

# Effects of dissolved salts on calcite-water oxygen stable isotope fractionation at elevated temperatures and pressures

T. Driesner  
T.M. Seward

*Institut für Mineralogie und Petrographie, ETH Zentrum,  
CH-8092 Zürich*

## Introduction

Since the pioneering experimental work of Taube and coworkers (e.g. Taube, 1954) it is well known that the addition of salts may significantly alter oxygen isotope fractionation between water and other phases at room temperature. Data on oxygen isotope fractionations involving aqueous electrolyte solutions reveal valuable information about solution structure. In addition accurate and precise knowledge of fractionation factors is crucial to the interpretation of stable isotope geochemical data (e.g. in the evaluation of fossil and recent fluid-rock interaction processes). However, there is controversial evidence in the literature about the existence and magnitude of measurable salt effects at elevated temperatures (i.e. up to 550°C, Truesdell, 1974, Zhang *et al.*, 1989, Horita *et al.*, 1993 and references therein).

## Experimental

In this study we investigated the oxygen isotope fractionation between calcite and 4 m aqueous NaCl, KCl and CaCl<sub>2</sub> solutions at 350°C, 500 and 8000 bars and 500°C, 8000 bars. The experiments were done in conventional piston cylinder and hydrothermal apparatus using platinum capsules. Typical charges comprised 7 to 10 mg of calcite and 5 to 25 mg of fluid.

## Results

In all experiments, only partial exchange was achieved. Standard extrapolation procedures were used to calculate equilibrium fractionation factors (table 1).

At 350°C/500 bars, fractionation factors for NaCl and KCl solutions are close to calcite-water (O'Neil *et al.*, 1969). A minor salt effect in the order of 0.8 to 1 per mil cannot be excluded. For CaCl<sub>2</sub>, a significant salt effect seems to be present.

At 350°C/8000 bars, no salt effect could be detected. Data for NaCl and KCl solutions agree with calcite-water fractionations within the limits of analytical uncertainty. Due to some scatter in the data a small effect in CaCl<sub>2</sub> solutions might be possible.

At 500°C/8000 bars, fractionation factors for NaCl and KCl again are very close to calcite-water fractionations. First data for CaCl<sub>2</sub> indicate a salt effect in the order of up to 3 per mil.

## Discussion

The salt effect on oxygen isotope fractionations involving aqueous solutions has, since Taube's (1954) work, commonly been attributed to inner shell cationic hydration. In general the heavy isotope becomes more enriched in the inner hydration shell around small and/or highly

TABLE 1. Equilibrium fractionation factors for oxygen isotope exchange between calcite and aqueous salt solutions. Data are extrapolated from partial exchange experiments. Estimated uncertainty of 1000 ln $\alpha$  is 0.3.

	350°C/500 bar, 35days 1000ln $\alpha$	350°C/8 kbar, 1 day 1000ln $\alpha$	500°C/8 kbar, 2 days 1000ln $\alpha$
Calcite-4m NaCl	2.9	3.9	1.5
Calcite-4m KCl	3.0	3.9	1.3
Calcite-4m CaCl <sub>2</sub>	<2.6	4.0	<-1.3
Calcite-water	4.0	4.1	1.5
Calcite-water (O'Neil <i>et al.</i> , 1969)	4.27	4.27	1.76

charged cations like  $\text{Li}^+$  or  $\text{Mg}^{2+}$  and depleted in the hydration shell of large single-charged cations like  $\text{Rb}^+$ . Therefore, in addition to the influence of temperature on isotopic fractionation processes, the measured magnitude of salt effects is critically dependent on the number of cations present and the bond strength between the cation and water molecules in the first hydration shell.

It is well known that electrolytes in aqueous solutions become highly associated at elevated temperatures and at equilibrium saturated water pressure. Therefore, the number of cations present at temperatures above  $\sim 300^\circ\text{C}$  is expected to be low, leading to a decrease in the magnitude of the salt effect. On the other hand there is evidence from the partial molar volumes of electrolytes and Born model computations of inner shell bond lengths (Shock *et al.*, 1992) that bonds in the inner hydration shell become much stronger near the critical point of water. This would lead to stronger isotopic fractionation between the hydration shell and bulk water.

Our results indicate that under the conditions investigated, the inferred stronger fractionation in the inner hydration shell does not lead to a major salt effect for solutions containing  $\text{Na}^+$  and  $\text{K}^+$ . Most likely it is cancelled out by both the temperature effect on isotopic equilibrium fractionation and the strong increase in ion association. The observed effects in  $\text{CaCl}_2$  solutions could be the result of hydration phenomena around polar ion pairs like  $\text{CaCl}^+$  as well as the 'free' aquated  $\text{Ca}^{2+}$ . Also, hydrolysis of Ca-ions should be taken into account although x-ray diffraction patterns of

the run material shows no evidence for the formation of portlandite or other hydroxy-phases.

### Conclusions

A series of pilot experiments at elevated temperature and pressure shows that salt effects on oxygen isotope fractionation are small or negligible for  $\text{NaCl}$  and  $\text{KCl}$  solutions at least up to a concentration of 4 m under 'hydrothermal' and 'metamorphic' conditions. Thus interpretations of fluid-rock interaction processes under these conditions can be based on mineral-water equilibrium fractionation factors. Significant salt effects, however, cannot be excluded for other electrolytes like  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{HCl}$ .

The data cannot be unambiguously interpreted in terms of solution structure, and information from spectroscopy and theoretical studies (e.g. molecular dynamics simulations) is required to provide deeper insight into the nature of the experimental results.

### References

- Horita, J., Wesolowski, D.J. and Cole, D.R. (1993) *Geochim. Cosmochim. Acta*, **57**, 2797–817.  
 O'Neil, J.R., Clayton, R.N. and Mayeda, T.K., (1969) *J. Chem. Soc. Farad. Trans.*, **88**, 803–26.  
 Taube, H. (1954) *J. Phys. Chem.*, **58**, 523–8.  
 Truesdell, A.H., (1974) *Earth Planet. Sci. Lett.*, **23**, 387–96.  
 Zhang, L., Liu, J., Zhou, H. and Chen, Z. (1989) *Econ. Geol.*, **84**, 1643–50.