biozones of Anticosti Island (Canada) and Nevada (USA), such as *Tanuchitina anticostiensis, Hercochitina longi,* and *Eisenackitina ripae*. The Brassfield Formation (Silurian) overlies the "Fort Atkinson" Formation in the F688 core and here we infer a substantial stratigraphic gap that comprises at least all the Hirnantian Stage and likely the uppermost part of the Katian Stage.
The combination of these complementary methods has produced a high-resolution chronostratigraphic record for the Upper Ordovician succession in the F688 core. Not only is this suite of data from a pivotal locality in our emerging Upper Ordovician chronostratigraphic synthesis of the eastern U.S., but these results also highlight the promise of chitinozoan biostratigraphy to refine temporal correlations within Laurentia. Our integrated approach is yielding chronostratigraphic context for Maquoketa Group REE-enriched phosphate deposits allowing us to disentangle the signatures of the cryptic oceanic anoxic events from which they originated.

Keywords: Integrated stratigraphy, Palynology, Graptolites, Conodonts, Stable Carbon Isotopes, REE