

Abstract

Dissolution of halite slices was performed in diluted Dead Sea (DS) brines, with and without stirring. The range of DS dilutions used in the experiments was wide, from 10% to 90%, and the ratios between solution volume to surface area of the halite slices varied from 6.7 to 27 ml solution per cm^2 halite. In the experiments with stirring, data interpretation was performed by applying first order kinetics. The initial dissolution rate (at time zero) in 200 ml of 50% diluted brine was about 0.4 – 0.5 g/min (or about 13 – 17 mg NaCl/min cm^2) and it decreased exponentially with time. In the experiments without stirring, the data were best fitted to a power function and the dissolution rates have been estimated by the derivative of the power function. During the first half hour in 50% diluted brine, the rates are about twice slower in runs without stirring, than in runs with stirring; they become comparable after about two hours. The data obtained with the varying experimental conditions permit a reasonable estimate of halite dissolution rates in natural environments (such as the subsurface interaction between groundwater and old halite layers and the dissolution of halite crusts from the lake floor by diluted DS surface brines). The DSH calculations performed for all the experimental data enable us to predict the maximal amount of halite that can be dissolved by brines diluted to a wide range of salinities.

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Introduction

Previous studies on halite dissolution

Halite dissolution has been studied by several workers. Alkattan et al. (1997a) and Alkattan et al. (1997b) have performed experimental studies of halite dissolution kinetics in concentrated NaCl solutions (300 g NaCl / liter, degree of saturation (DSH) = 0.94)) in the absence and in the presence of dissolved trace metals and of anions. Dijk et al (2002) studied flow and dissolution patterns in rough walled halite fractures. Saturated NaCl solutions flowed through rock fractures at $\sim 1 \text{ mm sec}^{-1}$ during NMRI measurements and pulses of unsaturated solutions flowed in between the NMRI measurements, to induce dissolution of the rock fracture walls. The above studies were performed with almost saturated NaCl solutions. But, the chemical composition of the Dead Sea (DS) brines is very different from these pure NaCl solutions, and includes high concentrations of magnesium, calcium and potassium chlorides, as well as relatively high concentrations of trace metals. In 1993 the average chemical composition of major ions in the Dead Sea was K 7.81 g / liter, Na 36.4 g / liter, Mg 45.9 g / l, Ca 17.3 g / liter, Cl 225 g / liter and Br 5.6 g / liter (Gavrieli 1997). Data on the rate of halite dissolution in Dead Sea brine, whose chemical composition is so more complex than pure NaCl solutions, are not yet available.

The purpose of the present study is to provide preliminary data on the dissolution kinetics of halite in under-saturated Dead Sea brines under static or dynamic flow conditions. This study has also practical aspects as dissolution of halite in the subsurface is the direct cause for the development of sinkholes along the shores of the Dead Sea.

The hydrological system of the Dead Sea and the formation of sinkholes

The level of the Dead Sea has dropped drastically, by more than 20 meters during the past 50 years (Gertman and Hecht, 2002; Gavrieli and Oren, 2004; Lensky et al. 2005). Concomitant with the lake level drop, during the late 1980's and more so during the 1990's, large sinkholes began to develop on the western shore of the Dead Sea. This process continues nowadays, at the beginning of the 21st century. The sinkholes appear

in clusters, they differ in size and shape, their diameter reaches 25 meters and their depth up to 20 meters. The size of the sinkholes increases with time and several adjacent sinkholes sometimes merge into a bigger one.

The mechanism of the formation of the sinkholes is related to dissolution of salt in the subsurface by groundwater unsaturated with respect to halite (Wachs et al., 2000; Yechieli et al., 2006). As the lake level drops, groundwater level and the interface between fresh groundwater and DS brines are dropping too (Yechieli 2004). Consequently salt layers at depths of about 20m to 60m, that were previously in contact with DS brines, become exposed to contact with groundwater that is much less saline than the saturated DS brine. The salt dissolves and large voids are produced within the sedimentary column. Finally, the roof of unconsolidated sediments collapses and a new sinkhole appears on the lake shore.

The ‘sinkholes phenomenon’ raises the following question: how fast does halite dissolve in groundwater, what is the dependence of the dissolution rate on the salinity of the groundwater and more importantly, can we then predict, combined with available stratigraphical and hydrogeological data, the timing, location and extent of formation of new sinkholes.

Experimental procedures

1. Experimental set-up

Halite slices. Cores (about 3.7cm diameter) were drilled in pieces of rock salt from Mount Sdom, a salt diaper on the western shore of the southern basin of the Dead Sea (Zak, 1967). The cores were then cut into slices, ranging in thickness from about 8 mm to about 28 mm, with a water cooled saw. The thicker slices were used in experiments with more diluted brines and in experiments of longer duration. The exact dimensions of each slice were measured with a caliber. Upon cutting, slices had polished surfaces with no cracks and fractures, so that the initial surface area of each could be calculated quite accurately. During the experiments this polished appearance deteriorated a bit along with

some decrease in the thickness of the slices. **Therefore, each slice was used only once.** The initial dimensions of all slices are given in Table 1.

Dilutions of Dead Sea brines. Dilutions of DS brine sampled in June 2003 and in December 2004 were prepared with distilled water: 10%, 50%, 70% and 90% (% volume DS).

Dissolution with no stirring. All experiments with no stirring were performed in a thermo-stated water bath at 28 °C. A pre – weighed halite slice was fixed with a rubber band to the top of a three legs pizza fork (Fig. 1). 200 ml. of diluted brine, measured with a 250 ml cylinder, were added into a 250 ml pre-weighed beaker which was then re-weighed. The halite slice was carefully introduced into the beaker, with the fork holder upside down, so that the entire surface area of the slice was exposed to contact with the fluid (Fig. 1). The beaker was then placed in the thermo-stated water bath. Several experiments were also performed with 300 ml and 800 ml diluted brine in 400 ml and 1000 ml beakers, respectively. In the 250 ml and 400 ml beakers, the slices on the forks were positioned at mid-height of the solution. In the 1000 ml beakers the slices were below mid height, at about 35% of the solution's height in the beaker. But, most of the 800 ml experiments were performed with two forks, one on top of the other, thus increasing the height of the slice above bottom to about 62%. At the end of the experiment (minutes or hours) the fork was withdrawn from the solution using a pair of tweezers and the halite slice was dried with paper towel and weighed. The weight loss of the slice at the end of the experiment represents the amount of halite that was dissolved, though it may also include some insoluble matter from the rock salt, which became suspended in solution or sank to the bottom of the beaker. The beaker with the solution (brine + dissolved rock salt) was weighed again at the end of the experiment, the solution filtered through a pre-weighed 0.45 μ membrane filter and its density measured with a Paar density meter. The filtrate was then submitted to chemical analysis of major ions. The membrane filter was dried on a paper towel, and then weighed in order to assess the amount of insoluble matter that was released from the halite slice (Table 1).

Dissolution with shaking. During the early stages of the study, several dissolution runs were conducted in beakers, in a shaking thermo-stated bath at 28 °C (runs M2, M3, M10,

M11, M16, M17, M19 and M20 in Tables 2 and 3). In these experiments the handling of the halite slice and of the solution at the end of the experiment was similar to that described above for the *no stirring experiments*. It turned out however, that intensive shaking that would ensure complete mixing could not be achieved without spilling losses. Yet, closed vessels, like erlenmeyers, could not be used because it was not possible to introduce into them the halite rock slice and its holder.

Moderate shaking was however used in several of the saturation experiments.

Dissolution with magnetic stirring. To overcome the above problem, experiments were run using a small magnet (length 3cm, diameter 0.7cm) that was placed in 250 ml beakers. The halite slice was placed in a round cotton net, which was rimmed to the top of the beaker by a thin elastic band (the empty beaker was pre-weighed with the magnet and the net). The height of the halite slice above the beaker bottom was adjusted to be the same as in the *no-stirring* experiments, by carefully sliding the elastic rim on the outside wall of the beaker (Fig. 1). The beaker was immediately placed on a magnetic stirrer plate, at 350 rpm. The efficiency of mixing was checked with a drop of 0.1% Rhodamine B, which became dispersed instantly at 350 rpm. The temperature of the solution was about 22.5 °C at start and 24.5 °C at the end of the experiment. The procedure at the end of the experiment was identical to the *no-stirring* experiments.

Dissolution with ground halite rock. Several experiments were performed with ground halite rock; the size of the halite crystals was irregular, in the range of 0.5 – 2.0 mm. The experiments were conducted with 50% DS diluted brine and with no stirring. In these experiments no forks and no nets were used; the ground halite was placed on the bottom of the beaker. The surface area of the ground rock crystals could not be calculated because of the irregular size and shape of the crystals.

Saturation with respect to Halite. Several experiments, with and without shaking, were conducted to achieve saturation with NaCl, in each of the four dilutions of Dead Sea brines used for the kinetic experiments. In several experiments regular salt and ground halite rock were used instead of halite slices (without forks or nets). Instead of magnetic

stirring, a thermo-stated shaker bath, at 28 °C, was used. All the beakers were tightly closed with Parafilm, to avoid evaporation losses during the long run of the experiments (one to two weeks). The rest of the procedural steps were identical with the experimental procedure described above.

2. Calculation methods

Calculations with the weighing data.

w_1 is the weight of the empty beaker (g)

w_2 is the weight of the beaker with 200 ml diluted brine (g)

w_3 is the weight of 200 ml diluted brine (g)

w_4 is the weight of the beaker with the solution at the end of the experiment (g)

w_5 is the weight of the brine at the end of the experiment; this weight includes the halite rock that was dissolved (i. e. NaCl and some insoluble matter)

w_6 is the initial weight of the halite slice (g)

w_7 is the weight of the halite slice at the end of the experiment (g)

w_8 is the weight loss of the halite slice (g)

w_9 is the initial weight of the membrane filter (g)

w_{10} is the weight of the membrane filter bearing the insoluble portion of halite that has been dissolved from the halite slice (g)

w_{11} is the net weight of the insolubles (g)

w_{12} is the net amount of NaCl that has been dissolved from the halite slice

w_{13} is the net weight of NaCl added to the solution

$w_3 = w_2 - w_1$ weight of 200 ml brine

$w_5 = w_4 - w_1$ weight of brine at end of experiment (including insolubles)

$w_8 = w_6 - w_7$ weight loss of halite slice

$w_{11} = w_{10} - w_9$ weight of insolubles

$w_{12} = w_8 - w_{11}$ loss of NaCl from the halite slice

$w_{13} = w_5 - w_3 - w_{11}$ net weight of NaCl added to solution

In principle w_{13} , the net weight of NaCl added to the solution, should be identical to w_{12} , the net loss of NaCl from the halite slice, but in reality w_{13} is usually somewhat lower than w_{12} by about 1 to 2 g. This discrepancy is due to some loss of solution (some loss from w_5 onto the slice and onto the fork while withdrawing them from the beaker at the end of the experiment), and possibly also due to some loss by evaporation from the beaker.

By dividing the weight of the initial brine to its density (ρ_1 , g cm⁻³) the exact initial volume of solution (V_1 , cm³) can be calculated: $V_1 = w_3 / \rho_1$

The volume of solution at the end of the experiment is V_2 . It could be calculated as:

$$V_2 = (w_5 - w_{11}) / \rho_2$$

where ρ_2 is the measured density at the end of the experiment. But, because as mentioned above, there are some weight losses from w_5 , we have chosen an alternative way to calculate V_2 more exactly:

$$V_2 = (w_3 + w_{12}) / \rho_2$$

V_1 and V_2 will be needed in the calculations of NaCl that has been dissolved during the experiments, calculations which will be based on the chemical analysis of the brines.

Calculations based on chemical analysis.

Chemical analyses were performed on the initial diluted Dead Sea brine solution and on the brine at the end of the experiment.

Calculation of g NaCl dissolved, (w_{12Na}) based on Na analysis (mg / L):

$$w_{12Na} = (((Na_{meas} - (Na_{init} * V_1/V_2)) * V_2) / (1000 * 1000)) * 58.5/23$$

where Na_{meas} and Na_{init} are the Na concentrations (mg / L) in the brine at the end of the experiment and in the initial diluted Dead Sea brine, respectively.

Similarly, calculations were performed for g NaCl dissolved (w_{12Cl}) based on Cl analysis (mg / L)

$$w_{12Cl} = (((Cl_{meas} - (Cl_{init} * V_1/V_2)) * V_2) / (1000 * 1000)) * 58.5/35.5$$

A routine check of the chemical analysis (Appendix 1) was performed by calculating the expected Na (or Cl) concentration at the end of the experiment based on the weight loss from the halite slice and comparing it to the measured value, Na_{meas} (or Cl_{meas}) as following:

$$Na_{expected} = (((w_{12} * 23 / 58.5) * 1000) / V_2) * 1000 + (Na_{init} * V_1 / V_2)$$

$$Cl_{expected} = (((w_{12} * 35.5 / 58.5) * 1000) / V_2) * 1000 + (Cl_{init} * V_1 / V_2)$$

The above calculations enable us to report the results of NaCl dissolution in several ways:

- (a) a plot of the losses of NaCl from the halite slices (g) vs. the duration of the experiments i.e. a plot of w_{12} (or w_{12Na} or w_{12Cl}) vs. time (min); (see below, section Results, Figs. 4 and 5)
- (b) a plot of NaCl slice losses per initial surface area of the respective slices (g / cm²) vs time (min) ; (see below, section Discussion, Figs. 8a, 8c, 8d)
- (c) a plot of the rate of NaCl slice loss, i.e. of NaCl dissolved, per initial surface area of the slice (cm²) into the initial brine volume V_1 (ml), expressed per liter brine in units of g / cm² L vs. time. The calculation is: $(w_{12} / (\text{slice area} * V_1)) * 1000$. (see also below, section Discussion, Fig. 8i).

For the sake of simplicity we will refer from now on to w_{12} , w_{12Na} and w_{12Cl} as **W**, **W_{Na}** and **W_{Cl}**, respectively.

The molalities (mole/kg water) of all ions in solution, needed for the calculation of DSH, were computed as following:

Molality = molarity / weight of water in the brine

where molarity (mole/L) = ion concentration (mg / L) / (A * 1000)

A is the atomic weight of the respective element

and the weight of water in the brine = kg water / L Brine =

= ((density * 1000) – (TDS/1000)) / 1000

density is in g/cm³ and TDS (Total Dissolved Solids) in mg/L units

Results

The analytical data for all the experiments are listed in Table 2. At first only Na and Cl were measured. At a later stage complete chemical analyses were performed. The complete chemical analysis is useful because:

- a. it indicates the quality of the analytical data, expressed by R.E. (%), the percent Reaction Error :

$$\text{R.E. (\%)} = ((\text{sum of cations} - \text{sum of anions}) / \text{sum of cations and anions}) * 100$$

- b. full chemical analysis enables to calculate the degree of saturation with respect to halite (DSH) for each experiment.

The analytical procedure was further improved by weighing the brines at the beginning and at the end of the experiment and by measuring their densities.

Table 3 summarizes the experimental conditions for all the experiments and the respective amounts of NaCl that have been dissolved. The initial volumes, measured by cylinders are listed in Table 3, although the exact initial volumes, V_1 , are usually somewhat smaller, due to small losses on the measuring cylinder wall. The V_1 were of course calculated according to the net weight of the initial brine and its density and were used in further calculations, but are not shown in Table 3. The final volumes, V_2 , are always larger than V_1 ; they increase with the increasing amounts of dissolved NaCl. The amounts of dissolved NaCl were calculated according to weight loss of NaCl from the slice (W), and according to the chemical analyses (W_{Na} and W_{Cl}). The three values are usually very close to each other as can be seen in Figs 2a, 2b and 2c. The increase in volume ($V_2 - V_1$) in the 200 ml experiments vs. the amount of NaCl dissolved (W) is shown in Fig. 3, exhibiting a linear correlation ($R^2 = 0.994$) which almost passes through the origin. Accordingly, each gram of NaCl dissolved in 200 ml, causes a volume increase of about 0.37 ml or

0.074 ml / g NaCl dissolved / L. It should be mentioned that the correlation of Fig. 3 holds over a wide range: it is based on all the experiments at the different DS dilutions, including the saturation experiments.

Dissolution of halite vs time in 50% DS.

The following experiments were conducted in 50% DS:

dissolution of halite rock slices in 200 ml (Fig. 4a, 4b) with no stirring

dissolution of halite rock slices in 300 ml (Fig. 4c) with no stirring

dissolution of halite rock slices in 800 ml (Fig. 4d) with no stirring

dissolution of halite rock slices in 200 ml (Fig.4e) with magnetic stirring

dissolution of ground halite in 200 ml (Fig.4f) with no stirring

complete dissolution of certain amounts of NaCl in 200 ml 50% DS, prior to the dissolution experiment with halite rock slices (Fig. 4g), with no stirring

With the exception of Fig. 4b where the dissolution is based on chemical analysis, i.e. on W_{Na} and W_{Cl} , all other Figures are based on slice loss of weight, W .

In the 200 ml experiments shown in Figs. 4a and 4b the ratio between solution volume and the slice surface area is about 6.7 ml solution / cm² initial surface area of the halite slice. It can be seen that dissolution does not increase linearly with the duration of the experiment. (It should be made clear that each data point in Figs. 4, and in all other Figures as well, is a separate experiment with a new halite slice). Duplicate experiments, as regards the duration of the experiment, are approximately within 10% reproducibility.

In Figs. 4c and 4d are shown experiments that were conducted in 300 ml and 800 ml, respectively, and the ratio between solution volume and slice area was about 10 and 27, respectively. Despite the increase in the ratio volume/slice area by about 50% and 300%, the amount of NaCl dissolved is only about 20% larger in 300 ml and about 100% larger in 800 ml. It seems like not all the larger, available volume of brine participates in the dissolution process. The 'effective' volume probably becomes restricted by stratification that builds up during the experiment (see Appendix 2).

In the experiments with magnetic stirring, the volume to slice area varies gradually from about 7 in the shorter runs to about 4.8 in the longest ones. In these experiments (Fig. 4e), dissolution from the halite slice is more than twice larger than in runs with no stirring (Fig.4a). Moreover it seems that in the 4 hours run, saturation with respect to halite has

almost been reached (32 g halite have been dissolved in 4 hours and 32.4 g in the saturation experiments, see also section ‘saturation’ below).

The experiments with ground halite, with no stirring, are shown in Fig. 4f. The same amount of about 22 g, has been used in all the experiments. No clear dissolution trend could be observed. There are two possible reasons: first, despite the equal initial weights of ground halite, the surface area might have been very different from run to run, because the size and shape of the particles was very irregular and second, the experimental set-up was different from all the other runs. The ground halite lied on the beaker’s bottom, while the halite slices were suspended in the beaker at about mid – depth of the brine column. However, this set of experiments is important because it gives the order of magnitude of dissolution in conditions that might occur in a natural environment.

The set of experiments with initially dissolved NaCl (Fig.4g) was performed in order to see if the initial dissolution rate is about the same at different NaCl concentrations, in a 50% DS solution. In these experiments, prior to the slice dissolution runs, different amounts of NaCl were dissolved in 200 ml 50% DS . All the runs were of equal duration, 60 minutes. Fig. 4g shows that as more NaCl is initially dissolved, the slower the halite slice dissolves. In other words, the initial dissolution rate is, as expected, dependent on salinity.

Dissolution of halite vs. time in 10%, 70% and 90% DS

All the experiments with these DS dilutions were run in 200 ml. The ratio of solution volume (ml) per slice area (cm²) was about 7.

In 10% DS dilution relatively large amounts of NaCl can be dissolved in a relatively short time (Fig. 5a). The agreement between the weight data W , and the chemical analysis data, W_{Na} and W_{Cl} is very good (Fig.5b).

In the runs with 70% DS, the agreement between the duplicates is satisfactory, in some cases within less than 10% (Fig. 5c).

The slowest and smallest dissolution was measured, as expected, in the 90% DS runs (Fig. 5d; note the different time scale for these runs). The duplicate runs are good and in two cases even undistinguishable from each other on the plot.

Saturation with respect to halite

Experiments for halite saturation attainment were conducted with various DS dilutions at 28 °C. Most of the experiments were run in parallel with halite rock slices and with commercial table salt. The experiments lasted between 5 and 18 days.

The saturation experiments are important because they indicate the maximum amount of salt that can be dissolved in a certain dilution of Dead Sea brine. The amounts of NaCl that have been dissolved in the various runs are given in Table 3 and in Figs. 6a, 6b and 6c. The amounts that have dissolved in 200 ml, as calculated by all 3 methods, (W , W_{Na} and W_{Cl}), are about 61.5 g, 32.4 g, 19.5 g and 7.7 g in 10%, 50%, 70% and 90% DS, respectively (Table 3).

Figs. 6a, 6b and 6c show, according to the W , W_{Na} and W_{Cl} results respectively, that there is a clear inverse linear correlation between the amount of NaCl needed to attain saturation with respect to halite and the initial degree of dilution of the DS brine. In Fig. 6d the concentrations of NaCl at saturation are expressed as molalities. It is interesting to note that the extrapolation to 0% DS content in Fig. 6d, yields a NaCl solubility of 6.05 mole / kg water, quite similar with the Handbook value of 6.27 mole / kg water, at 28 °C. Extrapolation to 100% DS in Fig. 6d yields 1.75 mole Na / kg water, not very different from the measured value in DS brine, sampled in June 2003, of 1.57 ± 0.03 mole / kg water.

Discussion

The rate of halite dissolution with magnetic stirring

The aim of the experiments with shaking or stirring was to assess the dissolution rate of halite in a well mixed environment, free of concentration gradients that may build up around the halite slice. Magnetic stirring at room temperature (22°C to 24°C), in beakers, proved to be more suitable than shaking and was used in experiments M111-M114, M127-M131 and M135 (Table 3). We describe the kinetics of the dissolution rate of NaCl in these experiments as a first order reaction.

The initial concentration of NaCl in the DS dilution is C_0 . NaCl can dissolve in the DS dilution until saturation with respect to NaCl, C_{sat} , is reached. The concentration of dissolved NaCl at time t is C_t (C_t is the sum of C_0 and the amount of NaCl that has been dissolved during time t). The rate of dissolution, dC_t / dt , at any time t is given by:

$$dC_t / dt = \lambda (C_{sat} - C_0)e^{-\lambda t} \quad (1)$$

where λ (min^{-1}) is the dissolution constant, C_{sat} and C_t are as defined above. The term $(C_{sat} - C_0)$ decreases exponentially with time, which means that the dissolution rate decreases exponentially with time.

Integrating Eq. 1 yields:

$$C_t = - (C_{sat} - C_0) e^{-\lambda t} + C_{sat} \quad (2)$$

Rearranging Eq. 2

$$C_{sat} - C_t = (C_{sat} - C_0) e^{-\lambda t}$$

And in logarithmic form

$$\ln (C_{sat} - C_t) = \ln (C_{sat} - C_0) - \lambda t \quad (3)$$

A plot of $\ln (C_{sat} - C_t)$ vs. time t , should be a straight line with slope λ and intercept $\ln (C_{sat} - C_0)$.

The plot of $\ln (C_{sat} - C_t)$ vs. time t for the runs with magnetic stirring is shown in Figs. 7a and 7b. The runs performed with DS sampled in June 2003 (sample M111- M114, Fig.7a) were plotted separately from those performed with DS sampled in Dec 2004 (samples M127-M130, Fig.7b) because the two DS samples have somewhat different C_{sat} ,

saturation concentrations (in June 2003 the surface water of the Dead Sea brine was still somewhat diluted following the abundant rainy winter of 2002/3 and the increased freshwater inflow to the lake). C_{sat} for 50% DS sampled in June 2003 was measured by experiments M48-M51. For this model calculation we used the data of M50 (amount of NaCl added to C_o was 34.5 g), in which the highest density and DSH were achieved. For 50% DS sampled in Dec 2004 saturation was almost achieved in run M135 (amount of NaCl added to C_o was 32 g; degree of saturation with respect to halite was $\text{DSH} = 0.98$). It seems that C_{sat} in the Dead Sea decreased from June 2003 to Dec 2004 by about 2g. The correlation coefficients for the linear plots in Figs. 7a and 7b are good, but the slopes are somewhat different. It is remarkable that the calculated values of C_{sat} (from the intercepts of Figs. 7a and 7b) confirm the measured decrease in C_{sat} from June 2003 to Dec 2004, by about 2 g NaCl.

Using the dissolution constants derived from Figs. 7a and 7b, the instantaneous dissolution rates (dC_t / dt) could be calculated. The dissolution rates were calculated for the two sets separately (by Eq.1) and were plotted together in Fig 7c. They decrease exponentially with time. The maximal dissolution rate, at $t = 0$, is about 0.4 – 0.5 g/min. The average dissolution rate for each run, calculated by dividing the amount of dissolved NaCl (g) by the duration (min) of the experiment, are shown in Fig, 7d and for comparison with the calculated instant rates, they were also plotted on Fig.7c.

It must be mentioned that in the above kinetic model the slice area has not (and could not) been taken into account. Also, it must be noted that the initial slice area changes during the experiment and that all the above rates are within an initial volume of 200 ml.

However, it is useful to express the instantaneous dissolution rate under stirring conditions per surface area of the halite slice, (by dividing the dissolution rate to surface area, Fig. 7e), in order to compare them with those obtained under no stirring conditions (see below).

The dissolution rate of halite with no stirring

Dissolution in 50% DS

In the experiments with no stirring the simple model from above cannot be applied because stratification builds up around the slice and C_t is not homogenous in the whole

beaker at a certain point in time. We do measure W , W_{Na} and W_{Cl} , but these reflect average concentrations at the end of the run, after the stratification has been destroyed. Therefore, in *no stirring* conditions we cannot express properly $C_{\text{sat}} - C_t$.

A power best fit has been chosen to express the empirical relationship between the amounts of NaCl dissolved and the dissolution time. In all the power best fits, the amounts of dissolved NaCl have been expressed per cm^2 initial slice area. This is done in order to minimize the effect of the surface area of the slice, which varies from run to run (see in Table 1) and affects therefore the rate of dissolution.

Figs. 8a, 8c and 8e show the power best fits for the experiments performed in 200 ml, 300 ml and 800 ml, respectively. As at the beginning of each run, at time $t = 0$, there is no dissolved NaCl, a (0,0) data point should be added. However, it is not possible to apply a power best fit if the coordinates of one point are (0,0). Instead, a very close to zero data point, such as (0.001; 0.001) was used. The coordinates of this 'zero' data point have been slightly changed until a best fit (highest R^2) was achieved. In order to improve the power best fit for the 800 ml runs, samples M57 and M58 which are outliers of the general trend shown in Fig.4d, have been excluded from Fig. 8e.

The rate of dissolution of NaCl decreases with time and is given (approximately) by the time derivative of the power best fit equation. The (approximate) instantaneous rates of dissolution at the end of each run have been calculated and are shown in

Figs. 8b, 8d, and 8f. In Fig. 8g, the rates in the different reaction volumes are compared. The rate is about the same in 200 ml and 300 ml and about twice larger in 800 ml. It should be kept in mind that these sets of experiments were performed with no stirring and that stratification developed in the beakers. The elevation -in the beaker- of the stratification coincides with that of the halite slice, which is determined by the height of the pizza holder (see Appendix 2). The volume below the slice is apparently well mixed. Thus, the increased rate in the 800 ml experiments is probably due to the larger volume that participates in these experiments, in which the halite was kept at a higher elevation, of two pizza holders.

An attempt to express the rates in terms of unit volume (L) is shown in Fig. 8h. It should be noted that the volume increases slightly when dissolution takes place. The data shown in Fig. 8h refer to the initial reacting volume. Also, it should be mentioned that due to the

specific experimental set up in each case, one cannot be sure that extrapolation to 1 L really holds

Dissolution in 10% DS, 70% DS and 90% DS

The same approach described above, of power best fit to the experimental data of the runs with 50% DS and no stirring, has been adopted for the runs with the other DS dilutions. The best fits for the runs in 10% DS, 70% DS and 90% DS, shown in Figs. 9a, 9c and 9e, are based on the W data (run M88 was excluded from the 10% DS best fit). Very similar best fits were obtained with the W_{Na} and W_{Cl} data.

The instantaneous dissolution rates, estimated by the respective derivatives are shown in Figs. 9b, 9d, and 9f. For comparison, the rates obtained from the W_{Na} data are shown too in Fig. 9d. The rates decrease with time and decrease with increasing DS concentration (i.e. less DS dilution)

Fig. 10a is a summary of the dissolution data in the different DS dilutions. In Fig. 10b the instantaneous rates in 200 ml and 50% DS, with and without stirring, are compared. It can be seen that during the first half hour, they are about twice larger with stirring and become comparable after about 2 hours.

The degree of halite saturation (DSH) in the different DS dilutions

From the analytical data given in Table 2 the concentrations of all the major elements in terms of molalities (mole / kg water) have been calculated. The degree of halite saturation, DSH, has been calculated following Pitzer's approach for hypersaline solutions (Pitzer, 1973; Pitzer, 1975) and adopted for the Dead Sea (Krumgalz, 1982).

In Fig. 11a the molalities of Na (mole / kg water), measured in solution at the end of each experiment have been plotted vs. the respective DSH values. For each initial DS dilution (marked by open shapes) the gradual approach to saturation (marked by filled shapes) follows a distinct pathway. The 'saturation experiments' have also been included in this Figure and mark the approximate end of each pathway. Unlike the rest of the figures in this report, (where dissolution was given as a function of time), Fig. 11a shows

amounts of NaCl that **can be** dissolved in a certain DS dilution, regardless of time and of experimental set up,. In Fig. 11b this feature appears even more clearly as only the ‘dissolution added’ molalities of Na (mole / kg water) have been plotted vs. DSH (the ‘added’ molality was calculated by subtracting the initial molality of the DS dilution from the measured molality at the end of the experiment).

Summary and Conclusions

1. The present set of experiments shows that the dissolution rate of halite is relatively fast, on the order of up to a few mg NaCl / cm² min, even in saline solutions such as 50% DS - 90% DS.
2. The wide range of DS dilutions, from 10% to 90%, the varying solution to surface area ratios (from 6.7 to 27 ml solution per cm² halite) and the comparison between stirring and no-stirring conditions (at 50% DS) enables us to estimate dissolution rates of halite within a reasonable limit for a wide range of salinities and flow conditions.
3. As expected, the dissolution rate is related to the initial salinity of the solution, the higher the salinity the slower the dissolution rate.
4. It is interesting to compare the dissolution rates obtained in this study with published data. Alkattan et al. (1997a) report the dissolution rates of halite in solutions of 300 g NaCl / liter (DSH = 0.94), at 25°C, for runs of 10 minutes performed at various stirring speeds (the ratio liquid volume to solid surface is not given). At 35 rpm, 340 rpm and 2000 rpm the average dissolution rates were 2.1, 6.0 and 13 mg NaCl / cm² min, respectively. We have worked with relatively more diluted solutions than Alkattan et al (1997a), representing concentrations of brines and groundwater that do occur in the Dead Sea system. The largest initial concentration in our experiments was 90% DS (DSH = 0.4). From the power best fit of the runs with 90% DS and no stirring, it can be calculated that during the first 10 min 0.061 g NaCl / cm² have been dissolved or on the average about 6.1 mg NaCl / cm² min. Figure 10b, which compares dissolution rates with and without stirring, suggests that if we would have applied stirring in 90% DS, we would have obtained during the first 10 minutes, a dissolution rate about twice larger than

the above $6.1 \text{ mg} / \text{cm}^2 \text{ min}$. Thus, although a direct comparison with published data is not possible, our results are well within the range of published data.

5. The derived dissolution rates become relevant in two environments: a. at the subsurface where groundwaters that are usually less saline than 50% DS (Yecheieli et al 2006; Abelson et al. 2006), can dissolve halite layers, provided their flow is fast enough (otherwise saturation will be reached soon and dissolution stops). A possible application is the estimate of the rate of formation of sinkholes. Such a preliminary study was done by Shalev et al (2006) which used the lowest dissolution rate ($1.2 \text{ mg} / \text{cm}^2 \text{ min}$) measured in the experiments of Alkattan et al. (1997a). It seems that a better estimate of sinkhole formation can be obtained with the results of the present study. b. the DS surface layer, when it becomes diluted by floodwater it dissolves halite from the lake floor in shallow areas and from the delta of the end brine (Beyth et al., 1998). A possible application is the estimate of the amounts of halite that can be dissolved from these areas by rising DS lake levels in winter.

6. Technical conclusions: a. experiments with stirring are reliable and exact, because the solution is homogenous during the entire experiment and saturation with respect to halite can be easily approached. In experiments with no stirring, stratification within the reaction vessel hinders the dissolution rate and a fast approach to saturation. In natural environments, the 'real' situation is somewhere in-between these two extremes. b. the fact that saturation was observed in experiments with stirring suggests that the quantitative calculations based on the analytical data and on the DSH program for the Dead Sea system are satisfactory.

Acknowledgements

We thank Dr. Vladimir Lyakhovsky for mathematical advice, insight and support. We are grateful to Dr. Olga Yoffe, Dr. Sara Ehrlich and Yoetz Deutsch for their dedicated help with the chemical analyses. Robert Cnafo, Shlomo Ashkenazy and Chaim Huri are acknowledged for their technical help. Special thanks are due to Dina Stiber for the reliable chemical analyses and from one of us (M.S.) for her friendly and warm hospitality.

References

- Abelson, M., Yechieli, Y., Crouvi, O., Baer, G., Wachs, D., Bein, A., and Shtivelman, V., 2006. Evolution of the Dead Sea sinkholes, in “New Frontiers in Dead Sea Paleoenvironmental Research”, eds. Y. Enzel, A. Agnon, M. Stein, *Geological Society of America, Special Paper*, pp. 241-253.
- Alkattan M., Oelkers E.H., Dandurand J.L. and Schott J. 1997a. Experimental studies of halite dissolution kinetics 1, The effect of saturation state and the presence of trace metals. *Chem.Geol.* 137: 201-219.
- Alkattan M. Oelkers E.H., Dandurand J.L. and Schott, J. 1997b. Experimental studies of halite dissolution kinetics: II. The effect of the presence of aqueous trace anions and $K_3Fe(CN)_6$. *Chem.Geol.*143: 17-26.
- Beyth M., Katz O. and Gavrieli I. 1998. Propagation and retrogradation of the Salt Delta in the Southern Dead Sea: 10985 – 1992. *Isr. J. Earth Sci.* 46:95 – 106.
- Gertman I. and A. Hecht, 2002. The Dead Sea hydrography from 1992 to 2000. *J. of Marine Systems* 35:169-181.
- Gavrieli, I. Halite deposition from the Dead Sea 1960-1993. 1997. In: *The Dead Sea : the lake and its setting* (eds. T. Niemi, Z. Ben-Avraham and J.R. Gat) p.161 – 170. Oxford University Press
- Gavrieli I. and Oren A. 2004. The Dead Sea as a dying lake. In: *Dying and Dead Seas; Climatic versus Anthropogenic causes* (eds. Nihoul J.C.J., Zavialo P. and Micklin P.P.) NATO ARW/ASI Series, Kluwer Academic Pub.
- Krumgalz, B. S. and Millero, F.J. 1982. Physico-chemical study of the Dead Sea waters, I. Activity coefficients of major ions in Dead sea water. *Marine Chemistry* 11: 209-222.
- Lensky, N.G., Dvorkin Y., Lyakhovsky V. Gertman I. and Gavrieli I. 2005. Water , salt and energy balances of the Dead Sea. *Water Resour Res.* 41: W12418, doi:10.1029/2005WR004084,2005
- Pitzer, K. S. 1973. Thermodynamics of electrolytes. Theoretical. basis and general equations. *J. of Physical Chemistry* 77: 268-277.
- Pitzer, K. S. 1975. Thermodynamics of electrolytes. V. Effect of higher- order electrostatic terms. *Journal of Solution Chemistry* 4: 249-265.
- Shalev, E., Lyakhovsky, V. and Yechieli, Y. 2006. Salt dissolution and sinkhole formation along the Dead Sea shore. *J. Geophysical Research* 111, doi: 10/1029/2005JB004038.

- Wachs, D., Yechieli, Y., Stivelman, V., Itamar, A., Baer, G., Goldman, M., Raz, E., Riebekov, M. and Shatner, U. 2000. Formation of sinkholes along the shore of the Dead Sea – summary of finding from the first stage of research: Geological Survey Report GSI/41/2000 (in Hebrew), 49 p.
- Yechieli, Y., Abelson, M., Bein, A., Shtivelman, V., Crouvi, O., Wachs, D., Baer, G., Kalvo, R. and Lyakhovsky, V., 2004. Formation of sinkholes along the shore of the Dead Sea – summary of finding from the second stage of research: Geological Survey Report GSI/41/2004 (in Hebrew), 34 p.
- Yechieli, Y., Abelson, M., Bein, A., Crouvi, O. and Shtivelman, V., (2006). Sinkholes “swarms” along the Dead Sea coast: Reflection of disturbance of lake and adjacent groundwater systems. *GSA Bulletin* 118, 1075-1087.
- Zak I. 1967. Mount Sdom. Ph.D. thesis , Hebrew university, Jerusalem.

Table 1.								
Dimensions, weight and insoluble mater content of halite slices used in experiments.								
slice	diameter	width	total surface	volume	initial	at end	insoluble	calculated
no.			area		weight	weight	residue	density
	cm	cm	cm ²	cm ³	g	g	%	g cm ⁻³
M2 (T1)	~ 3.6	0.73	28.6	7.41	17.6272	14.7712	13.0	
M3 (T2)	~ 3.6	0.63	27.5	6.46	15.3620	12.6985	10.8	
M4 (LT1)	~ 3.6	0.86	30.1	8.76	20.8471	2.2632*	10.9	
M5 (LT2)	~ 3.6	0.70	28.3	7.10	16.8906	0.872*	5.2	
M8 (LT1b)	~ 3.6	0.60	27.1	6.09	14.4926	5.1954	17.7	
M9 (LT2b)	~ 3.6	0.52	26.2	5.28	12.5569	2.3368*	18.6	
M10 (T3)	~ 3.6	0.73	28.6	7.44	17.6990	16.2947	16.7	
M11 (T4)	~ 3.6	0.73	28.6	7.45	17.7338	16.7775	23.1	
M13 (LT3)	3.60	0.51	26.11	5.21	12.4083	9.0092	6.6	
M14 (LT4)	3.60	0.58	26.90	5.95	14.1527	10.5316	5.9	
M16 (T5)	~ 3.6	0.69	28.1	7.05	16.7675	9.2776	5.4	
M17 (T6)	~ 3.6	0.65	27.7	6.66	15.8401	8.0036	6.1	
M19 (T7)	~ 3.6	0.64	27.6	6.47	15.4040	14.0543	16.4	
M20 (T8)	~ 3.6	0.66	27.8	6.72	15.9936	13.2444	9.1	
M22 (LT5)	3.55	0.84	29.15	8.31	16.3951	9.0234	5.0	1.97
M23 (LT6)	3.61	0.84	29.98	8.59	16.0878	8.3872	3.7	1.87
M24 (LT7)	3.51	0.87	28.88	8.37	14.8842	8.6559	4.0	1.78
M25 (LT8)	3.68	0.90	31.60	9.52	17.7185	12.8435	6.9	1.86
M27 (LT9)	3.67	0.84	30.83	8.88	17.6158	7.2469	4.6	1.98
M28 (LT10)	3.64	0.75	29.37	7.80	16.6477	6.9987	5.7	2.13
M29 (LT11)	3.68	0.86	31.20	9.14	19.7677	8.0349	5.3	2.16
M30 (LT12)	3.69	0.79	30.53	8.44	17.4343	5.298	2.5	2.07
M31 (LT13)	3.70	0.56	28.00	6.02	11.7097	9.3838	10.2	1.95
M32 (LT14)	3.68	0.65	28.77	6.91	14.8816	12.1767	5.6	2.15
M33 (LT15)	3.72	0.80	31.07	8.69	16.3812	12.6591	8.9	1.89
M34 (LT16)	3.69	0.73	29.84	7.80	16.0468	11.8529	5.5	2.06
M35 (LT17)	3.71	0.75	30.35	8.10	16.6403	10.5313	6.3	2.05
M36 (LT18)	3.66	0.90	31.37	9.46	19.1036	12.8629	4.9	2.02
LT19	3.56	0.68	31.08	6.72	13.7776	6.0213	7.3	2.05
LT20	3.64	0.66	32.23	6.87	14.4926	6.6928	5.2	2.11
LT21	3.57	0.66	31.22	6.60	13.7724	8.7718	4.3	2.09
LT22	3.63	0.63	32.09	6.52	13.2284	8.0456	4.5	2.03
LT23	3.64	0.75	32.23	7.80	15.8928	14.9243	19.4	2.04
LT24	3.63	0.69	32.09	7.14	15.1824	13.951	12.7	2.13
M46	3.65	0.67	28.60	7.01	14.4596	3.6875	2.4	2.06
M47	3.62	0.69	28.42	7.10	14.4718	4.6712	4.9	2.04
M57	3.56	0.71	27.83	7.06	14.3744	1.2426	9.6	2.03
M58	3.66	0.77	29.88	8.10	15.7866	1.8534	6.1	1.95
M59	3.63	0.90	30.95	9.31	18.1344	4.3827	3.9	1.95
M60	3.62	0.83	30.01	8.54	16.968	3.7629	2.6	1.99
M62	ground halite				21.27		3.3	
M63	ground halite				22.66		3.4	
M64	ground halite				21.69		2.6	
M65	ground halite				20.05		3.5	
M66	ground halite				24.94		2.6	
M72	3.60	0.88	30.29	8.95	20.6093	6.0301	4.1	2.30
M73	3.60	0.88	30.29	8.95	19.7527	5.5819	5.3	2.21
M74	3.45	0.70	26.27	6.50	13.6400	1.459	3.2	2.10

Table 1 continued

slice no.	diameter cm	width cm	total surface area cm ²	volume cm ³	initial weight g	at end weight g	insoluble residue %	calculated density g cm ⁻³
M76	3.68	0.83	30.85	8.82	17.2110	1.9278*	11.2	1.95
M77	3.60	0.95	31.09	9.66	19.0802	2.0072	6.7	1.97
M78	3.60	1.05	32.22	10.68	21.8664	11.8104	2.5	2.05
M79	3.83	1.00	35.06	11.52	22.7772	12.173	3.0	1.98
M81	3.64	0.78	32.23	8.11	16.3283	7.7088	5.2	2.01
M82	3.62	0.69	31.94	7.10	13.7008	5.5232	3.3	1.93
M83	3.61	0.86	30.15	8.75	17.8328	7.6528	5.1	2.04
M84	3.60	0.85	29.96	8.65	17.1565	6.9222	6.0	1.98
M87	3.58	0.92	30.46	9.26	18.6928	4.2947	2.7	2.02
M88	3.46	1.18	31.62	11.09	22.9968	3.4056	5.0	2.07
M89	3.57	1.16	33.01	11.61	22.7464	0.6267	6.5	1.96
M90	3.60	1.30	35.04	13.23	27.3808	3.0612	8.0	2.07
M94	3.65	0.68	28.71	7.11	14.1321	9.2342	5.1	1.99
M95	3.55	0.82	28.93	8.11	15.0150	8.6688	5.0	1.85
M97	3.55	1.06	31.60	10.49	20.8538	14.5823	6.1	1.99
M98	3.68	1.00	32.82	10.63	19.0928	12.4805	4.1	1.80
M101	3.44	0.87	27.98	8.08	15.1015	11.6218	7.1	1.87
M102	3.45	0.72	26.49	6.73	13.1672	9.6591	6.0	1.96
M103	3.55	0.90	29.82	8.90	18.1171	12.1543	3.6	2.04
M104	3.58	0.88	30.01	8.85	17.4662	11.4901	3.6	1.97
M105	3.62	0.86	30.35	8.85	15.112	10.191	3.4	1.71
M106	3.65	0.83	30.43	8.68	16.1417	11.5354	3.8	1.86
M109	3.59	0.74	28.58	7.49	15.4712	3.1999	2.7	2.07
M110	3.55	0.78	28.48	7.72	15.8553	4.9836	2.4	2.05
M111	3.54	0.70	27.46	6.89	12.4295	1.435	4.8	1.81
M112	3.63	0.66	28.21	6.83	11.9375	2.4654	2.7	1.75
M113	3.60	1.30	35.04	13.23	27.3915	9.6701	2.7	2.07
M114	3.60	1.34	35.49	13.63	26.9017	6.0786	3.6	1.97
M115	3.69	1.40	37.60	14.96	30.1345	5.293	2.7	2.01
M116	3.64	1.29	35.55	13.42	27.3614	5.4783	3.0	2.04
M121	3.52	1.25	33.27	12.16	24.4140	15.6016**	2.9	2.01
M122	3.35	1.25	30.77	11.01	21.9029	14.4003**	8.3	1.99
M123	3.6	0.85	29.96	8.65	16.6507	10.8442**	7.5	1.93
M124	3.28	0.83	25.44	7.01	14.3502	8.9755**	4.6	2.05
M125	3.41	0.76	26.39	6.94	13.1739	7.7963**	4.3	1.90
M127	3.60	1.44	36.62	14.65	29.9896	4.5395	3.1	2.05
M128	3.68	1.51.	38.72	16.05	33.3779	5.9659	0.8	2.08
M129	3.65	1.77	41.20	18.51	39.2884	10.216	2.0	2.12
M130	3.67	1.81	42.00	19.14	40.2401	11.3754	1.7	2.10
M132	3.67	1.75	41.31	18.50	37.5541	6.3959	1.8	2.03
M133	3.64	1.83	41.72	19.03	38.8135	6.8374	1.3	2.04
M135	3.63	1.94	42.80	20.07	42.4530	3.3907	1.9	2.12
M136	3.48	0.99	29.83	9.41	18.3752	3.3907		1.95
							average***	2.003
							std.dev.	0.104
* slice completely dissolved; this is the weight of the insoluble residue								
** NaCl was added into the Dead Sea dilution, prior to the slice with added NaCl								
*** errors in halite density estimates are due to errors in measurements of slice dimensions								

Table 2. Analytical data for all experiments

Lab no.	% Dead Sea	Na mg / L	K mg / L	Ca mg / L	Mg mg / L	Sr mg / L	Cl mg / L	Br mg / L	SO4 mg / L	TDS mg / L	density g / cm ³	temp. °C	Cations meq / L	Anions meq / L	R.E. %	
M1	50%	15800					111400									
M2,T1	50% +	21370					121000									
M3,T2	50% +	20650					118000									
M4,LT1	50% +	49800					159400									
M5,LT2	50% +	45800					156350									
M6	50%	16000	3600	8900	21750	160	107870	3200	<400	161480			3026	3082	0	
M7	90%	28600	6600	15600	40100	285	193980	5900	<400	291065			5498	5544	-0.4	
M8,LT1b	50%+	31900	3700	8900	22000	160	135280	3150	400	205490			3741	3863	-1.6	
M9,LT2b	50%+	36000	3700	8800	21850	165	140380	3200	400	214495			3902	4007	-1.3	
M10,T3	90%+	31200	6500	15600	40100	285	197600	5850	400	297535			5609	5653	-0.4	
M11,T4	90%+	30750	6600	15800	40500	285	199160	6000	400	299495			5635	5700	-0.6	
M12	90%	29100					196535	5800					1266	5615		
M13,LT3	90%+	35150					203800	5800					1529	5820		
M14,LT4	90%+	35500					205150	5900					1544	5856		
M15	50%	16400	3820	8800	22200	166	109115	3000		163501	1.1173	24.5	3080	3115	-0.6	
M16,T5	50%+	30000	3680	8620	21770	163	130988	3200		198421	1.1391	23.6	3624	3735	-1.5	
M17,T6	50%+	29900	4100	8720	21780	164	129570	3050		197284	1.1390	23.7	3636	3693	-0.8	
M18	90%	28600	6660	15500	39800	270	194940	5450		291220	1.2053	23.7	5468	5567	-0.9	
M19,T7	90%+	31300	6600	15700	39950	275	197600	5400		296825	1.2085	24.0	5606	5641	-0.3	
M20,T8	90%+	33500	6550	15500	39700	270	201050	5400		301970	1.2128	24.0	5670	5738	-0.6	
M21	50%	16135	3690	8849	22000	162	107000	3010		161408	1.1174	23.3	3051	3067	-0.3	
M22,LT5	50%+	29345	3757	8734	21660	160	128517	3009		195616	1.1388	22.4	3594	3672	-1.1	
M23,LT6	50%+	30695	3753	8834	22110	162	130890	3040		199974	1.1403	22.5	3695	3740	-0.6	
M24,LT7	50%+	27695	3734	8724	21800	160	125290	2990		190860	1.1362	22.3	3532	3581	-0.7	
M25,LT8	50%+	25110	3746	8870	22070	162	122500	3044		186000	1.1318	22.3	3450	3504	-0.8	
M26	50%	16200	3750	8900	22500	155	109600	2600		164205	1.1179	22.1	3099	3134	-0.6	
M27,LT9	50%+	34700	3850	8750	22000	150	137830	2600		210380	1.1470	21.8	3858	3931	-0.9	
M28,LT10	50%+	33600	3850	8850	22100	150	135306	2650		207006	1.1452	21.9	3823	3860	-0.5	
M29,LT11	50%+	37000	3700	8750	22000	150	140734	2650		215484	1.1506	22.4	3954	4013	-0.7	
M30,LT12	50%+	38500	4000	8800	22400	150	144444	2700		221494	1.1524	22.5	4062	4118	-0.7	

Table 2 continued

M31,LT13	70%+	27100	5300	12300	41550	225	161945	3700	500	242620	1,1682	24.8	4529	4625	-1.0
M32,LT14	70%+	27650	5200	12250	31520	220	163020	3600	500	243960	1,1696	24.8	4545	4654	-1.2
M33,LT15	70%+	29100	5150	12170	31150	220	162630	3550	500	244470	1,1723	23.9	4572	4642	-0.8
M34,LT16	70%+	30350	5150	12120	31220	220	164530	3600	500	247690	1,1741	23.9	4630	4696	-0.7
M35,LT17	70%+	34200	5200	12450	31100	225	169960	3550	500	257185	1,1788	24.0	4805	4849	-0.4
M36,LT18	70%+	34400	5350	12450	31150	225	172360	3650	500	260085	1,1794	24.0	4822	4918	-1.0
M37	70%	22600	5150	12400	31650	225	153800	3650	500	229975	1,1618	23.6	4342	4394	-0.6
M38	70%	22450	4950	12200	31270	220	153519	3900		228509	1,1620	23.1	4289	4379	-1.0
LT19	70%+	36450	4880	12150	31080	225	174095	3950		262830	1,1835	23.1	4878	4960	-0.8
LT20	70%+	36200	4855	12100	31000	220	175906	3950		264231	1,1834	24.4	4858	5011	-1.6
LT21	70%+	32400	5200	12300	31800	230	168065	4000		253995	1,1764	23.9	4777	4791	-0.1
LT22	70%+	31300	4780	12000	30700	220	167090	3950		250040	1,1764	23.9	4613	4762	-1.6
LT23	70%+	24000	4800	12050	30770	225	154414	4000		230259	1,1651	23.7	4304	4406	-1.2
LT24	70%+	24700	5050	12300	31450	225	156091	4050		233866	1,1659	23.7	4410	4453	-0.5
M39;LT50P	50%+sat	69700	3600	8400	21200	160	192100	2500		297660	1,2002	23.8	5291	5450	-1.5
M40;LT50N	50%+sat	75000	3450	8550	21500	155	200210	2460		311325	1,2121	22.6	5549	5678	-1.1
M41,LT70P1	70%+sat	57100	5200	11700	30300	220	205620	3650		313790	1,2122	24.2	5698	5845	-1.3
M42,LT70P2	70%+sat	58200	5000	11600	30050	220	207660	3700		316430	1,2150	23.7	5715	5904	-1.6
M43	50%	16000	3650	8700	22550	165	111400	2700		165165	1,1177	23.1	3082	3176	-1.5
M44	70%	22300	5100	12100	31400	225	152070	3800		226995	1,1627	20.4	4292	4337	-0.5
M45	50%	15900	3350	8900	22700	160	109410	2550		162970	1,1178	22.4	3092	3118	-0.4
M46	50%+	29600	3600	8500	21900	165	130338	2600		196703	1,1386	26.5	3609	3709	-1.4
M47	50%+	27500	3400	8670	22300	155	127360	2570		191955	1,1361	26.2	3554	3825	-1.0
M48	50% +sat	78150	3400	8525	20900	156	201750	2250	500	315631	1,2119	21.5	5835	5729	-0.8
M49	50% +sat	78500	3400	8700	21260	167	203840	2350	500	318717	1,2118	21.9	5888	5789	-0.9
M50	50% +sat	79000	5000	8400	20870	155	203430	2400	500	319755	1,2133	21.5	5704	5778	-0.7
M51	50%+sat	78650	3370	8525	21000	164	204280	2350	500	318839	1,2119	21.3	5664	5802	-1.2
M52	70% +sat	60250	5000	11650	29800	220	202070	3550	500	313040	1,2193	22.4	5786	5754	0.3
M53	70% +sat	59950	4950	11950	30150	228	200570	3570	500	311868	1,2187	22.8	5818	5712	0.9
M54	70% +sat	60970	4900	12130	30280	228	208600	3550	500	321158	1,2191	21.5	5879	5939	-0.5
M55	70%	22700	5150	12000	31200	230	152600	3600	500	227980	1,1631	21.6	4290	4360	-0.8
M56	50%	16220	3650	8650	22150	165	108980	2750	500	183065	1,1185	21.5	3056	3119	-1.0
M57	50%+	21750	3600	8670	22090	163	114570	2600	500	173943	1,1270	23.0	3292	3275	0.3
M58	50%+	22230	3600	8770	22230	162	114340	2500	500	174332	1,1277	22.8	3329	3267	0.9
M59	50%+	32450	3600	8700	22010	162	130620	2500	500	200542	1,1437	22.8	3752	3728	0.3
Table 2 continued															

M60	50%+	31800	3650	8750	22120	162	129980	2500	500	199462	1.1409	22.8	3737	3708	0.4
M61	50%	16150	3700	8950	22460	185	106230	2500	500	160655	1.117	22.8	3095	3038	0.9
M62	50%+	33000	3800	8950	22500	165	135190	2600		206205	1.1429	24.6	3834	3846	-0.2
M63	50%+	34300	3600	8580	22500	162	137630	2600		209372	1.1450	24.5	3867	3915	-0.6
M64	50%+	35200	3500	8450	22000	160	136830	2500		208640	1.1466	24.5	3856	3891	-0.5
M65	50%+	32700	3580	8550	22500	162	134510	2550		204552	1.1430	24.4	3795	3826	-0.4
M66	50%+	39800	3550	8420	22250	160	144990	2550		221720	1.1540	24.4	4076	4122	-0.6
M67	50%	16000	3600	8600	22800	164	108720	2600		162484	1.1160	24.5	3097	3099	0.0
M68	50%+sat	72650	3550	8050	20450	150	193460	2480	470	301260	1.205	25.5	5338	5338	-1.5
M69	70%+sat	60900	5050	11200	29300	215	209990	3370	448	320473	1.2171	25.2	5752	5752	-1.9
M70	70%	22200	5200	11900	30700	225	152750	3460	335	226770	1.1625	24.8	4223	4223	-1.6
M71	100%	33250	7500	17250	45750	330	216810	5500		326390	1.2270	23.0	6270	6184	0.7
M72	50%+	22200	3900	9060	23200	174	116730	2800		178064	1.1178	22.8	3430	3328	1.5
M73	50%+	22200	3800	8850	22700	170	117460	2850		178030	1.117	25.4	3376	3349	0.4
M74	50%+	39750	3700	8600	22200	165	143500	2800		220715	n.m.	n.m.	4083	4063	0.0
M75	50%	16850	3800	8850	22700	170	107700	2850		162920	1.1160	24.5	3143	3073	1.1
M76	50%+	36000	3900	8950	22100	165	137790	2650		211555	1.1478	25.4	3934	3920	0.2
M77	50%+	36850	3900	8850	22500	166	137740	2750		212756	1.1485	25.1	3999	3920	1.0
M78	50%+	21200	3750	8720	22750	168	115930	2750		175268	1.1249	23.4	3329	3304	0.4
M79	50%+	23600	3750	8650	22650	167	116900	2750		178467	1.1284	24.1	3421	3332	1.3
M79b	50%+	24400	4000	9000	23650	158	127620	n.m.	635	189463	1.1284	24.1	3562	3613	-0.7
M80	50%	16450	3750	8670	23000	167	110800	2750		165587	1.1171	23.4	3140	3160	-0.3
M81	70%+	38050	5300	11550	30800	202	175450	3600	800	265752	1.1841	24.8	4905	5011	-1.1
M82	70%+	39950	5250	11750	31400	210	172430	3700	295	264985	1.1854	24.9	5046	4916	1.3
M83	10%+	22200	830	1700	4400	31	51377	525	460	81523	1.0552	24.1	1434	1465	-1.1
M84	10%+	22500	785	1735	4600	32	49620	540	225	80037	1.0543	24.2	1464	1411	1.9
M85	70%	22400	5200	11900	31350	210	148880	3550	190	223680	1.161	24.1	4285	4248	0.4
M86	10%	3350	840	1650	4300	31	21117	510	160	31958	1.0224	24	604	605	-0.1
M87	10%+	29300	855	1750	4350	40	62150	540	<1000	98985	1.0672	23.9	1742	1780	-0.5
M88	10%+	39900	830	1900	4280	40	78110	530	<1000	125590	1.086	24	2205	2210	-0.1
M89	10%+	42600	850	1750	4320	33	80110	540	<1000	130203	1.0883	24	2318	2266	1.1
M90	10%+	45600	870	1950	4320	50	87325	530	<1000	140645	1.0948	24.2	24600	2470	-0.2
M91	10%	3120	775	1700	4530	34	21740	540	<1000	32439	1.0226	23.5	614	620	-0.5
M92	10%+sat	112000	790	2000	4050	45	188770	490		309145	1.1968	24.8	5326	5351	-0.2
M93	10%+sat	115400	800	1950	4080	48	192590	490		316558	1.2007	25.1	5474	5463	0.1
Table 2 continued															

Table 3. List of all experiments and experimental conditions:											
	Stirring (yes or no), type of slice holder: pizza fork (P) or net (N) or none.										
	Amounts of NaCl dissolved derived from slice data (W) and from Na and Cl analyses in solution at end of experiment (W_{Na} and W_{Cl})										
Lab no.	DS content	Volume of DS dilution	Volume at end exp. V_2	Stirring and holder	Initial slice surface area	Duration of exp.	Density	Temp.	NaCl dissolved		Remarks
		ml	ml		cm ²	min	g cm ⁻³	°C	W	W_{Na}	W_{Cl}
M1	50% of Dead Sea, surface, sampled June 2003						n.m.	n.m..			
M2 (T1)	50%	200	n.m.	yes*, none	28.58	30	n.m.	n.m..	2.486	2.833	3.164
M3 (T2)	50%	200	n.m.	yes*, none	27.52	30	n.m.	n.m..	2.377	2.467	2.175
M4 (LT1)	50%	200	n.m.	no, P **	30.08	4 days	n.m.	n.m..	18.584	17.296	15.820
M5 (LT2)	50%	200	n.m.	no, N **	28.23	4 days	n.m.	n.m..	16.019	15.261	14.815
M6	50% of Dead Sea, surface, sampled June 2003										
M7	90% of Dead Sea, surface, sampled June 2003										
M8 (LT1b)	50%	200	n.m.	no, P	27.11	140	n.m.	n.m..	7.652	8.088	7.743
M9 (LT2b)	50%	200	n.m.	no, N	26.21	140	n.m.	n.m..	10.220	10.174	9.184
M10 (T3)	90%	200	n.m.	yes*, none	28.61	120	n.m.	n.m..	1.170	1.323	1.193
M11 (T4)	90%	200	n.m.	yes*, none	28.63	120	n.m.	n.m..	0.736	1.094	1.707
M12	90% of Dead Sea surface sampled June 2003										
M13 (LT3)	90%	200	n.m.	no, P	26.14	240	n.m.	n.m..	3.174	3.078	2.394
M14 (LT4)	90%	200	n.m.	no, N	26.95	240	n.m.	n.m..	3.406	3.256	2.839
M15	50% of Dead Sea surface sampled June 2003						1.1173	24.5			
M16 (T5)	50%	200	n.m.	yes*, P	28.17	40	1.1391	23.6	7.088	6.920	7.209
M17 (T6)	50%	200	n.m.	yes*, P	27.74	40	1.1390	23.7	7.362	6.868	6.742
M18	90% of Dead Sea surface sampled June 2003						1.2048	24.6			
M19 (T7)	90%	200	n.m.	yes*, none	27.54	122	1.2085	24.0	1.128	1.374	0.877
M20 (T8)	90%	200	n.m.	yes*, P	27.81	122	1.2128	24.0	2.498	2.492	2.014
M21	50% of Dead Sea surface sampled June 2003						1.1174	23.3			
M22 (LT5)	50%	200	201.8	no, P	29.15	40	1.1388	22.4	7.005	6.880	7.580
M23 (LT6)	50%	200	201.7	no, P	29.98	40	1.1403	22.5	7.415	7.573	8.383
M24 (LT7)	50%	200	201.1	no, P	28.88	20	1.1362	22.3	5.980	5.994	6.409
M25 (LT8)	50%	200	201.3	no, P	31.60	20	1.1318	22.3	4.540	4.654	5.399
M26	50% of Dead Sea surface sampled June 2003						1.1179	22.1			
M27 (LT9)	50%	200	202.5	no, P	30.83	70	1.1470	21.8	9.888	9.677	10.061

Table 3 continued												
M28 (LT10)	50%	200	202.5	no, P	29.37	70	1.1452	21.9	9.103	9.092	9.160	
M29 (LT11)	50%	200	203.2	no, P	31.20	110	1.1506	22.4	11.111	10.912	11.144	
M30 (LT12)	50%	200	203.9	no, P	30.53	110	1.1524	22.5	11.835	11.741	12.482	
M31 (LT13)	70%	200	199.1	no, P	28.00	22	1.1682	24.8	2.088	2.319	2.849	
M32 (LT14)	70%	200	199.6	no, P	28.77	22	1.1696	24.8	2.553	2.613	3.249	
M33 (LT15)	70%	200	199.4	no, P	31.07	41	1.1723	23.9	3.392	3.361	3.185	
M34 (LT16)	70%	200	198.9	no, P	29.84	41	1.1741	23.9	3.963	3.995	3.848	
M35 (LT17)	70%	200	200.4	no, P	30.35	81	1.1788	24.0	5.726	6.028	5.843	
M36 (LT18)	70%	200	200.7	no, P	31.37	81	1.1794	24.0	5.934	6.141	6.661	
M37	70% of Dead Sea, surface sampled June 2003											
LT19	70%	200	201.2	no, P	31.08	136	1.1835	23.1	7.187	7.305	7.477	
LT20	70%	200	202.1	no, P	32.23	136	1.1834	24.4	7.395	7.220	8.158	
LT21	70%	200	200.1	no, P	31.22	60	1.1764	23.9	4.787	5.158	5.245	
LT22	70%	200	200.6	no, P	32.09	60	1.1764	23.9	4.948	4.617	4.968	
LT23	70%	200	198.2	no, P	32.23	10	1.1651	23.7	0.780	0.790	0.361	
LT24	70%	200	199.7	no, P	32.09	10	1.1659	23.7	1.075	1.158	0.944	
M38	70% of Dead Sea, surface sampled June 2003											
M39	sat. in 50% DS		210.1	no, P		5 days	1.2002	23.8	29.788	29.147	29.983	to saturation at 29°C
M40	sat. in 50% DS		211.6	no, P		15 days	1.2121	22.6	33.870	32.265	33.254	to saturation at 29°C
M41	sat. in 50% DS		207.1	no, P		5 days	1.2122	24.2	18.493	18.732	20.051	to saturation at 29°C
M42	sat. in 50% DS		207.6	no, P		5 days	1.2150	23.7	19.680	19.386	20.918	to saturation at 29°C
M43	50% of Dead Sea surface sampled June 2003											
M44	70% of Dead Sea, surface sampled June 2003											
M45	50% of Dead Sea surface sampled June 2003											
M46(LT30)	50%	300	301.9	no, P	28.60	61	1.1386	26.5	10.513	10.674	11.096	
M47(LT30)	50%	300	301.5	no, P	28.42	61	1.1361	26.2	9.323	9.034	9.533	
M48	sat. in 50% DS		208.8	no, 4 slices		9 days	1.2119	21.5	32.118	33.353	33.944	to saturation at 28°C
M49	sat. in 50% DS		209.4	no, salt		9 days	1.2118	21.9	33.010	33.664	34.893	to saturation at 28°C
M50	sat. in 50% DS		211.1	yes*, 4 slices		9 days	1.2133	21.5	34.829	34.252	35.233	to saturation at 26°C
M51	sat. in 50% DS		209.5	yes*, salt		9 days	1.2119	21.3	32.980	33.759	35.053	to saturation at 26°C
M52	sat. in 70% DS		205.2	no, 4 slices		9 days	1.2193	22.4	20.905	20.239	19.516	to saturation at 28°C
M53	sat. in 70% DS		203.3	no, salt		9 days	1.2187	22.8	18.800	19.935	19.011	to saturation at 28°C
M54	sat. in 70% DS		204.1	yes*, salt		9 days	1.2191	21.5	18.550	20.606	22.055	to saturation at 26°C
Table 3 continued												

M90	10%	200	205.7	no, P	35.04	71.25	1.0948	24.2	22.374	22.280	22.491	
M91	10% of Dead Sea surface sampled June 2003						1.0226	23.5				
M92	sat. in 10% DS	200	220.7	no		14 days	1.1968	24.8	61.500	60.993	60.713	
M93	sat. in 10% DS	200	219.6	no		14 days	1.2007	25.1	60.850	62.574	61.779	
M94	10%	200	200.4	no, P	28.71	9.5	1.0377	22.1	4.650	4.116	3.939	
M95	10%	200	200.3	no, P	28.93	10.66	1.0443	22.0	6.030	6.152	6.009	
M96	10% of Dead Sea surface sampled June 2003						n.m.	n.m..				
M97	90%	200	199.8	no, P	31.60	1476	1.2218	24.7	5.890	5.956	6.086	
M98	90%	200	200.6	no, P	32.82	1476	1.2235	24.7	6.344	6.444	6.599	
M99	sat. in 90% DS	200	199.8	salt		15 days	1.2289	25.1	6.655	8.460	8.334	sat. 28°C
M100	sat. in 90% DS	200	199.4	salt		15 days	1.2287	25.0	6.928	9.123	8.619	sat. 28°C
M101	90%	200	199.0	no, P	27.98	182	1.2160	24.2	3.231	3.337	3.387	
M102	90%	200	199.4	no, P	26.49	182	1.2165	24.0	3.299	3.773	4.753	
M103	90%	200	200.9	no, P	29.82	1100	1.2211	24.1	5.747	5.809	6.119	
M104	90%	200	200.2	no, P	30.01	1099	1.2219	24.0	5.763	5.652	6.071	
M105	90%	200	199.7	no, P	30.35	442	1.2199	26.3	4.755	4.842	5.894	
M106	90%	200	199.4	no, P	30.43	441	1.2199	26.0	4.430	4.408	4.648	
M107	90% of Dead Sea surface sampled June 2003						1.2057	24.0				
M108	90% of Dead Sea surface sampled June 2003						1.2054	24.8				
M109	50%	800	810.2	no, 2P	28.58	61	1.1265	23.4	11.853	11.654	9.310	holder one above other
M110	50%	800	807.7	no, 2P	28.48	50	1.1256	23.3	10.494	12.007	5.524	holder bottom to bott.
M111	50%	200	203.1	yes, N****	27.46	30	1.1481	23.9	10.466	9.737	10.095	
M112	50%	200	202.3	yes, N****	28.21	28	1.1444	23.6	9.218	8.398	8.446	
M113	50%	200	204.1	yes, N****	35.04	59	1.1667	23.4	17.243	19.825	16.981	Na too high
M114	50%	200	205.9	yes, N****	35.49	75	1.1743	24.0	20.068	19.260	19.521	
M115	50%	800	810.9	no, 2P	37.60	121	1.1387	24.4	24.018	19.889	19.908	bad Na, Cl? bott. to bott
M116	50%	800	809.2	no, 2P	35.55	101	1.1395	24.9	21.473	21.691	20.138	bott. to bott
M117	50% of Dead Sea surface sampled June 2003						1.1171	23.9				
M118	100% of Dead Sea surface sampled Dec 2004						1.2370	24.0				
M119	50% of Dead Sea surface sampled Dec 2004						1.1229	23.5				
M120	100% of Dead Sea surface sampled June 2003						1.2271	23.0				
M121	50% ***	200	203.4	no, P	33.27	60	1.1628	24.1	8.560	8.244	8.261	
M122	50% ***	200	203.5	no, P	30.77	60.5	1.1649	24.4	6.879	6.554	6.734	
M123	50% ***	200	203.7	no, P	29.96	61	1.1665	24.3	5.374	5.087	5.149	
Table 3 continued												
M124	50% ***	200	204.5	no, P	25.44	61	1.1698	24.3	5.129	4.702	5.520	

M125	50% ***	200	205.3	no, P	26.39	61	1.1716	24.4	5.145	5.193	5.332	
M126	50% of Dead Sea surface sampled	200	205.3	no, P			1.1234	24.3				
M127	50%	200	208.5	yes, N****	36.62	90	1.1910	24.2	24.653	23.036	24.656	
M128	50%	200	209.8	yes, N****	38.72	106	1.1968	24.7	27.190	24.978	26.442	
M129	50%	200	209.8	yes, N****	41.20	121	1.2015	24.7	28.499	26.481	27.696	
M130	50%	200	210.3	yes, N****	42.00	137	1.1999	25.0	28.373	26.444	27.782	
M131	50% of Dead Sea surface sampled	200	205.3	no, P			1.1239	23.0				
M132	10%	200	209.6	no, P	41.31	90	1.1178	25.0	30.598	30.1595	29.963	
M133	10%	200	210.6	no, P	41.72	100	1.1179	25.7	31.552	30.3871	30.782	
M134	10% of Dead Sea surface sampled	200	205.3	no, P			1.0233	24.4				
M135	sat. 50% DS, Dec 04	200	211.8	yes, N****	42.80	235	1.2084	27.7	31.988	32.153	32.843	to saturation at 23°C
M136	50% stratification exp.			appendix	29.83							
M137	50% of Dead Sea surface sampled	200	205.3	no, P			1.1229	26.4				
*in thermostated shaking bath												
** slice completely dissolved												
***NaCl was dissolved into the 200 ml Dead Sea dilution, before introducing the slice; 5.262g to M121												
7.237g to M122, 9.481g to M123, 11.039g to M124 and 11.767g to M125												
****with magnetic stirrer, 348 rpm at about 23 °C												

