Palaeozoic biosphere and climate: Modes of marine primary production and methane cycling feedbacks

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Lipid biomarker records of microbial community structure during the Late Ordovician through Early Silurian (~449-439 Ma) indicate substantial differences in the balance of bacterial versus algal primary production through the Late Ordovician, largely in response to climatic change associated with the Hirnantian glaciation ([1]. Our biomarker records suggest that these warm Palaeozoic intervals were associated not only with elevated atmospheric pCO_2 (~4-16x preindustrial atmospheric levels, PAL), but also with a higher average flux of oceanic methane, exerting a potential positive feedback on hothouse climates in the Paleozoic. To refine the assessment of a methanotrophic contribution to lipid biomarkers, we have conducted compound-specific carbon isotope analyses on hydrocarbon extracts from Anticosti Island (Canada) the Vinini Formation (USA), the Maquoketa Formation (USA), and OM9 drill core (Estonia).

Recent models have demonstrated that a relatively modest increase of 4-5x preindustrial pCH_4 can generate 2-3°C of warming [2]. Methane cycling feedbacks on climate must have been of similar or greater impact in the Palaeozoic, a period of warm conditions and reduced oxidant availability [3] which may have driven a larger proportion of remineralized organic matter through microbial methanogenesis and attenuated the efficacy of combined anaerobic methane oxidation processes as a throttle for methane fluxes to the atmosphere. Because the loss rate of atmospheric methane scales inversely with atmospheric methane abundance [4], increased fluxes to the atmosphere will often translate into higher steady-state concentrations. We explore the possible effects of this for Palaeozoic times with a series of simple mass balance calculations given a range of carbon flux and anaerobic remineralization scenarios.

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Solubility and TRLFS studies on Nd(III)/Cm(III) complexation with gluconate in NaCl and CaCl$_2$ media.

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Radionuclide sorption and solubility in cementitious systems can be affected by the presence of organic ligands. Gluconic acid (GLU) is a poly-hydroxocarboxylic acid expected in repositories for low and intermediate–level radioactive waste as a component of cementitious materials. The formation of very stable An(III)–GLU complexes has been reported in the literature, although in contrast to An(IV) no ternary species Ca–An(III)–GLU have been described so far. These species may play a relevant role in cementitious and saline environments, where high Ca^{2+} concentrations are expected in certain scenarios.

Undersaturation solubility studies with $Nd(OH)_3$(am) were conducted in inert gas (Ar) gloveboxes at 22±2°C. Samples were prepared in dilute NaCl (0.1 M) and $CaCl_2$ (0.1 and 0.25 M) solutions as background electrolytes. Parallel experimental series were prepared with pH_c = constant ~12 and $10^{-6} \leq$ [GLU] $\leq$ 10^{-2} M, and with [GLU] = constant = 10^{-3} M and $9 \leq pH_c \leq 13$. TRLFS measurements were performed with ~10^{-7} Cm(III) per sample, with NaCl (0.1 M) and $CaCl_2$ (0.1 and 0.25 M) as background electrolytes. In the NaCl systems, three different concentration levels of Ca^{2+} were considered: 0, 10^{-3} M and 10^{-2} M. The initial concentration of GLU in all samples (10^{-6} M) was increased to $3 \cdot 10^{-3}$ M by step–wise additions of NaCl-NaGLU or $CaCl_2$-CaGLU$_2$ solutions of appropiate ionic strenght.

The solubility of $Nd(OH)_3$(am) remains unaffected by GLU in 0.1 M NaCl solutions. On the other hand, solubility of $Nd(OH)_3$(am) in 0.1 and 0.25 M $CaCl_2$ solutions is clearly increased by GLU under hyperalkaline conditions. The species forming are pH–dependent and unequivocally involve the participation of Ca^{2+}, with the likely formation of a Nd–GLU complex with stoichiometry 1:2. No further increase of Nd(III) concentration is observed at [GLU]tot $\geq 10^{-3}$ M, resulting in an upper solubility limit at [Nd] $\sim 10^{-6.5}$ M which suggest the formation of a new Ca–Nd–GLU solubility limiting solid phase. Consistently with Nd(III) solubility data, TRLFS confirms the key role of Ca^{2+} in the complexation process, with the likely formation of a Ca–Cm(III)–GLU complex with Ca:GLU ratio 1:1. Two Ca–Cm–GLU species are further identified in 0.1 M and 0.25 M $CaCl_2$ solutions.