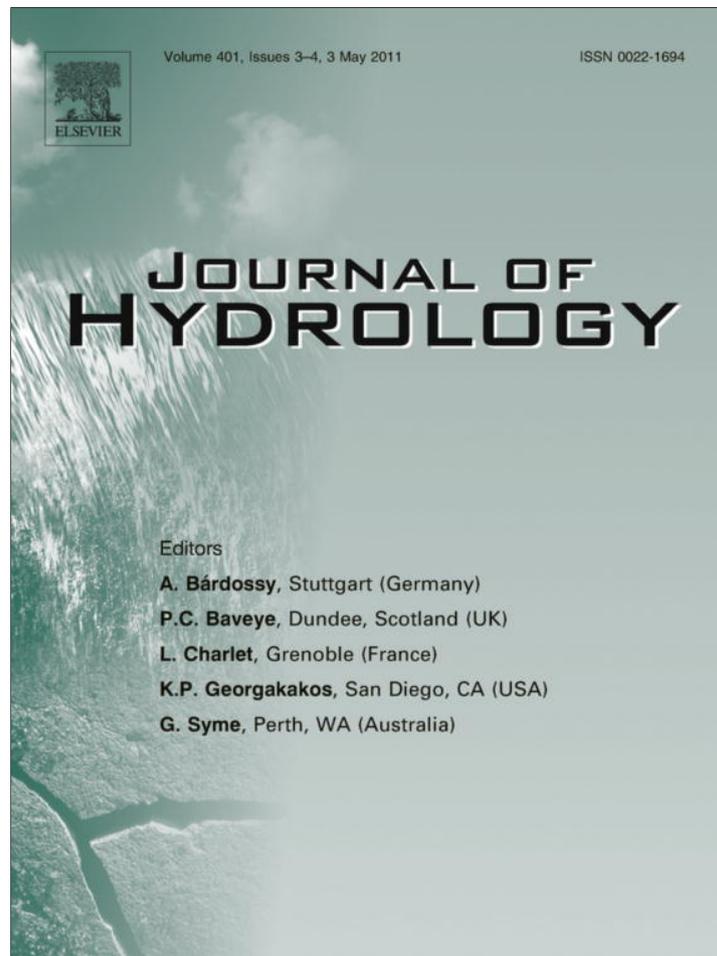


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## Modeling the interaction between evaporation and chemical composition in a natural saline system

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### SUMMARY

Evaporation controls the salinity of many natural and anthropic brine systems, but the reverse is also true. By controlling water activity, salinity affects evaporation rates. We present a method to compute the evolution of water activity in high salinity systems so as to evaluate evaporation rates. We place special emphasis on the assessment of invariant points, where activity is controlled by the set of precipitated minerals. The algorithm is tested on a natural Mg–SO<sub>4</sub> rich brine evaporation experiment. In accordance with the experiments, the model predicts two intervals (invariant points) in which water activity, the concentration of all species and the amount of liquid water remain constant, because evaporating water comes from the dissolution of hydrated minerals. This suggests that mineral paragenesis might have a considerable influence on shallow brine lake evolution by fixing chemical composition for a significant portion of time. This conjecture was tested with a simplified model of a perennial saline playa lake. An analytical solution was developed to illustrate the evolution of the proposed system. According to the calculations, the system tends to a cyclical steady state for both lake level and chemical composition. The latter remains fixed at invariant points during long time intervals, where hydrated minerals act as the water source for evaporation. This situation is to be expected in epsomite lakes where two invariant points can be found in equilibrium with relative humidities of 57% and 50%.

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### 1. Introduction

Natural saline systems occur broadly worldwide. They may be of significant hydrological, economic and ecological importance. Playas, sabkhas and saline lakes often represent the discharge point of regional water flow systems and are important for water resource assessments (Yecheili and Wood, 2002). Moreover, due to their high concentrations and density differences, hypersaline water can significantly affect groundwater quality and flow (Simmons and Narayan, 1998; Holzbecher, 2005). Evaporation is the critical process to understand the evolution of these natural systems. In fact, evaporation is also a key process to understand the formation of evaporitic deposits (Jankowski and Jacobson, 1989; Donovan and Rose, 1994), and plays a main role in the formation of water-soluble efflorescent salts on tailings in arid climates (Acero et al., 2009). Such salts may increase the risk of human exposure to heavy metals such as Cu, Ni, and Zn through wind transport (Dold, 2006; Bea et al., 2010b). Therefore, under-

standing the evaporation mechanisms and quantitative modeling of the formation of these salts is crucial for the design of remediation measures. Evaporation also plays a leading role in the production of industrial salt (halite, magnesium and sodium sulfate, potassium chloride). Nearly all forms of salt production require evaporation of water to concentrate brine and ultimately produce salt crystals (Akridge, 2008).

The chemical evolution of brines under evaporation has been extensively modeled (Hardie and Eugster, 1980; Eugster et al., 1980; Sanford and Wood, 1991; Wood and Sanford, 1990; Ayora et al., 1994; Yan et al., 2002). However, most of these works are oriented to model geochemical features, either mineral sequences or brine composition or both and they take evaporation as given and do not pursue understanding evaporation dynamics. Ironically, geochemistry may exert a key control on evaporation rate.

Ever since Dalton (1802), evaporation has been seen as a balance between vaporization and condensation. The latter depends on the quantity and energy of water molecules in the gas phase, which can be evaluated as proportional to vapor pressure,  $pV_{air}$ . Vaporization depends on the energy of liquid molecules to overcome the surface barrier. In hydrology, vaporization has been traditionally taken as proportional to the saturation vapor pressure,

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