

The Many Roles of Boron in Controlling Lithium-Brine Geochemistry

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For lithium extraction, lithium-rich brines are pumped from salt flats, primarily in the Lithium Triangle (Chile, Argentina, and Bolivia) of South America. Yet the mechanisms controlling the geochemistry of these brines are not yet fully understood. Here we demonstrate the functionality of boron as a key element in controlling the geochemistry of lithium-rich brines during the evaporative concentration of inflows as well as in controlling the pH of both natural brines from the salt flats and in the evaporation ponds used for lithium extraction.

The precipitation of evaporite minerals (gypsum, halite) from inflow waters during evaporative concentration in the delta system largely determines the geochemistry of the resulting brines. This follows a series of geochemical divides in which the ions that are in a greater stoichiometric proportion in the initial water becomes further concentrated in the residual brine, while the others become depleted upon equal removal to salts. Here we investigate the evaporative concentration of the Rio Grande as it flows into the Salar de Uyuni (SDU), Bolivia, where initial inflow waters have Ca/SO_4 and $\text{Na}/\text{Cl} > 1$, which would indicate that the resulting brine should evolve to have $[\text{Ca}] \gg [\text{SO}_4]$ and $[\text{Na}] \gg [\text{Cl}]$ following gypsum and halite precipitation. Evaporation, however, yields a brine with $[\text{Ca}] \ll [\text{SO}_4]$ and $[\text{Na}] \ll [\text{Cl}]$, which suggests that another mechanism is influencing these geochemical divides. Given the occurrence of ulexite, a Ca-Na-borate that forms in the Rio Grande Delta, we propose that its precipitation removes both Ca and Na allowing for the observed deviations from the predicted evaporation path.

Despite the precipitation of ulexite, boron becomes highly concentrated in SDU brines (~50 mmol/kg), and consequently, borate/polyborate ions become the dominant alkalinity species. Evaporative concentration of both inflow waters and of brines in evaporation ponds further increases the salinity and boron content which intensifies the dissociation of boric acid allowing for observed decreases in the pH from >7.8 in inflows to ~7 in natural brines to 3.2 in brine evaporation ponds. Consequently, we posit that these observed decreases in pH from inflows to natural brines to evaporation ponds derive from the dominance of the alkalinity of the boron species.