## The Biodegradation of [omim][PF<sub>6</sub>] with activated sludge in anoxic conditions

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Many Ionic Liquids have significant solubility in water, which can result in the potential problems with degradation or persistence in environment. Biodegradation is the microbial breakdown of chemical compounds, such as Ionic Liquids. Compared to chemical or physical methods, it seems to be more environmentally friendly. This study focuses on the biodegradation efficiency and the pathways of [omim][PF<sub>6</sub>] under anoxic conditions. Biodegradation efficiency of [omim][PF<sub>6</sub>] under anoxic conditions was studied by acclimatizing the activated sludge with the UASB reactor. The proposal of possible metabolic pathways of [omim]+ in anoxic conditions was analyzed by identification of the breakdown products using GC-MS. The biodegradation experiments were also performed under aerobic conditions. It suggests faster flow enhanced the contact frequency of [omim][PF<sub>6</sub>] and microbe, but was not conducive to the removal rate with the increase of run-time. The results showed that the  $[omim][PF_6]$ removal efficiency reached the highest as the flow velocity of UASB was 0.75 mL·min<sup>-1</sup> in this study. The molecular weights of the main degradation products were 83, 155, 102, 170 and 109, respectively. It is predicted that there were 3 main pathways for anoxic biodegradation of [omim]<sup>+</sup>, which were different from the aerobic process because of the different electron acceptor. Similar to the aerobic process, N-C bond ruptured first, but the metabolism of [omim]<sup>+</sup> did not appear to undergo oxidation reactions but reduction reactions in anoxic conditions. The toxicity of the breakdown products was reduced under anoxic conditions according to their polarities and EC<sub>50</sub> in references.

Acknowledgements: This research was financially supported the National Science & Technology Pillar Program during the Eleventh Five-Year Plan of China (2009BADC2B01-01)

## Controls on and effects of surface ocean oxygenation prior to the Great Oxidation

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Multiple lines of evidence suggest that organisms that produced free oxygen had evolved by ~2.7Ga, while geochemical evidence shows pervasive oxygenation of ocean margins prior to the Great Oxidation Event (GOE) at 2.4Ga [1]. However, given the likely heterogeneous spatial distribution of environments supporting oxygen-producing ecosystems, it is unclear whether oxygen production would have resulted in a significant flux to the atmosphere, or remained a local phenomenom restricted to "oxygen oases" in the surface ocean or mat-based environments. Here we use a combination of ocean GCM and box-model coupled atmosphere-ocean-ecosystem studies, in combination with constraints from proxy data, to investigate: (i) factors controlling the prevalence of surface ocean oxygenation prior to the GOE, (ii) the (local) geochemical signature of early oxygenic photosynthesis in different environments (i.e., restricted to shelf seas, or widespread in the surface ocean), and (iii) the likely impacts on atmospheric oxygen, including constraints on the relative timing of the evolution of oxygen photosynthesis relative to the GOE.

As an initial geochemical diagnostic for spatial structure we focus on factors controlling the production of isotopically light organic carbon via methane recycling. We show that oxygenation of the surface ocean could have been widespread in upwelling regions, that consumption of oxygen in the surface ocean increases stability of a low atmospheric  $pO_2$  state, and that aerobic methanotrophy in open environments produces only relatively small changes in  $\delta^{13}$ C insufficient to explain the excursions seen at ~2.7Ga [2] which would then require a different mechanism and most likely restricted environments.

[1] Kendall, Reinhard, Lyons, Kaufman, Poulton, Anbar (2010) *Nature Geosci.* **3**, 647-652. [2] Eigenbrode & Freeman (2006), *PNAS* **103**, 15759-64.

Mineralogical Magazine

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