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Natural Oxidation of Bromide to Bromine in Evaporated Dead Sea Brines

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Highly evaporated Dead Sea brines are found in isolated sinkholes along the Dead Sea. Many of these brines reach densities of over 1.3 kg/L and pH<5 and are the product of evaporation of Dead Sea brine that drain into the sinkholes. The low pH and the reddish to brownish hue of these brines were an enigma until recently. Despite the rather high total alkalinity (TA) of the Dead Sea (3.826 mmol/kg) the pH of the Dead Sea brine is known to be slightly acidic with a value of ∼6.3. In comparison, seawater with the same alkalinity would have a pH value well above 8.3, meaning that H+ activity is 100 fold lower than that of Dead Sea brine.
In the present work we assess the apparent dissociation constant value of boric acid (K‘B) for the Dead Sea brine and use it to explain the brine’s low pH value. We then show that pH decreases further as the brine evaporates and salinity increases. Finally we explain the reddish hue of the hypersaline brines in the sinkholes as due to the presence of dissolved bromine. The latter is the product of oxidation of dissolved bromide, a process that is enabled by the low pH of the hypersaline brines and their high bromide concentration.