

The chemical evolution of brine and Mg-K-salts along the course of extreme evaporation of seawater – An experimental study

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Abstract

Extreme evaporation experiments of modern seawater, up to a degree of evaporation (DE) of 870 on Li scale and brine density of $1.40 \text{ g}\cdot\text{ml}^{-1}$ were conducted under controlled semi-natural conditions. This DE is well within the bischofite facies and, to the best of our knowledge, is the highest experimental DE ever reported. During the experiments, brine temperature varied between $\sim 20^\circ\text{C}$ and $\sim 40^\circ\text{C}$ with few excursions to higher temperatures, thereby demonstrating the effect of temperature on the precipitating mineral assemblages. Results were compared to a thermodynamic simulation of the evaporation experiment at 25°C , based on the Harvie-Møller-Weare activity coefficients correction.

The relative amounts of the precipitated minerals were evaluated from the bulk chemical composition of the collected precipitates, applying a Li-based methodology for subtracting the contribution of the brine adsorbed on the precipitated salts. The following minerals were identified during the evaporation experiments: halite (NaCl), epsomite ($\text{MgSO}_4\cdot 7\text{H}_2\text{O}$), kainite ($\text{KMgClSO}_4\cdot 3\text{H}_2\text{O}$), carnallite ($\text{MgKCl}_3\cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4\cdot \text{H}_2\text{O}$) and bischofite ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$). The precipitation of the Mg-salts was accompanied by continuous halite precipitation up to DE of ~ 170 . The experimental results are in good agreement with literature experimental data, available up to $\text{DE} = 98$, and generally follow the thermodynamic calculations, thereby supporting both the established methodology of the experiments and the simulation parameters and assumptions. Minor differences between the experiments and the thermodynamic calculation are mainly due to temperature variations. The experiments suggest that, at warmer temperatures ($\sim 50^\circ\text{C}$), kainite and bischofite precipitate instead of kieserite, which precipitates to a greater extent at lower temperatures ($25\text{--}30^\circ\text{C}$). The presence of organic matter (OM) in the brine was found to reduce the evaporation rate and the final DE at which evaporation ceased, but not to significantly affect the chemical evolution of the brine.

The detailed systematic data-set presented here is useful for both geochemical and applied purposes. For example, it can be used as a reference for reconstructing the evolution of ancient marine-derived brines, using evaporitic sequences far beyond the halite facies. Hence, this study provides new insights on the formation of such evaporitic minerals and opens

Abbreviations: DE, degree of evaporation; DEs, degrees of evaporation; DE_{Li} , degree of evaporation on Li-scale; $\text{DE}_{\text{H}_2\text{O}}$, degree of evaporation on water scale

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the way for further studies on these highly soluble evaporitic sequences as clues to the chemical composition of the ancient oceans.

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1. INTRODUCTION

Mg-K (potash) salts precipitate from highly evaporated seawater at degrees of evaporation (DE) > 50. DE is defined as the ratio of the mass of H₂O in a given mass of “mean” modern seawater (salinity of 35) divided by the mass of H₂O in the brine remaining from the original mass of seawater after evaporation (hereinafter DE_{H₂O}; e.g., Levy, 1977; Babel and Schreiber, 2014). For convenience, DE is calculated using the molal concentration (mol·kg_{H₂O}⁻¹) ratios of the most conservative elements, Br or Li (e.g., Braitsch, 1971; McCaffrey et al., 1987; Zimmermann, 2000, 2001; Warren, 2010; Babel and Schreiber, 2014). In nature, DE > 50 is typically reached only in fully or nearly enclosed basins. Potash salts are found in large volumes in giant evaporitic basins, such as the Permian Zechstein basins in northern Europe and the Messinian basins around the Mediterranean (e.g., Warren, 2010). In addition to their commercial importance, Mg-K evaporite minerals in the geological record are important archives for ancient (“fossil”) brines and can be used to estimate past seawater compositions and climate (e.g., Holland, 1972; Holland et al., 1986; Hardie, 1991; Horita et al., 2002; Warren, 2010). As chemical deposits, these evaporites are direct recorders of the chemistry of ancient marine-derived brines (e.g., Babel and Schreiber, 2014), whereby variations in ocean chemistry are reflected in changes in the depositional records and sequences of Mg-K salt deposits. These vary between the chloride type, composed mainly of sylvite and carnallite (for compositions see Table 1), and the sulfate type, characterized by MgSO₄-rich minerals (e.g., Zharkov, 1981; Hardie, 1991; Babel and Schreiber, 2014).

Reconstructions of past seawater composition from evaporitic sequences and studies of the evolution of different types of brines are based on comparison to modern seawater evaporation path (e.g., Holland, 1972; Holland et al.,

1986; Fontes and Mataray, 1993; Hanor, 1994). This modern path has been studied for more than 150 years using theoretical calculations, experimental work and field studies (e.g., Usiglio, 1849a, 1849b; Braitsch, 1971; Bassegio, 1974; Eugster et al., 1980; Harvie et al., 1980, 1984; Møller and Weare, 1986; McCaffrey et al., 1987; Millero, 2009; and others). Brine evolution and the precipitating salts sequence during the early stages of evaporation (the aragonite, gypsum and halite phases) are well known from studies on marine solar salt evaporation pans (Babel and Schreiber, 2014 and references therein), experimental data and theoretical calculations (e.g., Braitsch, 1971; Eugster et al., 1980; Harvie and Weare, 1980; Harvie et al., 1980; Lazar et al., 1983; McCaffrey et al., 1987; Usdowski and Dietzel, 1998; Millero, 2009). The evolution and sequence along the advanced stages of evaporation (the Mg-K salts phases), however, are not as well established and are based mainly on thermodynamic calculations (e.g., Eugster et al., 1980; Harvie and Weare, 1980; Harvie et al., 1980, 1984; Møller and Weare, 1986). Experimental data or data from solar salt pans of these advanced stages of natural seawater evaporation are limited and sporadic (e.g., Fontes and Mataray, 1993; and references therein) and show differences and inconsistencies, which may stem from the different physical settings of the system (temperature, evaporation rate, closure degree of the system, etc.; Babel and Schreiber, 2014). Fontes and Mataray (1993), for example, described the entire Mg-K salts sequence based on only several samples taken from previous studies of evaporation of different waters (Black Sea, Lake Sasyk-Sivash, Salins du Midi). Thus, they have sylvite, for example, instead of kainite and kieserite, making their results difficult to interpret. To the best of our knowledge, detailed and systematic experimental study of the chemical evolution of evaporated seawater into the Mg-K facies is available only up to DE = 98 (McCaffrey et al., 1987). This latter study, however, dealt only with the evolution of the brine whereas the precipitated salts were not analyzed.

Based on existing thermodynamic models for precipitation in a closed system (the solids and brine are continuously interacting while maintaining halite saturation), the precipitation order of Mg-salts is: epsomite, hexahydrate, kieserite, carnallite and bischofite (e.g., Harvie et al., 1980). When the precipitating salts are continuously separated from the brine during the course of evaporation (hereafter termed “fractional precipitation path”) the modeled precipitation order is epsomite, kainite, carnallite, kieserite and bischofite (e.g., Eugster et al., 1980). These thermodynamic calculations assume ideal conditions, with a solution at a constant temperature of 25 °C and at either full-equilibrium (all the solids are in thermodynamic equilibrium with the contemporaneous brine) or full-fractional

Table 1
The chemical formulas of some Mg-salts minerals.

Mineral	Symbol	Chemical composition
Bischofite	Bi	MgCl ₂ ·6H ₂ O
Bloedite	Bl	Na ₂ Mg(SO ₄) ₂ ·4H ₂ O
Carnallite	Car	MgKCl ₃ ·6H ₂ O
Epsomite	Ep	MgSO ₄ ·7H ₂ O
Hexahydrate	Hx	MgSO ₄ ·6H ₂ O
Kainite	Ka	KMgClSO ₄ ·3H ₂ O
Kieserite	Ki	MgSO ₄ ·H ₂ O
Leonite	Le	K ₂ Mg(SO ₄) ₂ ·4H ₂ O
Polyhalite	Poly	K ₂ Ca ₂ Mg(SO ₄) ₄ ·2H ₂ O
Sylvite	Syl	KCl

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