

## Laboratory experiments on the effect of microbial activities on iodine speciation in seawater

N. OKABE<sup>1\*</sup>, Y. MURAMATSU<sup>1</sup> AND S. AMACHI<sup>2</sup>

<sup>1</sup>Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan

(\*correspondence:12242003@gakushuin.ac.jp)

<sup>2</sup>Chiba University, 648 Matsudo, Matsudo-shi, Chiba 271-8510, Japan

In seawater, iodine concentration is relatively constant (0.3 – 0.5 micro M). However, chemical forms of iodine are known to be variable and there are species of iodide (I<sup>-</sup>), iodate (IO<sub>3</sub><sup>-</sup>) and organic iodine. Due to the oxic condition in seawater, iodate is thermodynamically stable and it is dominant. In surface seawater, iodide which is a reduced form, also exists, due to presence of microorganisms, e.g. nitrate-reducing bacteria which reduce iodate to iodide (Tsunogai and Sasa, 1969; Amachi *et al.* 2007). In our previous study on the speciation of iodine in pore water of marine sediments, we found the dominant species was iodide. This was explained by the anoxic condition created by the effect of microorganisms in the sediments.

In this study, we used seawater samples collected from site on Pacific Coast such as Numadu (Suruga Bay) and Odaiba (Tokyo Bay). The samples were introduced into 50 ml glass vials after following treatments; autoclaving, filtering or addition of antibiotic substances together with unfiltered fresh samples. They were incubated under light and dark conditions at 25 °C in a laboratory. The chemical forms of iodine were determined over time using HPLC-ICP-MS.

Analytical results showed that the concentration of iodide increased and that of iodate decreased with time under light condition. This result agrees with increased iodide proportion reported in the euphoric zone. However, under dark condition, no obvious changes of iodine chemical forms were observed.

In seawater samples that were either sterilized by autoclaving or filtering, chemical forms of iodine did not change as much. These findings indicate the role of microorganisms on the transformation of iodine species.

## Calcite and Chalk: Differences in Vapour Adsorption Behaviour

D.V. OKHRIMENKO\*, K.N. DALBY, L.L. SKOVBJERG, N. BOVET, M.P. ANDERSSON, M.H.M. OLSSON AND S.L.S. STIPP

Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark (\*denisokr@nano.ku.dk)

Calcite is a common mineral, widely used in industry and important in environmental processes. It is the main component of chalk and limestone, which serve as natural reservoirs for water and oil. Understanding adsorption energetics and wetting properties of calcite surfaces is important for developing remediation strategies for aquifers, for improving oil recovery, for minimising risk in CO<sub>2</sub> storage and for optimising industrial processes. We have compared the adsorption properties of synthetic calcite with those of chalk samples, composed of biogenic calcite.

We measured the heat of adsorption for water and several alcohols, from the gas phase, and determined the surface energy in order to learn more about the surface properties of these samples. XPS (X-ray photoelectron spectroscopy) was used to monitor changes in chalk surface composition when the organic content was decreased by extraction with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH. The affinity for vapour of polar longer chain organic compounds (e.g. alcohols) was higher for synthetic calcite than for chalk, giving enthalpies of adsorption typical for chemisorption (~100 kJ/mole). DFT/MD (density functional theory and molecular dynamics) simulations showed that the alcohols formed structured monolayers on calcite and that dispersive lateral interactions between the CH<sub>2</sub> tails of the adsorbed molecules contributed as much as 60% of the overall adsorption energy. Such behaviour was not observed for the chalk samples. Alcohol vapours adsorbed to chalk with lower binding energy (~80 kJ/mole), showing a distribution of adsorption energies typical for heterogeneous surfaces. After partially removing organic contamination by extraction, water and ethanol adsorption experiments showed that surface energy, mainly the dispersive component, increased. This increase might be a response to the low polarity of surface sites generated during extraction and could be connected to the presence of nanoscale clay lamellae, already seen using AFM (atomic force microscopy) chemical force mapping [1]. However, the response could also result from increased lateral interactions between the CH<sub>2</sub> tails of alcohols adsorbed on the calcite surface of the chalk.

[1] Skovbjerg *et al.* (2012) *Geochim. Cosmochim. Acta* **99**, 57-70