

## Nitrogen and carbon isotopes, and metals in waste work sediments, Kovik, Sweden

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Sediment samples were taken in the water upstream, near and downstream of the outflow of the purification plant of the Kovik Waste Plant in the Höggarnsfjärden Bay near Stockholm, Sweden. The waste plant receives, treats and deposits domestic and industry refuse and latrine.

An Otto Gravity Corer was used for sampling. The sediment was cut into centimetres slices, freeze-dried and analysed for the total content and isotopic signature of carbon and nitrogen with element analyser, NC2500. Freeze-dried sediment subsamples were digested in a microwave oven in the presence of nitric acid and hydrogen peroxide, and analysed for metals with ICP-AES, Varian Vista AX.

The isotopic signature of nitrogen has been a successful tool in identifying sources of nitrogen contaminated water and sediments. Carbon isotopes may be used in identifying carbon sources of sediments, with regard to terrigenous or marine sources, and organic or inorganic sources, for example.

In this investigation the  $\delta^{15}\text{N}$  values of nitrogen in the sediment near the outflow (16-19‰) suggest that the nitrogen comes from sewage, i.e. is likely to be derived from the waste work. Upstream of the outflow and 600 metres downstream, the  $\delta^{15}\text{N}$  are in a more natural range (2-3‰ resp. 7-9‰).  $\delta^{13}\text{C}$  values are also differentiating the outflow samples (-25 to -21‰) from the samples collected upstream (-25 to -23‰) and downstream the outflow (-27 to -25‰).

A lot of "new" metals like Al, Ga, Ge, As, In, Sn, Sb, Tl, and Bi are presently introduced into the environment, coming from the electronic industry. Some of these compounds are poisonous. Therefore, it is of general interest to find the amounts of the compounds that are released to the environment from waste plants. The concentrations of the "by the method detectable metals" are high but do not generally appear to be higher at the outflow than upstream or downstream, but the sediments are subject to further investigations and method development.

## Fractionation of $^{44}\text{Ca}/^{40}\text{Ca}$ between Aragonite and Calcite

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The  $^{44}\text{Ca}/^{40}\text{Ca}$  ratio decreases during precipitation of calcium carbonate from a fluid. The preferred incorporation of  $^{40}\text{Ca}$  in the crystal can be explained by kinetic fractionation during the diffusion of hydrated calcium ions at the mineral surface. This fractionation is temperature dependent and decreases with increasing temperature. Extending our earlier studies we present calcium isotope data measured on sclerosponge skeletons. These skeletons are of special interest because they are precipitated without significant biogenic modifications of the precipitating fluid in isotopic equilibrium with ambient sea water. This has been shown for carbon and oxygen isotopes and is very likely for boron isotopes

Ca isotope values of sponge skeletons grown at temperatures ranging from 7 to 27°C are compatible with the temperature-fractionation dependence of inorganic aragonite. The fractionation factors of the sponge aragonite and of inorganic aragonite are identical. There is no significant difference between Ca isotope values of aragonitic skeletons of three different sclerosponge species that grew at the same temperature. However, there is an offset of Ca isotope values of calcitic sclerosponge skeletons from the aragonite value. The calcitic sclerosponge skeletons show values that are in the range of Ca isotope ratios measured on calcitic foraminifera (*Orbulina universa*). We conclude that a systematic offset exists for Ca isotope fractionation between aragonite and calcite. This offset appears to be constant in the temperature range between 10 and 28°C. There is no significant isotopic offset between high-Mg calcite (HMC) and low-Mg calcite (LMC) for Ca isotopes. This is in contrast to oxygen and carbon isotopes for which there is an offset between LMC on the one hand and HMC/aragonite on the other hand.

We suggest that the observed Ca isotope offset is caused by kinetic fractionation related to the different lattice parameters of the aragonitic and calcitic crystals. This contrasts with the equilibrium fractionation offset of oxygen isotopes between LMC and aragonite, which is mainly controlled by the different internal vibration frequencies of the carbonate ions, while influences from external lattice vibrations are nearly equal for the two polymorphs (O'Neil et al., 1969).