

Mineral precipitation and hydrochemical evolution through evaporitic processes in soda brines

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INTRODUCTION

Soda lakes are saline lakes mostly typically fed by volcanic terrains. They are characterized by high pH and a large concentration of Na^+ , Cl^- , CO_3^{2-} and HCO_3^- , leading to active evaporite precipitation. Lakes Magadi, Nasikie Engida and Natron (MNN), are among the highly saline and alkaline soda lakes in the tectonic depressions of the East African Rift valley. Precipitation in MNN lakes follows a complex, recurrent cycle of undersaturation, evaporative concentration, and desiccation. During the evaporative concentration, trona grows as thin sheet-like rafts on the surface and as upward radiating needles at the bottom of the lake. After complete evaporation (desiccation stage), continued evaporation of interstitial brines causes expansion and buckling of the crust and precipitation of a variety of efflorescent crusts and inter-crystallite cement. During the undersaturation stage (flooding of the lake), dilute inflows partially dissolve the preexisting trona or nahcolite, creating layered deposits of upward radiating trona crystals (in Lake Magadi) or nahcolite crystals (in Nasikie Engida) with thin mud layers on top of the dissolution surfaces. The investigation of this complex hydro-chemical evolution, is relevant to geological and paleo-environmental studies of the area. Identifying the chemical and climatological factors controlling the precipitation sequence would simplify the decoding of the stratigraphic record and allow an efficient use of the mineral resources (evaporites are currently exploited by TATA Chemicals). To this end, we have performed *ex-situ* and *in-situ* (drop levitation) diffraction experiments during evaporation as well as hydrochemical modeling of the evaporation/precipitation sequences. The methodology for these studies is described in Getenet et al. (2022).

RESULTS AND DISCUSSION

Figure 1 shows the precipitation sequence during evaporation of levitated drops of (a) Lake Magadi brine, (b) Lake Nasikie Engida brine, (c) Nasikie Engida hot spring and (d) Lake Natron brine (left column) along with the output of the evaporative precipitation sequence modeled using the hydrochemical code PHREEQC (mineral phases in the center column and solution species in the right column). Trona and halite were observed to precipitate from all brines except the Nasikie Engida hot spring, where nahcolite is the first precipitate. Thermonatrite was observed to precipitate in all cases except Lake Nasikie Engida brine. The time (and therefore concentration factor) at which these phases start precipitating changes for different brine composition. The mineral precipitation sequences predicted by hydrochemical modeling agree for sodium carbonate phases with the outcome of evaporation experiments, with the only exception of natron, predicted to precipitate from Lake Nasikie Engida brine but not observed and trona, predicted to precipitate from Lake Nasikie Engida spring while thermonatrite is observed instead. The absence of natron in the evaporation experiments can be due to the thermal transformation of the mineral into trona (Eugster, 1980). The differences in the relative amount of the minerals among the experiments, the simulations and the natural setting arise mainly from the differences in partial CO_2 pressure ($p\text{CO}_2$) and in biogenic activity, leading to the dissolution of the early precipitated nahcolite. In the case of hot springs, the initial brine was dominated by HCO_3^- over CO_3^{2-} , allowing the precipitation of significant amount of nahcolite even though CO_2 input was minimal. In a later stage, nahcolite partially convert to trona. The precipitation of a significant amount of thermonatrite and halite in artificial pans exploited by TATA Chemicals is also explained by our results: the company pumps the HCO_3^- depleted lake brine (after trona precipitation) into shallow evaporation ponds where evaporation is very rapid and organic production of CO_2 is negligible.

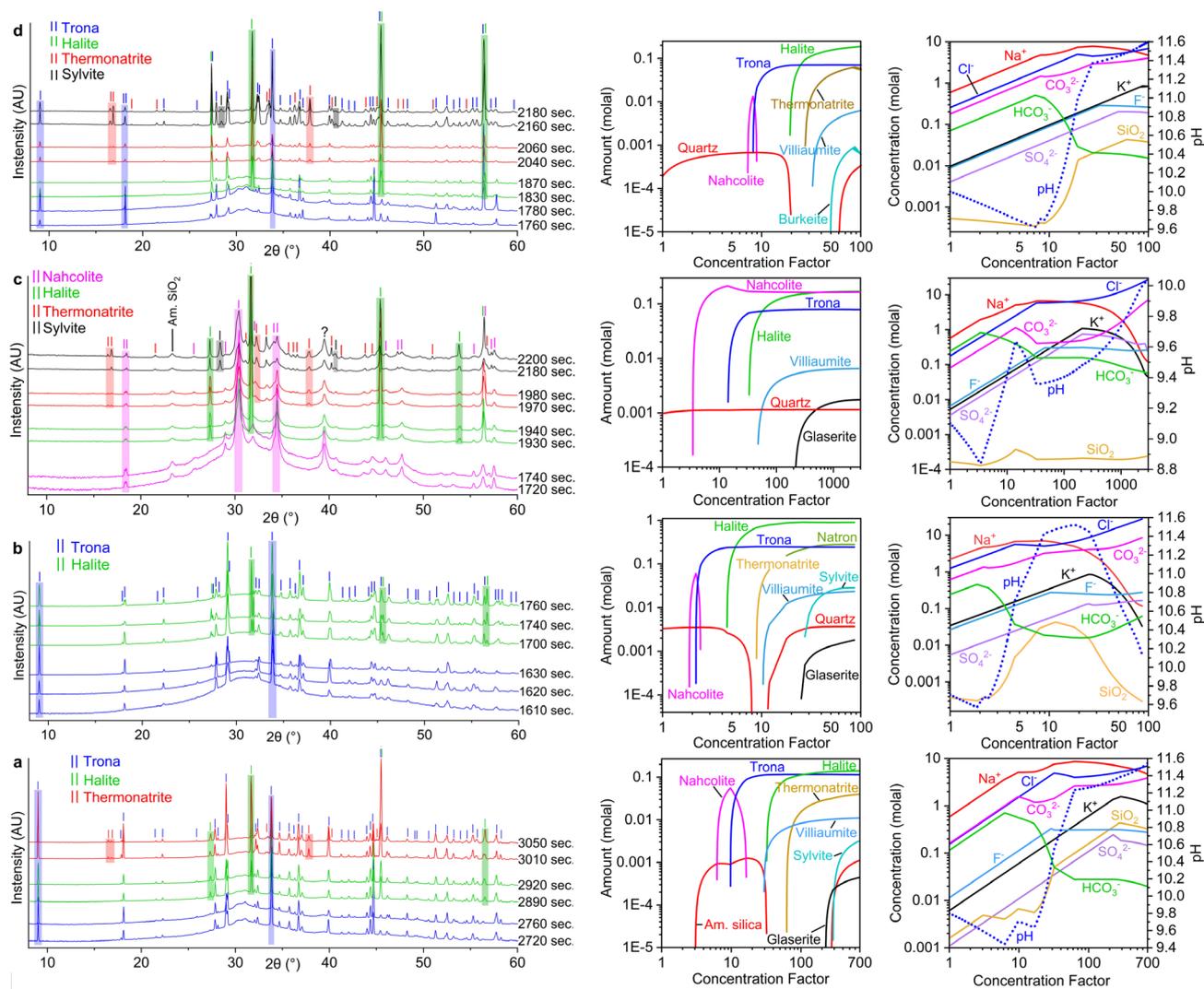


Fig 1. Powder X-ray diffraction data from *in-situ* (levitated drop) evaporation /precipitation experiments of (a) Lake Magadi brine, (b) Lake Nasikie Engida brine, (c) Nasikie Engida hot spring and (d) Lake Natron brine (left column). Simulation of the same process by hydrochemical modeling; precipitated mineral phase amounts and solution species concentrations are represented as a function of the concentration factor (initial solution weight divided by the current solution weight).

These results also reproduce the hydrochemical evolution observed in natural settings. In Lake Magadi, and in southern Nasikie Engida, trona precipitates currently at the bottom as a firm mesh of vertical acicular crystals and on the surface as crusts of smaller crystal aggregates. The successive growth of these crystals forms a layered trona deposits of 2-5 cm annual bands. The evaporite sediments of the northern Nasikie Engida are dominated by nahcolite. Drill cores on the lake bed revealed that the uppermost sediments are composed of intercalations of laminated mud with scattered nahcolite crystals and distinct beds of nahcolite resulting from abrupt precipitation at the sediment–water interface or within the water column. In Lake Natron, trona was reported both in ancient and modern evaporite deposits. The modern surface of Lake Natron is composed of 10-20 cm thick trona, thermonatrite and halite crust with alternating layers of black clay and trona. Thermonatrite and halite form only in the modern evaporite sequence of MNN lakes as efflorescent crusts and some local pools where there is intense evaporation.

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