Determination of the composition of H_2O-NaCl-$CaCl_2$ fluid inclusions based on microthermometric and microanalytical data

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1. Introduction

Aqueous fluids in which NaCl and $CaCl_2$ are the two most abundant salts and which may be adequately described by the system H_2O-NaCl-$CaCl_2$ are common in many geologic environments. The best source of information concerning the compositions of paleo-geologic fluids comes from fluid inclusions, including microthermometric (T_m) and microanalytical data (X_{NaCl}) (e.g., from LA-ICPMS).

Several numerical models have been developed to interpret data from H_2O-NaCl-$CaCl_2$ fluid inclusions (Oakes et al., 1990; Williams-Jones and Samson, 1990; Naden, 1996; Bakker, 2003; Chi and Ni, 2007). While each model appears to work well over a limited range of T-X conditions, none is capable of determining compositions over the whole reported range of natural fluid compositions, each is limited in the usable data types, and many predict wavy isotherms and boundary curves.

The model presented here incorporates those aspects of previous models that have been shown to work well, and adds new equations and methods to expand the T-X range of applicability, remove anomalies inherent in some previous statistical models, and expand the range of input data types that may be used to estimate compositions of H_2O-NaCl-$CaCl_2$ fluid inclusions.

2. Vapor-Saturated Phase Relations

Phase relations on the vapor-saturated liquidus of the H_2O-NaCl-$CaCl_2$ system are shown schematically in Figure 1. The system is characterized by at least eight fields in which a single solid phase is in equilibrium with liquid and vapor. Six of these fields are described in this study; two additional fields in the high salinity, low X_{NaCl} part of the system (near the $CaCl_2$ apex) for which experimental data are not available are not considered here.

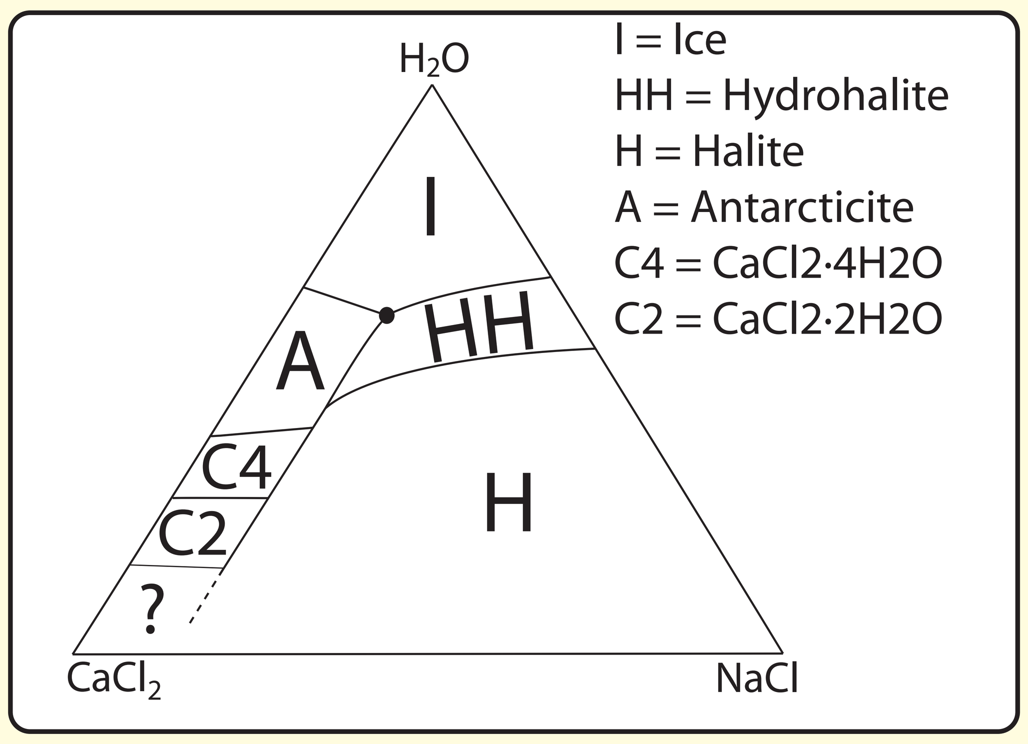

Fig. 1. Schematic vapor-saturated phase relations in the H_2O-NaCl-$CaCl_2$ system.

3. Experimental Data and Regression

Experimental data on the vapor-saturated H_2O-NaCl-$CaCl_2$ liquidus are shown in Figure 2 and Table 1. Data are sorted according to the solid phase(s) present at last melting. Regression modeling was done using SAS© JMP 7.0 software. Data on the two-solid boundary curves (cotectic and peritectic curves) are regressed to describe X_{NaCl} and salinity (S) each as a function of T_m, while data on the one-solid liquidi are regressed to describe S as a function of X_{NaCl} and T_m.

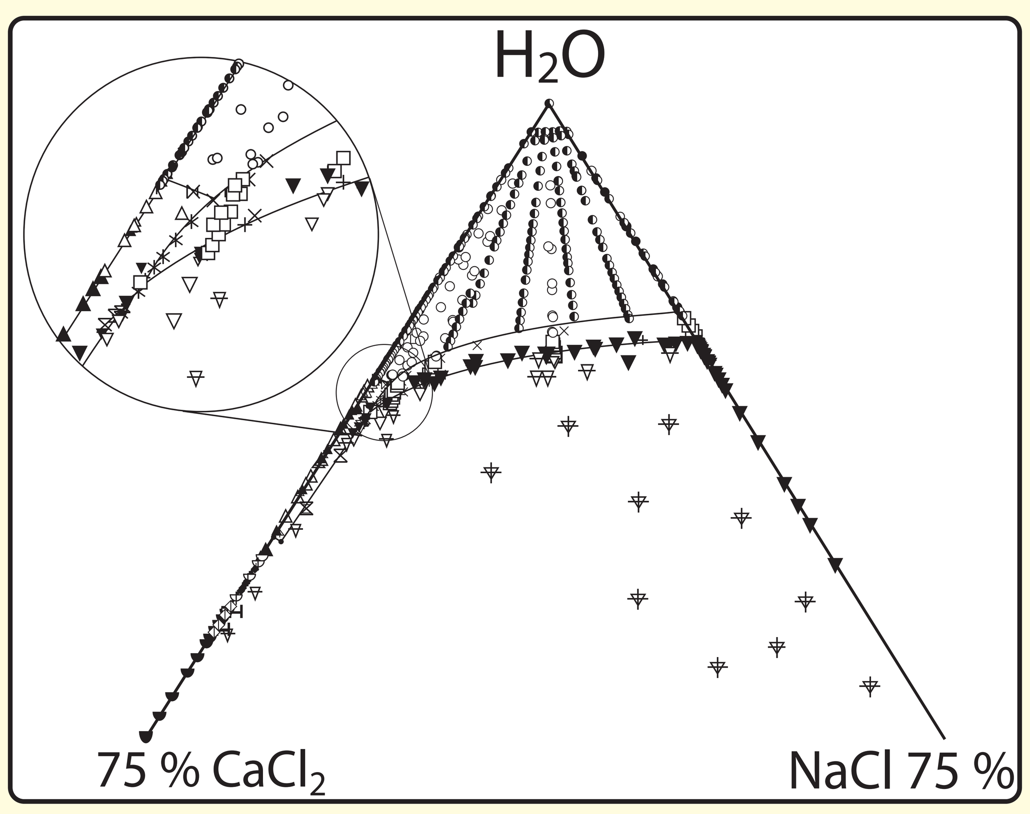

Fig. 2. Experimental data on the H_2O-NaCl-$CaCl_2$ liquidus. Symbols defined in Table 1 (below).

Source	I+HH	HH+H	I+A	HH+A	H+A	H+C2	I	H	HH	A	C4	C2
Nat. Research Council (1928)								(19)				
Yanatieva (1946)	×(9)	+(6)	⋈(3)	∗(7)	⧖(8)		○(57)	▽(13)	□(30)	△(20)		
Linke (1958)		+(4)			⧖(1)	⊢(2)	●(21)	▼(57)	■(1)	▲(15)	◆(7)	(12)
Potter and Clynne (1978)								(11)		(4)	(5)	(5)
Vanko et al. (1988)								(10)				
Oakes et al. (1990)	×(1)						◐(168)					
Oakes et al. (1992)	×(3)											
Sub-total							246	110	31	39	12	17
Total*	13	3	10	7	9	2	262	129	61	58	12	19

Table. 1. Summary of the sources of experimental data in the H_2O-NaCl-$CaCl_2$ system. Number of data points for each source for each phase assemblage is shown in parentheses. *(Total = sum of all data on liquidus and adjacent phase boundary curves)

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References

Bakker, R. J., 2003. Chem. Geol. 194, 3-23.
Chi, G., Ni, P., 2007. Yanshi Xuebao 23, 33-37.
Linke, W. F., 1958. Solubilities, inorganic and metal organic compounds; a compilation of solubility data from the periodical literature. Van Nostrand, Princeton, NJ.
Naden, J., 1996. PACROFI VI, Madison, WI.
National Research Council, 1928. International critical tables of numerical data, physics, chemistry and technology. McGraw-Hill, New York.
Oakes, C. S., Bodnar, R. J., Simonson, J. M., 1990. Geochim. Cosmochim. Acta 54, 603-610.
Oakes, C. S., Sheets, R. W., Bodnar, R. J., 1992. PACROFI IV Lake Arrowhead, CA.
Potter, R. W., II, Clynne, M. A., 1978. J. of Res. U. S. Geol. Survey 6, 701-705.
Vanko, D. A., Bodnar, R. J., Sterner, S. M., 1988. Geochim. et Cosmochim. Acta 52, 2451-2456.
Williams-Jones, A. E. and Samson, I. M., 1990. T. Can. Min. 28, 299-304.
Yanatieva, O. K., 1946.. Zhurnal Prikladnoi Khimii 19, 709-22.

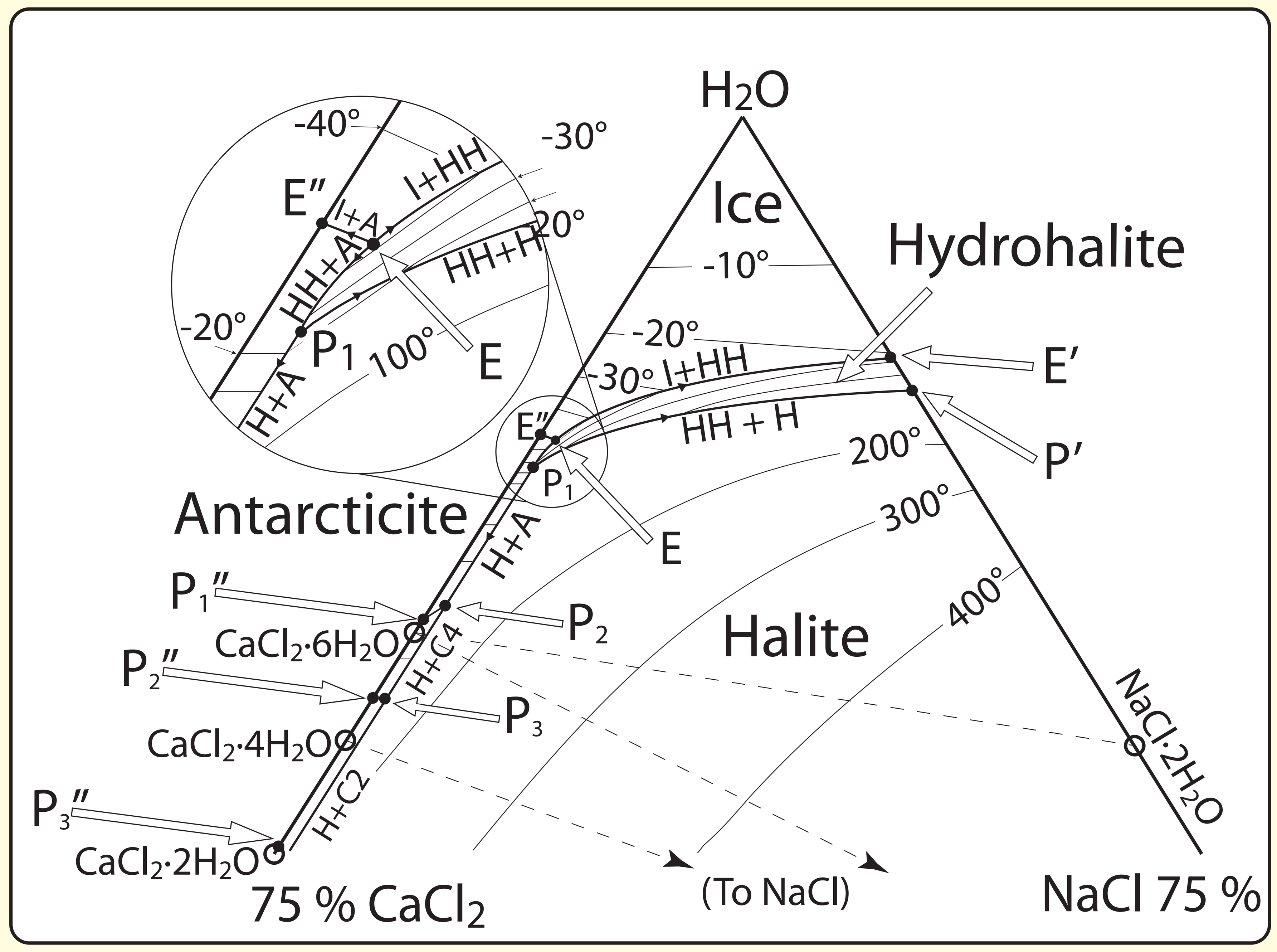


Fig. 3. Vapor-saturated liquidus for the H_2O-NaCl-$CaCl_2$ system. Phase boundaries and isotherms calculated from equations from the literature (Naden, 1996) and those derived in this study. Also shown are the invariant points (E = eutectic; P = peritectic; H_2O-NaCl and H_2O-$CaCl_2$ binary invariant points labelled prime(′) and double prime(″), respectively) as solid cirlcles. Compositions of solid phases shown as open circles.

4. Modeling the Vapor Saturated Liquidus

Phase boundary curves and isotherms calculated from the equations derived in this study are shown in Figure 3. The regression equations developed in this study completely describe liquid composition on the vapor-saturated liquidus between the H_2O apex, the NaCl apex and the composition of $CaCl_2 \cdot 4H_2O$ on the H_2O-$CaCl_2$ binary (Fig. 4). Residuals of the equations with respect to experimental data are shown in Figure 5. The equations predict smooth variation of composition along isotherms and phase boundary curves, removing the anomolous behavior exhibited by previous models (Fig. 6). The system of equations in the model is designed to allow compositional determination from either combination of two melting temperatures (a phase cotectic or peritectic curve melting temperature plus the final melting temperature) or the final melting temperature plus the known X_{NaCl}.

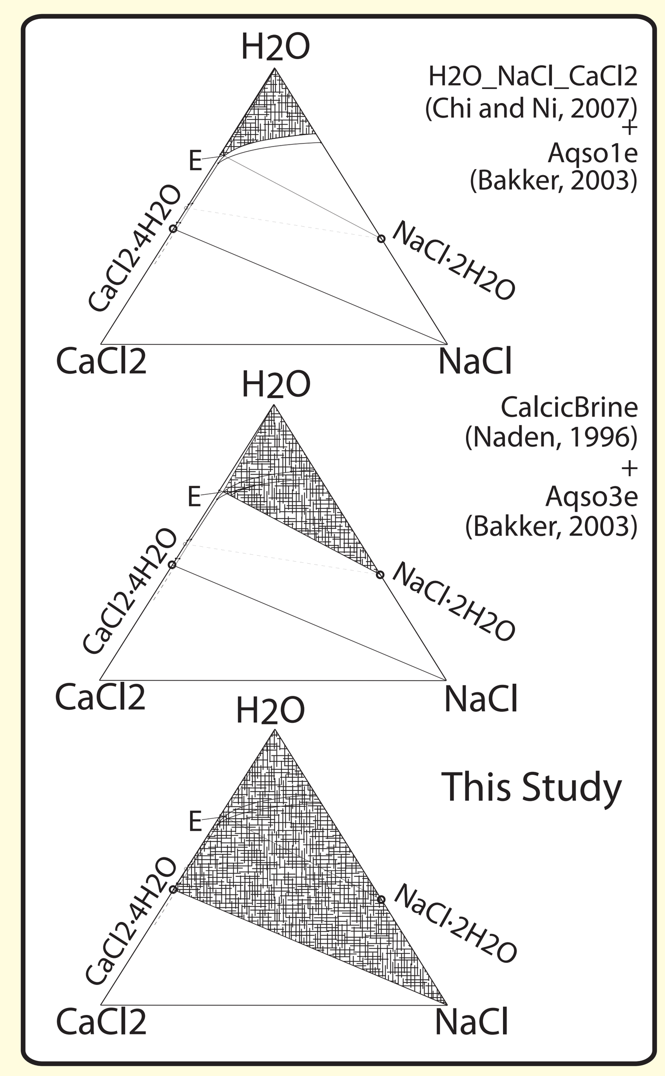


Fig. 4. (Above) Comparison of the compositional range of applicabiltiy of the model developed in this study (bottom) with previous models (top and middle).

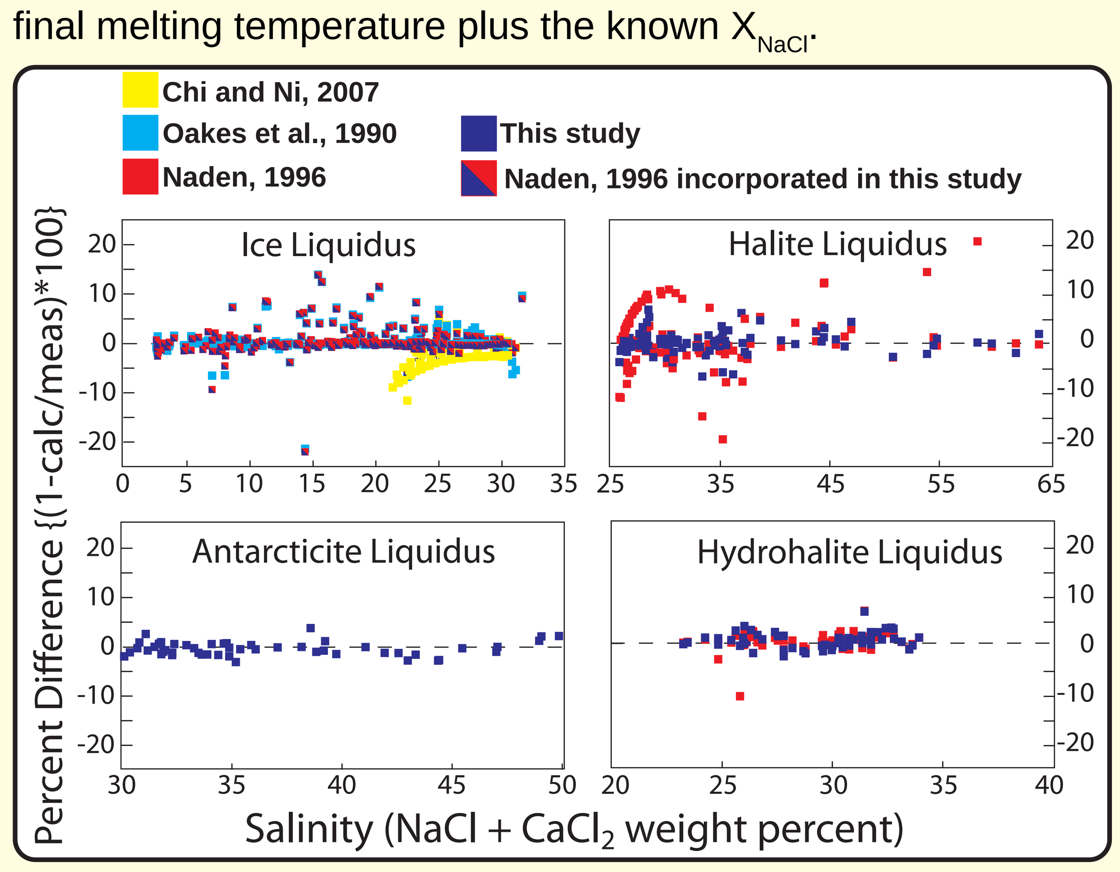
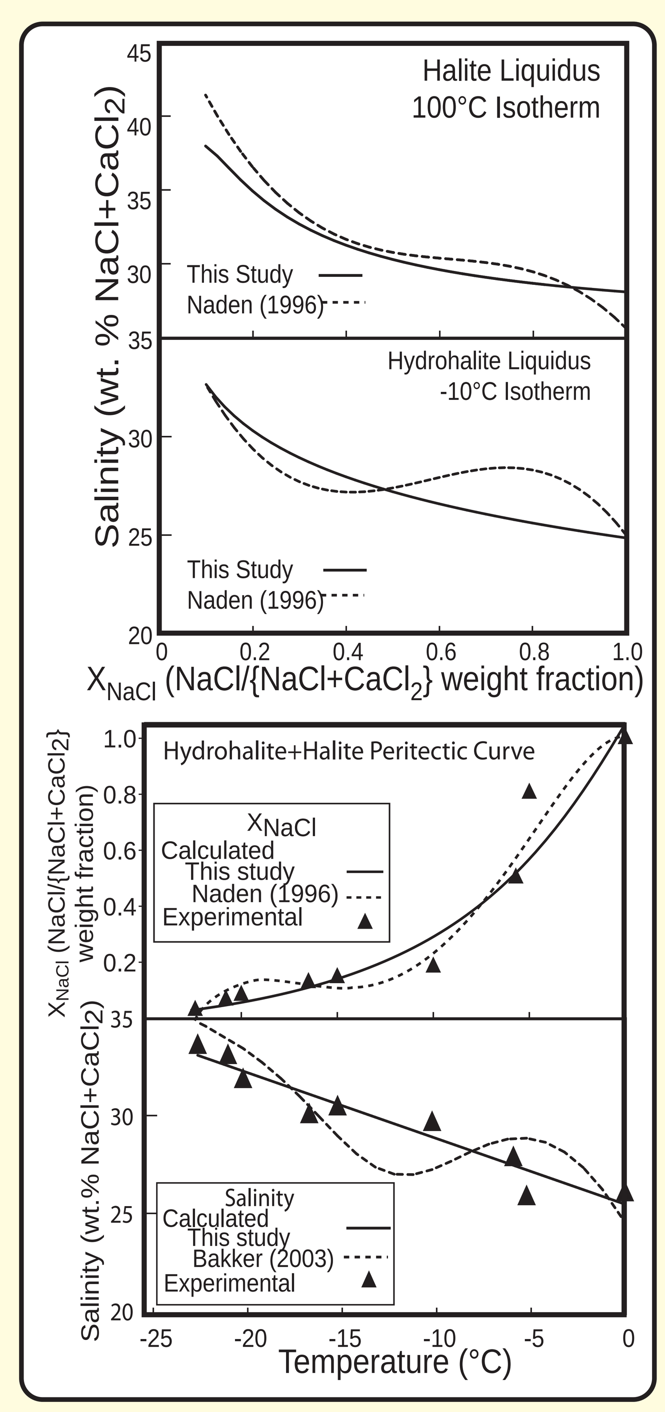


Fig. 5. (Above) Residuals associated with salinity determination for experimental data on the liquidus surfaces using the equations developed in this study and previous models.

Fig. 6. (Right) comparison of liquid composition on isotherms in the halite and hydorhalite fields (top), and on the HH+H peritectic curve (bottom), calculated from the equations developed in this study with those of previous models.



4. Summary

The numerical model described herein incorporates a comprehensive set of empirical equations to allow fluid inclusion compositions to be determined anywhere within the range of reported fluid compositions in the H_2O-NaCl-$CaCl_2$ system. A Microsoft© Excel program that implements the model to estimate fluid inclusion compositions is available for download at the Fluids Research Laboratory webpage, http://www.geochem.geos.vt.edu/fluids/.