

Geochemistry and Re-Os age for black shales from the Cambrian-Ordovician boundary, Green Point, western Newfoundland

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Chemical and isotopic signatures for black shales can serve as proxies for reconstruction of paleoenvironmental conditions. Here we bring Rock-Eval, major and trace elements and Re-Os isotopic data together to examine the environmental record at the Cambrian-Ordovician Global Stratotype Section and Point (*GSSP*) at Green Point in western Newfoundland. The Green Point shales are oil mature and contain Type-II organic material of marine origin. A Re-Os isochron for these shales provides the first depositional age for the *GSSP* boundary at 484 ± 16 Ma (2σ ; Model 3 age; MSWD = 21; n = 13), with an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.74 ± 0.05 .

Factor analysis of the geochemical dataset for Green Point shales shows association of most trace elements with TOC and S contents, ensuring an authigenic origin for most elements and hence, their validity for evaluating paleoredox state. Relatively high enrichment factors for redox-sensitive elements (*e.g.*, Re, U and Mo) compared to average shales, but lower enrichment factors relative to modern Black sea sediments, suggest deposition in anoxic waters. Comparison of global Cambrian-Ordovician shale geochemistry datasets leads us to suggest that anoxic conditions and warm oceanic regimes were restricted to the margins of Laurentia and Baltica whereas depositional basins with colder waters (*e.g.* Avalonia and Gondwana) show geochemically less reducing conditions. These outcomes underscore the important role of paleogeography in regulating ocean conditions and marine life.

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Nanoparticle interactions with lipid bilayers studied by nonlinear optics

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The goal of this work is to understand the fundamental chemistry of how nanoparticles (NPs) interact with biologically relevant interfaces *in situ* at the molecular level. Surface specific nonlinear optical spectroscopies, namely second harmonic (SHG) and sum frequency generation (SFG), are used to investigate the interactions of NPs with lipid bilayers as model cell membranes. Specifically, SHG allows us to probe binding interactions, while SFG allows us to investigate the effect of NPs interactions with the molecular structure of the lipids.

We use resonant and nonresonant SHG to quantify binding constants, adsorption free energies, and interfacial charge densities in real time for gold NPs and quantum dots interacting with bilayers of various lipid compositions. We also examine the relationship between the measured adsorption free energies and the electric double layer interfacial potential to determine the change in the charge state of the NPs during these interactions. Combining this knowledge with the SFG results, detailing molecular structural changes due to the NP-membrane interaction, allows us to predict possible pathways for the molecular level NP-lipid bilayer interactions.

The impact of lipid composition, NP core composition, and capping ligand on the NP-membrane interactions is investigated. Understanding how nanomaterials interact with lipid bilayers at the molecular level is important for predicting and controlling molecular interactions of nanomaterials with living systems as well as designing environmentally and biologically sustainable nanomaterials.