

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

MEGAN ROHRSEN<sup>1</sup>, GORDON D. LOVE<sup>\*1</sup>  
AND CHRISTOPHER T. REINHARD<sup>2</sup>

<sup>1</sup>Department of Earth Sciences, University of California,  
Riverside, CA, 92521, USA; \*Correspondence:  
glove@ucr.edu

<sup>2</sup>Department of Geological and Planetary Sciences, California  
Institute of Technology, Pasadena, CA, 91125, USA

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  $p\text{CO}_2$  (~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  $p\text{CH}_4$  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.

[1] Rohrsen, *et al.* (2013), *Geology* 47, 127-130. [2] Beerling, *et al.* (2011), *PNAS* 108, 9770-9775. [3] Luo, *et al.* (2010), *EPSL* 300, 101-111. [4] Schmidt & Shindell (2003), *Paleoceanography* 18, 1-9.

## Solubility and TRLFS studies on Nd(III)/Cm(III) complexation with gluconate in NaCl and CaCl<sub>2</sub> media.

H.ROJO<sup>1,2</sup>, X. GAONA<sup>1</sup>, TH. RABUNG<sup>1</sup>, M. GARCIA<sup>3</sup>,  
T. MISSANA<sup>3</sup> AND M. ALTMAIER<sup>1</sup>

<sup>1</sup>Institute for Nuclear Waste Disposal, Karlsruhe Institute of  
Technology, Karlsruhe, Germany (henar.rojo@kit.edu)

<sup>2</sup>Laboratory for Waste Management, Paul Scherrer Institut,  
Villigen PSI, Switzerland

<sup>3</sup>CIEMAT, Research Centre for Energy, Environment and  
Technology, Madrid, Spain

Radionuclide sorption and solubility in cementitious systems can be affected by the presence of organic ligands. Gluconic acid (GLU) is a poly-hydroxycarboxylic 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  $\text{Ca}^{2+}$  concentrations are expected in certain scenarios.

Undersaturation solubility studies with  $\text{Nd}(\text{OH})_3(\text{am})$  were conducted in inert gas (Ar) gloveboxes at  $22 \pm 2^\circ\text{C}$ . Samples were prepared in dilute NaCl (0.1 M) and  $\text{CaCl}_2$  (0.1 and 0.25 M) solutions as background electrolytes. Parallel experimental series were prepared with  $\text{pH}_c = \text{constant} \sim 12$  and  $10^{-6} \leq [\text{GLU}] \leq 10^{-2}$  M, and with  $[\text{GLU}] = \text{constant} = 10^{-3}$  M and  $9 \leq \text{pH}_c \leq 13$ . TRLFS measurements were performed with  $\sim 10^{-7}$  M Cm(III) per sample, with NaCl (0.1 M) and  $\text{CaCl}_2$  (0.1 and 0.25 M) as background electrolytes. In the NaCl systems, three different concentration levels of  $\text{Ca}^{2+}$  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  $\text{CaCl}_2$ -CaGLU<sub>2</sub> solutions of appropriate ionic strength.

The solubility of  $\text{Nd}(\text{OH})_3(\text{am})$  remains unaffected by GLU in 0.1 M NaCl solutions. On the other hand, solubility of  $\text{Nd}(\text{OH})_3(\text{am})$  in 0.1 and 0.25 M  $\text{CaCl}_2$  solutions is clearly increased by GLU under hyperalkaline conditions. The species forming are pH-dependent and unequivocally involve the participation of  $\text{Ca}^{2+}$ , with the likely formation of a Nd-GLU complex with stoichiometry 1:2. No further increase of Nd(III) concentration is observed at  $[\text{GLU}]_{\text{tot}} \geq 10^{-3}$  M, resulting in an upper solubility limit at  $[\text{Nd}] \sim 10^{-6.5}$  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  $\text{Ca}^{2+}$  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  $\text{CaCl}_2$  solutions.