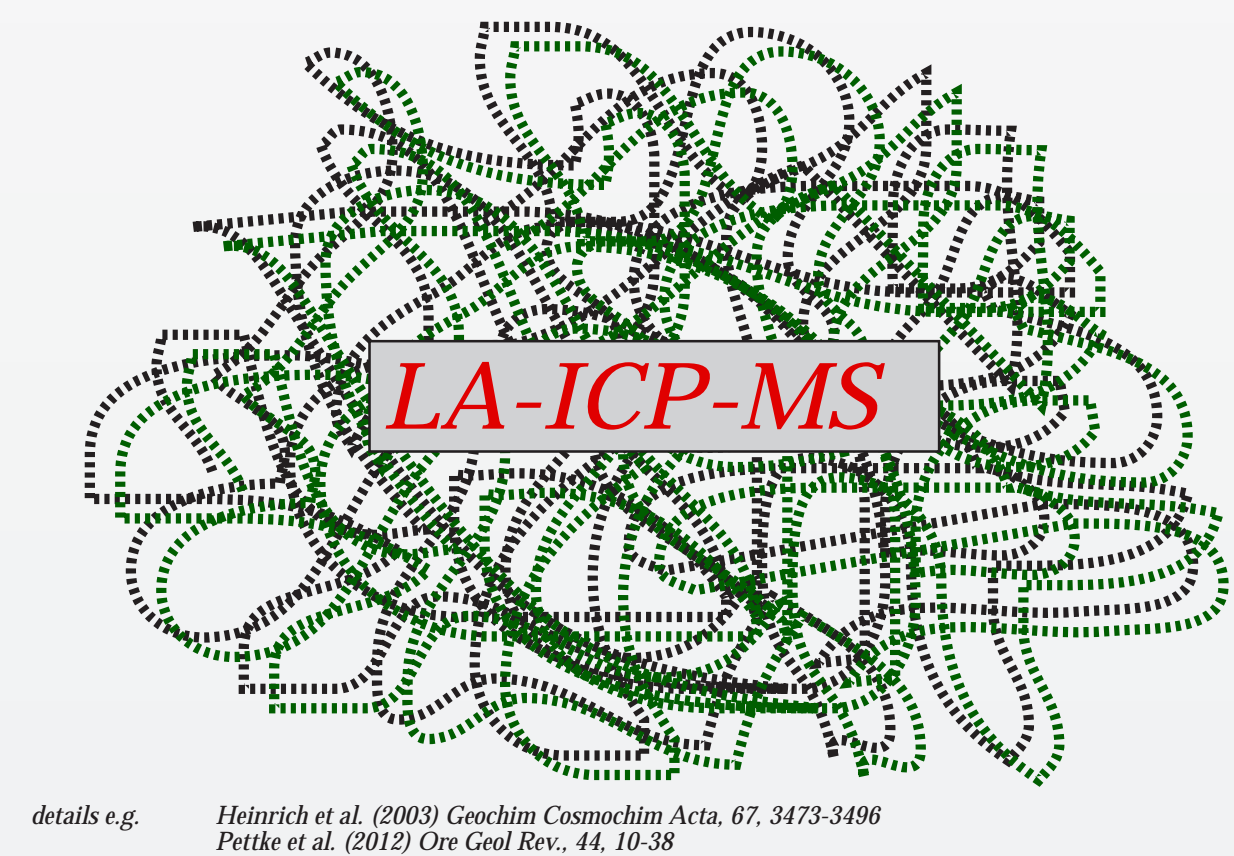


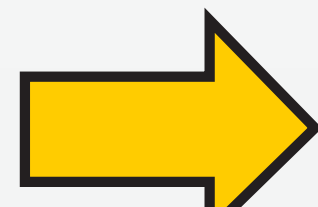
How microthermometry and eq. mass fraction NaCl can spoil your highly sophisticated LA-ICP-MS data of fluid inclusions

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details e.g. Heinrich et al. (2003) Geochim Cosmochim Acta, 67, 3473-3496
Pettke et al. (2012) Ore Geol Rev., 44, 10-38



Concentration type	Symbol	Definition	SI unit	other units
mass density	ρ	m/V	kg·m ⁻³	g(100 mL) ⁻¹
amount concentration	c_n	n_p/V	mol·m ⁻³	M (= mol/L)
molar concentration	c_m	n_p/V	mol·m ⁻³	M (= mol/L)
volume fraction	φ_{ij}	V_{ij}/V	m ³ ·m ⁻³	
Related quantities	Symbol	Definition	SI unit	other units
molality	b_i	n_i/m_{solvent}	mol·kg ⁻¹	
amount fraction	x_i	n_i/n	mol·mol ⁻¹	ppm, ppb
mole fraction	x_i	n_i/n	mol·mol ⁻¹	ppm, ppb
mass fraction	w_i	m_i/m	kg·kg ⁻¹	ppm, ppb

"fraction" is the correct concept

the result of the mass spectrometer is transformed in a **concentration** using standards:

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mass fraction	w_i	m_i/m	kg·kg ⁻¹	ppm, ppb

V = volume in m³
m = mass in kg
n = amount of substance in mole

correct = the amount divided by the mass of the "solvent",
not the mass of solution: mol/kg_{solvent} ≠ mol/kg_{solution}

"m" is not the symbol for molality

mmol/kg_{solution}

μg/g

mass% (= "wt.%")

mg/g

ppm

"weight" is a force, not a mass

"ppm", "ppb" should be avoided:
1) unclear whether mass or amount is involved
2) language: 10⁹ = billion (eng) = milliard (ger, fra, ned, it, esp)
10¹² = trillion (eng) = billion (ger, fra, ned, it, esp)

e.g. Leisen et al. (2012) Geochim. Cosmochim. Acta, 90, 110-125

e.g. Shepherd et al. (1998) Eur. J. Min., 10, 1097-1108
Audétat et al. (2000) Econ. Geol., 95, 1563-1581
Günther (2001) Short Course MAC, 29, 47-61
Heinrich et al. (2003) Geochim Cosmochim. Acta, 67, 3473-3496
Allan et al. (2005) Am. Mineral., 90, 1767-1775
Pettke et al. (2012) Ore Geol. Rev., 44, 10-38

LA-ICP-MS results in μg per gram
per gram of what?

put here your answer

Internal standard fluid inclusions

composition of fluid inclusions are usually given in relative numbers:

fractions of mass (g) or amount-of-substance (mole)

a fraction cannot be "absolute"

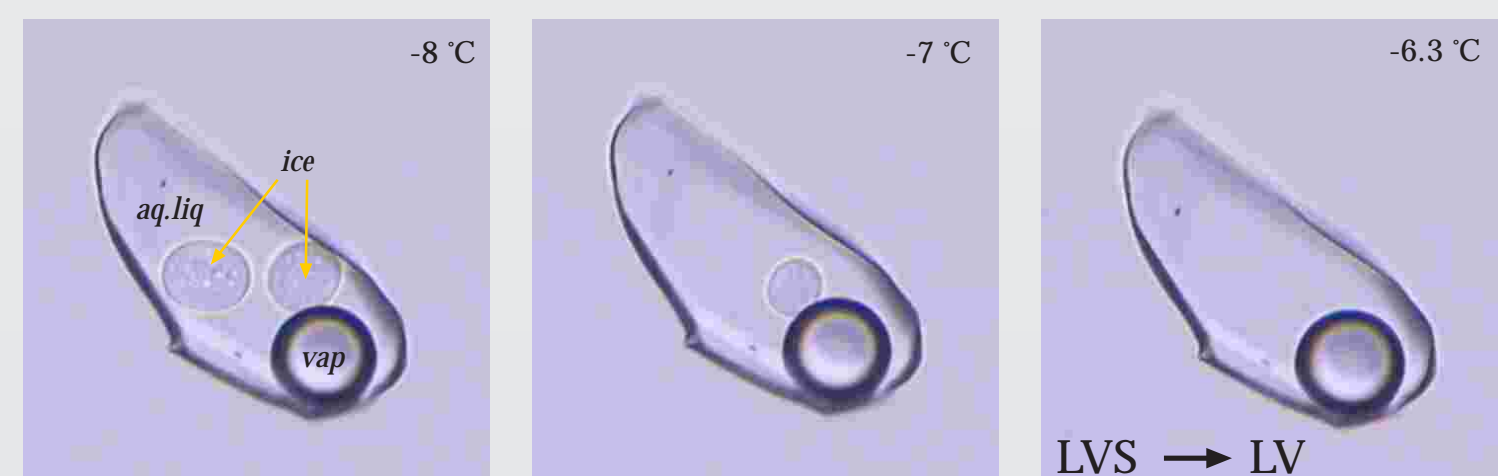
the elemental ratios obtained from LA-ICP-MS are transformed into "absolute" fractions in aqueous solutions ("concentrations") with the aid of an internal standard

microthermometry

microthermometry involves mainly dissolution temperatures of ice, hydrohalite, and halite in aqueous solutions. "Observed" eutectic temperatures in complex salt bearing solutions are regarded as unreliable (Bakker and Baumgartner, 2012, Cent. Eur. J. Geosci., 4, 225-237), and do not give sufficient information about the major types of dissolved salts. Metastable phase changes and assemblages are common in these types of inclusions (Bakker, 2004, Can Mineral., 42, 1238-1304).

common phase changes related to salinity:

1. final ice dissolution temperature



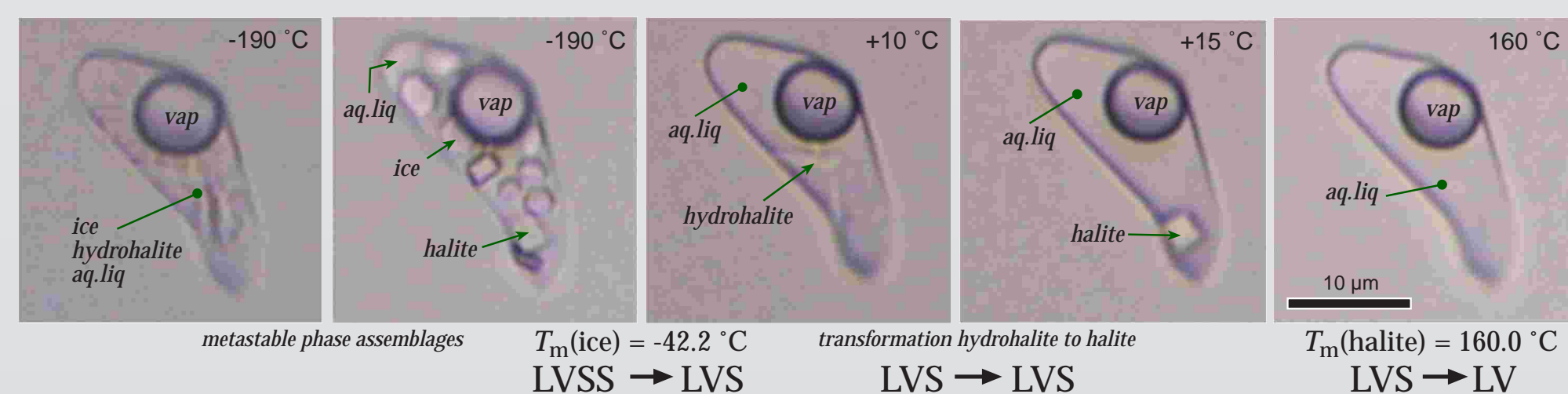
equivalent binary system: w(H₂O-eq.) = 90.41%
w(NaCl-eq.) = 9.59 %

2. dissolution temperature of halite



equivalent binary system: w(H₂O-eq.) = 32.79 %
w(NaCl-eq.) = 67.21 %

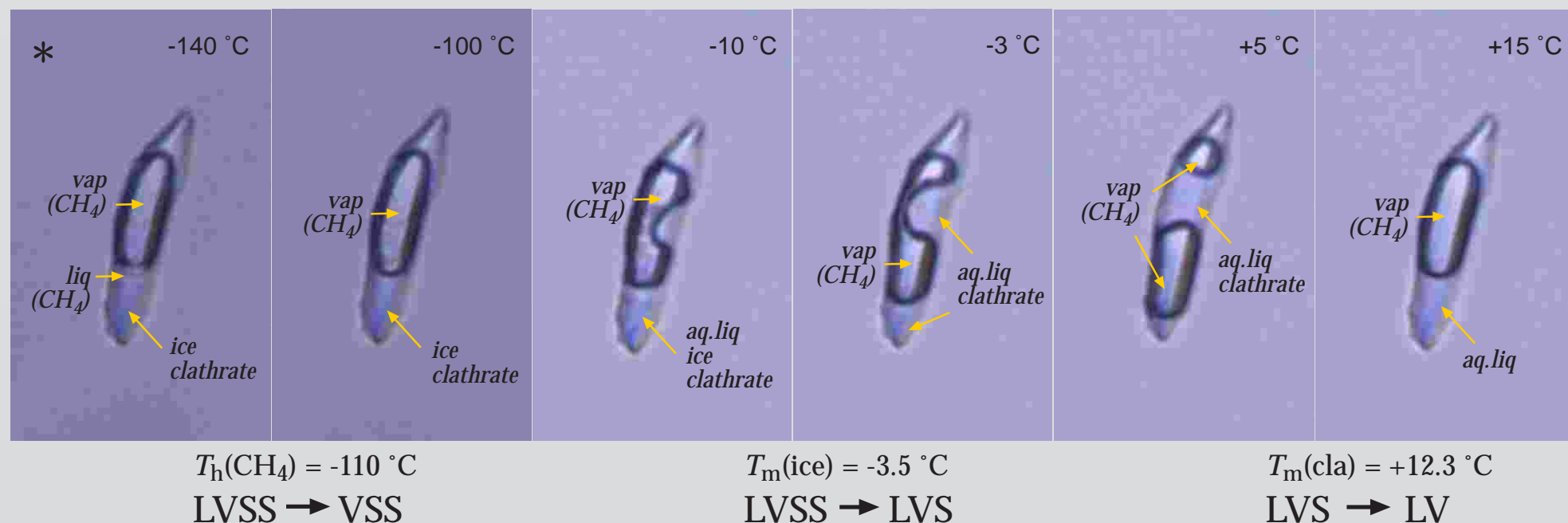
3. combination dissolution temperatures of ice/hydrohalite/halite



equivalent binary system: w(H₂O-eq.) = 69.87 %
w(NaCl-eq.) = 30.13 %

equivalent ternary system: w(H₂O-eq.) = 64.14 %
w(NaCl-eq.) = 14.47 %
w(CaCl₂-eq.) = 21.39 %

4. dissolution temperatures of ice and clathrate



T_m(CH₄) = -110 °C
LVSS → VSS

T_m(ice) = -3.5 °C
LVSS → LVS

T_m(cla) = +12.3 °C
LVS → LV

equivalent ternary system: x(H₂O-eq.) = 0.8887
x(CH₄-eq.) = 0.1057
x(NaCl-eq.) = 0.0056

w(H₂O-eq.) = 88.8 %
w(CH₄-eq.) = 9.4 %
w(NaCl-eq.) = 1.8 %

* phases are mainly identified by Raman spectroscopy

Correct analyses and interpretation of microthermometry is of major importance for additional uncertainties in the results from LA-ICP-MS. It is necessary to understand the existence of metastable phase assemblages in saline inclusions, in addition to metastable phase changes during heating experiments. Abundant mis-interpretations of microthermometry exist in literature. Most LA-ICP-MS studies do not provide sufficient information about the microthermometrical results. Knowledge and understanding of phase diagrams of water-salt systems at variable conditions are the minimum settings for a useful interpretation of fluid inclusion properties.

The illustrated examples are calculated with the software:

BULK (package "Fluids"): Bakker (2003, Chem. Geol., 194, 3-23)
ICE (package "Clathrates"): Bakker (1997, Comput. Geosci., 23, 1-18)
AqSo WHS: Bakker (2012, Mineral. Petrol., 105, 1-29)
AqSo Vir: R.J. Bakker's website: <http://fluids.unileoben.ac.at>

all programs can be downloaded from this website
... and others

Methods of calculation

A. charge-balance of aqueous solution e.g. Allan et al. (2005), Leisen et al. (2012)

basic equation: $\sum z_i \cdot x_i = 0$

anions: Cl⁻ (only chlorides are taken into account)

cations: Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺, ...

can also be expressed in molalities (replace x with b)

reorganization of this equation to have a direct link to LA-IC-MS data:

$$x_{Na} = x_{Cl} \cdot \left[1 + \frac{x_K}{x_{Na}} + \frac{2 \cdot x_{Ca}}{x_{Na}} + \frac{2 \cdot x_{Mg}}{x_{Na}} + \frac{2 \cdot x_{Fe}}{x_{Na}} \right]^{-1}$$

No clear definitions of uncertainties in literature

extremely increased uncertainties caused by:

- only Cl⁻ as anion, other anions are excluded
- no correction possibilities for additional cations
- dissolution temperatures are affected by numerous types of cations and anions
- chloridity is highly underestimated in the equivalent binary H₂O-NaCl system

the illustrated example on the left (3) already results in a 24% underestimation of x(Na⁺)

B. straight isotherm right angle to base (SIRAB) method e.g. Heinrich et al. (1992, 2003), Audétat et al. (2000)

basic assumptions:

- hypothetical ternary system of H₂O-NaCl-rest
- isotherms are perpendicular to the H₂O-NaCl base in a triangular diagram of mass fractions

geometry of triangular shapes: $eq. w(NaCl) = w(NaCl) + 0.5 \cdot \sum w(Q_i Cl_n)$

$$\frac{w(NaCl)}{MM_{NaCl}} \cdot \frac{MM_{Q_i Cl_n}}{w(Q_i Cl_n)} = \frac{w(Na^+)}{MM_{Na^+}} \cdot \frac{MM_{Q_i^{+n}}}{w(Q_i^{+n})}$$

and reorganization of the equation:

$$eq. w(NaCl) = w(NaCl) \cdot \left[1 + 0.5 \cdot \sum \mu_i \cdot \frac{w(Q_i^{+n})}{w(Na^+)} \right]$$

microthermometry

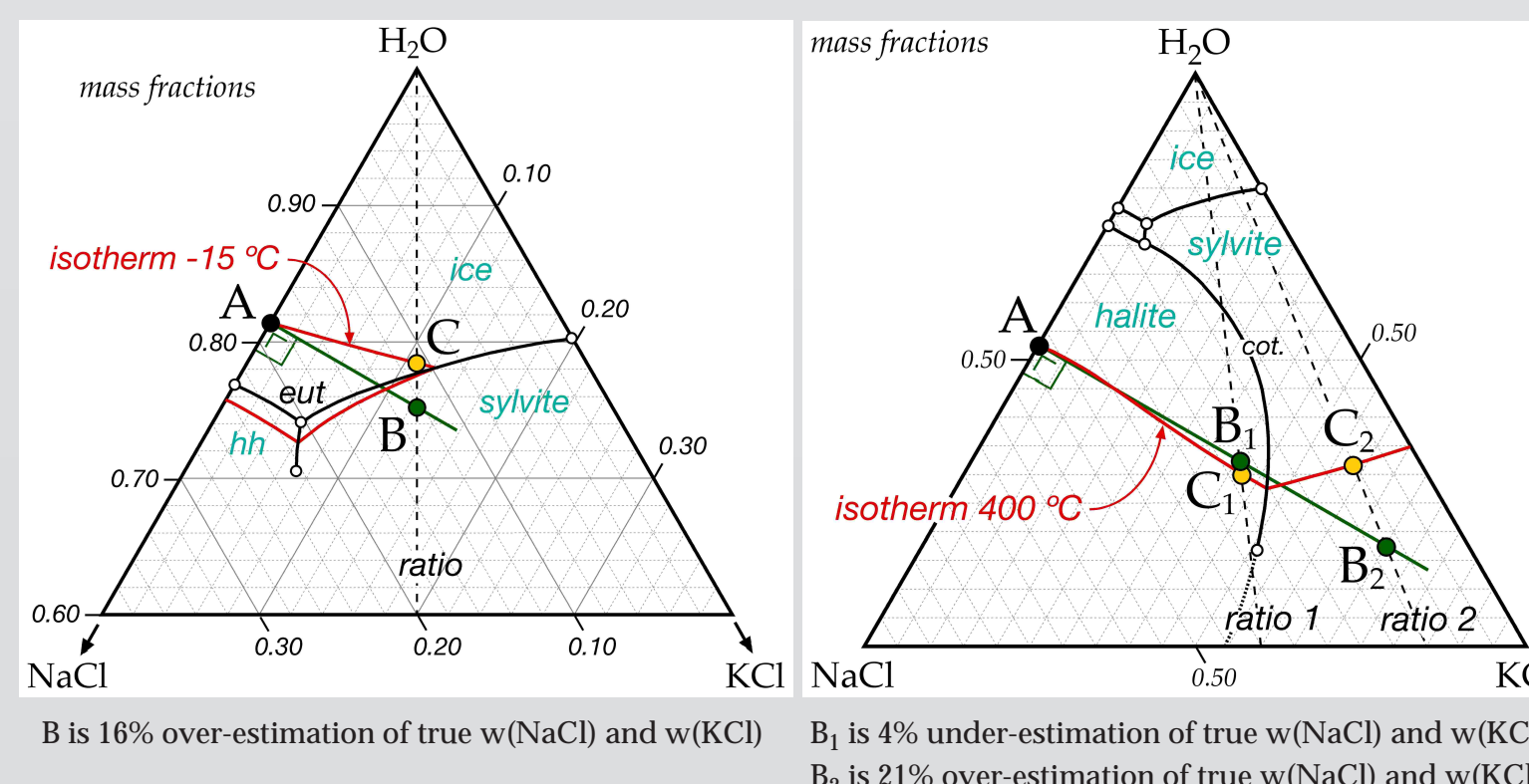
$$\text{where: } \mu_i = \left[\frac{MM_{Q_i Cl_n}}{MM_{NaCl}} \cdot \frac{MM_{Na^+}}{MM_{Q_i^{+n}}} \right]$$

No clear definitions of uncertainties in literature

extremely increased uncertainties caused by:

- isotherms are not perpendicular to the H₂O-NaCl base of triangular mass-fraction diagrams
- hypothetical phase diagram has no similarities to real triangular phase diagrams
- under- as well as over-estimations regularly occur

Examples of uncertainty H₂O-NaCl-KCl



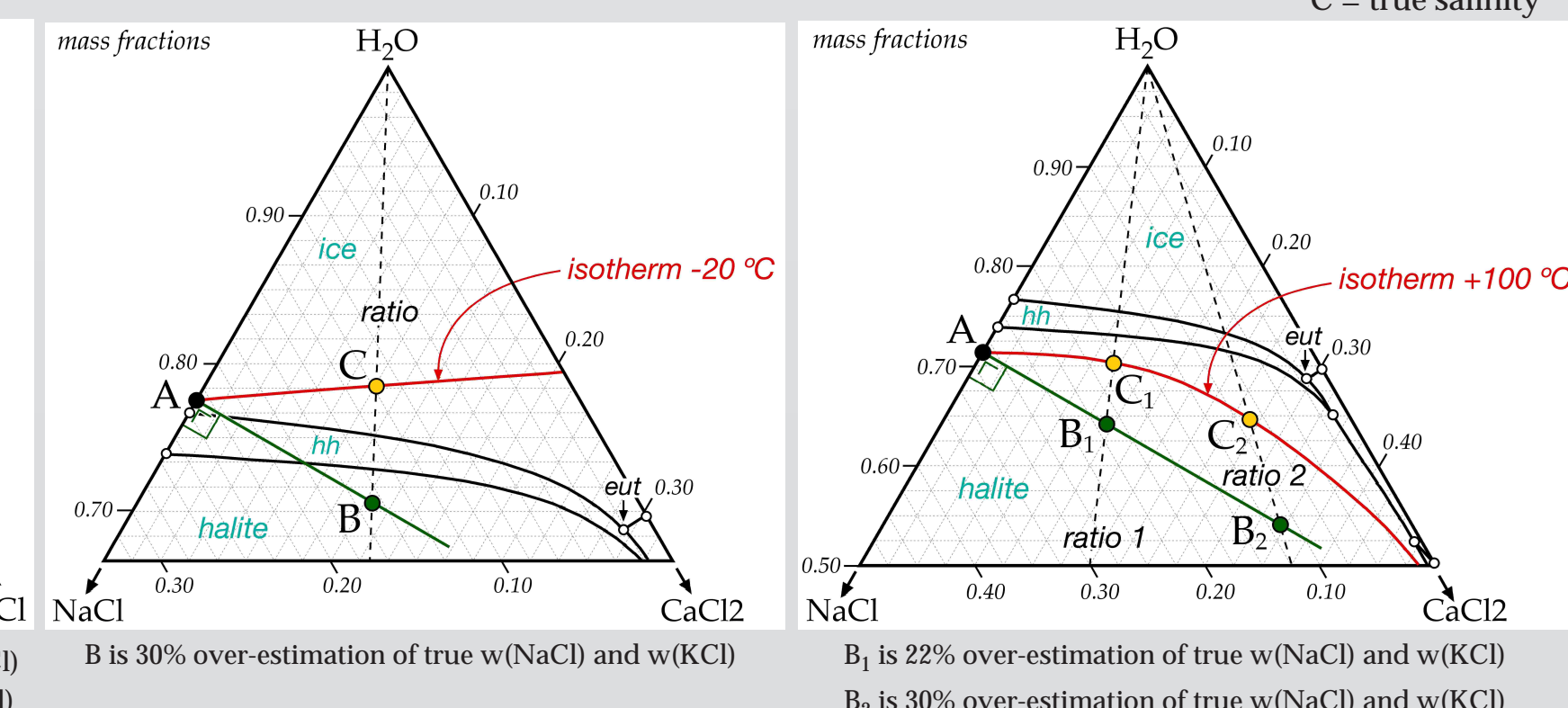
C. osmotic coefficients e.g. Leisen et al. (2012)

At relative low salinities, i.e. in the "ice-field", osmotic coefficients can be used to relate T_m(ice) with activity of H₂O and cation concentrations (Bakker, 2003, Chem. Geol., 194, 3-23).

not suitable for T_m(halite) or T_m(hydrohalite)

Component definition:
(1) predefined system (2) manually defined system
choose number: 2
Gas System: H2O-CO2-CH4-H2-C2H6-H2S-N2-He-O2-CO
Components included:
H2O y/n: y CO2 y/n: n CH4 y/n: n N2 y/n: n C2H6 y/n: n H2S y/n: n He y/n: n O2 y/n: n CO y/n: n
Ball System: NaCl-KCl-CaCl2-MgCl2-HeCl2
Components included:
NaCl y/n: y KCl y/n: n CaCl2 y/n: n MgCl2 y/n: n HeCl2 y/n: n
Bulk fluid V-X properties of inclusions are calculated from:
- Homogenization temperatures/pressures - Ice melting temperatures - Volume fraction estimates
Properties of individual phases are calculated at room temperature
Reference:
Bakker RJ (2003) Chemical Geology, vol.194, 3-23.

Examples of uncertainty H₂O-NaCl-CaCl₂



basic equations: $\Phi_{H_2O} = \frac{-1}{1000} \cdot \sum b_i \cdot \ln(a_{H_2O})$

$$\ln(a_{H_2O}) = (1 - \Phi_{H_2O}) \cdot \frac{MM_{H_2O}}{1000} \cdot \sum b_i$$

purely empirical fit to experimental data (Pitzer, 1991, CRC Press)

$$G_m^{excess} = A + \sum_i x_i B_i + \sum_{i,j} x_i x_j C_{ij}$$

Clear definitions of uncertainties in literature !

Aqueous Solution:	Salinity of dissolved salts:
Thermodynamic model for aqueous solution: (1) K2O-Salts Purely empirical/dissolved gases and P neglected (2) K2O-Salts Ion interaction model, osmotic coefficients (Pitzer, 1992)	(1) ice melting temperature (2) molality (3) mass% (4) amount-of-substance fractions associated salt (relative to H2O)
choose number: 1	choose number: 1
choose number: 2	choose number: 2
Ion interaction model: (1) Combination (Bakker, 1999) NaCl-KCl-CaCl2-MgCl2 (2) NaCl + NaCl (1983) KCl (3) Pitzer + Pitzer (1983) CaCl2 (4) NaCl + NaCl (1983) MgCl2 (5) NaCl + NaCl (1983) NaCl-KCl-CaCl2-MgCl2 (6) NaCl (1981) NaCl-CaCl2 (7) Spencer et al. (1990) NaCl-KCl-CaCl2-MgCl2 (8) Archer (1992) NaCl (9) NaCl et al. (1997) CaCl2-MgCl2	Final melting temperature of ice (in °Celsius) < -35 Mass ratio percentage of salts in solution (between 0 and 100) as obtained from e.g. hydrohalite melting: w(Ca ²⁺) = 53.17 w(Na ⁺) = 46.83 these numbers are calculated from cation ratios as obtained from LA-ICP-MS w(Ca ²⁺) / w(Na ⁺) = 0.88 Osmotic coefficients Successful calculation of salinity of aqueous solution Mass NaCl = 13.2908 Mass CaCl2 = 11.9945
choose number: 1	choose number: 1

et voilà!