

## The carbonate system in hypersaline brine: Dead Sea case study

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Aragonite precipitation in hypersaline Ca-rich Dead Sea (DS) and in its precursor, the late Pleistocene Lake Lisan, are a result of common ion effect induced by mixing of high bicarbonate freshwater runoff with the Ca rich brine ( $\text{Ca} \approx 0.38 \text{ mol} \cdot \text{kg}^{-1}$ ). Evaluating the aragonite precipitation kinetics and thermodynamics in the DS brines and its mixtures with freshwater is of great importance for understanding the limnological/hydrological regime under which the Holocene and Late Pleistocene aragonite laminae were deposited. Preliminary field and experimental data on the DS carbonate system are presented.

Depth profiles of total alkalinity, dissolved inorganic carbon (DIC) and its isotopic composition ( $\delta^{13}\text{C}_{\text{DIC}}$ ) were conducted bi-monthly in the DS. In the laboratory, DS brine was equilibrated with atmospheric  $\text{CO}_2$  in order to remove excess  $\text{CO}_2$  from the solution. Fine aragonite powder was added to the  $\text{CO}_2$ -equilibrated brine to serve as aragonite precipitation nuclei and the total alkalinity of the solution was measured regularly over several months.

The measured alkalinity was uniform throughout the water column during winter, when the lake is mixed. During summer, when the lake is stratified, alkalinity increase was measured in the epilimnion. The salinity-normalized alkalinity, however, remained constant ( $3.825 \text{ mmol} \cdot \text{kg}^{-1}$ ) throughout the year, implying conservative behaviour.

During the equilibration of DS brine with atmospheric  $\text{CO}_2$  in the laboratory the pH increased gradually while total alkalinity remained constant. Slow but continuous decrease in pH and alkalinity were observed following the addition of aragonite powder to the equilibrated brine. The experiments demonstrate that the DS remains oversaturated with respect to aragonite.

It should be noted that the brine remained oversaturated despite the dramatic decline in freshwater inflow during the last several decades that supplies the carbonate alkalinity. It is suggested that the aragonite laminae along the DS shores and inflow of suspended aragonite with scarce flashfloods did not provide enough crystallization surfaces to attain saturation.