

## Volcanic Gases and the Oxygenation of the Atmosphere

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There is now general agreement that the atmosphere was mildly reducing until ca. 2.5 Ga, that O<sub>2</sub> appeared in significant quantities not long thereafter, and that its level has increased somewhat irregularly since then [1]. This history is explained most readily by the invention of photosystem II, together with a progressive change in the composition of volcanic and hydrothermal gases.

Today the H<sub>2</sub> content of volcanic gases is sufficient to reduce 20% of the volcanic CO<sub>2</sub> to CH<sub>2</sub>O and to reduce half of the volcanic SO<sub>2</sub> to sulfide. The remaining SO<sub>2</sub> is oxidized to SO<sub>3</sub> and is removed as a constituent of CaSO<sub>4</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O [2]. Before 2.5 Ga ca 20% of the volcanic CO<sub>2</sub> was also reduced to CH<sub>2</sub>O, but nearly all volcanic SO<sub>2</sub> was reduced to sulfide, and excess H<sub>2</sub> was present in the atmosphere. This demands that volcanic gases were more reducing than today. A higher H<sub>2</sub>/H<sub>2</sub>O ratio is unlikely [3]; lower CO<sub>2</sub>/H<sub>2</sub>O and SO<sub>2</sub>/H<sub>2</sub>O ratios are a reasonable alternative. A simple model of mantle degassing, crustal recycling, and the invention of photosystem II predicts a progressive increase in the CO<sub>2</sub>/H<sub>2</sub>O and SO<sub>2</sub>/H<sub>2</sub>O ratios of volcanic gases and provides an explanation for the oxidation history of the atmosphere [4].

[1] Holland (2006) *Phil. Trans. Roy. Soc. B* **361**, 902-915

[2] Holland (2002) *Geochimica Cosmochimica Acta* **66**, 483-

493 [3] Li & Lee (2004) *Earth Planet. Sci. Letters* **228**, 483-

493 [4] Holland (2009) *Geochimica Cosmochimica Acta* **73**, 5241-5255

## Monitoring the interaction of divalent metal ions with surface bound ssDNA using second harmonic generation

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Non-linear optics (NLO) has been identified as a useful surface-specific approach to studying biofunctionalized surfaces. Most recently, second harmonic generation (SHG), a NLO technique, has been used to study DNA functionalized silica surfaces. The Eisenthal  $\chi^{(3)}$  method is used to quantify the thermodynamic parameters of the oligonucleotide-metal interaction. This approach is used to specifically monitor the divalent cations Sr (II), Mg (II), Ca (II), Ba (II), and Zn (II). The role of the background electrolyte concentration will also be addressed. The  $\chi^{(3)}$  technique is analogous to an optical voltmeter, and allows the interface to be monitored on a molecular level, that is surface specific, non-destructive, and can be done under flow conditions. For biofunctionalized surfaces, this technique is very useful, because there is no need for external labels.

A fused silica surface is functionalized with a short 21-mer of 3'-amine terminated ssDNA (5'-AAAAAAAAAAAAAAAAATTTTT-3') by a commonly used *N*-hydroxysuccinimidyl (NHS) ester linker. Adsorption isotherms for cation binding to this DNA interface have been obtained under flow conditions, at pH 7 and with 10mM NaCl background electrolyte. The resulting isotherms have been fit using the Gouy-Chapman surface complexation model. The Gibbs free energy of adsorption, in kJ/mol, ranges from -33.8 (4) for Ca (II), -33.6 (6) for Sr (II), -39.9 (4) for Mg (II), -31.1 (6) for Ba (II) and Zn (II). The ion density was determined to be 10 cations/21-mer for Sr (II), and 5 or 6 cations/21-mer for the other metals. Additionally, with Mg (II), the free energies of adsorption as a function of the interfacial potential have been studied. These measurements have shed light on possible binding motifs between the cations and the negatively charged phosphate backbone of DNA. Lastly, the role of the nitrogenous bases in cation binding has been addressed by varying the composition of the ssDNA sequences. Insofar as these surfaces model naturally occurring mineral/water interfaces, the thermodynamic results of this work can serve as valuable benchmarks for computer simulation of metal cation transport in biogeochemical environments.