Equations for calculation of NaCl/(NaCl + CaCl$_2$) ratios and salinities from hydrohalite-melting and ice-melting temperatures in the H$_2$O-NaCl-CaCl$_2$ system

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Abstract   The composition of fluid inclusions in the H$_2$O-NaCl-CaCl$_2$ system has been generally graphically estimated using the melting temperatures of hydrohalite ($T_{m\text{-}HH}$) and ice ($T_{m\text{-}ice}$). Here we present two equations that can be used to calculate the relative proportion of NaCl (i. e., NaCl/[NaCl + CaCl$_2$], or X_{NaCl}) and the total salinity (i. e., NaCl + CaCl$_2$, wt%) for fluid inclusions with ice as the last melting phase. X_{NaCl} can be calculated from $T_{m\text{-}HH}$ using the following equation:

$$y = (a + bx)^{-1/c}$$

where y is X_{NaCl}, x is $T_{m\text{-}HH}$, $a = 0.33124402$, $b = -0.031518028$, and $c = 0.22932736$. In the cases where only $T_{m\text{-}ice}$ is measured and $T_{m\text{-}HH}$ is not known, $T_{m\text{-}ice}$ can be used as the maximum possible $T_{m\text{-}HH}$ to calculate the maximum value of X_{NaCl} using the above equation. In these cases, the following equation can be used to calculate the maximum total salinity:

$$y = (a + bx + cx^2)^{-1}$$

where y is salinity, x is $T_{m\text{-}HH}$, $a = 0.057184817$, $b = 0.00078565757$, and $c = 5.7262766E\text{-}6$. Because the isotherms in the field of ice are sub-parallel to the NaCl-CaCl$_2$ binary side in the H$_2$O-NaCl-CaCl$_2$ ternary system, the errors in salinity calculation introduced by the above approximation are small (less than 2 wt%). A Windows program for calculation of X_{NaCl} and salinity is available at：http://uregina. ca/ ~ chiguox.

Key words   NaCl/[NaCl + CaCl$_2$], Total salinity, H$_2$O-NaCl-CaCl$_2$ system, Fluid inclusions

1   Introduction

Fluid inclusions from a variety of geologic environments can be approximated by the H$_2$O-NaCl-CaCl$_2$ system (Crawford, 1981; Oakes *et al.*, 1990; Williams-Jones and Samson, 1990). The H$_2$O-NaCl-CaCl$_2$ system was first thoroughly studied by Yanatieva (1946), whose experimental data were widely used in constructing phase diagrams of the system (Crawford, 1981; Vanko *et al.*, 1988; Williams-Jones and Samson, 1990). More recently, Oakes *et al.* (1990) carried out extensive experiments in the field of ice of the H$_2$O-NaCl-CaCl$_2$ system and constructed isotherms that are significantly different from those of Yanatieva (1946). These new isotherms were considered (Oakes *et al.*, 1990) to be superior to Yanatieva's (1946), and have been

adopted in most recent literatures (e. g., Bodnar, 2003; Kontak, 2004).

The composition of the fluid inclusions which are undersaturated with halite at room temperature can be plotted in the field of ice in the H$_2$O-NaCl-CaCl$_2$ phase diagram (Fig. 1) by using the final melting temperatures of hydrohalite ($T_{m\text{-}HH}$) and ice ($T_{m\text{-}ice}$) (Oakes *et al.*, 1990; Williams-Jones and Samson, 1990), thus providing a graphical estimation of the salinity (i. e., NaCl + CaCl$_2$, wt%) and the relative proportion of NaCl (i. e., NaCl/[NaCl + CaCl$_2$], or X_{NaCl}). Oakes *et al.* (1990) have established an equation relating salinities to X_{NaCl} and $T_{m\text{-}ice}$ ($> -35\,°C$). The solution of this equation, however, requires a known X_{NaCl} value, which must be graphically estimated from $T_{m\text{-}HH}$. Since a graphical estimation is of relatively
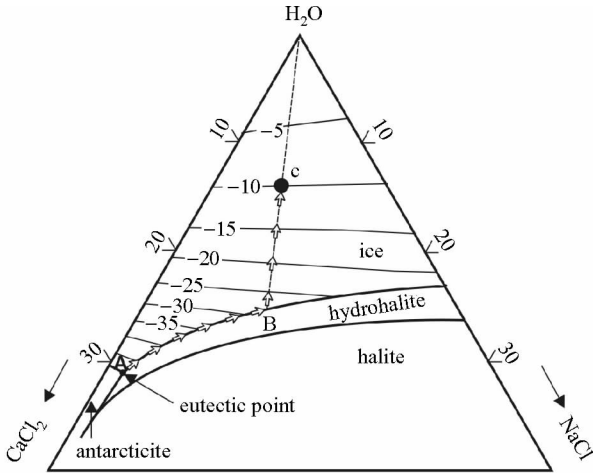
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Fig. 1　Phase diagram of the H_2O-NaCl-$CaCl_2$ system（based on the data of Yanatieva, 1946 and Oakes *et al*., 1990, 1992）. Arrows show the melting process of a fluid inclusion. The inclusion starts melting at the eutectic point at $-52℃$（point A）, where antarcticite is instantly molten, leaving hydrohalite, ice and a liquid. Further warming leads to co-melting of hydrohalite and ice, and the composition of the liquid changes along the ice-hydrohalite cotectic curve from A to B. At point B hydrohalite is completely molten, leaving only ice and a liquid, and afterwards ice continues to melt and the composition of the liquid follows the line toward the apex of H_2O. Ice is completely molten at point C, which indicates that composition of the final liquid, i. e., the composition of the fluid inclusion.

low precision and is time-consuming, it is desirable to develop an equation to calculate X_{NaCl} from T_{m-HH}, which is one of the objectives of this paper. A Microsoft Excel add-in program has been developed by Naden（1996）to calculate X_{NaCl} and salinities, but his data set did not include those of Oakes *et al*. （1992）, which provide more constraints on the ice-hydrohalite cotective curve.

　　In many cases, T_{m-HH} cannot be measured for fluid inclusions of the H_2O-NaCl-$CaCl_2$ system, and so X_{NaCl} as well as salinity cannot be graphically estimated or calculated using the methods discussed above. If T_{m-ice} is higher than $-21.2℃$, the system may be approximated by the H_2O-NaCl system, and the salinity is calculated using the equation for that system（Bodnar, 2003）. For T_{m-ice} lower than $-21.2℃$, T_{m-ice} may be considered as the maximum value of T_{m-HH}. Thus, T_{m-ice} may be used in the place of T_{m-HH} to calculate the maximum X_{NaCl} values and salinities. The equation for calculating salinities from T_{m-HH} along the ice-hydrohalite cotectic curve, and the potential error in salinity calculation introduced by this approximation（i. e., using T_{m-ice} in the place of T_{m-HH}）constitute the second part of this paper. It is noted that this paper only deals with fluid inclusions that are undersaturated with halite at room temperatures and that have ice as the last melting phase （Fig. 1）.
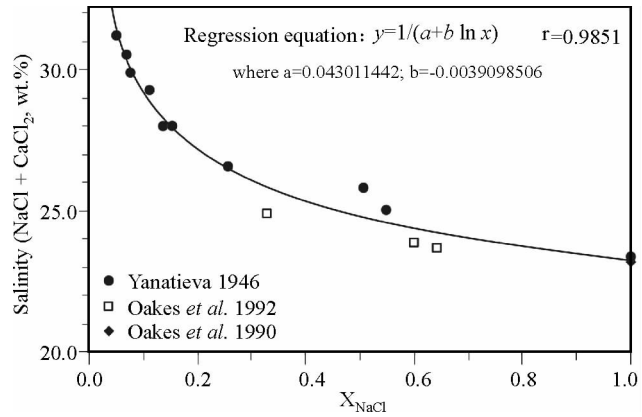

Fig. 2　X_{NaCl}-salinity diagram showing the experimental data of Yanatieva（1946）and Oakes *et al*. （1990, 1992）and the regression curve.

2　Equation for calculation of X_{NaCl} from T_{m-HH}

　　Limited amounts of data on the ice-hydrohalite cotectic curve are available from Yanatieva（1946）and Oakes *et al*. （1990, 1992）（table 1）. The data of Yanatieva（1946）are mainly distributed in the range of X_{NaCl} from 0.0577 to 0.2632. There are only five data between 0.3 and 1.0 of X_{NaCl}, with significant discrepancy between Yanatieva（1946）and Oakes *et al*. （1992）（Table 1; Fig. 2）. On the other hand, large amounts of data are available in the field of ice above $-35℃$ （Oakes *et al*., 1990）, and since the ice-hydrohalite boundary is part of the ice field, it is possible to use the isotherms in the ice field to constrain the X_{NaCl}-T_{m-HH} relationship on the ice-hydrohalite boundary. Based on the data presented in Table 1 and the isotherms in the field of ice（Oakes *et al*., 1990）, an equation correlating X_{NaCl} and T_{m-HH} is derived as follows.

　　First, an equation correlating X_{NaCl} and salinity（i. e., NaCl + $CaCl_2$, wt%）on the ice-hydrohalite boundary is regressed using the data of Yanatieva（1946）and Oakes *et al*. （1990, 1992）（Table 1）, with the CurveExpert（version 1.3）program. The best fit is found with a reciprocal logarithm curve （Fig.2）, and the equation is expressed as:

$$y = (a + b\ln x)^{-1} \qquad (1)$$

where y is salinity, x is X_{NaCl}, $a = 0.043011442$, and $b = 0.0039098506$.

　　Next, the above equation is coupled with the equation of Oakes *et al*. （1990）describing the relationship between salinities, X_{NaCl} and T_{m-ice}（$> -35℃$）to obtain paired data of X_{NaCl} and T_{m-ice} along the ice-hydrohalite boundary. The Oakes *et al*. 's（1990）equation is described as follows:

$$y = \sum_{i=0}^{6} a_i T^i + \sum_{j=1}^{4} b_j T^j x + \sum_{k=2}^{6} c_k T^k x^2 \qquad (2)$$

where y is salinity, x is X_{NaCl}, $T = T_{m-ice}/10$, and a_i, b_j and c_k are coefficients which are given in Table 3 of Oakes *et al*. （1990）. Since there are three unknowns（y, x and T）in the two equations, it is possible to eliminate y and obtain an equation correlating x and T. However, given the complexity of the equations, an analytical solution is unrealistic. Therefore, we

Table 1   Experimental data on the ice - hydrohalite cotectic of the H$_2$O-NaCl-CaCl$_2$ system

Point	NaCl (wt%)	CaCl$_2$ (wt%)	Salinity (NaCl + CaCl$_2$, wt. %)	XNaCl (NaCl/NaCl + CaCl$_2$)	Hydrohalite-melting temperature (℃)	Data sources
Y1	1.80	29.40	31.20	0.0577	− 52.0	
Y2	2.35	28.16	30.51	0.0770	− 46.8	
Y3	2.50	27.40	29.90	0.0836	− 45.0	
Y4	3.10	26.20	29.30	0.1183	− 40.0	Yanatieva, 1946
Y5	4.00	24.00	28.00	0.1429	− 36.0	
Y6	4.50	23.50	28.00	0.1607	− 35.0	
Y7	7.00	19.60	26.60	0.2632	− 30.0	
Y8	13.20	12.60	25.80	0.5116	− 26.7	
Y9	13.80	11.20	25.00	0.5520	− 25.0	
Y10	23.40	0.00	23.40	1.0000	− 21.2	
O1	23.20	0.00	23.20	1.0000	− 21.2	Oakes *et al.*, 1990
O2	8.30	16.60	24.90	0.3333	− 28.1	
O3	14.40	9.50	23.90	0.6025	− 23.8	Oakes *et al.*, 1992
O4	15.30	8.40	23.70	0.6456	− 23.1	

use an iterative method and a C^{++} program to calculate the X_{NaCl} and salinity values for a series of given $T_{m\text{-}ice}$ values. Since $T_{m\text{-}HH}$ is equal to $T_{m\text{-}ice}$ on the ice-hydrohalite boundary, paired X_{NaCl}-$T_{m\text{-}HH}$ data are obtained. The $T_{m\text{-}HH}$ values are specified from − 22℃ to − 35℃ with an increment of 1, and an x value is selected iteratively for each $T_{m\text{-}HH}$ value. The criterion of convergence for the iteration is |slt$_1$ - slt$_2$| < 0.0001, where slt$_1$ and slt$_2$ are salinity values calculated from Eq. 1 and 2, respectively. The calculated results of X_{NaCl} and salinity corresponding to the specified $T_{m\text{-}HH}$ values are listed in Table 2.

Finally, the calculated $T_{m\text{-}HH}$ and X_{NaCl} data (Table 2) and the experimental data of Yanatieva (1946) and Oakes (1992) are considered for constructing a regression equation. Figure 3 shows that the calculated $T_{m\text{-}HH}$ and X_{NaCl} data are quite different from the experimental data in the range of $T_{m\text{-}HH}$ from − 35 to − 21.2℃. Because the calculated data are constrained by large amounts of experimental data in the field of ice, and because of the discrepancy between the data set of Yanatieva (1946) and Oakes *et al.* (1992) in the $T_{m\text{-}HH}$ range from − 35 to − 21.2℃, we choose to use only the calculated data and five of Yanatieva's (1946) data (filled symbols, Fig. 3) for the regression. The regression equation is as follows:

$$y = (a + bx)^{-1/c} \qquad (3)$$

where y is X_{NaCl}, x is $T_{m\text{-}HH}$, $a = 0.33124402$, $b = -0.031518028$, and $c = 0.22932736$.

3   Equations for calculation of salinity from $T_{m\text{-}HH}$ and $T_{m\text{-}ice}$

The salinity of a fluid in the H$_2$O-NaCl-CaCl$_2$ system is equal to NaCl + CaCl$_2$ (wt%), which can be calculated using different methods depending on what have been measured: 1) both $T_{m\text{-}HH}$ and $T_{m\text{-}ice}$ have been measured, and 2) only $T_{m\text{-}ice}$ has been measured.

If $T_{m\text{-}HH}$ has been measured, X_{NaCl} can be calculated using
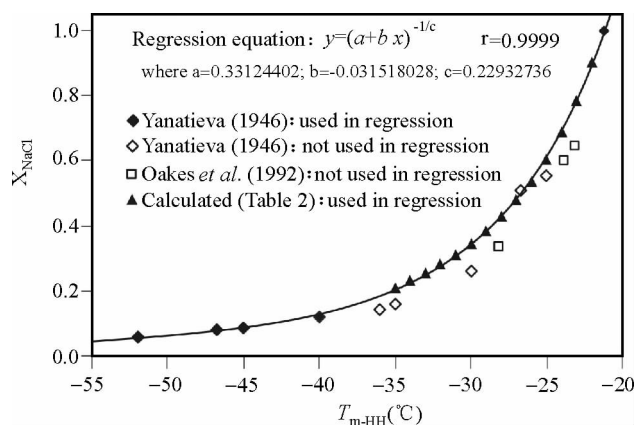

Fig. 3 $T_{m\text{-}HH}$-X_{NaCl} diagram showing the experimental data of Yanatieva (1946) and Oakes *et al.* (1990, 1992) and calculated data in Table 2. The regression curve is based on the calculated data and five of Yanatieva's (1946) data. See text for more detailed explanation.

Eq. 3 derived above. In the case of $T_{m\text{-}ice} > -35℃$, the X_{NaCl} value can then be used in conjunction with $T_{m\text{-}ice}$ to calculate the salinity using Eq. 2 (Oakes *et al.*, 1990). If $T_{m\text{-}ice}$ is lower than − 35℃, the salinity can be estimated using either the graphical method or the equation derived below with $T_{m\text{-}ice}$ being considered as the maximum possible $T_{m\text{-}HH}$.

When only $T_{m\text{-}ice}$ has been measured, the composition of the inclusions cannot be calculated because X_{NaCl} cannot be determined. However, an inspection of the phase diagram (Fig. 1) indicates that when $T_{m\text{-}ice}$ is lower than − 21.2℃ (the eutectic point in the H$_2$O-NaCl binary system), the isotherms in the field of ice are sub-parallel to the NaCl-CaCl$_2$ side, meaning that the total salinities along a given isotherm are similar. Thus, the salinity at the intersection of the isotherm with the ice-

hydrohalite boundary may be used to approximate the salinity of the fluid inclusions. It is also noticeable from the phase diagram (Fig. 1) that $T_{\text{m-ice}}$ represents the maximum possible value of $T_{\text{m-HH}}$, and so the X_{NaCl} value calculated from Eq. 3 using $T_{\text{m-ice}}$ to replace $T_{\text{m-HH}}$ represents the maximum possible X_{NaCl}.

Table 2   Salinities, X_{NaCl}, and melting temperatures along the ice-hydrohalite cotectic as calculated from coupling Eq (1) of this paper and Eq (2) of Oakes *et al.* (1990)

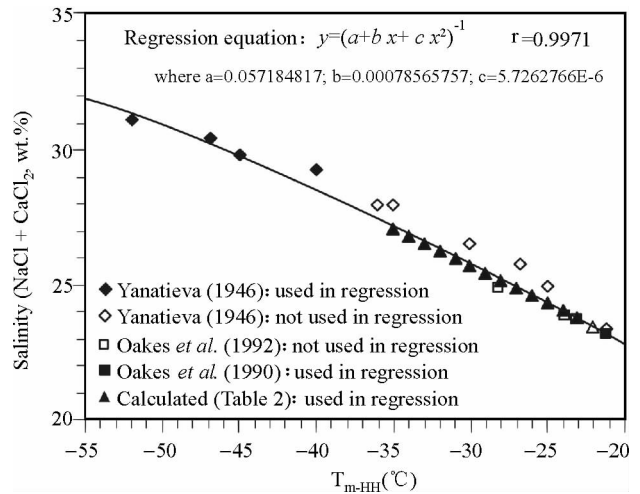| Point	$T_{\text{m-HH}}$ (℃)	X_{NaCl}	Salinity (wt%)
C1	−22.0	0.9065	23.46
C2	−23.0	0.7877	23.77
C3	−24.0	0.6898	24.06
C4	−25.0	0.6081	24.35
C5	−26.0	0.5392	24.63
C6	−27.0	0.4804	24.91
C7	−28.0	0.4298	25.18
C8	−29.0	0.3858	25.45
C9	−30.0	0.3472	25.72
C10	−31.0	0.3131	25.99
C11	−32.0	0.2826	26.27
C12	−33.0	0.2554	26.54
C13	−34.0	0.2308	26.83
C14	−35.0	0.2085	27.11

Fig. 4 $T_{\text{m-HH}}$-Salinity diagram along the ice-hydrohalite cotectic showing the experimental data of Yanatieva (1946) and Oakes *et al.* (1990, 1992) and calculated data in Table 2. The regression curve is based on the calculated data, the eutectic point of the H_2O-NaCl binary system (Oakes *et al.*, 1990), and five of Yanatieva's (1946) data. See text for more detailed explanation.

The equation correlating salinity and $T_{\text{m-HH}}$ along the ice-hydrohalite boundary is regressed from the same data set as for the X_{NaCl}-$T_{\text{m-HH}}$ equation (Eq. 3). Similarly, only the calculated data (Table 2) and five of Yanatieva's (1946) data are used in the regression. The regression curve is shown in Figure 4 and the equation is as follows:

$$y = (a + bx + cx^2)^{-1} \qquad (4)$$

where y is salinity, x is $T_{\text{m-HH}}$, $a = 0.057184817$, $b = 0.00078565757$, and $c = 5.7262766E-6$.

The potential errors on salinity estimation introduced by approximating $T_{\text{m-HH}}$ with $T_{\text{m-ice}}$ decrease with decreasing $T_{\text{m-ice}}$ values from −21.2 to −52℃. Thus, for a $T_{\text{m-ice}}$ of −21.2℃, the salinity calculated from Eq. 4 with $T_{\text{m-HH}}$ being replaced by $T_{\text{m-ice}}$ (i.e., −21.2℃, the maximum possible $T_{\text{m-HH}}$) is 23.20, whereas the salinity calculated from Eq. 2 with $T_{\text{m-HH}}$ being assigned to −52℃ (the minimum possible value of $T_{\text{m-HH}}$) is 21.25, thus a potential error of 1.95 wt.%. In contrast, if $T_{\text{m-ice}}$ is −35℃, the salinity calculated from Eq. 4 with $T_{\text{m-HH}}$ being replaced by $T_{\text{m-ice}}$ is 27.25, and the salinity calculated from Eq. 2 with $T_{\text{m-HH}}$ being assigned to −52℃ is 26.74, so the potential error is only 0.51 wt.%.

4   Discussion and conclusions

Fluid inclusions with first melting temperatures lower than −50℃ are usually modeled by the H_2O-NaCl-$CaCl_2$ system, unless there is evidence showing that other bivalent cations such as Mg^{2+} are more important than Ca^{2+} (e.g. from chemical analysis). Many of this type of inclusions show ice as the last melting phase and hydrohalite as the second last one. If stable final melting temperature of hydrohalite ($T_{\text{m-HH}}$) and final melting temperature of ice ($T_{\text{m-ice}}$) can be measured, the

composition of the fluid, including X_{NaCl} (i.e., NaCl/[NaCl + $CaCl_2$]) and salinity (i.e., NaCl + $CaCl_2$, wt%), can be graphically plotted on a H_2O-NaCl-$CaCl_2$ phase diagram.

We have developed two equations (Eqs. 3 and 4) to calculate the X_{NaCl} and salinities by the regression method using the $T_{\text{m-HH}}$, X_{NaCl}, and salinity data along the ice-hydrohalite cotectic curve. Because experimental data on the cotectic curve are relatively limited, and because there is a discrepancy between Yanatieva (1946) and Oakes *et al.* (1992), we use a method to extend the isotherms in the field of ice, where large amounts of experimental data (Oakes *et al.*, 1990) are available, to the ice-hydrohalite boundary. The equations (Eqs. 3 and 4) are thus compatible with Eq. 2 of Oakes *et al.* (1990) which is used to calculate the salinity for fluid inclusions in the field of ice with $T_{\text{m-ice}} \geqslant -35℃$.

If $T_{\text{m-ice}} = T_{\text{m-HH}}$, X_{NaCl} and salinity can be calculated using Eq. 3 and 4, respectively. When both $T_{\text{m-ice}}$ and $T_{\text{m-HH}}$ are measured, X_{NaCl} is calculated with Eq. 3, and the salinity is calculated in different ways depending on the value of $T_{\text{m-ice}}$. If $T_{\text{m-ice}} > -35℃$, salinity is calculated by using the X_{NaCl} value just obtained and Eq. 2 of Oakes *et al.* (1990), otherwise (i.e., $T_{\text{m-ice}} < -35℃$) the approximate salinity is calculated using Eq. 4 with $T_{\text{m-HH}}$ being replaced by $T_{\text{m-ice}}$ in the equation. The errors introduced by this approximation is less than about 0.5 wt.%. Finally, if $T_{\text{m-ice}}$ is measured and $T_{\text{m-HH}}$ is not and if $T_{\text{m-ice}} < -21.2℃$, $T_{\text{m-ice}}$ can be considered as the maximum possible value of $T_{\text{m-HH}}$. Therefore, the maximum possible values of X_{NaCl} and salinity can be calculated using Eq. 3 and 4, respectively, with $T_{\text{m-HH}}$ being replaced by $T_{\text{m-ice}}$ in the equation. The maximum error in salinity estimation introduced by this approximation is less than 2 wt.%. Considering the relatively high salinities for fluid inclusions with $T_{\text{m-ice}} < -21.2℃$, these potential errors of salinity estimation are not significant for most geological problems.

An executable Windows program for calculation of X_{NaCl} and salinity is available to run or download at: http://uregina. ca/ ~ chiguox. In the program, the equation of Bodnar (1993) is used for the H$_2$O-NaCl binary system instead of Eq. 4, even though the results obtained from the two equations are very similar. Thus, by entering $T_{m\text{-}HH}$ = − 21. 2℃, the program can be used for the H$_2$O-NaCl system as any other programs based on Bodnar's (1993) equation.

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