

## Rates and mechanisms of lead(IV) oxide reductive dissolution

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The Pb(IV) oxides plattnerite ( $\beta$ -PbO<sub>2</sub>) and scrutinyite ( $\alpha$ -PbO<sub>2</sub>) have very low solubility, but they can undergo reductive dissolution and release more soluble Pb(II). While PbO<sub>2</sub> solids are not common in nature, they can form in the presence of oxidants used for water disinfection and play a significant role in controlling lead concentrations in drinking water conveyed through lead pipes. Because PbO<sub>2</sub> is not stable in the absence of a strong oxidant, the dissolved Pb(II) concentrations achieved are governed by the kinetics and not the equilibrium of the dissolution reaction. The reductive dissolution of PbO<sub>2</sub> can be interpreted as a coupled process involving chemical reduction of Pb(IV) to Pb(II) at the PbO<sub>2</sub> surface followed by detachment of Pb(II) to solution.

The dissolution rates of plattnerite were measured as a function of water chemistry in continuously-stirred tank reactors that prevented the accumulation of reaction products and formation of secondary Pb(II) solids. Reaction rates were measured as functions of pH, a strong oxidant (hypochlorite) that might inhibit reductive dissolution, a reductant (iodide) that could accelerate the reduction of Pb(IV) to Pb(II), and a ligand (carbonate) with a high affinity for the Pb(II) formed during reduction.

PbO<sub>2</sub> is such a strong oxidant that soluble Pb(II) is produced even when water is the only possible reductant. The presence of hypochlorite at concentrations used in drinking water distribution systems strongly inhibited Pb release. The addition of iodide dramatically accelerated the dissolution of PbO<sub>2</sub> by driving the reduction of Pb(IV) to Pb(II) at the solid-water interface. The addition of dissolved inorganic carbon (DIC) to previously carbonate-free systems increased dissolution rates by facilitating the desorption of Pb(II) from the PbO<sub>2</sub> surface; however, once some DIC was present the dissolution rate was insensitive to further increases. The dissolution rate was higher at low pH, which could have been caused by its effect on the overall electrochemical driving force for PbO<sub>2</sub> dissolution, impact on the kinetics of a rate limiting step, and control of iodide adsorption and Pb(II) desorption. A kinetic model similar to those used for the reductive dissolution of other metal oxides (i.e., iron and manganese oxides) was successfully fit to the experimental data. The data suggest that chemical reduction is the rate-limiting step for PbO<sub>2</sub> dissolution in the presence of iodide.

The reductive dissolution of PbO<sub>2</sub> present as a corrosion product on lead pipes can produce lead concentrations that exceed drinking water standards. Such reductive dissolution can occur for drinking water systems that switch their secondary disinfectant from hypochlorite to a weaker oxidant such as chloramines. While iodide was chosen in the present study as a model reductant, the reductive dissolution mechanism will likely be similar for natural organic matter, Fe(II), and Mn(II), which are more common reductants found in drinking water.

## Isotopic evidence for sea ice and brine formation in the northern Labrador Sea at the terminations of Heinrich Events 1 and 2.

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Reconstructions of sea surface conditions in the Northern Labrador Sea (HU2008-029-004PC) have been created using dinoflagellate cyst assemblages for the last ~35 cal ka BP. They demonstrate that the temperatures were near freezing, the salinity below 31, and the area was under close to permanent ice cover. There were however occurrences of the planktonic foraminifera *Neogloboquadrina pachyderma* sinistral (Npl). Since Npl requires salinity above 34 (e.g., [1]), its growth had to occur either deeper in the water column, if suitable salinities prevailed, or more likely, in brine canals in the sea-ice itself, as it does in modern sea-ice environments [2]. Similarly to previous studies (e.g., [3]), an isotopic shift of -2.5‰ occurs between the beginning and end of Heinrich Event 1 (H1), and a less dramatic -1‰ shift during H2. These light isotope excursions would typically be acknowledged as low-salinity pulses and higher sea surface temperatures. However the dinocyst data indicates this was not the case. As demonstrated by Hillaire-Marcel and de Vernal [4], the light  $\delta^{18}\text{O}$  excursions are an effect of the foraminifera forming in isotopically light brines during sea ice formation. Perennial sea ice cover inferred from particularly low production of dinocysts occurred toward the end of the Heinrich events, concurrently with high abundance of ice rafted debris and Npl.

[1] Hilbrecht, H., 1996. Technische Hochschule und der Universität Zürich, Neue Folge, p. 300 (93 pp., Zürich).

[2] Spindler, M., (1996). *Polar Biology* **9**, 85-91.

[3] Hillaire-Marcel, C. and de Vernal, A. (2008). *Earth and Planetary Science Letters* **268**, 143-150.

[4] Hillaire-Marcel, C., de Vernal, A., Bilodeau, G., Wu, G. (1994). *Canadian Journal of Earth Sciences* **31**, 63-89.