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Marine Nanoparticle Metal Fingerprints via sp-ICP-TOF-MS: Evidence from the Black Sea

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Recent advancements in mass spectrometry, particularly time-resolved applications of ICP-MS and the integration of time-of-flight mass spectrometers, have enabled multi-element detection within single nanoparticles (NPs). Single-particle inductively coupled plasma time-of-flight mass spectrometry (sp-ICP-TOF-MS) is a powerful tool for analyzing natural marine nanoparticles, providing quantitative data on particle numbers and multi-element compositional information. Until recently, aquatic nanoparticle detection progress has focused primarily on freshwater matrices, and there remains an urgent need for novel method development in saltwater matrices. This is critical for advancing our understanding of multi-metal fingerprints and the complex interplay of marine metal cycles

Here, we present the first results from the analysis of seawater particles (>0.40 μm) collected from the Black Sea. The samples were analyzed using an IcpTOF instrument (TOFWERK, Thun, Switzerland) with a 7% H_2/He collision gas mixture, targeting essential cofactor metals such as Fe, Mn, Mo, Cu, Ni, V, and Zn. Seawater samples were collected using an oceanographic CTD-Rosette system during fieldwork in July 2024. Particles were collected on 0.40 μm pore-size Cytiva Nuclepore hydrophilic polycarbonate membranes, stored frozen until analysis, and re-collected in Milli-Q water before measurement. Nanoparticles attached to larger particles were retrieved via sonication and homogenized with vortex mixing before being introduced to the IcpTOF in single-particle mode. The first results showed a high abundance of Mn and Fe particles with many co-occurring MnFe particles and the occasional presence of Mo, Cu, Ni, and V as a function of redox state and distance from shore. These first multi-element metal (nano)particle distribution data from the Black Sea provide a foundation for understanding the complex biogeochemical processes and contribute to reconstructing biogeochemical evolution. In addition, metal fingerprints serve as critical indicators for habitability studies beyond Earth. The application of advanced mass spectrometry to complex environmental matrices enhances our knowledge of marine metal cycles and offers comparative data outputs for investigating ocean worlds, such as those targeted by the SUDA instrument of Europa Clipper.