

# KINETIC AND THERMODYNAMIC REASONS FOR FRACTIONATION OF ISOTOPES OF CHLORINE IN THE PROCESS OF SEDIMENTATION OF HALITE

A.V.Bochkarev, S.L.Belopukhov, A.V.Zhevnerov, A.A.Ovod

Russian State Agrarian University — Moscow Timiryazev Agricultural Academy

Timiryazevskaya St., 49

127550 Moscow, Russian Federation

## Abstract

Data on isotopic reduced partition functions ratios ( $\beta$ -factors) of hydrated chloride ion and crystalline halite obtained with application of *ab initio* methods have been used for theoretical modeling of process of fractionation of chlorine isotopes during sedimentation of NaCl from saturated solution. It has been shown that during precipitation of halite in the process of evaporation of natural water reservoirs appreciable separation of isotopes of chlorine may take place, thermodynamic contribution to isotope effect prevails.

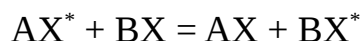
## 1 Introduction

In previous papers [1, 2] we have presented results of theoretical study of isotope fractionation of lithium, calcium and magnesium in the process of crystallization. However, in the process of crystallization from saturated aqueous solutions also occurs fractionation of isotopes of elements included in anions.

Fractionation of isotopes of carbon and oxygen has been studied in many works [3]. At the same time, fractionation of chlorine isotopes has been studied insufficiently. The present work is devoted to theoretical consideration of fractionation of isotopes in the process of sedimentation of halite from saturated solution.

## 2 Calculation of $\beta$ -factors and thermodynamic (equilibrium) isotope separation factor of chlorine.

According to the thermodynamics of chemical isotope exchange [4], the reaction



of element X isotope exchange is characterized by the isotope separation factor  $\alpha_{X^*/X}$  (here,  $X^*$  is heavy isotope of the element X), which is, by definition

$$\alpha_{X^*/X} = \frac{\{[X^*]/[X]\}_{in A}}{\{[X^*]/[X]\}_{in B}},$$

and can be calculated as

$$\alpha_{X^*/X} = \frac{\beta(A)}{\beta(B)}$$

Here,  $[X]$  and  $[X^*]$  are the concentrations of isotopes in the corresponding substance,  $\beta(A)$  and  $\beta(B)$  are the so-called “isotope reduced partition function ratios” or “ $\beta$ -factors”<sup>1</sup>, which are the ratios between the quantum partition functions of the isotope forms of the given substance divided by the ratios between the classical partition functions.

## 2.1 Estimation of equilibrium isotope separation factor.

As has been mentioned before, isotope separation coefficient can be calculated as

$$\alpha = \frac{\beta_{aqCl}^-}{\beta_{NaCl}}, \quad (1)$$

where  $\beta_{Cl_{aq}^-}$  and  $\beta_{NaCl}$  are  $\beta$ -factors of hydrated chloride ion and solid salt, accordingly.  $\ln \beta_{37Cl/35Cl}$  of solid NaCl we have calculated previously [1]; it equals  $\approx 0.0032$  at 300K.

Values of  $\beta$ -factors of hydrated chloride ion and hydrated ionic pairs  $NaCl \cdot nH_2O$  we calculated earlier [5]. Conditions of precipitation of halite (saturated solution of NaCl) correspond to ionic pairs with  $n \approx 5.5$ . Value of  $\ln \beta_{37Cl/35Cl}$  of these ionic pairs is 0.00289 at the temperature 300K. Thus, according to (1) value of  $\ln \alpha_{37Cl/35Cl}$  is 0.0003.

## 3 Model of fractionation of chlorine isotopes in the process of evaporation of water reservoir.

### 3.1 Quasi-equilibrium mode of precipitation.

Let us consider fractionation of isotopes of chlorine in the process of evaporation of reservoir with salt water by quasi-equilibrium mode of precipitation, when at every moment of precipitation chemical and isotopic equilibrium between solution and *surface* of crystalline phase takes place. Most crystals precipitate exactly in this mode provided the speed of precipitation is rather slow [6].

Because sedimentation of sodium chloride accompanied by small enthalpy change, change of temperature due to crystallization can be neglected [7].

So, we have saturated solution of salt which contains  $n^{H_2O}$  moles of water and  $n_{aq}^{NaCl}$  moles of salt, mole ratio  $\frac{n_{aq}^{NaCl}}{n^{H_2O}} = s(T)$  is determined by the solubility of

---

<sup>1</sup> The notation  $\left(\frac{S}{S'}\right)f$  is also used

salt. Dissolved salt consists of  $^{35}n_{aq}$  moles of  $\text{Na}^{35}\text{Cl}$  and  $^{37}n_{aq}$  moles of  $\text{Na}^{37}\text{Cl}$ ,  
 $^{35}n_{aq} + ^{37}n_{aq} = n_{aq}^{\text{NaCl}}$ .

In the process of evaporation of water from the solution the precipitation of crystalline phase begins, at any moment of this process

$$n_{aq}^{\text{NaCl}} = s(T)n^{\text{H}_2\text{O}} = s(T)(n_0^{\text{H}_2\text{O}} - n_{\text{evap}}^{\text{H}_2\text{O}}),$$

$$n_{\text{solid}}^{\text{NaCl}} = s(T)n_{\text{evap}}^{\text{H}_2\text{O}}.$$

Here  $n_0^{\text{H}_2\text{O}}$  — initial amount of water,  $n_{\text{evap}}^{\text{H}_2\text{O}}$  — amount of evaporated water,  $n_{\text{solid}}^{\text{NaCl}}$  — amount of precipitated salt (mole).

In quasi-equilibrium mode of precipitation the relation between  $\text{Na}^{35}\text{Cl}$  and  $\text{Na}^{37}\text{Cl}$  in surface layer of solid phase, which is in direct contact with solution, at every moment is determined by the isotope separation factor  $\alpha$ ; bulk crystal cannot exchange with solution because of exceptionally low rate of diffusion of ions in solid  $\text{NaCl}$ <sup>2</sup>.

Let  $dn_{\text{evap}}$  of water evaporated in quasi-equilibrium mode. Then  $dn_{\text{solid}}^{\text{NaCl}} = s(T)dn_{\text{evap}}$  of salt precipitated, accordingly the solution lost  $dn_{aq}^{\text{NaCl}} = -s(T)dn_{\text{evap}}$ . Because of

$$d^{35}n_{\text{solid}} + d^{37}n_{\text{solid}} = dn_{\text{solid}}^{\text{NaCl}} = s(T)dn_{\text{evap}}$$

$$d^{35}n_{aq} + d^{37}n_{aq} = dn_{aq}^{\text{NaCl}} = -s(T)dn_{\text{evap}}$$

and by definition separation factor (assuming homogeneity of composition of the liquid phase) is

$$\alpha_{35/37} = \frac{d^{35}n_{\text{solid}} / d^{37}n_{\text{solid}}}{^{35}n_{aq} / ^{37}n_{aq}},$$

we have

$$d^{35}n_{\text{solid}} = \frac{^{35}n_{aq}}{^{37}n_{aq}} \cdot \alpha_{35/37} \cdot d^{37}n_{\text{solid}}$$

Because of  $^{35}n_{aq} = ^{35}n_0 - ^{35}n_{\text{solid}}$  (analogically for isotope  $^{37}\text{Cl}$ ), we have equation with separable variables, known from the theory of coprecipitation:

$$\frac{d^{35}n_{\text{solid}}}{^{35}n_0 - ^{35}n_{\text{solid}}} = \alpha_{35/37} \cdot \frac{d^{37}n_{\text{solid}}}{^{37}n_0 - ^{37}n_{\text{solid}}}. \quad (2)$$

Integration of (2) gives equation similar to Doerner and Hoskins equation [6] which describe coprecipitation in quasi-equilibrium mode:

$$\ln\left(1 - \frac{^{35}n_{\text{solid}}}{^{35}n_0}\right) = \alpha_{35/37} \cdot \ln\left(1 - \frac{^{37}n_{\text{solid}}}{^{37}n_0}\right) \quad (3)$$

Solving equation (3) and taking into account that

<sup>2</sup> Self-diffusion coefficient of ions in crystalline  $\text{NaCl}$  cannot be measured at room temperature, extrapolation gives for  $D$  values less than  $10^{-20}$   $\text{cm}^2/\text{s}$  [8].

$$^{35}n_{solid} + ^{37}n_{solid} = s(T) \cdot n_{evap}, \quad (4)$$

where  $n_{evap}$  is amount of evaporated water, we have dependence of amounts of isotopes  $^{37}\text{Cl}$  and  $^{35}\text{Cl}$  in solid phase (sediment of salt) on  $n_{evap}$ . That, in turn, makes it possible to calculate isotope ratio in surface layer of crystal by the equation (2) and then calculate  $\delta^{37}\text{Cl}$  in surface layer of crystal and in stock solution as functions of  $n_{evap}$ :

$$\delta^{37}\text{Cl}_{solid} = 1000 \cdot \left( \frac{d^{37}n_{solid} / d^{35}n_{solid}}{SMOC} - 1 \right)$$

$$\delta^{37}\text{Cl}_{aq} = 1000 \cdot \left( \frac{d^{37}n_{aq} / d^{35}n_{aq}}{SMOC} - 1 \right)$$

Here SMOC (“Standard Mean Ocean Chloride”) is adopted as a standard ratio of concentrations  $^{37}\text{Cl}/^{35}\text{Cl}$  in ocean water, equal to 0.324. In order to take into account kinetic contribution to isotope effect, it is also necessary to take into account dependence of separation factor  $\alpha$  on rate of precipitation.

### 3.2 Account for influence of rate of precipitation. Diffusion mode of precipitation.

Because sedimentation of halite proceeds with not infinitely small but with finite rate, it is necessary to examine corrections which can contribute kinetic isotope effect. In order to study isotope fractionation it should be noted that fractionation of isotopes in the process of precipitation of crystal from solution which contains two or more isotopes of element which is a part of precipitated substance, can be considered as a special case of coprecipitation.

As is generally known [6], quantitative measure of coprecipitation is degree of coprecipitation  $x$  which is equal to ratio of mass of sedimented impurity to the mass of impurity in initial solution. Degree of coprecipitation is characterized by differential coefficient of coprecipitation  $K_{diff}$  which shows the degree of transition of coprecipitated component from initial medium to layer of solid phase. If  $y$  and  $\rho$  are mass and density of precipitate, accordingly, and  $V$  is the volume of medium, then  $K_{diff}$  is expressed as

$$K_{diff} = \frac{\rho V}{(1-x)} \frac{dx}{dy}.$$

For separation of isotopes in the process of precipitation, instead of coefficient of coprecipitation, the differential isotope separation factor  $\alpha$  should be used, which is equal to

$$\alpha_{35/37} = \frac{d^{35}n_{solid} / d^{37}n_{solid}}{^{35}n_{aq} / ^{37}n_{aq}}.$$

Let us consider the precipitation of some isotope of chlorine, for example  $^{35}\text{Cl}$ . Because of  $x = \frac{^{35}m_{solid}}{^{35}m_0} = \frac{^{35}n_{solid}}{^{35}n_0}$ , where  $m_0$  and  $n_0$  are initial mass and amount

of isotope in the system, differential coefficient of coprecipitation for this isotope may be expressed as

$${}^{35}K_{diff} = \frac{\rho_{solid} V_{aq}}{(1-x)} \frac{dx}{dy} = \frac{\rho_{solid} V_{aq}}{\left(1 - \frac{{}^{35}n_{solid}}{{}^{35}n_0}\right) {}^{35}n_0} \frac{d{}^{35}n_{solid}}{dy} = \frac{\rho_{solid} V_{aq}}{{}^{35}n_{aq}} \frac{d{}^{35}n_{solid}}{dy}. \quad (5)$$

For precipitation of other isotope ( ${}^{37}\text{Cl}$ ) we have analogous expression and finally we have

$$\alpha_{35/37} = \frac{{}^{35}K_{diff}}{{}^{37}K_{diff}}. \quad (6)$$

Equation (6) makes it possible to use results of studying of phenomenon of coprecipitation described in literature for analysis of fractionation of isotopes in the process of precipitation from solutions.

At diffusion mode of precipitation, at the surface a layer of the liquid phase is formed with thickness  $\delta$  (diffusion layer). Transport of precipitated ions through this layer occurs in a time commensurable with crystal growth rate, but less than time necessary to establish equilibrium distribution. In this mode coefficient of coprecipitation is given by Burton, Prim and Slichter equation [6]:

$$K_{diff} = \frac{K_{eq}}{[K_{eq} + (1 - K_{eq}) \exp(-G\delta/D)]}, \quad (7)$$

where  $G$  is linear growth rate of crystals,  $D$  is diffusion coefficient of ions in liquid phase,  $K_{eq}$  is equilibrium coefficient of coprecipitation which describes coprecipitation under conditions of low rate of crystal growth (in quasi-equilibrium mode).

Reverting to equation (6), for equilibrium separation factor of isotopes of chlorine one can write

$$\alpha_{35/37}^{eq} = \frac{{}^{35}K_{eq}}{{}^{37}K_{eq}}. \quad (8)$$

Equations (6), (7) and (8) give

$$\alpha_{35/37} = \alpha_{35/37}^{eq} \frac{{}^{37}K_{eq} + (1 - {}^{37}K_{eq}) \exp(-G\delta/{}^{37}D)}{{}^{35}K_{eq} + (1 - {}^{35}K_{eq}) \exp(-G\delta/{}^{35}D)}. \quad (9)$$

For practical usage of equation (9) one has to calculate values of  ${}^{35}K_{eq}$  and  ${}^{37}K_{eq}$ , using the above results, when consider quasi-equilibrium mode of precipitation. Because volume of phase where the isotope exchange occurs (surface + near-surface layer) is small in comparison with volume of mother waters, change of isotope composition of solution in the process of precipitation of slim layer of crystal can be neglected. In that case equilibrium coefficient of coprecipitation of isotope  ${}^{35}\text{Cl}$  is equal to

$${}^{35}K_{eq} = \frac{{}^{35}c_{solid}}{{}^{35}c_{aq}},$$

where  $c_{solid}$  and  $c_{aq}$  are concentrations of isotope in surface layer of solid phase and in the solution, accordingly (similarly for the other isotope). Taking into account evident equality

$$\frac{{}^{35}c_{solid} + {}^{37}c_{solid}}{{}^{35}c_{aq} + {}^{37}c_{aq}} = S,$$

where  $S$  is constant determined by solubility of salt, we have

$$\frac{{}^{35}K_{eq} {}^{35}c_{aq} + {}^{37}K_{eq} {}^{37}c_{aq}}{{}^{35}c_{aq} + {}^{37}c_{aq}} = S$$

and, taking into account equation (8), we have

$$\begin{aligned} {}^{37}K_{eq} &= S \frac{{}^{35}c_{aq} + {}^{37}c_{aq}}{\alpha_{35/37}^{eq} {}^{35}c_{aq} + {}^{37}c_{aq}} = S \frac{{}^{35}n_{aq} + {}^{37}n_{aq}}{\alpha_{35/37}^{eq} {}^{35}n_{aq} + {}^{37}n_{aq}}, \\ {}^{37}K_{eq} &= \alpha_{35/37}^{eq} S \frac{{}^{35}c_{aq} + {}^{37}c_{aq}}{\alpha_{35/37}^{eq} {}^{35}c_{aq} + {}^{37}c_{aq}} = \alpha_{35/37}^{eq} S \frac{{}^{35}n_{aq} + {}^{37}n_{aq}}{\alpha_{35/37}^{eq} {}^{35}n_{aq} + {}^{37}n_{aq}}. \end{aligned} \quad (10)$$

It is necessary to take into account the fact of change of  $\frac{{}^{37}c_{aq}}{{}^{35}c_{aq}}$  during the process of sedimentation. From equations

$$\frac{{}^{37}n_0}{{}^{35}n_0} = SMOC \quad (11)$$

and

$${}^{35}n_0 + {}^{37}n_0 = n_0 \quad (12)$$

we have

$${}^{35}n_0 = \frac{n_0}{1 + SMOC}, \quad {}^{37}n_0 = \frac{n_0 SMOC}{1 + SMOC}. \quad (13)$$

Further,

$$\frac{{}^{37}c_{aq}}{{}^{35}c_{aq}} = \frac{{}^{37}n_{aq}}{{}^{35}n_{aq}} = \frac{{}^{37}n_0 - {}^{37}n_{solid}}{{}^{35}n_0 - {}^{35}n_{solid}}, \quad (14)$$

where values  ${}^{37}n_0$  and  ${}^{35}n_0$  are given by equations (13). Values of  ${}^{37}n_{solid}$  and  ${}^{35}n_{solid}$  can be calculated from the system of equations (3) and (4). Accordingly, from equation (14) one can calculate  $C = \frac{{}^{37}n_{aq}}{{}^{35}n_{aq}} = \frac{{}^{37}c_{aq}}{{}^{35}c_{aq}}$ , and, taking into account (8), we have

$${}^{37}K_{eq} = S \frac{1+C}{\alpha_{35/37}^{eq} + C}, \quad {}^{35}K_{eq} = \alpha_{35/37}^{eq} S \frac{1+C}{\alpha_{35/37}^{eq} + C}. \quad (15)$$

Substitution of equation (15) in (9) gives final expression for differential coefficient of isotope fractionation for precipitation in diffusion mode:

$$\alpha_{35/37} = \alpha_{35/37}^{eq} \frac{SA + [1 - SA] \exp\left(-\frac{G\delta}{37D}\right)}{\alpha_{35/37}^{eq} SA + [1 - \alpha_{35/37}^{eq} SA] \exp\left(-\frac{G\delta}{35D}\right)}, \quad (16)$$

where  $A = \frac{1+C}{\alpha_{35/37}^{eq} + C}$ . As one can see from equation (16), if rate of crystal growth  $G$  approaches zero, separation factor approaches value for quasi-equilibrium precipitation  $\alpha_{35/37}^{eq}$  (full thermodynamic control of isotope fractionation). In the opposite case, when rate of crystal growth is large, growing crystal exhaustively captures ions from solution, and fractionation of isotopes cannot take place ( $\alpha=1$ ). At intermediate rate of precipitation different behavior of  $\alpha_{35/37}$  is possible. It should be noted that always  $\frac{35D}{37D} > 1$ , because light isotope migrates faster. Maximal upper limit of  $\frac{35D}{37D}$  is equal to square root of the ratio of reverse masses of atoms, but in fact this ratio approximately ten times small. Experimentally measured ratio of mobilities of ions  $^{35}\text{Cl}^-$  and  $^{37}\text{Cl}^-$  in nearly saturated solutions of sodium chloride is 1.0022 [9]. Thermodynamic isotope effect, on the contrary, favors the enrichment of solid phase by heavy isotope  $^{37}\text{Cl}$ . Accordingly, kinetic (diffusion) and thermodynamic effects in the process of precipitation of sodium chloride act in opposite directions. This leads to dependence of differential isotope separation factor on rate of precipitation which has an extremum. For quantitative estimate of influence of rate of precipitation on isotope separation factor it should be necessary to estimate numerical values of the quantities in equation (16). Value of  $S$  for NaCl is 6.951 and weakly depends on temperature. As an estimate for diffusion coefficient in near-surface layer one may assume value of diffusion coefficient of ion  $\text{Cl}^-$  in water ( $6 \cdot 10^{-6} \text{ cm}^2/\text{s}$ ). Ratio  $\frac{35D}{37D}$  and value of  $\alpha_{35/37}^{eq}$ , as mentioned above, are 1.0022 and 0.9997<sup>3</sup>, accordingly. As is obvious from Eq. (16), value of  $\alpha$  depends on the product of the growth rate of crystal on the thickness of diffusion layer. In several papers on studying of mechanism of crystallization [10, 11] it has been established that thickness of diffusion layer changes for different salts from  $5 \cdot 10^{-3}$  to  $10^{-5}$  cm, this value weakly depends on rate of flow of liquid round the crystal.

Dependence of isotope separation factor on product  $G\delta$  is presented in Fig. 1. As one can see from this figure, with increase of rate of precipitation  $\alpha_{35/37}$  at first increased from initial equilibrium value  $\alpha_{35/37}^{eq}$  and approaches maximum.

---

<sup>3</sup>  $\alpha_{35/37} = 1/\alpha_{37/35}$

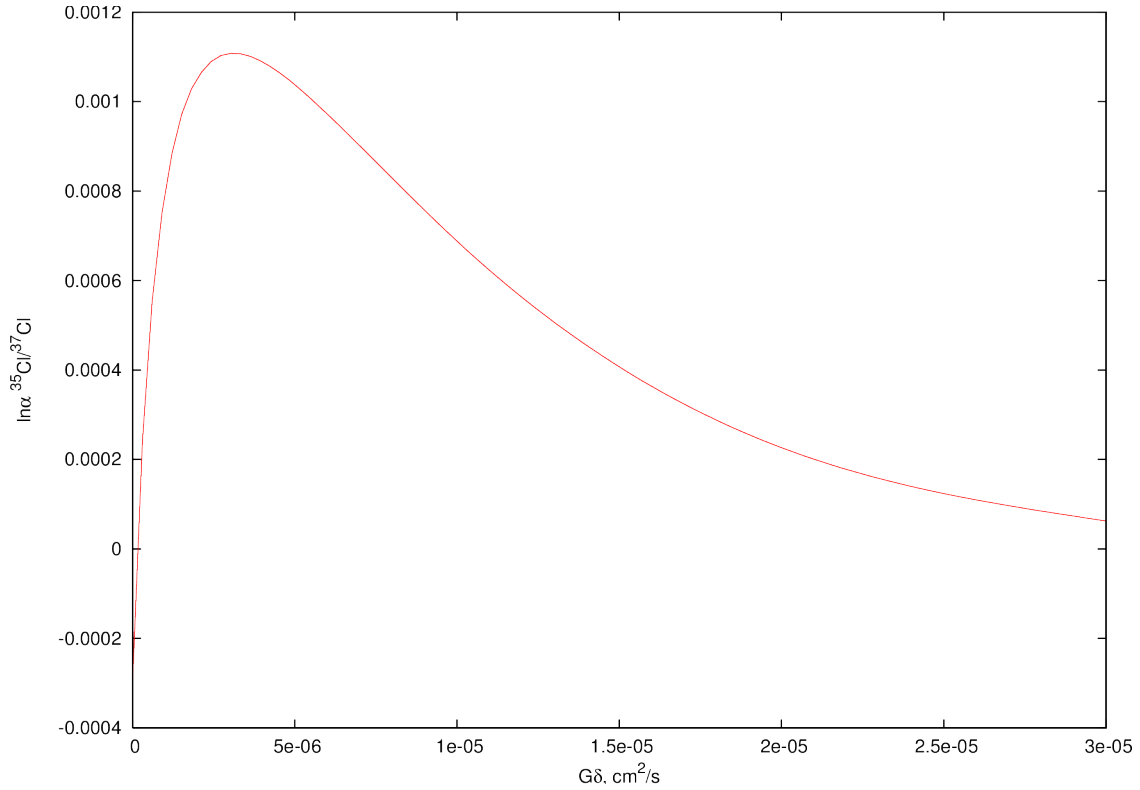


Figure 1. Dependence of differential isotope separation factor in the process of precipitation on linear rate of growth of solid phase.

At this rate influence of kinetic factor is maximal. It is also evident that at high rate of precipitation (high  $G\delta$ ) direction of isotope fractionation reverses, and crystal should be enriched with light isotope. Such an enrichment has not been observed in natural samples. Therefore it can be concluded that fractionation of isotopes during precipitation of halite is conditioned mainly by thermodynamical reasons.

As stated above,  $\ln\alpha_{35\text{Cl}/37\text{Cl}}$  is  $\approx -0.0003$  at 300K. One may calculate the depth distribution of  $\delta^{37}\text{Cl}_{\text{solid}}$  in the deposited layer. If  $n_{\text{solid}}^{\text{NaCl}} = s(T)n_{\text{evap}}^{\text{H}_2\text{O}}$  of salt precipitated, then height of the sediment layer will be

$$\frac{h}{h_{\text{max}}} = \frac{n_{\text{evap}}^{\text{H}_2\text{O}}}{n_0^{\text{H}_2\text{O}}},$$

where  $n_{\text{evap}}^{\text{H}_2\text{O}}$  is amount of water evaporated from surface of reservoir and  $h_{\text{max}}$  is thickness of layer of sediment after full evaporation of water.



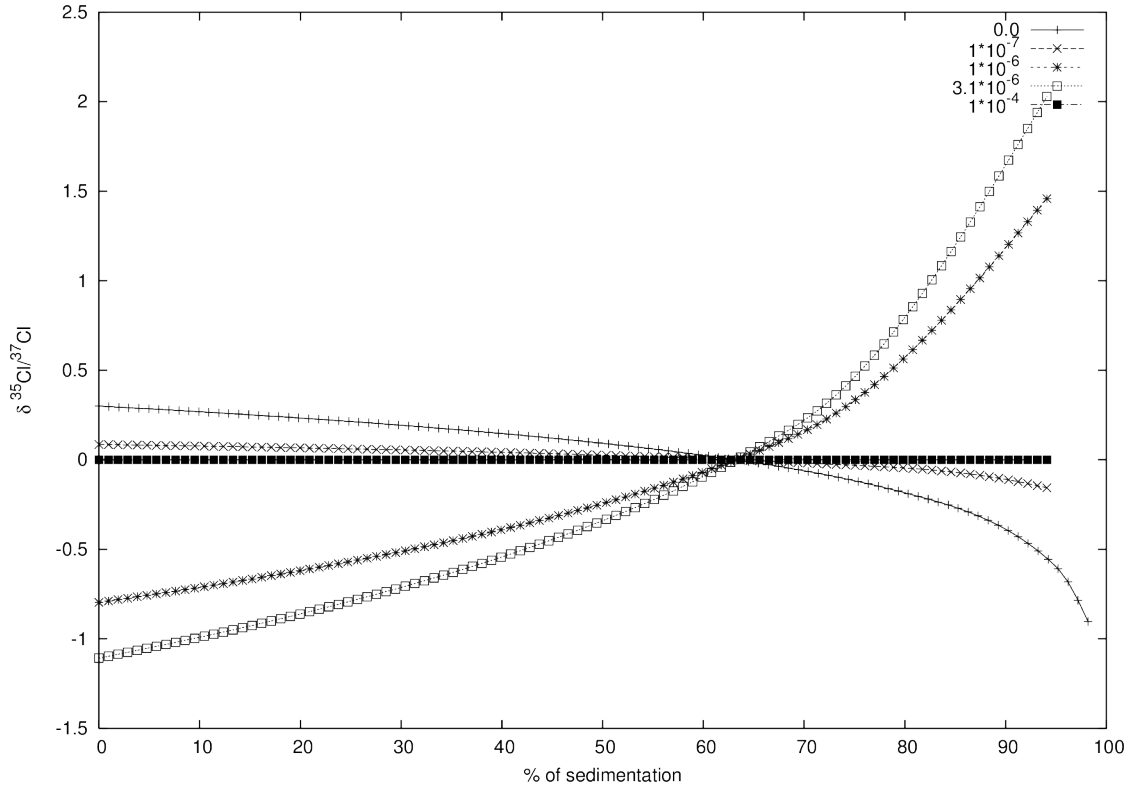


Figure 2. Profile of enrichment of salt layer with heavy isotope of chlorine  $^{37}\text{Cl}$  by exhaustive drying of water reservoir depending on the deposition rate.

Results of calculation are presented in Fig. 2. Because  $\beta$ -factor of solid salt greater than  $\beta$ -factor of hydrated chloride ion, at low rate of precipitation crystal will be enriched with heavy isotope, and solution, contrary, with light isotope (Rayleigh depletion).

As one can see from Fig. 2, under thermodynamic control of isotope fractionation lower layers of salt deposit should be enriched with heavy isotope, while under kinetic control they would be enriched with light isotope.

### 3.2.1 Adsorption-kinetic and others modes of precipitation.

In the process of precipitation from strongly supersaturated solution with intensive stirring rate of crystal growth is comparable both with rate of migration of ions in near-surface layer and with the rate of reaction of precipitation but significantly less than velocity of the ions in solution, that is diffusion (adsorption-kinetic mode of precipitation). However it is evident that in nature in the process of evaporation of water reservoirs intensive stirring (and strong supersaturation in case of precipitation of NaCl) cannot take place. Therefore, one may not examine adsorption-kinetic mode of precipitation.

There are also other reasons to refrain from consideration of adsorption-kinetic and other modes of precipitation. Recent experimental works on study of crystal growth from solution [10, 11] shows that crystal growth is always essentially inequilibrium process. In the process of crystal growth in the system solution — crystal dissipative structures always forms, leading to formation of solution flow around the crystal. As a result, at every real mode of sedimentation

the diffusion layer  $\delta$  forms near the crystal surface. It is precisely this fact that explains why Burton, Prim and Slichter equation describes coprecipitation in most cases.

## 4 Discussion.

### 4.1 Experimental data on fractionation of isotopes of chlorine in the process of precipitation.

It was supposed earlier that variations of isotope composition of chlorine in natural specimens are small. In paper [12] almost no variation of the isotopic composition of natural specimens<sup>4</sup> has been found. In this work the experiment on separation of isotopes of chlorine in the system halite — water solution of NaCl has been carried out. However, authors could not measure isotope separation factor with enough precision (it appeared to be  $1.0002 \pm 0.0003$ , halite was enriched with heavy isotope  $^{37}\text{Cl}$ ). In later works [13] such variations have been found out due to improvement of methods of mass-spectrometric analysis. In [14] many natural samples have been studied, including specimens of halite from different deposits and specimens of underground saline waters. It has been stated that, as a rule, specimens of halite and salted hydrothermal waters are enriched with heavy isotope of chlorine relative to standard (ocean water). Particularly, enrichment of specimen of halite  $\delta^{37}\text{Cl}$  depending on deposit varies from  $+0.52\text{‰}$  to  $+0.24\text{‰}$ . In [15] chlorine isotope separation factor in the process of precipitation of halite in the system NaCl(solid) — solution has been measured. It appeared to be  $0.00026 \pm 0.00007$  at  $22 \pm 2^\circ\text{C}$ . That confirms data of work [12] and our estimate. In [15] also has been studied fractionation of chlorine isotopes in the process of precipitation from saturated solutions of KCl and bischofite  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , values of  $\ln \alpha_{^{37}\text{Cl}/^{35}\text{Cl}}$  were  $0.00009 \pm 0.00009$  and  $-0.00006 \pm 0.00010$ , accordingly.

It should be noted that in all aforementioned works except [15], authors describe variations of isotopic composition of natural salt waters exclusively by kinetic reasons, in the first place by diffusion. Probability of isotope fractionation due to thermodynamical reasons, particularly enrichment of halite by heavy isotope, has not been studied at all. However, in the process of precipitation of crystal from saturated solution crystal should be enriched with heavy isotope of chlorine  $^{37}\text{Cl}$ , because  $\beta$ -factor of crystal greater than  $\beta$ -factor of hydrate chloride ion. This is in accordance with observations in nature. Were fractionation of isotopes controlled by kinetics, then lower layers of solid phase would have to be enriched with light isotope.

Actually in the process of deposition of salt formation isotope exchange at every moment of deposition takes place only on the surface of the deposit. That inevitably causes variations of the isotopic composition of the salt layer, depending on the depth of salt deposit. There is only one paper [15] which investigated the variation of the isotopic composition of chlorine, depending on the depth of the salt

---

<sup>4</sup> only one specimen of halite has been studied.

deposit. Unfortunately, in this work only one salt deposit has been studied, with complex layered structure. Besides, this deposit was not deposit of pure halite — on the depths studied (from 1628 to 1786 m) composition of salt sediments was very different, concentration of halite was from 19 to 97%, other salts were carnallite, bischofite and kieserite. Obviously, precipitation of salts took place in several stages.

Enrichment of salt deposit depending on depth of sediment (decrease of  $\delta^{37}\text{Cl}$  with height of salt sediment, in particular, enrichment of upper layers with light isotope) has been mentioned in [16].

## 4.2 Experimental data on estimate of rate of precipitation of halite in nature.

There are enough reliable data on rate of evaporation of Caspian sea. Surface area of Caspian sea is  $3.864 \cdot 10^{15} \text{ cm}^2$ . Total evaporation of water from surface is  $400 \text{ km}^3/\text{year} = 4 \cdot 10^{17} \text{ cm}^3/\text{year}$ . Thus, mean rate of evaporation from surface of  $1 \text{ cm}^2$  is  $103.53 \text{ g}/(\text{year} \cdot \text{cm}^2) = 5.75 \text{ mole}/(\text{year} \cdot \text{cm}^2) = 1.82 \cdot 10^{-7} \text{ mole}/(\text{s} \cdot \text{cm}^2)$ .

Data on evaporation from World Ocean give similar values. Every year from surface area of World Ocean ( $361.1$  million  $\text{km}^2$ ) evaporate about  $450000 \text{ km}^3$  of water.

For verification of these natural observations in a saturated solution we have carried out an experiment on precipitation of sodium chloride from freely evaporating saturated solution. Concentrated (not saturated) solution of NaCl has been prepared in water and crystalline NaCl(pur.). The solution was placed in a glass cylinders with different internal diameter (see. Tab. 1). Cylinders were placed in a room and solutions given the opportunity to freely evaporate. There was no protection of surface from dust because such protection is absent in natural conditions and specks of dust may be centers of nucleation.

Results presented in Tab. 1. As one can see, rate of evaporation of water weakly depends both on type of reservoir and degree of saturation of solution.

Table 1: Mean rate of evaporation of water from different reservoirs and corresponding linear rate of growth of NaCl crystals.

Reservoir	Mean rate of evaporation of water from the surface of reservoir, $\text{mole}/(\text{cm}^2 \cdot \text{s})$	Corresponding mean linear rate of crystal growth $G$ , $\text{cm}/\text{s}$
Caspian sea	$1.82 \cdot 10^{-7}$	$5.5 \cdot 10^{-7}$
World Ocean	$2.20 \cdot 10^{-7}$	$6.6 \cdot 10^{-7}$
Cylinder with a diameter 204 mm	$(1.2 \div 1.5) \cdot 10^{-7}$	$(3.6 \div 4.5) \cdot 10^{-7}$
Cylinder with a diameter 62 mm	$(0.7 \div 0.9) \cdot 10^{-7}$	$(2.1 \div 2.8) \cdot 10^{-7}$

Cylinder with a diameter 36.5 mm	$(0.5 \div 0.7) \cdot 10^{-7}$	$(1.4 \div 2.1) \cdot 10^{-7}$
----------------------------------	--------------------------------	--------------------------------

### 4.3 Comparison of calculated data with experimental results.

As stated above, mean linear rate of growth of crystal of NaCl in natural conditions is  $G=(3-7) \cdot 10^{-7}$  cm/s. Even if we take maximal value of  $\delta$  ( $5 \cdot 10^{-3}$  cm), we have  $\delta G \approx 10^{-10}$  cm<sup>2</sup>/s, that corresponds to virtually full thermodynamic control of isotope fractionation.

As one can see from not numerous experimental data, observed enrichment of natural samples confirms the assumption about thermodynamic control of fractionation of isotopes of chlorine, but observed enrichment less than predicted by theory. For this fact, there are two possible explanations. Firstly,  $\beta$ -factor of surface of the crystal less than  $\beta$ -factor of ion in bulk crystal [17]. Secondly, under real conditions precipitation of NaCl to a considerable extent takes place on the surface of the reservoir, formed floating pyramids consist of small crystals [18]. These pyramids may grow by means of flow solution by capillary forces following by exhausting evaporation, that decreases effective separation factor.

Now we can only establish a fact that experimental data on precipitation of halite in nature are in accordance with proposed model. In particular, the model explains both enrichment of halite with heavy isotope and discrepancy of literature data on  $\delta^{37}\text{Cl}$  in natural halite (discrepancy apparently due to the fact that the samples were taken from different depths of salt deposit).

## 5 Conclusion

As seen from above, proposed model of fractionation of isotope of chlorine in the process of precipitation of halite is in accordance with experimental observations in nature. However, this information is very scant. Therefore, extremely useful would be a detailed study of isotope composition of salt layers taking into account the non-uniformity of ratio  $^{37}\text{Cl}/^{35}\text{Cl}$ . Such studies could be an important source of information on the geological environment in which the deposition of halite took place.

On the grounds of available data it is possible to state that main increment in fractionation of isotopes of chlorine in the process of sedimentation of halite gives exactly thermodynamic isotope effect, diffusion in natural conditions can decrease this effect, but cannot change the whole feature.

## 6 Acknowledgments

Research supported by Government of Russian Federation under Grant 11 G34.31.0079.

## References

- [1] *Bochkarev A.V., Trefilova A.N., Bobrov M.F.* Calculation of the Ratios between the Reduced Partition Functions of Isotopic Forms ( $\beta$ -Factors) for

- Ionic Crystals // *Russian Journal of Physical Chemistry*. — 2003. — Vol. 77, no. 8. — Pp. 1207–1214.
- [2] *Bochkarev A.V.* Calculation of  $\beta$ -factors of aqua- and amminocomplexes of lithium // *Russian Journal of Physical Chemistry*. — 2001. — Vol. 75, no. 9. — Pp. 1566–1569.
- [3] *Galimov E.M.* The Biological Fractionation of Isotopes. — Academic Press Inc, 1985. — 262 pp.
- [4] *Knyazev D.A., Bochkarev A.V., Myasoedov N.F.* Quantum-Statistical and phenomenological analysis of equilibrium isotope effects // *Separation Science and Technology*. — 2001. — Vol. 36, no. 8–9. — Pp. 1595–1675.
- [5] *Bochkarev A.V.* Counterion Effects on the Isotopic Properties of the  $\text{Cl}^-$  and  $\text{Li}^+$  Ions in Aqueous Solution // *Russian Journal of Physical Chemistry A*. — 2008. — Vol. 82, no. 5. — Pp. 723–727.
- [6] *Melikhov I.V., Merkulova M.S.* Co-crystallization. — Moscow: Khimiya, 1975. — 280 pp. — (in Russian).
- [7] *Al-Jibbouri S., Ulrich J.* The growth and dissolution of sodium chloride in a fluidized bed crystallizer // *Journal of Crystal Growth*. — 2002. — Vol. 234, no. 1. — Pp. 237–246.
- [8] *Murin A.N., Lure B.G.* Diffusion of labelled atoms and conductivity in ionic crystals. — Leningrad: Publishing House of Leningrad State University, 1967. — 100 pp. — (in Russian).
- [9] *Konstantinov B.P., Bakulin E.A.* Separation of isotopes of chlorine in water solutions of  $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{HCl}$  // *Zhurnal fizicheskoi khimii (Russian Journal of Physical Chemistry)*. — 1965. — Vol. 39, no. 3. — Pp. 592–596. — (in Russian).
- [10] *Askhabov A.M.* Quantitative estimate of kinetic parameters and mechanism of crystal growth. — Syktyvkar: Geoprint, 1996. — 28 pp. — (in Russian).
- [11] *Troshev S.A.* Structure and dynamics of border layer in the process of crystal growth. Dissertation Cand. Geol.-Miner. Sciences. Institut of geology of Komi. Ural Branch of RAS. Syktyvkar, 1994. — (in Russian).
- [12] *Hoering T., Parker P.* The geochemistry of the stable isotopes of chlorine // *Geochimica et Cosmochimica Acta*. — 1961. — Vol. 23, no. 3/4. — Pp. 186–199.
- [13] *Willmore C.C., Boudreau A.E., Spivack A., Kruger F.J.* Halogens of Bushveld Complex, South Africa:  $\delta^{37}\text{Cl}$  and  $\text{Cl/F}$  evidence for hydration melting of the source region in a back-arc setting // *Chemical Geology*. — 2002. — Vol. 182, no. 2–4. — Pp. 503–511.
- [14] *Kaufmann R.S., Long A., Bentley H.W., Davis S.N.* Natural chlorine isotope variations // *Nature*. — 1984. — Vol. 309, no. 5966. — Pp. 338–340.
- [15] *Eggenkamp H.G.M., Kreulen R., Koster van Groos A.F.* Chlorine stable isotope fractionation in evaporites // *Geochimica et Cosmochimica Acta*. — 1995. — Vol. 59, no. 24. — Pp. 5169–5175.

- [16] Hongbing T., Haizhou M., Yingkai X., Haizhen W., Xiying Z., Wandong M. Characteristics of chlorine isotope distribution and analysis on sylvinite deposit formation based on ancient salt rock in the western Tarim Basin // *Science in China Series D*. — 2005. — Vol. 48, no. 11. — Pp. 1913–1920.
- [17] Bochkarev A.V., Trefilova A.N., Bobrov M.F., Tsurkov N.A. Isotope Separation During Ionic Crystal Growth from Solution // *Russian Journal of Physical Chemistry*. — 2003. — Vol. 77, no. 11. — Pp. 1868–1872.
- [18] Mendeleev D.I. *Foundations of Chemistry*. — M.-L.: State Scientific-Technikal Publishing House, 1931, 10 edition. — 639 pp. — (in Russian).

Captions in article A.V.Bochkarev “KINETIC AND THERMODYNAMIC REASONS FOR FRACTIONATION OF ISOTOPES OF CHLORINE IN THE PROCESS OF SEDIMENTATION OF HALITE”

Fig.1. Dependence of differential isotope separation factor in the process of precipitation on linear rate of growth of solid phase.

Fig.2. Profile of enrichment of salt layer with heavy isotope of chlorine  $^{37}\text{Cl}$  by exhaustive drying of water reservoir depending on the deposition rate.