## EXTRACTION OF FOSSIL MICROMETEORITES FROM TERRESTRIAL ROCKS

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**Introduction:** The Earth experienced three major extinctions during the Paleozoic Era, usually related to rapid and sudden climate changes that were caused by one or both internal and external events such as plate tectonics, large volcanic eruptions, changes in the Earth's orbit, and/or asteroid impacts [1]. Indeed, the Devonian–Carboniferous boundary is characterized by a record of widespread oceanic anoxia, which coincided with massive marine biodiversity losses. Astronomical insolation changes, linked to Earth's eccentricity, may have played a role in the increase of ocean anoxia and other environmental perturbations [2].

The flux of extraterrestrial material to the Earth does not appear to have been constant over time. Discrete events in the solar system may have led to increases in the flux of asteroids, meteorites, and micrometeorites with time. While most of this material weathers away quickly under the oxidizing conditions at the Earth surface, some refractory minerals or fossil micrometeorites may resist alteration and diagenesis [3,4]. To date, various increases in the extraterrestrial influx have been identified in the geological record, based on enrichments in spinel group minerals but also I-type micrometeorites in various types of sediments [5]. However, none of these higher extraterrestrial fluxes has convincingly been linked to a mass extinction event, or changes in the eccentricity of the Earth's orbit.

Schmitz et al. [6] worked on the sedimentary records at the Frasnian–Famennian boundary, which marks another Late Devonian extinction (the Upper Kellwasser Event), searching for an increase in the extraterrestrial materials, looking for Cr-spinel as a proxy using heavy acid dissolution of the rocks. They did not find clear evidence for an increased flux of extraterrestrial Cr-spinel crystals, potentially due to insufficiently high amounts of those minerals in the rock. However, Cr-spinels are not found in all types of extraterrestrial materials, and heavy acid extraction methods could have dissolved any remaining extraterrestrial silicate-rich material, which represents an important fraction of the extraterrestrial flux. In addition, Suttle and Genge [7] reported the discovery of fossil micrometeorites, as pristine silicates, iron-type spherules and magnetite or Fe-silicate pseudomorphic spherules, from Late Cretaceous chalk. They investigated both acid dissolution and mechanical separation and discovered different results, both in abundance and type of extraterrestrial materials depending on the extraction methods.

In this study, we will compare different methods to extract fossil micrometeorites and other extraterrestrial materials from different lithologies, in order to evaluate the most effective method for the extraction of extraterrestrial materials, while trying to limit any procedural biases.

**Methods**: We collected rocks (carbonates, limestones, and shales) from around the Devonian–Carboniferous boundary that records the Hangenberg extinction event. We plan to apply various extraction methods of extraterrestrial materials on the different lithologies: (i) HCl dissolution, (ii) consecutive HCl and HF dissolution, (iii) consecutive HCl, HF and H<sub>2</sub>SO<sub>4</sub>, (iv) surfactant Rewoquat following Jarochowska et al. method [8], (v) heavy liquids separation, and (vi) mechanical disaggregation (crushing). We will examine the residue of those methods and look for extraterrestrial materials, including Cr-spinel crystals as well as whole micrometeorites (silicates, glassy, oxides and irontypes), using optical microscopy, scanning electron microscope (SEM) and micro-X-ray fluorescence (XRF).

**Discussion**: We will first discuss the comparison between the efficiency of the different acids processing, the Rewoquat processing, the heavy liquids processing and the manual separation, with the various difficulties caused by the rock compositions, and the different methodological biases arising from the differences between extraction procedures. We propose the most effective extraction methods to extract the various types of extraterrestrial material (from silicate to iron-type micrometeorites) to assess the global extraterrestrial flux, and compare our results to more conventional proxies, such as the iridium and helium-3 contents of the bulk rocks, to trace past variations in the extraterrestrial fluxes to the Earth. We also aim to determine the best extraction methods to preserve the oxidized iron-type spherules, as their oxygen isotopic compositions may contain information on their oxidation during atmospheric entry during the late Devonian. By comparison with other time intervals as well as current Antarctic and urban micrometeorite collections we aim to build a framework that will allow us to evaluate fluctuations in the extraterrestrial material influx on Earth, as well as any effects from preservation biases.

**References:** [1] Erwin D.H. (1990) Annu Rev Ecol Syst 21, 69–91; [2] Da Silva A.-C. et al. (2020) Scientific reports, 10(1), 1-12; [3] Thorslund P. and Wickman F.E. (1981) Nature 289, 285–286; [4] Meier M.M.M. et al. (2010) Earth Planet Sci Lett 290, 54–63; [5] Schmitz B. (2013) Chemie der Erde-Geochemistry 73, 117-145; [6] Schmitz B. et al. (2019) Earth Planet Sci Lett 522, 234–243; [7] Suttle M. D. & Genge M. J. (2017) Earth and Planetary Science Letters, 476, 132-142; [8] Jarochowska E et al. (2013) Palaeontologia Electronica, 16(3), 7T-16.