ISOTOPE EFFECTS ASSOCIATED WITH δ^2H, $\delta^{18}O$ AND $\delta^{17}O$ ANALYSES OF BRINES USING PICARRO L2140-i SPECTROMETER: insights from dedicated laboratory experiments

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INTRODUCTION

Stable isotope analyses of concentrated saline solutions (brines) play an important role in deciphering the origin of fluids encountered in deep sedimentary basins, fluids associated with exploration and exploitation of oil and gas reserves, as well as the origin of water appearances in mines. Stable isotope analysis of heavy brines using classical IRMS technique typically requires troublesome and time-consuming sample preparation procedures and usage of appropriate correction factors [1-3]. With the advent of laser spectroscopic methods of water isotope analyses there is a need to determine if, and to which extent concentrated saline solutions can be analysed directly using this methodology.

Here we present the results of dedicated laboratory experiments aimed at quantifying isotope effects associated with δ^2H, $\delta^{18}O$ and $\delta^{17}O$ analyses of single and double-salt mixtures, as a function of their molality.

METHODOLOGY

Four single-salt (NaCl, $CaCl_2$ and $MgSO_4$, $MgCl_2$) solutions and two double-salt (NaCl-$CaCl_2$ and NaCl-$MgSO_4$) mixtures were prepared and investigated for a large range of molalities, from ca. 0.5 mol/kgH_2O till saturation conditions. The solutions were prepared using anhydrous salts, on the basis of deionised water of known isotopic composition.

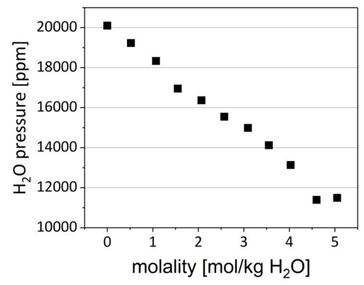


Fig.1. Pressure of H_2O signal in the cavity of L2140-i as a function of $MgCl_2$ content in the tested solutions

δ^2H, $\delta^{18}O$ and $\delta^{17}O$ were measured directly with Picarro L2140-*i* spectrometer based on the CRDS technique. To avoid excessive accumulation of salt at the injection port of the vaporizer unit, a salt liner was used [Fig. 2-4]. Salt liner was cleaned after each measurement run.

Due to high salt content in the solutions, it was necessary to adjust the volume of the injected sample in order to maintain H_2O pressure in the measurement cavity recommended by the manufacturer (17000-23000 ppm). For constant sample volume of 1.8 µl, a decrease in the pressure of H_2O in the cavity with the increasing concentration of salt in the solutions was observed. The effect was particularly strong for $MgCl_2$ [see Fig. 1].

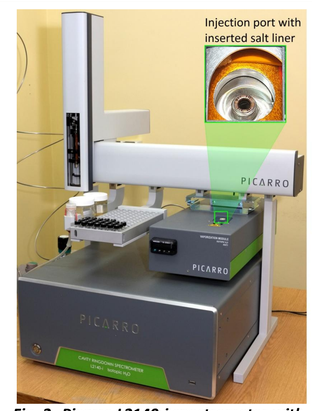


Fig. 2. Picarro L2140-i spectrometer with salt-liner inserted into the injection port of the vaporizer unit



Fig. 3. Salt-liner



Fig.4. Salt-liner and injection septa after measurement run with $MgSO_4$ solutions measured

RESULTS

Single-salt solutions

To facilitate presentation of the results of laboratory experiments an offset (Δδ) was defined as the difference between measured δ value of the salt solution and the δ value of deionised water used for preparation of the investigated solution:

$$\Delta\delta = \delta_{measured} - \delta_{deionised\ water}$$

Single-salt solutions (NaCl and $CaCl_2$) revealed small, roughly constant negative offsets Δδ equal -0.066±0.026‰ (^2H), -0.0861±0.0075‰ (^{18}O), and 0.0197±0.0058‰ (^{17}O) for NaCl and -0.292±0.050‰ (^2H), -0.046±0.014‰ (^{18}O), -0.018 ±0.011‰ (^{17}O) for $CaCl_2$, independent on the molality of the solution. In contrast, $MgSO_4$ solution revealed roughly one order of magnitude higher offsets, gradually increasing with the growing molality of the solution [Fig. 5].

Strongest impact of the molality on the measured Δδ offset was observed for $MgCl_2$ solutions. Only in the case of these solutions, the effects observed for hydrogen and the oxygen isotopes are opposite: for ^2H Δδ increases rapidly with increasing concentration of $MgCl_2$, whereas it decreases for both ^{18}O and ^{17}O [see Fig. 5]. What is more, for ^2H the offset is negative for low molalities (up to ca. 1.5 mol/kg H_2O) and turns positive for higher molalities.

The observed isotope effects are most probably linked to the processes occurring during injection of the analysed salt solutions to the vaporizer unit of Picarro L2140-*i* spectrometer. Fast evaporation of the injected water sample leads to super-saturation and crystallization of salts occurring predominantly in the salt liner of the vaporizer. Precipitating salts retain certain amount of the analysed water, thus leading to the observed isotope offsets.

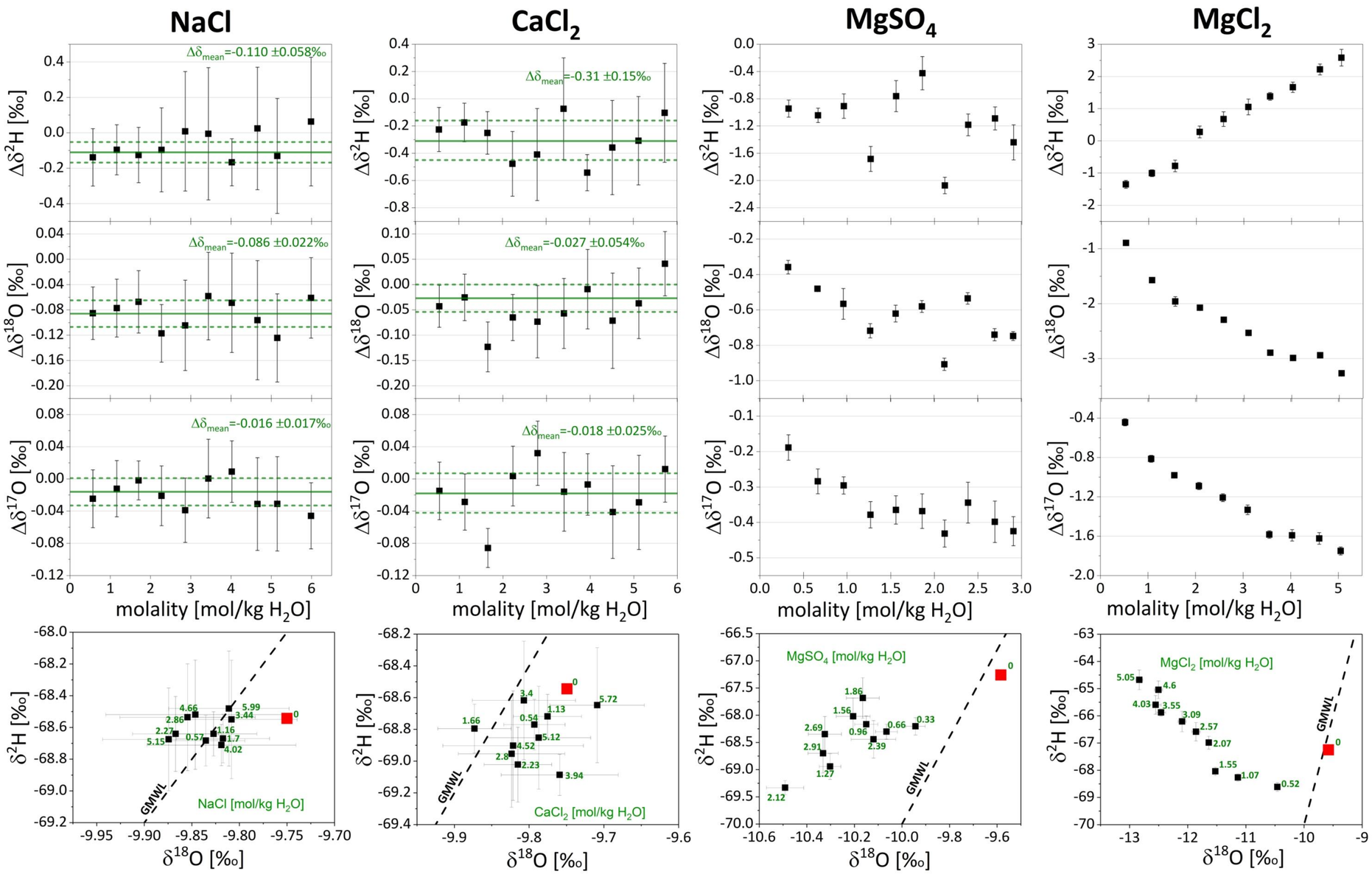


Fig. 5. Upper graphs: isotope effects observed for four single-salt solutions (NaCl, $CaCl_2$, $MgSO_4$, $MgCl_2$) expressed as a difference between measured δ value of the solution and the δ value of deionised water used for preparation of the investigated solution. Error bars are weighted uncertainties of the mean values generated from at least five measurement runs. Lower graphs: Measured δ values of the investigated solutions shown in the δ^2H- $\delta^{18}O$ space. Deionised water used to prepare the solutions is marked in red.

Double-salt mixtures

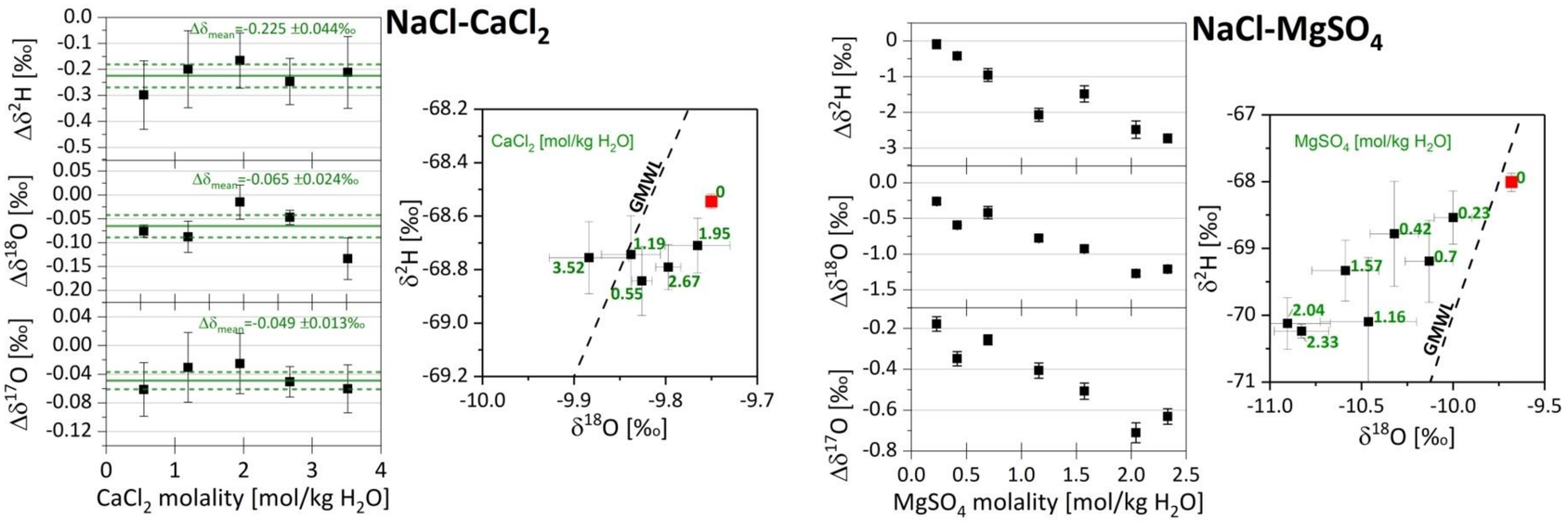


Fig. 6. Isotope effects observed for NaCl-$CaCl_2$ and NaCl-$MgSO_4$ double-salt mixtures, combined with the δ^2H- $\delta^{18}O$ plots of the measured δ values (deionised water used to prepare the solutions is marked in red). Error bars are weighted uncertainties of the mean values generated from at least five measurement runs.

Isotope offsets observed for double-salt mixtures mirror the effects observed for single-salt solutions. NaCl-$CaCl_2$ mixture reveals roughly constant offsets of similar magnitude to those observed for single NaCl and $CaCl_2$ solutions [Fig. 6]. They are equal to -0.225±0.044‰ for ^2H, -0.065±0.024‰ for ^{18}O and -0.049±0.013‰ for ^{17}O.

NaCl-$MgSO_4$ solution reveals gradually increasing offsets reaching significantly higher values: -2.73 ±0.14‰ for ^2H, -1.21 ±0.15‰ for ^{18}O and -0.63 ±0.08‰ for ^{17}O, for the molality of $MgSO_4$ equal to 2.33 mol/kg H_2O. In contrast, measured offset for single $MgCl_2$ solution which revealed peculiar behaviour (cf. Fig. 5) the measured offsets for NaCl-$MgSO_4$ are all negative and increase with increasing molality.

It should be noted that the observed isotope offets are not additive, neither for NaCl-$CaCl_2$ nor for NaCl-$MgSO_4$ mixtures.

CONCLUSIONS

- **Stable isotope analysis of brines using classical IRMS technique requires troublesome and time-consuming sample preparation methods and usage of appropriate correction factors [1-3]. Laser spectroscopic methods offer attractive possibilities to analyse directly such waters.**
- **Single-salt solutions (NaCl and $CaCl_2$) revealed small, negative offsets Δδ which are independent of the molality of the solution. In practical applications they can be neglected. In contrast, $MgCl_2$ and $MgSO_4$ solutions revealed significantly higher offsets, which need to be accounted for in direct analyses of concentrated brines in which those salts are present.**
- **The isotope offsets observed for double-salt mixtures mirror the effects observed for single-salt solutions. However, they are not additive, neither for NaCl-$CaCl_2$ nor for NaCl-$MgSO_4$ solutions which were investigated in this study.**

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