Isotope effects accompanying δ^2H, $\delta^{18}O$ and $\delta^{17}O$ analyses of brines using cavity ring-down laser spectroscopy:

insights from dedicated laboratory experiments

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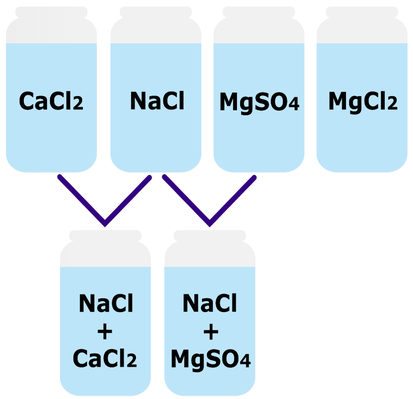
INTRODUCTION

Stable isotope analyses of heavy brines using classical IRMS technology typically require 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 salt solutions and double-salt mixtures, as a function of their molality.

METHODS

PREPARED SOLUTIONS AND MIXTURES:



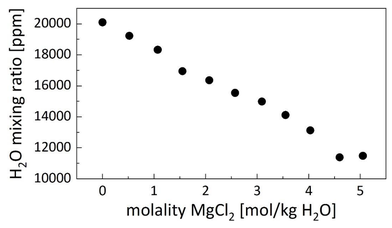
Solutions were prepared using anhydrous salts, on the basis of deionised water of known isotopic composition.

Solutions and mixtures were prepared and investigated for a large range of molalities, **from ca. 0.5 mol/kg H_2O up to the saturation conditions**.

Triple-isotope composition of the prepared solutions was analysed with **Picarro L2140-*i* analyser**.

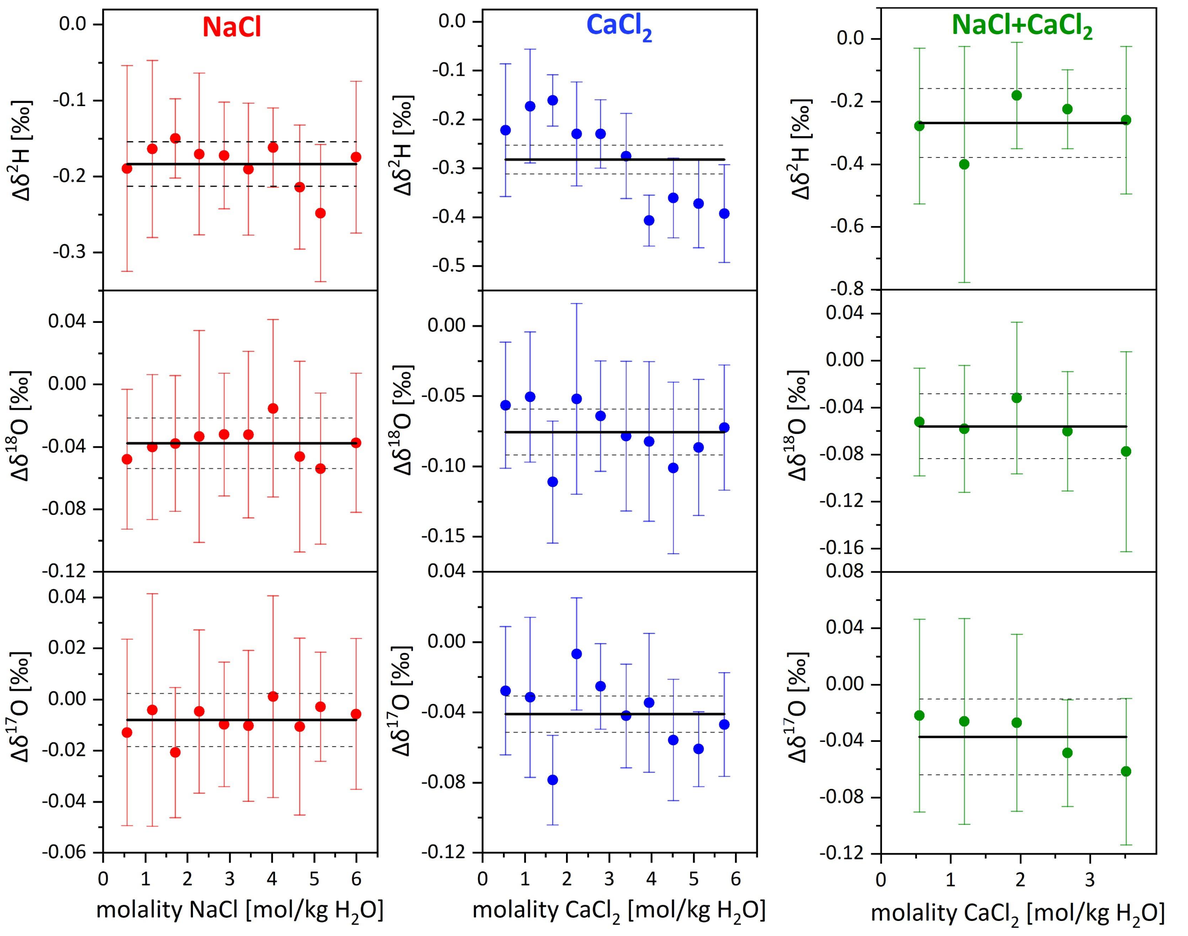
To avoid excessive accumulation of salt in the vaporizer unit, small stainless steel mesh (**salt liner**) was placed in the injection port of the vaporizer. The salt liner has been cleaned after each measurement run.

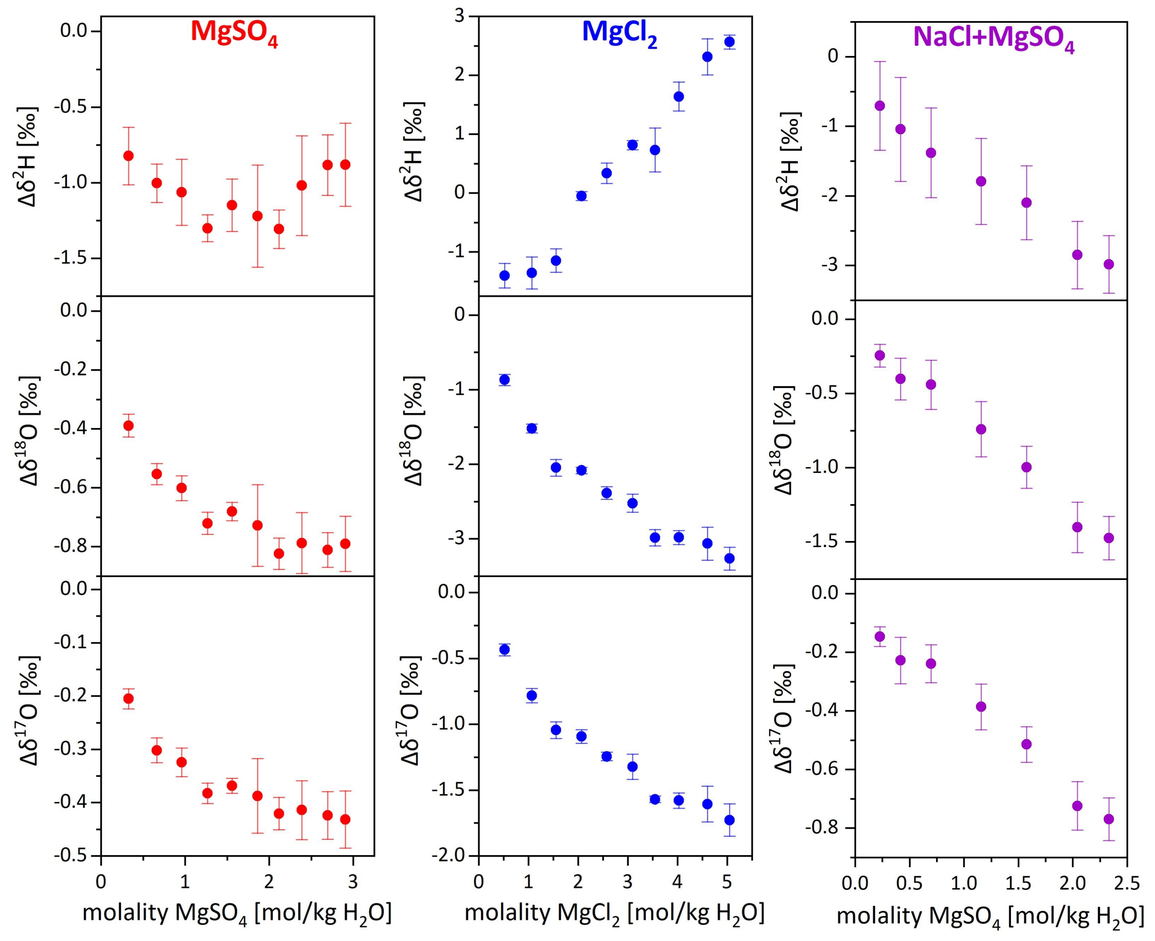
Due to high salt content in the solutions **the volume of the injected sample was adjusted** in order to maintain proper H_2O pressure in the optical cavity of the analyser.





RESULTS

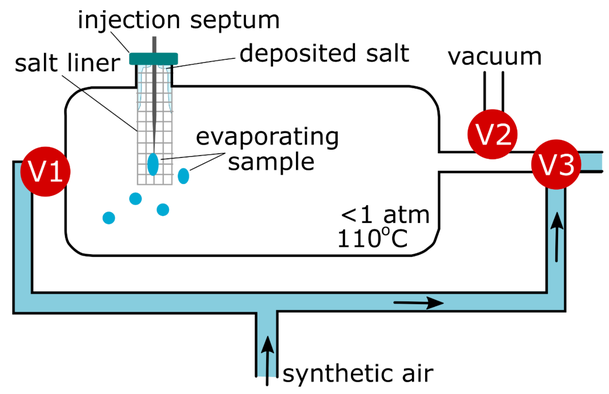




Negligible salt effect up to saturation

Significant salt effect, increasing with molallity

Salt effect $\Delta\delta \equiv \delta_{measured} - \delta_{source\ water}$



The evaporation of the sample modelled as a Rayleigh-type evaporation:

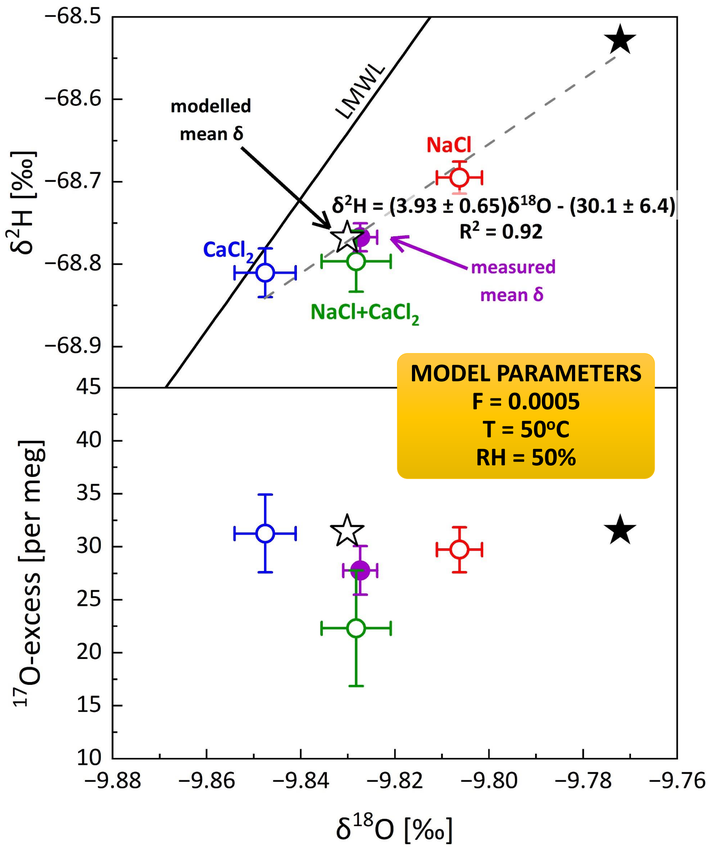
mean isotope ratio of the vapour phase

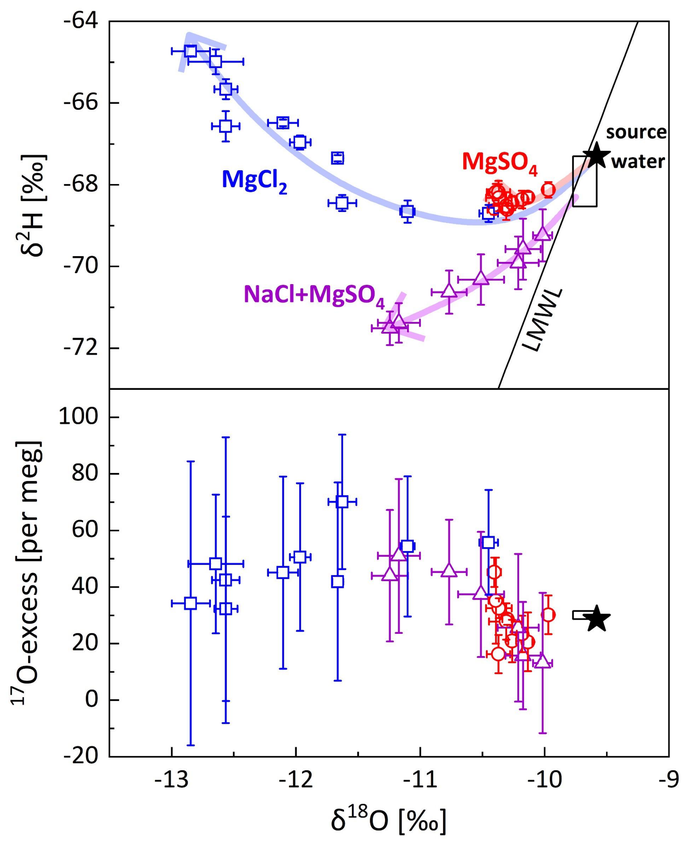
effective isotope fractionation (T and RH dependant)

$$R_v = R_0 \frac{1 - F^{1/\alpha_{eff}}}{1 - F}$$

initial isotope ratio of water

remaining fraction of water





CONCLUSIONS

① **Only solutions of monovalent ions can be analysed with the aid of laser technology without significant salt effects. However, it still causes serious detoriation of vaporizer unit and substantial reduction of syringe lifetime.**

② **For monovalent salts the presented modelling approach well reproduces observed salt effect for all three isotope systems investigated. For bivalent ions only the trends in the observed salt effects as a functions of salinity are confirmed.**

③ **The lack of additivity in case of direct isotope analyses of concentrated saline solutions which contain several ions, seems to be a general characteristics of laser-based analytical systems**

REFERENCES

[1] Sofer, Z. and Gat, J.R. The isotope composition of evaporating brined; effect on the Isotopic activity ratio in saline solutions. Eart Planet. Sci. Lett. 26 (1975) 179-186.

[2] Horita, J., Wesolowski, D.J., and Cole, D.R. The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions. I: Vapor-liquid water equilibration of single salt solutions from 50 to 100°C. Geochim. Cosmochim. Acta 57 (1993a) 2797-2817.

[3] Horita, J., Cole, D.R., and Wesolowski, D.J. The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions. II: Vapor-liquid water equilibration of mixed salt solutions from 50 to 100°C and geochemical implications. Geochim. Cosmochim. Acta 57 (1993b) 4703-4711.

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